INORGANIC CHEMISTRY



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SECTION OVERVIEW

1.5: An Introduction to Wave Mechanics

Topic hierarchy

1.5A: Wave Mechanics of Electrons

1.5B: The Uncertainty Principle

1.5C: The Schrödinger Wave Equation

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1.5A: Wave Mechanics of Electrons

All matter has intrinsic wave properties. These are described mathematically by the Schrödinger Equations and it's solutions. The wavenature of electrons and other fundamental principles (eg charge and momentum) together produce the wave mechanics of electron. The effects of electron wave mechanics are far reaching, responsible for such phenomena as electricity, emission and absorption, and bonding and hybridization.

Background

Wave-Nature of Matter

Accurate explanations of atomic natural physical chemical phenomena are dependent on energy quantization. The realization of this fundamental characteristic of matter was developed through treatment of a couple well known experiments, notably Max Planck's explanation of black body radiation and Einstein's explanation of the photoelectric effect. The conclusions of energy quantization were consolidated by Louis De Broglie as

$$\Lambda = \frac{h}{p}$$

and, by rearrangement:

$$f = \frac{E}{h}$$

On Waves

Quantum mechanically, an electron can be described by a wave function oscillating in space and time that has mean values equal to the expectation values of observables corresponding to given operators. According to the Born interpretation of quantum mechanics, the complex conjugate of this wavefunction correlates to the electron's positional probability density.

Electrons are fermions. They are charged particles. When they are confined by a potential to a limited space they display harmonics analogous to those of other wavelike phenomena. This occurs most notable in atoms and molecules. The hydrogen atom proves the most simple atomic example. The three dimensional harmonics of an electron bound within the potential energy well of a proton results in what are conventionally called orbitals. Orbitals are commonly depicted as contours of some percent of the complex conjugate of the electron's approximate wave function, though realistically without external potentials they diffuse infinitely.

A bound electron occupies higher harmonics of the bound state with increasing energy. Energy can only be increased in specific quanta as demanded for the wave function to exist. The discrete energy levels of higher harmonics correspond to higher orbitals.

Electrons can gain energy to exist in a higher orbital. When this process occurs via interaction with electromagnetic radiation, it is referred to as absorption. Similarly, the regression of an electron into a lower energy orbital results in the release of electromagnetic radiation, and is referred to as emission. Because of the quantized energy levels demanded by a bound system, electrons in a molecule or atom can only absorb or emit light at specific frequencies, which depend on the properties of the system.

Certain materials have energy level spacing such that excitation by an energy source can produce a greater number of electrons in an excited state than in the ground state. This is known as population inversion. When this happens for a transition which releases light upon relaxation, light of a specific nature is produced that has great practical importance. This light is monochromatic, and can be channeled back and forth through the medium (gain medium) and allowed only to disperse through a very narrow slit to produce monochromatic, directional, coherent light source. The apparatus is called a LASER, which is an acronym for light amplification by stimulated emission of radiation.

The inherent charge of electron incites movement of the particle in accordance to the forces described by coulomb's law. Rotational motion of a charged particle produces an electric field. The potential of an electron attraction to positive charge can be used to store energy in chemical form. The motion of electrons by batteries or other sources through conductive media, such as copper wire can be facilitated to do work. Computer. Light.

Electronic absorption and emission within roughly 350 to 750 nm produces radiation that is in the visible spectrum. the sky is blue because of the interaction of light from the sun with electrons in atoms in the atmosphere in what's known as scattering. Scattering

of this type occurs to the inverse cube of wavelength so light with shorter wavelength (blue in the visible) is scattered much more than other wavelengths. The other light passes through the atmosphere or something. maybe i have this backwards.

electrons can tunnel due to their wave nature. quantum mechanical tunneling is where a particle goes somewhere that is classically impossible, meaning that it simply did not have enough energy to to past a potential barrier, ut it did. We experts in science call this quantum weirdness. There are a lot of electrons, but perhaps not more than there are stupid people in the world. This page needs revision.

Most basic wave to satisfy boundary conditions (which are...) is

$$A\sin(n\pi x/L)$$

The superposition principle allows for the fourier theorem which allows an infinite number of such waves to be combined to form any any curve that obeys the requirements of a bound system.

Such a wave provides an accurate (nonrelativistic) description of the electron.

References

1. D.A.McQuarrieandJ.D.Simon,PhysicalChemistry:AMolecularApproach (1997)
2. P. W. Atkin and R. S. Friedman, Molecular Quantum Mechanics, 4th Ed. Oxford University Press, 2005.

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1.5C: The Schrödinger Wave Equation

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SECTION OVERVIEW

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1.6A: Electronic Quantum Numbers

1.6B: The Radial Part of the Wave Function

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1.6E: Orbital Energies in a Hydrogen-like Species

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1.6H: The ground state of Hydrogen

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1.6A: Electronic Quantum Numbers

There are four quantum numbers (n, l, m_l, m_s). No two electrons in the same atom can have the same four quantum numbers. Each quantum number describes a different aspect of the electron and its orbital. These numbers are obtained from the solution of the Schrödinger Equation for atoms in spherical coordinates.

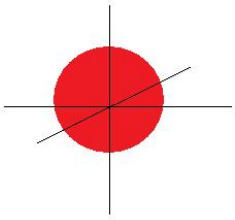
n, the principal quantum number

n tells you about the size of the orbital. It is related to how far the electron is from the atom. It is also related to the energy of the electron. n can be any positive integer number. An orbital has $n-1$radial nodes as well, which describe a radius at which the probability of finding the electron is 0.

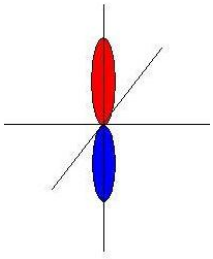
l, azimuthal quantum number

lt tells you about the angular momentum of the electron in the orbital. It defines the shape of the orbital. lt can be any integer between (and including) 0 and ($n-1$). Each orbital has $l$planar nodes.
Some examples of orbitals with different l:

$l=0$is an s orbital, with no planar nodes.



$l=1$gives a p orbital, which has one planar node.

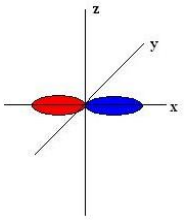


m_l, magnetic quantum number

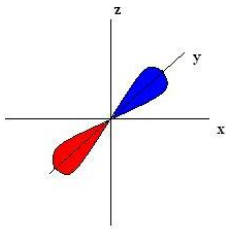
m_l tells you about the angular momentum projected on to the z axis. It tells you of the orientation of the orbital. It can be any integer between $-l$ and l.

$l=1$ has 3 different (but degenerate) m_l possible values:-1,0 or 1.

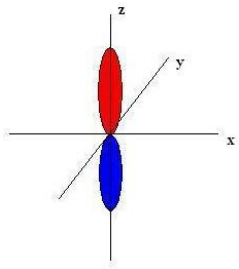
p_x



p_y



p_z



m_S spin projection quantum number

m_s tells you about the spin of the electron. An electron is a fermion, a type of quantum particle which is only allowed to have $m_s$equal to -1/2 or 1/2.

Pauli Exclusion Principle

The Pauli Exclusion principle states that no two identical fermions can share the same quantum state simultaneously. An electron, being a fermion, obeys this principle, so no two electrons in the same atom can have the same quantum numbers. Each orbital has space for 2 electrons, with m_s values with opposite sign. These electrons are considered spin-paired.

Energies of the Orbitals

The energies of the orbitals depend solely on n and l so there are degenerate states that result from various m_l values. For example, there are 3 p orbitals, all of which are equal in energy and therefore degenerate. Here is a table of possible quantum number arrangements and the corresponding orbitals from $n = 1$ to $n = 5$:

n	l	m_l	m_s	**Orbital**
1	0	0	$\pm\frac{1}{2}$	$1s$
2	0	0	$\pm\frac{1}{2}$	$2s$
2	1	±1 or 0	$\pm\frac{1}{2}$	$2p_x, 2p_y$ *or* $2p_z$
3	0	0	$\pm\frac{1}{2}$	$3s$
3	1	±1 or 0	$\pm\frac{1}{2}$	$3p_x, 3p_y$ *or* $3p_z$
3	2	$\pm2, \pm1$ or 0	$\pm\frac{1}{2}$	$3d_{z^2}, 3d_{x^2-y^2}, 3d_{xy}, 3d_{xz}$ *or* $3d_{yz}$
4	0	0	$\pm\frac{1}{2}$	$4s$
4	1	±1 or 0	$\pm\frac{1}{2}$	$4p_x, 4p_y$ *or* $4p_z$
4	2	$\pm2, \pm1$ or 0	$\pm\frac{1}{2}$	$4d_{z^2}, 4d_{x^2-y^2}, 4d_{xy}, 4d_{xz}$ *or* $4d_{yz}$
4	3	$\pm3, \pm2, \pm1$ or 0	$\pm\frac{1}{2}$	$4f_{x^3}, 4f_{y^3}, 4f_{z^3}$, $4f_{x(z^2-y^2)}, 4f_{y(z^2-x^2)}, 4f_{z(x^2-y^2)}$ *or* $4f_{xyz}$
5	0	0	$\pm\frac{1}{2}$	$5s$
5	1	±1or 0	$\pm\frac{1}{2}$	$5p_x, 5p_y$ *or* $5p_z$
5	2	$\pm2, \pm1$ or 0	$\pm\frac{1}{2}$	$5d_{z^2}, 5d_{x^2-y^2}, 5d_{xy}, 5d_{xz}$ *or* $5d_{yz}$
5	3	$\pm3, \pm2, \pm1$ or 0	$\pm\frac{1}{2}$	$5f_{x^3}, 5f_{y^3}, 5f_{z^3}, 5f_{x(z^2-y^2)}, 5f_{y(z^2-x^2)}$, $5f_{xyz}$
5	4	$\pm4, \pm3, \pm2, \pm1$ or 0	$\pm\frac{1}{2}$	$5g_{z^4}, 5g_{z^3x}, 5g_{z^3y}, 5g_{z^2xy}, 5g_{z^2(x^2-y^2)}, 5g_{x^4+y^4}$ or

References

1. J Goldstone, F Wilczek, Fractional quantum numbers on solitons - Physical Review Letters, 1981 - APS
2. *Harris, R. ,2007, Modern Physics*, 2e, *Addison Wesley*

Example 1.6A.1

How many electrons can have the quantum numbers $n = 2$ and $l = 0$? List the acceptable values for m_l and m_s for these values.

Solution

There may be 2 electrons with these quantum numbers, one with $m_l = 0$ and $m_s = \frac{1}{2}$ and the other with $m_l = 0$ and $m_s = -\frac{1}{2}$.

Example 1.6A.2

How many electrons can have the quantum numbers $n = 2$ and $l = 2$?

Solution

This is not a permitted value of l for $n = 2$, since the greatest acceptable value is given by $l = n - 1$.

Example 1.6A.3

Which set of orbitals do the quantum numbers $n = 3$ and $l = 2$describe? How many radial and planar nodes do these orbitals have?

Solution

This represents the 3d orbitals. They have 2 planar orbitals and 0 radial nodes.

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1.6B: The Radial Part of the Wave Function

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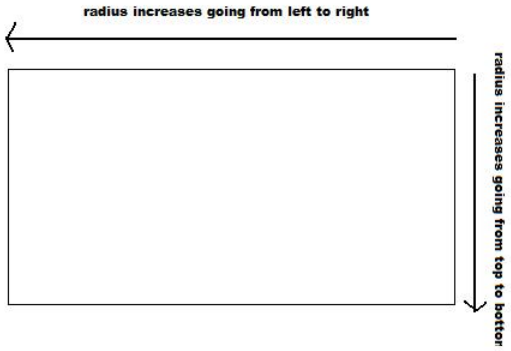
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1.6F: Size of Orbitals

Figure 1. General Trend of how the radius change within the Periodic Table



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1.6H: The ground state of Hydrogen

Hydrogen is the simplest atoms, which only contains an electron and a proton. The ground state of hydrogen is the lowest allowed energy level and has zero angular momentum. However, it is the most stable state in which a single electron occupied the 1s atomic orbital.

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SECTION OVERVIEW

1.7: Many Electron Atoms

Topic hierarchy

1.7A: The Helium Atom - Two Electrons

1.7B: Ground State Electronic Configurations - Experimental Data

1.7C: Penetration and Shielding

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1.7A: The Helium Atom - Two Electrons

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1.7B: Ground State Electronic Configurations - Experimental Data

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1.7C: Penetration and Shielding

Learning Objective

- To quantify the shielding effect experienced by atomic electrons.

We have previously described the concepts of electron shielding, orbital penetration and effective nuclear charge, but we did so in a qualitative manner. In this section, we explore one model for quantitatively estimating the impact of electron shielding, and then use that to calculate the effective nuclear charge experienced by an electron in an atom. The model we will use is known as Slater's Rules (J.C. Slater, *Phys Rev* **1930**, *36*, 57).

Slater's Rules

The general principle behind Slater's Rule is that the actual charge felt by an electron is equal to what you'd expect the charge to be from a certain number of protons, but minus a certain amount of charge from other electrons. Slater's rules allow you to estimate the effective nuclear charge Z_{eff} from the real number of protons in the nucleus and the effective shielding of electrons in each orbital "shell" (e.g., to compare the effective nuclear charge and shielding 3d and 4s in transition metals). Slater's rules are fairly simple and produce fairly accurate predictions of things like the electron configurations and ionization energies.

Slater's Rules

- **Step 1**: Write the electron configuration of the atom in the following form:

  (1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) . . .

- **Step 2**: Identify the electron of interest, and ignore all electrons in higher groups (to the right in the list from Step 1). These do not shield electrons in lower groups
- **Step 3**: Slater's Rules is now broken into two cases:
  - the shielding experienced by an s- or p- electron,
    - electrons within same group shield **0.35**, except the 1*s* which shield **0.30**
    - electrons within the n-1 group shield **0.85**
    - electrons within the n-2 or lower groups shield **1.00**
  - the shielding experienced by n*d* or n*f* valence electrons
    - electrons within same group shield **0.35**
    - electrons within the lower groups shield **1.00**

These rules are summarized in Figure 1.7*C*.1 and Table 1.7*C*.1.

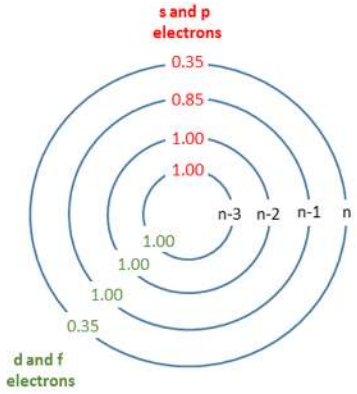


Figure 1.7*C*.1: Graphical depiction of Slater's rules with shielding constants indicated.

Shielding happens when electrons in lower valence shells (or the same valence shell) provide a repulsive force to valence electrons, thereby "negating" some of the attractive force from the positive nucleus. Electrons really close to the atom (n-2 or lower) pretty

much just look like protons, so they completely negate. As electrons get closer to the electron of interest, some more complex interactions happen that reduce this shielding.

Table 1.7C.1: Slater's Rules for calculating shielding constants

Group	Other electrons in the same group	Electrons in group(s) with principal quantum number n and azimuthal quantum number < l	Electrons in group(s) with principal quantum number n-1	Electrons in all group(s) with principal quantum number < n-1
[1s]	0.30	-	-	-
[*n*s,*n*p]	0.35	-	0.85	1
[*n*d] or [*n*f]	0.35	1	1	1

The shielding numbers in Table 1.7C.1 were derived semi-empirically (i.e., derived from experiments) as opposed to theoretical calculations. This is because quantum mechanics makes calculating shielding effects quite difficult, which is outside the scope of this Module.

Calculating S

Sum together the contributions as described in the appropriate rule above to obtain an estimate of the shielding constant, S, which is found by totaling the screening by **all electrons** except the one in question.

$$S = \sum n_i S_i \tag{1.7C.1}$$

where

- n_i is the number of electrons in a specific shell and subshell and
- S_i is the shielding of the electrons subject to Slater's rules (Table 1.7C.1)

Example 1.7C.1: The Shielding of 3*p* Electrons of Nitrogen Atoms

What is the shielding constant experienced by a 2*p* electron in the nitrogen atom?

Given:

Nitrogen (N)

Asked for:

S, the shielding constant, for a 2*p* electron (Equation 1.7C.1)

Strategy:

A. Determine the electron configuration of nitrogen, then write it in the appropriate form.

B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Step A

N: $1s^2\ 2s^2\ 2p^3$

N: $(1s^2)(2s^2,2p^3)$

Step B

$$S[2p] = \underbrace{0.85(2)}_{\text{the 1s electrons}} + \underbrace{0.35(4)}_{\text{the 2s and 2p electrons}} = 3.10$$

As Table 1.7C.1 indicates,

- the 1s electrons shield the other 2p electron to 0.85 "charges".
- the 2s and 2p electrons shield the other 2p electron equally at 0.35 "charges".

Exercise 1.7C.1: The Shielding of valence *p* Electrons of Bromine Atoms

What is the shielding constant experienced by a valence *p*-electron in the bromine atom?

Answer

The electronic configuration of Bromine is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$

We are asked about shielding of a 4p electron so the electrons that contribute to the calculation (in a reorganized configuration)

Reorganized the configuration is $(1s^2)(2s^2,2p^6)(3s^2,3p^6)(3d^{10})(4s^2,4p^4)$

$$S[4p] = \underbrace{(2\times 1)}_{1s\text{ electrons}} + \underbrace{(8\times 1)}_{2s\text{ and }2p\text{ electrons}} + \underbrace{(8\times 0.85)}_{3s\text{ and }3p\text{ electrons}} + \underbrace{(10\times 1)}_{3d\text{ electrons}} + \underbrace{(6\times 0.35)}_{4s\text{ and }4p\text{ electrons}} = 28.9$$

Example 1.7C.2: The Shielding of 3*d* Electrons of Bromine Atoms

What is the shielding constant experienced by a 3*d* electron in the bromine atom?

Given:

Bromine (Br)

Asked for:

S, the shielding constant, for a 3*d* electron

Strategy:

A. Determine the electron configuration of bromine, then write it in the appropriate form.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Step A

Br: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$

Br: $(1s^2)(2s^2,2p^6)(3s^2,3p^6)(3d^{10})(4s^2,4p^5)$

Ignore the group to the right of the 3d electrons. These do not contribute to the shielding constant.

Step B

$$S[3d] = 1.00(18) + 0.35(9) = 21.15$$

Exercise 1.7C.2: The Shielding of 3*d* Electrons of Copper Atoms

What is the shielding constant experienced by a valence *d*-electron in the copper atom?

Answer

S = 21.15

Calculating Effective Nuclear Charge

Previously, we described Z_{eff} as being less than the actual nuclear charge (Z) because of the repulsive interaction between core and valence electrons. We can quantitatively represent this difference between Z and Z_{eff} as follows:

$$S = Z - Z_{eff} \tag{1.7C.2}$$

Rearranging this formula to solve for Z_{eff} we obtain:

$$Z_{eff} = Z - S \tag{1.7C.3}$$

We can then substitute the shielding constant obtained using Equation 1.7C.3 to calculate an estimate of Z_{eff} for the corresponding atomic electron.

Example 1.7C.3: The Effective Charge of p Electrons of Boron Atoms

What is the effective nuclear charge experienced by a valence *p*- electron in boron?

Given:

Boron (B)

Asked for:

Z_{eff} for a valence *p*- electron

Strategy:

A. Determine the electron configuration of boron and identify the electron of interest.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.
C. Use the Periodic Table to determine the actual nuclear charge for boron.
D. Determine the effective nuclear constant.

Step A

B: $1s^2\ 2s^2\ 2p^1$. The valence p- electron in boron resides in the 2*p* subshell.

B: $(1s^2)(2s^2,2p^1)$

Step B

$S[2p]$ = 1.00(0) + 0.85(2) + 0.35(2) = 2.40

Step C

Z = 5

Step D

Using Equation 1.7C.3,

$$\begin{aligned} Z_{eff} &= Z - S \\ &= 5 - 2.50 \\ &= 2.60 \end{aligned}$$

Exercise 1.7C.3

What is the effective nuclear charge experienced by a valence d-electron in copper?

Answer

Z_{eff}= 7.85

Summary

Slater's Rules can be used as a model of shielding. This permits us to quantify both the amount of shielding experienced by an electron and the resulting effective nuclear charge. Others performed better optimizations of Z_{eff} using variational Hartree-Fock methods. For example, Clementi and Raimondi published "Atomic Screening Constants from SCF Functions." J Chem Phys (1963) 38, 2686–2689.

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1.8: The Periodic Table

For the most part, the introduction to this chapter is about why inorganic chemistry tends to be more complicated to understand and learn than organic:

- Number of elements
- Variation of properties (size, DH_{IP}, DH_{EA}, c) even among similar ones
- Covalency, electrovalency and multiple valencies
- Physical state, molecular aggregation and stability range (temperature) and solubility
- Air and water stability
- Coordination number and respect for the octet rule
- s, pp-pp, pp-dp and dp-dp bonding possibilities

Much order can be introduced into this potential chaos by relating the properties of the elements to their position in the periodic table (or, as was originally done by Mendeleev et al, arranging the elements into the periodic table according to their properties.

Heavier Elements

There is little chemistry to learn about for many of the transuranium elements especially the newest (104 - 108) because of their extremely short half-lives. In some cases only one or two atoms have been made!

The rest of the chapter is divided into secions A and B which, respectively, describe the pure elements themselves and then the general group trends and non-trends.

Part A - The Nature and types of the Elements

Monatomic Elements

Includes all the noble gases and many metal vapours. The noble gases do not form bonds to each other because of their closed valence shell configuration, and the metals have their own kind of bonding which does not work in the gas phase (see below).

Diatomic Elements

These are H_2, the simplest of all neutral molecules, the halogens which also have single bonds, and N_2 and O_2 which have multiple pp-pp bonding.

Discrete (Small) Polyatomic Molecules: S_n and Se_8, P_4.

Since pp-pp bonding is not a very useful option for elements below the first short period because of core-core repulsion at useful p-bonding distances, P, S and Se can form clusters (or chains - see the next group).

Sulphur, which can form two single bonds to itself, comes in various ring sizes up to S_{20}, S_8 being the most stable ("orthorhombic" sulphur).

White phosphorus, which can form three, comes as P_4 with P-P at 2.21 Å, which is more or less normal. A particularly strained P-P, i.e. "bent" would be longer. Nevertheless, P_4 is the most reactive form of phosphorus, for example, spontaneously inflaming in air.

Boron and carbon, capable of forming 3 and 4 bonds, respectively, could have been included here too, but see below.

Elements with Extended Structures

Boron is a somewhat anomalous case because it is electron deficient. The allotropic forms of boron are all hased on the icosahedral B_{12} unit. In this unit, each boron has 5 nearest neighbours, and since the units are weakly bonded to form more extended 3-frameworks, the borons that will have more remote neighbours as well. There are nowhere near enough electrons and atomic orbitals to do this using localized 2-electron - 2-centre Lewis type bonds. As usual molecular orbital theory comes to the rescue, but the B_{12} cage alone is a rather complex system to use as an example. The topic of the boranes (boron hydrides), to be covered later, might help shed some light on how the molecular orbitals might be set up. The allotropes of crystalline boron are the most complex of the structures of the elements, and their study has been futher complicated by the presence of small (but stoichiometric) amounts of carbon or nitrogen leading to some false ones.

 The basic icosohedral B_{12} unit

Depending on the number of bonds that they can form the following elements can form chain, sheet, or three dimensional structures:

C	P	S
Si	As	Se
Ge	Sb	Te
Sn	Bi	

"Plastic" sulphur (S_n) has a rubbery texture and is thermally unstable at room temperature with respect to conversion to S_8. Selenium also forms chains, but infinite spirals in an ordered (crystalline) structure. Tellurium is similar and the solid has semiconductor propeties.



Crystalline black phosphorus has a "double sheet" structure. This structure is shared by its cogeners (members of the same group) but they are metals. Red phosporus, the other common form, contains chains of phosphorus tetrahedra.)



Graphite has 2-dimensional sheets of trigonal sp^2 carbon atom arranged in aromatic six membered rings. Because of the extended delocalized orbitals, graphite is a conductor, especially parallel to the sheets.



Diamond is a 3-dimensional lattice of tetrahedral sp^3 carbon atoms arranged in saturated six-membered rings all in the chair form. Diamond is an insulator.



A number of additional carbon structures have been discovered quite recently. Buckmeisterfullerene C_{60}, the simplest of the "bucky balls" is shown on the right. It was discovcerd in soot. (Its shape, like an international soccer ball, is an icosahedron with all 10 corners cut off to 1/3 of the way along each edge which generates 10 new pentagonal faces and converts the old triangular ones to hexagons.) There are a number of elongated spheroidal structures and tubes capped by hemispheres known all made by cooling carbon vapour from and arc or plasma discharge. Chemists are still trying to make them do something useful!

Heats of formation for carbon forms are: Graphite, 0 ; diamond, 2.9; and C_{60}, 38.1 kJ mol^{-1}.

Metals

The structures of many metals are based on hexagonal or cubic close packing (Chapter 4 section 7), or the less efficient body-centered cubic (Fig 8-6). Figure 8-7 shows the distribution of these structures.

Metals are sometimes described as a regular array of cations immersed in a sea of valence electrons which are completely delocalized and free to roam through the entire mass. A simplified theoretical picture of this follows:

In the molecule Li_2 the bond results from overlap of the 2s orbitals each of which contains 2 electrons. The diagram below shows several representations of this:



The part of the diagram on the left shows the energy levels at the observed internuclear distance marked with a vertical dotted line on the right hand diagram. A crude representation of the two molecular orbitals is also shown. (The internal spherical nodes that the 2s orbitals possess are omitted.)

The next four diagrams show orbital energies (and orbitals) for hypothetical linear molecules, Li_3, Li_4, Li_5 and $Li_¥$.



Variation of orbital enery with internuclear separation for a hypothetical linear Li_3 molecule



.

Variation of orbital enery with internuclear separation for a hypothetical linear Li_4 molecule.



Variation of orbital enery with internuclear separation for a hypothetical linear Li_5 molecule.



At the left is the diagram for the hypothetical $Li_¥$. The infinite number of morse curves merge together to give the "band" shown.

Because lithium has the $2s^1$ valence shell configuration, only half of this band will be filled, and electrons can easily move into the empty orbitals accounting for the metallic conduction observed. The occupied levels/orbitals are shown by the shaded area in the diagram below:



The situation described above is not real. Real crystals are three-dimensional, and in addition to the molecular orbitals formed by the atomic s-orbitals, there will be another set formed by overlap of the atomic p-orbitals. The text figures 8.8 and 8.9 are a more realistic representation.

Cohesive Energies of the Metals

See figure 8-10. Note that the main group metals have relatively low enthalpies of atomization correlating roughly with the number of valence electrons. Maxima occur at the half-filled shell after which antibonding parts of the conduction bands begin to be populated.

Part B - The Chemistry of the Elements in Relation to their Position in the Periodic Table

Hydrogen: $1s^1$

With an intermediate electronegativity and one valence electron, hydrogen might range from H+ to H- in its compounds:

- The proton (radius = 1.5×10^{-13} cm) cannot exist in condensed states (liquid or solids) because it exerts too powerful a polarizing influence on molecules near to itself. Therefore, it is always complexed, for example as H_3O^+.
- Covalent compounds are the normal situation.
- When combined with very electropositive elements e.g. Na, K, Ca it behaves as H^- (hydride ion) and is a very powerful reducing agent.

Helium ($1s^2$) and the noble gases (ns^2np^6)

- The energy necessary to make a valence state is not compensated by bond formation above krypton which forms a few flourides. The rest of the group have fairly extensive chemistry with fluorine, chlorine and oxygen.

  (The first noble gas compound, originally thought to be $Xe^{2+}[PtF_6]^{2-}$ by analogy with $[O_2]^{2+}[PtF_6]^{2-}$, was made by Bartlett in 1962. Prior to that they had been thought to be inert.)

Elements of the First Short Period (Li - F)

They are poor representatives of their groups. (The second short period elements are much better for this.) The reason is connected to their small size and lack of (empty) d-orbitals which limits their coordination number to 4 in the absence of multicentre bonding.

- To achieve their normal valencies, Be, B and C "use" a valence state where one of the 1s electrons is promoted to the p-subshell.
- "Electron deficient" Li, Be and B compounds are Lewis acids. This involves a change in hybridization. The extent to which the coordination number can be increased is limited by negative charge build-up on the acceptor.
- Li, Be and B also tend to be involved in molecules featuring 3-centre, 2 e^- bonding as a way to reduce their electron deficiency.
- N, O and (perhaps) F compounds can be Lewis bases because of the available electon pairs on these atoms. The sharing of more than one pair is opposed by positive charge build-up on the donor atom, and sometimes steric factors.
- Li^+ exists in rather few compounds because of its small size. Covalent and multicenter bonding is common e.g. the lithium alkyls.
- Be^{2+} would be even more polarizing than Li^+ so no compounds containing it exist. Covalency is the norm e.g. BeF_2 and $[Be(H_2O)_4]^{2+}$, which hydrolyses extensively to BeOH containing species.
- for Li, Be and B there is a marked similarity to the diagonally related Mg, Al and C. Although the valencies differ, the chemical behaviour such as covalency of halides or coordination chemistry tends to be somewhat similar. For example, there are close parallels between the lithium alkyls and the magnesium alkyls or between beryllium halides and the aluminium halides.
- For B, C and N, there are no (long-lived) compounds in which the elements are cationic. Covalency dominates the chemistry of these elements.
- There are compounds containing anions e.g. C_2^{2-} (acetylide) and N^{3-}, which is a major product when Mg burns in air.
- The chemistry of O and F is dominated by anion formation and covalency. Remember, O^{2-} is too strong a base to exist in water though solid compounds are known. Fluoride, F^- is only a weak base and so known in solids and aqueous solution.

- C, N and O commonly participate in multiple bonding by the use of p-orbitals. N_2 is a rather unreactive molecule because of the great strength of the triple bond. O_2 is much more reactive, partly because it is a bi-radical. F_2 is very reactive because the filled p-orbitals perpendicular to the bond repel each other.

Covalent Bonds

Covered as part of the previous section.

Elements of the Second Short Period (Na to Ar)

These elements are much more representative of the chemistry of the elements below them in their groups. This specially true for the non-metalic elements:

- The elements of this period and those below it do not tend to use their p-orbitals for p-bonding. Rather the empty d-orbitals are used if p-bonding occcurs.

  For example, aside from special sterically encumbered cases, there are few compounds containing Si=Si, P=P or S=S bonds. An example of an exception is $(CH_3)_3C\text{-}P\text{=}P\text{-}C(CH_3)$. pp-pp-bonding is not stable with respect to addition reactions: a kinetic effect.

- Multiple bonding that does occur usually involves a first short period element such as oxygen or nitrogen. Examples include Cl_3PO, SO_2 or ClO_2. Such molecules may contain pp-dp-bonding, and the octet rule is often violated. On the other hand, there is no analogue in silicon chemistry of O=C=O. SiO_2 is a network solid although the Si-O-Si groupings are linear which does hint and p-interactions.
- The d-obitals can be invoked to explain valence states where the coordination number exceeds 4 (and the octet is exceeded also.) Examples include PCl_5, SF_6 and IF_7. The possibility of higher coordination numbers lead also to different reactivity, e.g. CCl_4 which is inert to hydrolysis and $SiCl_4$.
- The metals differ from the first memeber of their group, e.g. sodium does not form covalent compounds, aluminum is a cation-forming metal quite unlike boron, and the coordination numbers are often 6 rather than 4 for these second row elements.

The Remainder of the Non-Transition Elements

This section contains a group-by-group summary of the properties characterizing each group and indicating, again, how the top member of each group differs. The following is list of key properties appropriate for comparisions:

1. Metallic character.
2. Properties of the oxides:
   a. Ionic *vs* covalent
   b. Acidic *vs* basic
3. Properties of the halides:
   a. Ionic *vs* molecular
   b. Ease of hydrolysis
4. General trends in electrovalence and covalence.
5. Trends in structure:
   a. Coordination numbers for discrete species
   b. Aggregation in the solid state to increase coordination number
6. Properties of the hydrides.
7. Tendency to catenate.
8. The relative importance of pp-pp *vs* pp-dp *vs* dp-dp bonding.
9. The general strength of covalent bonding.
10. The relative importance of the lower valent states vs the hight valent states.

Group IA or 1

See text Table 8.1. The elements have chemistry dominated by the ionic 1+ state. The behaviour going down a group is well-behaved. The following decrease down a group:

a. melting points and heats of sublimation.
b. lattice energies (mostly).
c. Effective hydrated radii and hydration energies.
d. Ionization Enthalpies.

Group IIA or 2 and IIB or 12

See text Table 8.2. For group IIA (Mg, Ca, Sr, Ba and Ra) which all form the 2+ ionic state there are again well-behaved trends including those mentioned for group IA and adding:

a. Solubility of the sulphates and carbonates.
b. Thermal *instability* of the carbonates and nitrates.

which decrease going down the group. Group IIB metals (Zn, Cd and Hg) have two s-electrons outside filled d-subshells. In Zn and Cd the d-electrons do a somewhat poorer screening job than the closed shells of the group IIA so that the 2+ ions (which are more polarizing) are more inclined to form complex ions with NH_3, halides and CN^-.

Mercuric ion, Hg^{2+}, where the f-subshell also has been filled, is quite different in that it is even more inclined to form complexes. The oxidation potential for mercury is positive, whereas the others are all negative, which means that mercury metal is rather easily produced in its reactions. It also readily forms the mercurous ion, Hg_2^{2+}.

Group IIIA or 3 and IIIB or 13

See text Table 8.3. The text includes the group IIIA elements and the rest of the lanthanides among the non-transition metals because of the relative simplicity of their chemistry. They all behave as quite electropositive elements and form the 3+ ion. Scandium behaves as if it falls somewhere between aluminum and gallium in terms of its covalency. The lanthanides are so similar to each another that separation is difficult. (Cation exchange chromatography is used.)

All the group IIIB elements form compounds containing the 3+ ion, but there is a marked tendency towards covalency especially for aluminum e.g. its alkyls are volatile liquids and its chloride sublimes.

Group IIIB is the first group to clearly demonstrate the "inert pair effect". On descending the group, there is a tendency for the 1+ ions to become more and more stable. Tl^+ is more stable than Tl^{3+} and its chemistry is complicated by its redox behaviour.

(The unusual stability of Hg^0 could also be ascribed to the inert pair effect.)

Group IVB or 14

See text Table 8.4. This is the group in which the property differences between the first member, carbon, and the rest is perhaps most marked. Knowing the chemistry of carbon is almost useless for predicting the chemistry of the remaining elements! The chemistry of carbon is dominated by its extraordinary ability to catenate. While silicon can form analogues to the hydrocarbons, multiple bonding is not viable, and the Si-O bond is the important bond in silicon chemistry.

The chemistry of the group IVB elements in their IV oxidation state is predominantly covalent: $SiCl_4$ is a liquid as is $Pb(C_2H_5)_4$, the infamous anti-knock gasoline additive.

The covalent bonds generally weaken on descending the group.

The divalent state of carbon (in carbenes) is very reactive and it comes in both singlet and triplet forms. Silicon has virtually no chemistry in this state.

For the rest of the group, the II state becomes successively more stable going down the group. The "inert pair" is usually stereoactive in both molecular and solid state aggregated compounds. The M(II) compounds can never be considered truly ionic. The trend is probably associated with decreasing covalent bond strengths compared to the energy needed to obtain the valence state because the ionization potential differences are small:

> *$GeCl_2 + Cl_2$ alt $GeCl_4$ (Rapid at 25 ^oC)*
> *$SnCl_2 + Cl_2$ alt $SnCl_4$ (Slow at 25 ^oC)*
> *$PbCl_2 + Cl_2$ alt $PbCl_4$ (Does not go except at higher temperature and pressure)*

$PbBr_4$ and PbI_4 cannot be made.

Group VB or 15

See text Table 8.5. The oxidation states V and III are normal for this group. Phosphorus compounds are all covalent, but the tendency towards ionic behaviour increases down the group especially for the III state, *but*, the only species that can be considered as predominantly cations are $SbO^+$and BiO^+ and Bi^{3+} in its fluoride.

Group VIB or 16

See text Table 8.6. This group is relatively well-behaved so that its features can be tablulated:

a. The 2- ions exist in salts with electropositive elements.
b. There are also anions containing one covalent bond e.g. RS^- or HS^-.
c. There are covalent compounds of type (for example) R_2E or X_2E (R is organic, X is a halogen and E is the group VIB element).
d. There are monocations of type R_3E^+
e. There are anionic ompounds where the group VI element is in the IV or VI state, and with coordination numbers 4, 5 and 6 e.g. SCl_4, SeF_5^-, TeF_6. There are stereoactive lone pairs to worry about!
f. The hydrides, H_2E decrease in stability down the group.
g. The elements themselves become gradually more metallic.
h. The tendency to form anionic complexes increases e.g. $SeBr_6^{2-}$, $TeBr_6^{2-}$ and even PoI_6^{2-}.

Group VIIB or 17

See text Table 8.7. With the elements of group IA, this group is the most well-behaved. The properties progress nicely down the group:

a. The elements all form th X^- ion and compounds with one covalent bond e.g. RX or HX.
b. Interhalogens e.g. ClF have properties somewhat intermediate between the parent dihalogens, but they are polar in the expected sense.
c. The higher oxidation states are II, V and VII.
d. There are no simple cationic ions X^+ but Br_2^+, I_2^+, Cl_3^+, Br_3^+ and several larger iodine cations have been prepared.

The Transition Elements of the d and f-Blocks

Not covered in Chem 242. (Winter 1999)

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SECTION OVERVIEW

1.9: The Aufbau Principle

Topic hierarchy

1.9A: Ground State Electronic Configurations

1.9B: Valence and Core Electrons

1.9C: Diagrammatic Representations of Electronic Configurations

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1.9A: Ground State Electronic Configurations

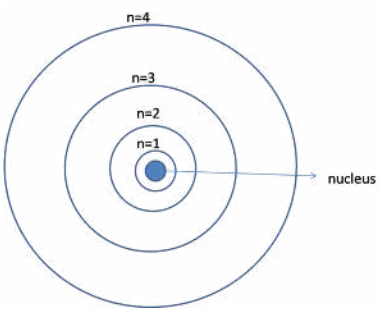
Ground state electron configurations are the foundation for understanding molecular bonding, properties, and structures. From the electrons in an atom, to the differing orbitals and hybridization, the ground state electron configuration sheds light on many different atomic properties. Fundamentally, understanding electron configuration leads to an understanding of the periodic table.

Introduction

In 1913, Niels Bohr proposed that electrons could orbit an atom at a certain distance without collapsing into the atom, and that each orbit distance had its own energy level. He proposed that each orbital's angular momentum, M, was equal to a multiple, n, of Plank's constant, h, divided by 2π. This gives the equation:

$$M = n\hbar \text{ where } \hbar = h/2\pi \text{ and } n = 1,2,3,4$$

This model proposed the Bohr atom, which shows circular orbits surrounding the nucleus.



Orbitals

In addition to having different energy levels, orbitals also have different shapes and orientations, and each can be occupied by two electrons. For each principal quantum number, n, there is one s orbital, three p orbitals, five d orbitals and seven f orbitals. Therefore, an s orbital can hold two electrons, a p orbital can hold six electrons, a d orbital can hold ten electrons, and an f orbital can hold 14 electrons.

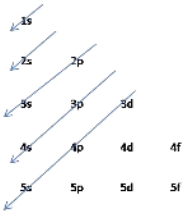
Ground State Electron Configuration

Quantum numbers

There are four quantum numbers n, l, m_l, and m_s. The principal quantum number n is a positive integer (1,2,3,4) and it represents the energy of the orbital. The angular momentum quantum number l, is from 0 to $n - 1$. The l values of 0, 1, 2, and 3 correspond to the s, p, d and f orbitals, respectively. The magnetic quantum number m_l ranges from $-l$ to $+l$. This quantum number dictates the orbital orientation, such as p_x, p_y, or p_z. The quantum spin number m_s, is either +1/2 or -1/2 and it dictates the electron spin.

Aufbau Principle

The Aufbau principle states that electrons must fill lowest energy shells first.



Following the model, electrons fill the 1s orbital with two electrons, then the 2s with two electrons, then the 2p with six electrons, then the 3s with two electrons, etc.

There are some exceptions to the Aufbau Principle. This occurs mainly with electrons in the d orbital where extra stability is obtained from a half filled or fully filled d orbital. Therefore, if there are 4 electrons, or 9 electrons in the d orbital, it will move one

electron from the s orbital below it to fill the extra space.

Example 1.9A.1: Chromium

The electron configuration of chromium

Solution

Cr's electron configuration, following the model would be: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4 \backslash 0, butinsteaditis \backslash (1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$, because there is extra stability gained from the half-filled d orbital.

Hund's Rule

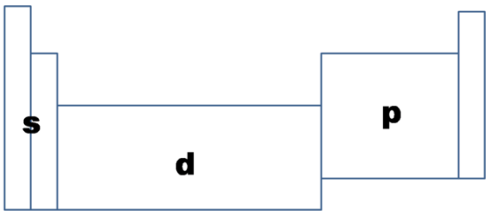
Hund's rule states that when filled sub-levels other than s orbital, electrons must not be spin paired in the orbitals until each orbital contains one electron, and no orbital can have two electrons with the same spin (m_s).

Pauli Exclusion Principle

Pauli Exclusion Principle states that no two electrons can have the same quantum numbers. An orbital can only hold 0, 1, or 2 electrons. They must have opposite spins if there are 2 electrons in the orbittal.

Periodic Trend

Valence electron shells in the periodic table follow a trend. This can be referred to as the s block, the p block, the d block and the f block (lanthanides and actinides) meaning that, in its ground state, an element in a certain "block" will have its valence electrons in the s, p, d, or f orbitals depending.

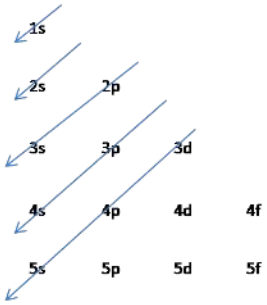


How to Write Ground State Electron Configurations

Basics

Electron configurations are written using the principal quantum number n, followed by the orbital (s, p, d, or f) with the total number of electrons written as a superscript. Example: $1s^2$ For writing ground state electron configurations, a few main steps should be followed.

1. Find the amount of electrons in the atom. Example: Na: 11 e^- Na^+: 10 e^-
2. Fill orbitals following the model until all electrons have been accounted for.



Example: Na: 11 e^- $1s^2$ $2s^2$ $2p^6$ $3s^1$ or Na^+: $1s^2$ $2s^2$ $2p^6$

3. After that, it is important to check for a nearly half-filled or filled d orbital (d^4 or d^9) and adjust accordingly by removing an electron from the s orbital beneath it.

Example 1.9A.2: Chromium

What is the electronic configuration of chromium

Solution

Cr: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 \mathbf{4s^2 3d^4}$ half filled orbital, s orbital beneath it

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{4s^1 3d^5}$

Shorthand

Because writing the entire electron configuration can become cumbersome, there is a shorthand option. It is done by using the symbol of the noble gas in the period above the element to represent the electron configuration before it.

Example: Na: [Ne] $3s^1$

References

1. Housecroft, Catherine E. and Alan G. Sharpe, “Inorganic Chemistry,” 3rd ed. England: Pearson Education Limited: 2008.
2. Tro, Nivaldo J. “Chemistry: A Molecular Approach,” 8th ed. Upper Saddle River, New Jersey: Prentice Hall: 2007.
3. Silberberg, Martin S. "Chemistry: The Molecular Nature of Matter and Change," 4th ed. Boston: McGraw Hill: 2006.

Problems

1. Write the expanded and shortened ground state electron configuration for Cl.
2. Write the expanded and shortened ground state electron configuration for Cr.
3. Write the expanded and shortened ground state electron configuration for Cu.
4. Write the expanded and shortened ground state electron configuration for Co^{2+}
5. Write the ground state electron configuration for P^{3-}

Solution 1. Expanded: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

Shorthand: [Ne] $3s^2\ 3p^5$

Solution 2. Expanded: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1 3d^5$

Shorthand: [Ar] $4s^1 3d^5$

Solution 3. Expanded: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1 3d^{10}$

Shorthand: [Ar] $4s^1 3d^{10}$

Solution 4. Expanded: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2 3d^5$

Shorthand: [Ar} $4s^2 3d^5$

Solution 5. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

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1.9B: Valence and Core Electrons

The electrons of an atom are typically divided into two categories: valence and core electrons. Valence electrons occupy the outermost shell or highest energy level of an atom while core electrons are those occupying the innermost shell or lowest energy levels. This difference greatly influences the role of the two types of electrons in a chemical reaction. Generally, valence electrons can participate in the formation of chemical bonding, but core electrons cannot. While core electrons are not involved in bonding, they influence the chemical reactivity of an atom.

The electron configuration of a oxygen atom is

$$\text{O}: 1s^2 2s^2 2p^4 \tag{1.9B.1}$$

which may be shorted

$$\text{O}: [He] 2s^2 2p^4 \tag{1.9B.2}$$

where the $[He]$ stands for the configuration of helium ($1s^2$). Similarly, the configuration of calcium with 20 electrons can be written

$$\text{Ca}: [Ar] 4s^2 \tag{1.9B.3}$$

where the $[Ar]$ stands for the configuration of argon ($1s^2 2s^2 2p^6 3s^2 3p^6$). Electronic configurations that are the same as noble gases are very stable since they have a full octet (except helium with a full 1s orbital).

The $1s$ electrons in oxygen do not participate in bonding (i.e., chemistry) and are called **core electrons**. The valence electrons (i.e., the $2s^2 2p^4$ part) are **valence electrons**, which do participate in the making and breaking of bonds. Similarly, in calcium (Equation 1.9B.3), the electrons in the argon-like closed shell are the core electrons and the the two electrons in the 4s orbital are valence electrons.

Example $1.9B.1$: Cobalt

What are the core and valence electrons in cobalt?

Solution

Start by writing the electron configuration of cobalt with 27 electrons:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$$

However, argon has the electronic structure $1s^2 2s^2 2p^2 3s^2 3p^6$, so we can rewrite the configuration as

$$[Ar] 4s^2 3d^7$$

The two electrons in the $4s$ orbital and the seven electrons in the $3d$ are the valence electrons: all others are core electrons.

The periodicity of valance electrons can be seen in the Periodic Table. Basically, the periodicity is only applied to the main group elements, while in transition metals, rules are complex.

The core electrons remain the same in the increase of group numbers in the main group elements. On the other hand, the valance electrons increase by one from left to right of a main period, and remain the same down the column of a main group. This evolution gives periodical change in property of a period, and similar chemical property of a group, which is called periodical trend. The number of valence electrons in a main period is the same as its group number. The table below shows this rule clearly.

Under construction

Figure 1: 1A + 2A are metals. 3A to 8A are non-metals.

However, this periodicity cannot be applied to the transition group, which is more complicated than that of the main group. Although the outermost electrons can be easily determined, the apparent valence electrons considered in chemical reactivity are complex and fluctuated. Electrons going into d sublevel can play either a role of valence electrons or shielding electrons. So there is not always a certain number of apparent valence electrons. The number of apparent valence electrons for the first transition metal period is shown in the table below.

Under construction

Figure 2: Valence electrons for transition metals.

Relationship with Chemical Reactivity

The chemical reactivity of an atom is mainly determined by valence electrons. Atoms which have a complete shell of valence electrons tend to be chemically inert. Atoms with one or two valence electrons are highly reactive. This phenomenon can be explained by Hund's rule, which states that orbitals that are empty, half-full, or full are more stable than those that are not. For example, Ne is chemically inert because it has two valence electrons that fill its outermost shell which makes it stable compared to atoms such as Al, which has three valence electrons, but its valence electrons does not fill its outermost shell.

Although core electrons do not take part in chemical bonding, they play a role in determining the chemical reactivity of an atom. This influence is generally due to the effect it has on valence electrons. The effect can be observed from the gradual change of chemical reactivity in a group. As you go down a group, more shells are occupied by electrons, which increases the size of the atom. The more core electron shells an atom has, the larger the size of the atom, and the farther the valence electrons are from the nucleus, thus the valence electrons will experience less effective nuclear charge and will be easily lost. For example, Na and K can both react with water, but K has a more radical reaction because it has more shells of core electrons which makes the valence electron in its outermost orbital much easier to lose than the valence electron of Na.

References

1. Miessler, Gary L., and Donald A. Tarr. *Inorganic Chemistry*. Upper Saddle River, NJ: Pearson Prentice Hall, 2010. Print.
2. Brown, Ian David. *The Chemical Bond in Inorganic Chemistry the Bond Valence Model*. Oxford: Oxford UP, 2006. Print.

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1.9C: Diagrammatic Representations of Electronic Configurations

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1.10: Ionization Energies and Electron Affinities

Example of IE_1 of Magnesium: **$Mg(g) \rightarrow Mg^+(g) + e^- \; I_1 = 738$ kJ/mol**

IE_1 stands for the first ionization energy: the energy the atom requires to expel the first electron from its orbital. Similarly, the second ionization energy, will be the energy needed to expel the second electron.

$Mg^+(g) \rightarrow Mg^{2+}(g) + e^- \; I_2 = 1{,}451$ kJ/mol

However, IE_2 of Magnesium will be larger than that of IE_1 because it is not energetically favorable to separate an electron from a positively charged ion.

The general pattern of the ionization energy as they are in regard to the period table is that the IE increases across a period, and decreases down a group. Because it requires more energy to remove an electron from a stable atom, the noble gases are usually associated with the highest IE_1. Because their valence shells are already filled and stablized, they will require much more energy to disrupt that stability. The first electron that is expelled is the most loosely held to the atom.

On the other hand, the group 1 elements are usually associated with the lowest IE_1. Since only one electron occupies the valence shell of these atoms, it will be more energetically favorable for them to lose the electron in order to achieve a full orbital shell.

However, there are few exceptions. The IE1 decreases when crossing from element in group 15 to the element in group 16. The group 15 has half-filled electronic configuration ns^2 np^3. This type of configuration is very stable; it's hard to remove electron from valence shell. Therefore, element in group 15 requires greater value of IE1 than group 16. Another exception is that going from Be (group 2) to B (group 13), the IE1 decreases because Be has the filled shell $2s^2$ which is more stable than the electronic configuration of B $2s^2$ $2p^1$. Hence, Be will require more IE1 than B. Similarly, the IE1 decreases when going from elements in group 12 to group 13

Electron Affinities

Electron affinity, often abbreviated as EA, is the energy released when an electron is added to a valence shell of the atom.

$F(g) + e^- \rightarrow F^-(g)$ EA = -328 kJ/mol

[When an electron is added to an atom, energy is given off. This process is exothermic.]

Atoms like the noble gases will not gain an electron because they are already in their most stable state with a full shell. Atoms like F will most likely gain an electron because when a free electron is added to the outer shell of fluorine, it will have obtained a full shell. Generally, atoms increasing across a period will increase in EA also.

Exothermic vs endothermic process

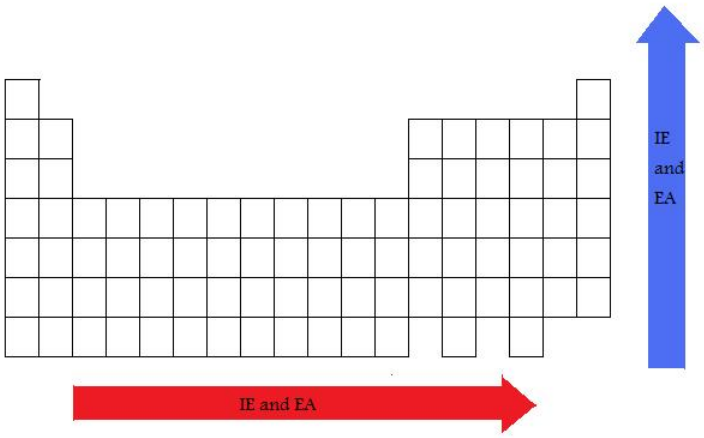
$O(g) + e^- \rightarrow O^-(g)$ EA_1= -141.0 kJ/mol

$O^-(g) + e^- \rightarrow O^{2-}(g)$ EA_2 = +744kJ/mol

When an electron is added to an atom, the energy change is exothermic because of the attraction of the electron to the nucleus. However, in the case of EA_2 where the electron is added to an anion, the repulsion between the anion and this newly added electron will overwhelm the attraction of the electron to the nucleus. Therefore, this process will be endothermic, as opposed to EA_1.

Periodic Trend

The general trend of IE and EA along a periodic table.



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1. Vedeneyer, Vladimir Ivanovich. Bond Energies Ionization Potentials and Electron Affinities. London: Edward Arnold, 1966. Print.
2. Petrucci, Ralph. General Chemistry: Principles and Modern Applications. New Jersey. Pearson Prentice Hall, 2006.

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- Link to outside sources. Wikipedia entries should probably be referenced here.

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2.1B: Lewis Structures

2.2: Homonuclear Diatomic Molecules - Valence Bond Theory

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2.2B: Covalent Bond Distance, Covalent Radius, and van der Waals radius

2.2C: Valence Bond model of Bonding in H_2

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2.7A: MO Theory- Orbital Interactions

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2.9.1: Trigonal Bipyramidal Species

2.9.2: Trigonal Bipyramidal Structures
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2.1: Bonding Models - An Introduction

Topic hierarchy

2.1A: A Historical Overview

2.1B: Lewis Structures

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2.1A: A Historical Overview

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2.1B: Lewis Structures

Lewis Structures are very similar to electron dot diagrams except for the fact that shared electrons between atoms are shown as lines. Lone pairs of electrons themselves are usually represented by dots around the atoms. These diagrams are helpful because they allow us to predict the shape of the molecule and see the positions of each atom relative to the others.

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SECTION OVERVIEW

2.2: Homonuclear Diatomic Molecules - Valence Bond Theory

Topic hierarchy

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2.2B: Covalent Bond Distance, Covalent Radius, and van der Waals radius

2.2C: Valence Bond model of Bonding in H_2

2.2D: Valence Bond model of bonding in F_2, O_2, and N_2

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2.2C: Valence Bond model of Bonding in H 2

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2.2D: Valence Bond model of bonding in F 2 , O 2 , and N 2

The bonding in simple homonuclear molecules such as F_2, O_2, and N_2 is quite similar in principle, but have fundamental differences in structure that can be described easily using Valence Bond models. The three molecules are comprised of atoms that are adjacent to one another in their period, and will thus have similar size and mass. The atoms do reside in different columns of the table though, and as such will have fundamentally different characteristics such as valence electron count and bond order in their respective diatomic molecules in which the elements are found naturally.

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SECTION OVERVIEW

2.3: Homonuclear Diatomic Molecules - Molecular Orbital (MO) Theory

Topic hierarchy

2.3A: An Overview of the MO Model

2.3C: MO Applied to \(He_2\), \(Li_2\), and \(Be_2\)

2.3D: MO Applied to \(F_2\) and \(O_2\)

2.3E: What happens if s-p separation is small?

2.3b: MO theory of bonding in H_2^+

2.3: Homonuclear Diatomic Molecules - Molecular Orbital (MO) Theory is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

2.3A: An Overview of the MO Model

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2.3C: MO Applied to H_2, Li_2, and Be_2

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2.3D: MO Applied to F 2 and O 2

Molecular orbitals (MO) are constructed from atomic orbitals. In O_2 and F_2, there is a crossover of the sigma and the pi ortbials: the relative energies of the sigma orbitals drop below that of the pi orbitals'. Information from the MO diagram justify O2's stability and show that it's bonding order is 2. The LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital) of difluoride's MO diagram help explain why the molecule is very stable - the diagram also tells us that the bond order is 1.

Contributors and Attributions

- Dieu Huynh

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2.3b: MO theory of bonding in H_2^+

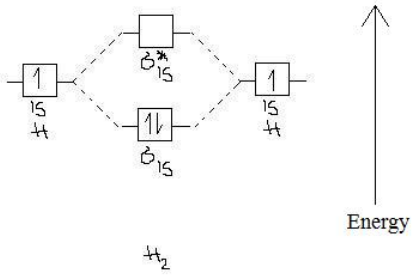


Figure 3: Schematic represenation of antibonding molecular orbital σ*(1s)

Note that there is a nodal plane in the anti-bonding MO.

Bond order

Bond order = 1/2 (#e- in bonding MO - #e- in antibonding MO)

For H_2, bond order = 1/2 (2-0) = 1, which means H_2has only one bond. The antibonding orbital is empty. Thus, H_2 is a stable molecule.

Again, in the MO, there is no unpaired electron, so H_2 is diamagnetic.

References

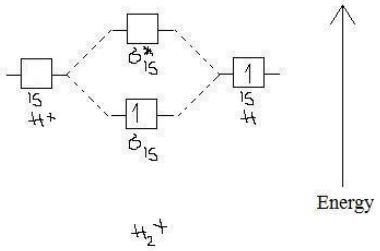
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Problems

1. What does the MO of H_2^+ look like? What is its bond order? What is its magnetic property? Explain.
2. What does the MO of H_2^- look like? What is its bond order? What is its magnetic property? Explain.
3. Which one is the most stable: H_2, H_2^+, or H_2^-? Why?
4. When a hydrogen atom accepts an electron, it becomes a hydride H^-. Theoretically would it be possible to form a molecule from two hydrides, that is to form H_2^{2-}? Why?

Answers:

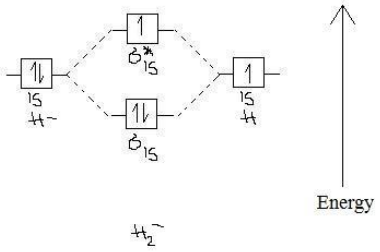
1-



Bond order = 1/2 (1-0) = 1/2

Paramagnetic because it has one unpaired e- in the σ(1s) orbital.

2-



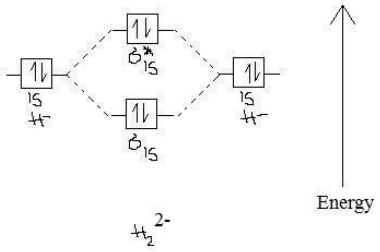
H_2^-

Bond order = 1/2 (2-1) = 1/2

Paramagnetic because it has one unpaired e- in the σ*(1s) orbital.

3- H_2 is the most stable because it has the highest bond order (1), in comparison with the bond orders (1/2) of H_2^+ and H_2^-.

4- Theoretically it would not be possible to form a molecule from two hydrides because the anti-bonding and bonding orbitals would cancel each other out. So, the bond order is zero. Because the antibonding ortibal is filled, it destabilizes the structure, making the "molecule" H_2^{2-} very non-stable.



H_2^{2-}

Bond order = 1/2 (2-2) = 0 ---> no bond formation. Thus, this molecule doesn't exist.

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SECTION OVERVIEW

2.4: The Octet Rule and Isoelectronic Species

Topic hierarchy

2.4.D: Periodic Trends

2.4A: The Octet Rule - First Row p-block Elements

2.4B: Isoelectronic Molecules

2.4C: The Octet Rule - Heavier p-block Elements

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2.4.D: Periodic Trends

Introduction

Trends across a period follow from the increasing number of protons in the nucleus and the decrease in radius. Both contributions can be explained by the change in **effective nuclear charge**.

Trends down a group follow from the increasing number of electron shells and the increased distance of the outer electrons from the nucleus. The major factor is the **increasing size**.

The properties of an element are largely determined by their electronic configurations, giving rise to recurring patterns or periodic behaviour. Examples are shown in the diagrams below including ionization energy, electron affinity, electronegativity and atomic radii. It is this periodicity of properties, manifestations of which were noticed well before the underlying theory was known, that led to the establishment of the periodic law (the properties of the elements recur at varying intervals) and the development of the first periodic tables. The modern periodic table is a tabular arrangement of the chemical elements, organized on the basis of their atomic number (number of protons in the nucleus), electronic configurations, and recurring chemical properties.

In the RSC Tutorial Chemistry Text on Main Group Chemistry, it notes that "When an element forms a chemical compound, electrons can be considered to be either lost, gained or shared with other atoms. These tendencies can be assessed by the parameters of ionization energy (IE), electron affinity (EA) and electronegativity (E). Prediction of bond types as either ionic or covalent then allows prediction of the chemical and physical properties of chemical substances."

So how are these parameters defined and how do they vary with atomic number?

Effective nuclear charge

The concept of the effective nuclear charge (often symbolized as Z_{eff} or Z^*) relates to the net positive charge experienced by an electron in a multi-electron atom. The term "effective" is used because the shielding effect of negatively charged inner electrons prevents higher orbital electrons from experiencing the full nuclear charge due to the repelling effect of the lower inner-layer electrons.

In an atom with one electron, that electron experiences the full charge of the positive nucleus. In this case, the effective nuclear charge can be calculated from Coulomb's law.

However, in an atom with many electrons the outer electrons are simultaneously attracted to the positive nucleus and repelled by the inner negatively charged electrons. The effective nuclear charge on such an electron is given by the following equation:

$Z_{eff} = Z - S$

where
Z is the number of protons in the nucleus (atomic number), and
S is the shielding calculated from the electrons between the nucleus and the electron in question. A systematic method for determining this is given by "Slater's rules".

These can be summarised as follows:
Arrange the electrons into a sequence of groups in order of increasing principal quantum number n, and for equal n in order of increasing azimuthal quantum number l, except that s- and p- orbitals are kept together.

[1s] [2s,2p] [3s,3p] [3d] [4s,4p] [4d] [4f] [5s, 5p] [5d] etc.

Any electron higher in the sequence to the electron under consideration contributes nothing to the shielding, S, and is ignored.

For an electron in an **ns or np** orbital:

0.35 comes from each other electron within the same group except for the [1s] group, where the other electron contributes only

0.30.

0.85 for each electron with principal quantum number n one less than that of the group, i.e (n-1) shell

1.00 for each electron with principal quantum number two or more less, i.e (n-2) etc. shell

For an electron in an **nd or nf** orbital:
0.35 comes from each other electron within the same group

1.00 for each electron "closer" to the atom than the group. This includes electrons with the same principal quantum number but in s or p orbitals.

In tabular form, the rules are summarized as:

Group	Other electrons in the same group	Electrons in group(s) with principal quantum number n and azimuthal quantum number < *l*	Electrons in group(s) with principal quantum number n-1	Electrons in all group(s) with principal quantum number < n-1
[1s]	0.30	-	-	-
[*n*s, *n*p]	0.35	-	0.85	1
[*n*d] or [*n*f]	0.35	1	1	1

Example 1.
Consider a sodium cation, Na^+, a fluorine anion, F^-, and a neutral neon atom, Ne. Each has 10 electrons, $1s^2\ 2s^2\ 2p^6$ so the shielding from the 1s and 2s/2p electrons is 2 * 0.85 + 7 * 0.35 = 4.15 but the effective nuclear charge varies because each has a different atomic number:

Z_{eff} F^- = 9 - 4.15 = 4.85
Z_{eff} Ne = 10 - 4.15 = 5.85
Z_{eff} Na^+ = 11 - 4.15 = 6.85

So the sodium cation has the largest effective nuclear charge, and can be expected to have the smallest radius.

Example 2.
Predict whether K would be more energetically stable with a configuration of
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{4s^1}$ or $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^1}$

For K, Z=19 and considering the 4s electron then the screening constant S can be calculated from:

S= (8 * 0.85) + (10 * 1.0) = 16.8

Z_{eff} = 19 - 16.8 = 2.2

For the 3d calculation of S:

S= (18 * 1.0) = 18

Z_{eff} = 19 - 18 = 1

Accordingly, an electron in the 4s (as opposed to the 3d) orbital would come under the influence of a greater effective nuclear charge in the ground state of potassium and so will be the orbital that is occupied.

Ionization Energy

The Ionization Energy (IE_n) of an element is defined as the internal energy change associated with the removal of an electron from the gaseous atom, E, in its ground state, i.e. at 0 K. The first IE is therefore the energy required for the reaction:

$E_{(g)} \rightarrow E^+_{(g)} + e^-$ energy required = IE

This energy change is generally considered equivalent to the enthalpy change at 298 K ($\Delta H_{298\ K}$). Estimates of the error suggest < 10 kJmol^{-1} which when compared to typical IE values often in their thousands, is insignificant.

The diagrams above show the variation in the values of the 1st five IE's as a function of Z up to Nd (60).

Features to note for **IE_1** are:

- the values associated with the noble gases are the highest in each period
- the values associated with the group 1 elements are generally the lowest in each period, (group 2 elements for the 2nd IE and group 3 for the 3rd IE etc.)
- the gradual increase in values across a given period (applies to $IE_{2\text{-}5}$ as well)
- the drop in values on going from an element in group 15 to its neighbour in group 16 e.g. for N-O, P-S, As-Se
- the drop in values on going from an element in group 2 or 12 to its neighbour in group 13, e.g. for Be-B, Mg-Al and Zn-Ga, Cd-In
- the rather similar values for a given row of d-block elements

These observations can be accounted for in terms of the effective nuclear charge since the further away from the positively charged nucleus that a negatively charged electron is located, the less strongly that electron is attracted to the nucleus and the more easily it can be removed. So, as the atomic radius decreases from left to right across the Period the 1st Ionization Energy increases.

Electron Affinity

The electron affinity(EA) of an element E is defined as minus the internal energy change associated with the gain of an electron by a gaseous atom, at 0 K :

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \tag{2.4.D.1}$$

Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be positive (energy is released when an electron is added), negative (energy must be added to the system to produce an anion), or zero (the process is energetically neutral).

Chlorine has the most positive electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element, EA= 348.6 kJmol^{-1} and the Group 17 elements have the largest values overall. The addition of a second electron to an element is expected to be much less favored since there will be repulsion between the negatively charged electron and the overall negatively charged anion. For example, for O the values are:

$$O_{(g)} + e^{\rightarrow} O^-_{(g)} \quad EA = +141\ kJmol^{-1} \tag{2.4.D.2}$$

$$O^-_{(g)} + e^- \rightarrow O^{2-})(g) \quad EA = -798\ kJmol^{-1} \tag{2.4.D.3}$$

Electronegativity

The concept of Electronegativity originated with Linus Pauling in the 1930's and was defined as **"the power of an atom in a molecule to attract electrons to itself"**.

The values proposed by Pauling were calculated based on differences in bond dissociation enthalpy values found when comparing homo-diatomic molecues with hetero-diatomic molecules. For example , the bond energy of chlorine monofluoride, ClF, is about 255 kJ mol^{-1} which is significantly greater than for either of the two homo-nuclear species Cl_2 and F_2 (242 and 153 kJ mol^{-1} respectively). Pauling attributed this to an electrostatic attraction between the partially charged atoms in the heternuclear species. That is the excess bond energy came from an ionic contribution to the bond.

The method of calculating the Pauling values is:

$D(XY) = [D(XX).D(YY)]^{1/2} + 96.48 * (\chi_Y - \chi_X)^2$ where the 96.48 factor means D values are in kJ mol^{-1}

In Housecroft and Sharpe the average, rather than geometric mean is used, and this is rearranged to give:

$\Delta D = D(XY) - \{½ * [D(XX) - D(YY)]\} = (\chi_Y - \chi_X)^2 = (\Delta\chi)^2$

or $\Delta\chi = \sqrt{(\Delta D)}$

As only differences in electronegativity were defined, it was necessary to choose an arbitrary reference point in order to construct a scale. Hydrogen was chosen as the reference, since it formed covalent bonds with a large variety of elements: its electronegativity was fixed at 2.20.

The **Mulliken scale** was calculated by taking the average of the Ionization Energy and the Electron Affinity (when both were given in units of eV).

$\chi^M = ½ (IE_1 + EA_1)$ where both IE_1 and EA_1 are in eV

A variant of this (2006) that converts the values to roughly the Pauling scale is:

$\chi^M = 0.00197 * (IE_1 + EA_1) + 0.19$ where IE_1 and EA_1 are now given in kJ mol^{-1}

The plots above indicate that while the absolute values are different, the trends are quite similar and the 2 curves are comparable when scaled appropriately.

The **Allred-Rochow scale** considered that electronegativity was related to the charge experienced by an electron on the "surface" of an atom: the higher the charge per unit area of atomic surface the greater the tendency of that atom to attract electrons. Their scale was dependent on Z_{eff} and inversely proportional to the square of the covalent radius, r_{cov}.

$\chi^{AR} = (3590 * Z_{eff} / r^2_{cov}) + 0.744$ where r_{cov} is in pm

The values range between 0 and 10. Once again a good correlation to the Pauling scale was found and this applies as well to other Electronegativity scales.

Atomic Radius

Have a look at an interactive visual display (JSmol) showing the periodic table of elements with atomic and ionic radii.

The atomic radius of a chemical element is a measure of the size of its atoms, usually the mean or typical distance from the center of the nucleus to the boundary of the surrounding cloud of electrons. Since the boundary is not a well-defined physical entity, there are various non-equivalent definitions of atomic radius. Three widely used definitions of atomic radius are Van der Waals radius, ionic radius, and covalent radius.

Covalent radius is defined as half the covalent bond length when the two atoms bonded are homonuclear (½ X-X bond).

van der Waals radius is defined as half of the internuclear separation of two non-bonded atoms of the same element on their closest possible approach.

It is not possible to measure the sizes of both metallic and nonmetallic elements using a single technique and method. To get values for comparison, theoretical quantum mechanical functions have been used instead to calculate atomic radii.

In the periodic table, atomic radii decrease from left to right across a period and increase from top to bottom down the groups. As a result of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper right corner.

The radius increases sharply between the noble gas at the end of each period and the alkali metal at the beginning of the next period. These trends of the atomic radii (and of various other chemical and physical properties of the elements) can be explained by the electron shell theory of the atom; they provided important evidence for the development and confirmation of quantum theory. The atomic radii decrease across the Periodic Table because as the atomic number increases, the number of protons increases across

the period, but the extra electrons are only added to the same quantum shell. Therefore, the effective nuclear charge towards the outermost electrons increases, drawing the outermost electrons closer. As a result, the electron cloud contracts and the atomic radii decreases.

The Lanthanide Contraction
The chart on the right above can be used to explain why Zirconium and Hafnium are two of the hardest elements in the Periodic Table to separate. In addition why the teaching of Transition Metal Chemistry is often covered in 2 courses since the properties of the first row elements are expected to be quite different to those of the second and third row.

Considering that the size of Gallium is smaller than Aluminium suggests that the 3d contraction is having an impact as well.

Ionic Radius

Although neither atoms nor ions have sharp boundaries, they are sometimes treated as if they were hard spheres with radii such that the sum of ionic radii of the cation and anion gives the distance between the ions in a crystal lattice.

Ions may be larger or smaller than the neutral atom, depending on the ion's charge. When an atom loses an electron to form a cation, the lost electron no longer contributes to shielding the other electrons from the charge of the nucleus; consequently, the other electrons are more strongly attracted to the nucleus, and the radius of the atom gets smaller. Similarly, when an electron is added to an atom, forming an anion, the added electron shields the other electrons from the nucleus, with the result that the size of the atom increases. Typical values range from 50 pm to over 220 pm.

Atomic and Ionic Radius Retrieved 24 November 2014
Return to the course outline or move on to Lecture 2: Polarizing power and polarizability, Anomalous behavior of row 2 elements.

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2.4A: The Octet Rule - First Row p-block Elements

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2.4B: Isoelectronic Molecules

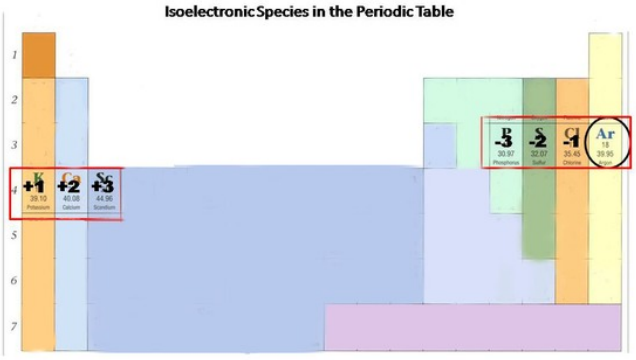


Figure 2 shows how Isoelectronic Species vary in atomic radii. Within a species, the radii differs depending on charge and shielding character of the electrons.

Isoelectronic Species Periodic Trends

The observation that isoelectronic species are usually isostructural, first made by Penny and Southerland in 1936, known as the isoelectronic principle (Geoff). Table 1 shows an example of isostructural isoelectronic species periodic trends. All of these molecules are octahedral and isoelectronic within their periods.

Isostructural Isoelectronic Species in Differeing Groups and Periods

Table 1	Group 13	Group 14	Group 15	Group 16	Group 17
Period 3	AlF_6^{3-}	SiF_6^{2-}	PF_6^-	SF_6	ClF_6^+
Period 4	GaF_6^{3-}	GeF_6^{2-}	AsF_6^-	SeF_6	BrF_6^+
Period 5	InF_6^{3-}	SnF_6^{2-}	SbF_6^-	TeF_6	IF_6^+

Other interesting trends appear in the periodic table including:

- Isoelectronic matricies--all isoelectronic species in a matrix defined by total electrons and valence electrons vary by progression in group number. For example, a 14 electron/10 valence electron diatomic matrix would have molecules such as CN^-, CO, and N_2.
- Isoelectronic arrays--an atom is replaced with another which alters the charge and continues the isoelectronic relationship. For example: BeF_4^{2-}, BF_4^-, and CF_4.

References

1. Smith, Michael, and Jerry March. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure.* Hoboken, NJ: Wiley-Interscience, 2007.
2. Rayner-Canham, Geoff. "Isoelectronic Series: a Fundamental Periodic Property." *Foundations of Chemistry* 11.2 (2009): 123-29.

Problems

1) Why is it important to understand the term "isoelectronic" and its trends throughout the periodic table?

2) Which isoelectronic species has the largest radius?

a. Mg2+ b.N3- c. O2- d. F-

3) Name 3 isostructural molecules

Answers:

1) Isoelectronic can help predict chemical reactions and interactions between molecules.

2) N3-

3) AlF_6^{3-}, SiF_6^{2-}, PF_6^-

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2.4C: The Octet Rule - Heavier p-block Elements

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SECTION OVERVIEW

2.5: Electronegativity Values

There are a few different 'types' of electronegativity which differ only in their definitions and the system by which they assign values for electronegativity. For example, there is Mulliken electronegativity which is defined as "the average of the ionization energy and electron affinity of an atom"[3], which as we will see, differs slightly from Pauling's definition of electronegativity.

Topic hierarchy

2.5A: Pauling Electronegativity Values

2.5B: Mulliken Electronegativity Values

2.5C: Allred-Rochow Electronegativity Values

2.5D: Electronegativity - final comments

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2.5A: Pauling Electronegativity Values

Linus Pauling described electronegativity as “the power of an atom in a molecule to attract electrons to itself.”[1] Basically, the electronegativity of an atom is a relative value of that atom's ability to attract election density toward itself when it bonds to another atom. The higher the electronegativity of an element, the more that atom will attempt to pull electrons towards itself and away from any atom it bonds to. The main properties of an atom dictate it's electronegativity are it's atomic number as well as its atomic radius. The trend for electronegativity is to increase as you move from left to right and bottom to top across the periodic table. This means that the most electronegative atom is Fluorine and the least electronegative is Francium.

There are a few different 'types' of electronegativity which differ only in their definitions and the system by which they assign values for electronegativity. For example, Mulliken electronegativity defines electronegativity as the "the average of the ionization energy and electron affinity of an atom."[3] As we will see, this definition differs slightly from Pauling's definition of electronegativity.

Pauling Electronegativity

Linus Pauling was the original scientist to describe the phenomena of electronegativity. The best way to describe his method is to look at a hypothetical molecule that we will call XY. By comparing the measured X-Y bond energy with the theoretical X-Y bond energy (computed as the average of the X-X bond energy and the Y-Y bond energy), we can describe the relative affinities of these two atoms with respect to each other.

$$\Delta\text{Bond Energies} = (X-Y)_{measured}–(X-Y)_{expected}$$

If the electonegativities of X and Y are the same, then we would expect the measured bond energy to equal the theoretical (expected) bond energy and therefore the Δ bond energies would be zero. If the electronegativities of these atoms are not the same, we would see a polar molecule where one atom would start to pull electron density toward itself, causing it to become partially negative.

By doing some careful experiments and calculations, Pauling came up with a slightly more sophisticated equation for the relative electronegativities of two atoms in a molecule:

$$EN(X) - EN(Y) = 0.102\sqrt{\Delta}.$$

In that equation, the factor 0.102 is simply a conversion factor between kJ and eV to keep the units consistent with bond energies.

By assigning a value of 4.0 to Fluorine (the most electronegative element), Pauling was able to set up relative values for all of the elements. This was when he first noticed the trend that the electronegativity of an atom was determined by it's position on the periodic table and that the electronegativity tended to increase as you moved left to right and bottom to top along the table. The range of values for Pauling's scale of electronegativity ranges from Fluorine (most electronegative = 4.0) to Francium (least electronegative = 0.7). [2] Furthermore, if the electronegativity difference between two atoms is very large, then the bond type tends to be more ionic, however if the difference in electronegativity is small then it is a nonpolar covalent bond.

? Exercise 2.5A.1

Explain the difference between Electronegativity and Electron Affinity

? Exercise 2.5A.2

Predict the order or increasing electronegativity from the following elements

a. F, Li, C, O
b. Te, Cl, S, Se
c. Cs, At, Tl, I

References

1. Zumdahl, Steven S. "Chemical Principles" 5th Edition. Houghton Mifflin Company 2005. Chapter 13.2 "Electronegativity" pgs. 587-590.
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3. International Union of Pure and Applied Chemistry. "Electronegativity". goldbook.iupac.org/E01990.html.

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2.5B: Mulliken Electronegativity Values

A method for estimating electronegativity was developed by Robert Mulliken (1896–1986; Nobel Prize in Chemistry 1966) who noticed that elements with large first ionization energies tend to have very negative electron affinities and gain electrons in chemical reactions. Conversely, elements with small first ionization energies tend to have slightly negative (or even positive) electron affinities and lose electrons in chemical reactions. Mulliken recognized that an atom's tendency to gain or lose electrons could therefore be described quantitatively by the average of the values of its first ionization energy and the absolute value of its electron affinity.

Robert S. Mulliken proposed that the arithmetic mean of the first ionization energy (E_{I_1}) and the electron affinity (E_{ea}) should be a measure of the tendency of an atom to attract electrons. As this definition is not dependent on an arbitrary relative scale, it has also been termed *absolute electronegativity.* Using our definition of electron affinity, we can write Mulliken's original expression for electronegativity as follows:Mulliken's definition used the magnitude of the ionization energy and the electron affinity. By definition, the magnitude of a quantity is a positive number. Our definition of electron affinity produces negative values for the electron affinity for most elements, so vertical lines indicating absolute value are needed in Equation 2.5B.1 to make sure that we are adding two positive numbers in the numerator.

$$\chi = \frac{|E_{I_1} + E_{ea}|}{2} \tag{2.5B.1}$$

Elements with a large first ionization energy and a very negative electron affinity have a large positive value in the numerator of Equation 2.5B.1, so their electronegativity is high. Elements with a small first ionization energy and a small electron affinity have a small positive value for the numerator in Equation 2.5B.1, so they have a low electronegativity. Inserting the appropriate data into Equation 2.5B.1 gives a Mulliken electronegativity value for fluorine of 1004.6 kJ/mol. To compare Mulliken's electronegativity values with those obtained by Pauling, Mulliken's values are divided by 252.4 kJ/mol, which gives Pauling's value (3.98).

However, it is more usual to use a linear transformation to transform these absolute values into values that resemble the more familiar Pauling values. For ionization energies and electron affinities in electronvolts:

$$\chi_{Mulliken} = 0.187(E_{I_1} + E_{ea}) + 0.17 \tag{2.5B.2}$$

and for energies in kJ/mol,

$$\chi_{Mulliken} = (1.97 \times 10^{-3})(E_{I_1} + E_{ea}) + 0.19 \tag{2.5B.3}$$

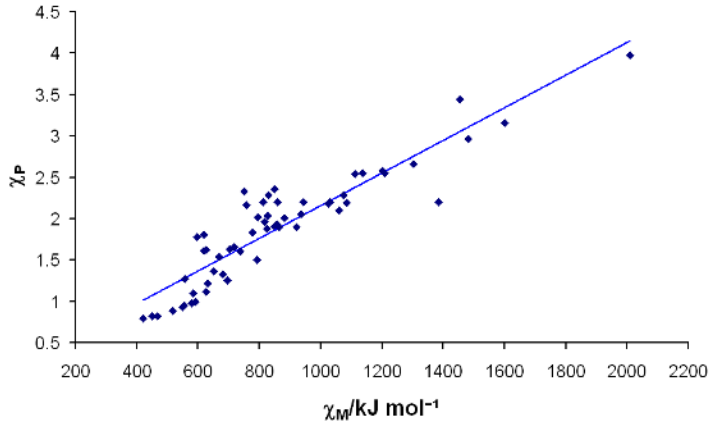
The Mulliken electronegativity can only be calculated for an element for which the electron affinity is known, fifty-seven elements as of 2006. The Mulliken electronegativity of an atom is sometimes said to be the negative of the chemical potential. By inserting the energetic definitions of the ionization potential and electron affinity into the Mulliken electronegativity, it is possible to show that the Mulliken chemical potential is a finite difference approximation of the electronic energy with respect to the number of electrons., i.e.,

$$\mu_{Mulliken} = -\chi_{Mulliken} = -\frac{E_{I_1} + E_{ea}}{2} \tag{2.5B.4}$$

All electronegativity scales give essentially the same results for one element relative to another. Even though the Mulliken scale is based on the properties of individual *atoms* and the Pauling scale is based on the properties of atoms in *molecules*, they both apparently measure the same basic property of an element. In the following discussion, we will focus on the relationship between electronegativity and the tendency of *atoms* to form positive or negative ions. We will therefore be implicitly using the Mulliken definition of electronegativity. Because of the parallels between the Mulliken and Pauling definitions, however, the conclusions are likely to apply to atoms in molecules as well.

Significance

Despite being developed from a very different set of principles than Pauling Electronegativity, which is based on bond dissociation energies, there is a good correlation between Mullikin and Pauling Electronegativities for the atoms, as shown in the plot below.



Although Pauling electronegativities are usually what are found in textbooks, the Mullikin electronegativity more intuitively corresponds to the "ability of an atom to draw electrons toward itself in bonding," and is probably a better indicator of that property. However, because of the good correlation between the two scales, using the Pauling scale is sufficient for most purposes.

References

1. Mulliken, R. S. (1934). "A New Electroaffinity Scale; Together with Data on Valence States and on Valence Ionization Potentials and Electron Affinities". Journal of Chemical Physics 2 (11): 782–793.
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5. This second relation has been recalculated using the best values of the first ionization energies and electron affinities available in 2006.

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2.5C: Allred-Rochow Electronegativity Values

Allred-Rochow Electronegativity is a measure that determines the values of the electrostatic force exerted by the effective nuclear charge on the valence electrons. The value of the effective nuclear charges is estimated from Slater's rules. The higher charge, the more likely it will attract electrons. Although, Slater's rule are partly empirical. So the Allred-Rochow electronegativity is no more rigid than the Pauling Electronegativity.

Electronegativity

Pauling established Electronegativity as the "power" of an atom in a molecule to attract electron to itself. It is a measure of the atom's ability to attract electron to itself while the electron is still attached to another atom. The higher the values, the more likely that atom can pull electron from another atom and into itself. Electronegativity correlates with bond polarity, ionization energy, electron affinity, effective nuclear charge, and atomic size.

Table 1: Pauling Electronegativity Values

H **2.1**																
Li **1.0**	Be **1.6**											B **2.0**	C **2.50**	N **3.0**	O **3.5**	F **4.0**
Na **0.9**	Mg **1.3**											Al **1.6**	Si **1.9**	P **2.2**	S **2.5**	Cl **3.0**
K **0.8**	Ca **1.3**	Sc **1.4**	Ti **1.5**	V **1.6**	Cr **1.7**	Mn **1.6**	Fe **1.8**	Co **1.9**	Ni **1.9**	Cu **1.9**	Zn **1.7**	Ga **1.6**	Ge **2.0**	As **2.2**	Se **2.6**	Br **2.8**
Rb **0.8**	Sr **1.0**	Y **1.2**	Zr **1.3**	Nb **1.6**	Mo **2.2**	Te **2.1**	Ru **2.2**	Rh **2.3**	Pd **2.2**	Ag **1.9**	Cd **1.7**	In **1.8**	Sn **2.0**	Sb **2.1**	Te **2.1**	I **2.7**
Cs **0.8**	Ba **0.9**	La **1.1**	Hf **1.3**	Ta **1.5**	W **1.7**	Re **1.9**	Os **2.2**	Ir **2.2**	Pt **2.2**	Au **2.4**	Hg **1.9**	Tl **2.0**	Pb **2.3**	Bi **2.0**	Po **2.0**	At **2.2**

The periodic trend for electronegativity generally increases from left to right and decreases as it go down the group. The exception are Hydrogen and the noble gases because the noble gases are content with their filled outermost shells, and hydrogen cannot bear to lose a valence electron unlike the rest of the group 1 metals. The elements in the halogen group usually have the highest electronegativity values because they only need to attract one valence electron to complete the octet in their outer shell. Whereas the group 1 elements except for Hydrogen, are willing to give up their only valence electron so they can fulfill having a complete, filled outer shell.

Slater's rules

Slater's rules are rules that provides the values for the effective nuclear charge concept, or Z_{eff}. These rules are based on experimental data for electron promotion and ionization energies, and Z_{eff} is determined from this equation:

$$Z_{eff} = Z - S \tag{2.5C.1}$$

where

- Z is the nuclear charge,
- Z_{eff} is the effective nuclear charge, and
- S is the shielding constant

Through this equation, this tells us that electron may get reduced nuclear charge due to high shielding. Allred and Rochow used Z_{eff} because it is accurate due to the involvement of shielding that prevents electron to reach its true nuclear charge: Z. When an atom with filled s-shell attracts electrons, those electrons will go to the unfilled p-orbital. Since the electrons have the same negative charge, they will not only repel each other, but also repel the electrons from the filled s-shell. This creates a shielding

effect where the inner core electrons will shield the outer core electrons from the nucleus. Not only would the outer core electrons experience effective nuclear charge, but it will make them easily removed from the outer shell. Thus, It is easier for outer electrons to penetrate the p shell, which has little likelihood of being near the nuclear, rather than the s shell. Consider this, each of the outer electron in the (ns, np) group contributes S = 0.35, S = 0.85 in the (n - 1) shell, and S = 1.00 in the (n - 2) or lower shells.

Example 1: Slater's Rules

What is the Z_{eff} for the 4s electrons in Ca.

Solution

Since Ca has atomic number of 20, $Z = 20$.

Then, we find the electron configuration for Ca, which is **$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$**.

Now we got that, we can use Slater's rules:

$$\begin{aligned} Z_{eff} &= Z - S \\ &= 20 - ((8 \times 0.85) + (10 \times 1.00)) \\ &= 3.2 \end{aligned}$$

So, Ca has a Z_{eff} of 3.2.

Allred-Rochow Electronegativity

Allred and Rochow were two chemists who came up with the Allred-Rochow Electronegativity values by taking the electrostatic force exerted by effective nuclear charge, Z_{eff}, on the valence electron. To do so, they came up with an equation:

$$\chi^{AR} = \left(\frac{3590 \times Z_{eff}}{r_{cov}^2} \right) + 0.744 \qquad (2.5C.2)$$

At the time, the values for the covalent radius, r_{cov}, were inaccurate. Allred and Rochow added certain perimeters so that it would more closely correspond to Pauling's electronegativity scale.

Table 2: Allred-Rochow Electronegativity Values

H **2.20**																
Li **0.97**	Be **1.47**											B **2.01**	C **2.50**	N **3.07**	O **3.50**	F **4.10**
Na **1.01**	Mg **1.23**											Al **1.47**	Si **1.74**	P **2.06**	S **2.44**	Cl **2.83**
K **0.91**	Ca **1.04**	Sc **1.20**	Ti **1.32**	V **1.45**	Cr **1.56**	Mn **1.60**	Fe **1.64**	Co **1.70**	Ni **1.75**	Cu **1.75**	Zn **1.66**	Ga **1.82**	Ge **2.02**	As **2.20**	Se **2.48**	Br **2.74**
Rb **0.89**	Sr **0.99**	Y **1.11**	Zr **1.22**	Nb **1.23**	Mo **1.30**	Te **1.36**	Ru **1.42**	Rh **1.45**	Pd **1.35**	Ag **1.42**	Cd **1.46**	In **1.49**	Sn **1.72**	Sb **1.82**	Te **2.01**	I **2.21**
Cs **0.86**	Ba **0.97**	La **1.08**	Hf **1.23**	Ta **1.33**	W **1.40**	Re **1.46**	Os **1.52**	Ir **1.55**	Pt **1.44**	Au **1.42**	Hg **1.44**	Tl **1.44**	Pb **1.55**	Bi **1.67**	Po **1.76**	At **1.90**

In this table, the electronegativities increases from left to right just like Pauling's scale because the Z is increasing. As we go down the group, it decreases because of the larger atomic size that increases the distance between the electrons and nucleus.

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3. Sarah Anderson. *Intro to Inorganic Chemistry*. University Science Books, September 2004.
4. Linus Pauling. *General Chemistry*. University Science Books, March 2002.
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Problems

1. From lowest to highest, order the elements in terms of Z_{eff}: Ni, Cu, Zn, Ga, Ge
2. Using the equations above, find the Z_{eff} for the Br by using Slater's rules.
3. Using the equations above, Find the X^{ar} for Br.

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2.5D: Electronegativity - final comments

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SECTION OVERVIEW

2.6: Dipole Moments

Topic hierarchy

2.6A: Polar Diatomic Molecules

2.6B: Molecular Dipole Moments

Template:HideTOC

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2.6A: Polar Diatomic Molecules

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2.6B: Molecular Dipole Moments

Molecular geometry and coordinates

Consider a diatomic molecule AB. Imagine fixing this molecule at a very specific spatial location, as shown below:

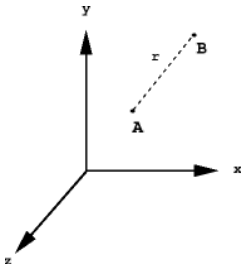


Figure 1

To locate the molecule so specifically, we would need to give the x, y, and z coordinates of each of its atoms, i.e.,

$$(x_A, y_A, z_A) = r_A$$
$$(x_B, y_B, z_B) = r_B$$

which is a total of 6 numbers.

However, we note that the molecule looks the same, no matter where in space it is located. This is called *translational invariance*, and it implies that we can give only the coordinates of one of the atoms *relative* to the other, which is equivalent to giving the vector difference between r_B and r_A (or vice-versa), which we will call the vector r:

$$r = r_B - r_A = (x, y, z)$$

which is only 3 numbers. This is the same as arbitrarily placing atom A at the origin of our xyz coordinate system.

We also note that the spatial orientation of the molecule is arbitrary, since the molecule looks the same at any viewing angle. For a diatomic, its orientation can be specified by giving two angles: the angle it makes with the z-axis and the angle of its projection onto the xy plane with the x-axis. The choice of these angles is arbitrary. This leaves only 1 number left, which is the distance between A and B, called the molecule's *bond length*.

$$\begin{aligned} r = |r| &= \sqrt{x^2 + y^2 + z^2} \\ &= |r_b - r_A| = \sqrt{(x_B - x_A)^2 + (y_B - y_A)^2 + (z_B - z_A)^2} \end{aligned}$$

This is an *internal degree of freedom* and is the only important number we need to give in order to convey the geometry of the diatomic.

In spite of this simplification, it is often necessary to specify *all* of the coordinates of the atoms in a molecule. Molecular modeling packages, which are becoming increasingly important in chemical research, require a full set of coordinates for each atom as input. Similarly, molecular data banks, such as the protein data bank (PDB) will give molecular structures as files of x, y, and z coordinates. Thus, being able to determine a set of coordinates given only bond lengths and bond angles, and conversely being able to determine bond lengths and angles from a set of coordinates is an extremely important skill. A few examples of how to do this will be illustrated below.

Example 1

The diatomic AB. How do we determine a set of coordinates for AB given only its bond length r. Since its absolute location in space and its orientation are arbitrary, any set of coordinates that reproduces the correct bond length will suffice. Thus, since a diatomic is linear, we may place it along one of the axes of our coordinate system with one of the atoms at the origin:

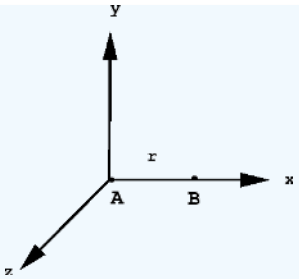


Figure 2

Now we see that the coordinates of atom A will simply be

$$r_A = (0, 0, 0)$$

and the coordinates of atom B, since B lies on the x-axis a distance r away from A, will be

$$r_B = (r, 0, 0)$$

Clearly, this set of coordinates reproduces the correct bond length:

$$|r_B - r_A| = \sqrt{r^2 + 0^2 + 0^2} = r$$

Thus, for the molecule HCl, whose bond length is $r = 1.284 \ \mathring{A}$, a set of coordinates could be

$$r_H = (0, 0, 0)$$
$$r_Cl = (1.284, 0, 0)$$

in $\mathring{A}$. This is just one possibility. We could have chosen either atom to be at the origin (or anywhere else in space for that matter), and chosen the bond to lie along any axis (or not along any particular axis), as we choose, so long as the correct bond length is reproduced.

Example 2

Water, H_2O: The geometry of water is bent (we will see how to determine this later), with a bond angle of 104.5° and an OH bond length of approximately $1.0 \ \mathring{A}$.

To determine a set of coordinates for H_2O, we note that the molecule is planar, so we may choose it to lie in the xy plane. We will place the oxygen at the origin with the hydrogens as shown below:

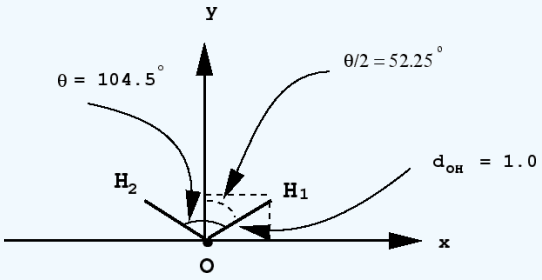


Figure 3

The coordinates of the oxygen can be written down immediately:

$$r_O = (0, 0, 0)$$

For each of the hydrogens, note that the y-axis bisects the angle, giving two right triangles. An OH bond forms the hypotenuse of one of these triangles, so that the x and y coordinates will be determined from the sine and cosine of the angle $\theta/2$, as can be shown using simple trigonometry:

$$r_{H_1} = (d_{OH} sin\theta/2, d_{OH} cos\theta/2, 0) = (0.7907, 0.6122, 0)$$
$$r_{H_2} = (-d_{OH} sin\theta/2, d_{OH} cos\theta/2, 0) = (-0.7907, 0.6122, 0)$$

To verify that the bond lengths are correctly reproduced, we compute the magnitudes of the vector differences $r_{H_1} - r_O$ and $r_{H_2} - r_O$:

$$|r_{H_1} - r_O| = \sqrt{(0.7907)^2 + (0.6122)^2 + 0^2} = 1.0 \ \mathring{A}$$
$$|r_{H_2} - r_O| = \sqrt{(0.7907)^2 + (0.6122)^2 + 0^2} = 1.0 \ \mathring{A}$$

In order to verify that the bond angle is correct, we note that the angle between two vectors a and b is given by the formula:

$$\theta_{ab} = cos^{-1}\left(\frac{a \cdot b}{|a||b|}\right)$$

where $a \cdot b$ is the *dot product* of a and b defined to be

$$a \cdot b = a_x b_x + a_y b_y + a_z b_z$$

Thus, the $H_1 - O - H_2$ angle is given by

$$\begin{aligned}\theta_{H_1-O-H_2} &= cos^{-1}\left(\frac{(r_{H_1} - r_O) \cdot (r_{H_2} - r_O)}{|r_{H_1} - r_O||r_{H_2} - r_O|}\right) \\ &= cos^{-1}\left(\frac{-(0.7907)^2 + (0.6122)^2}{1.0 * 1.0}\right) \\ &= cos^{-1}(-0.2504) = 104.5^\circ\end{aligned}$$

Periodic trends in bond lengths and bond energies

Within a group of the periodic table, bond lengths tend to increase with increasing atomic number Z. Consider the Group 17 elements:

$$\begin{aligned}&F_2 \quad d = 141.7 \ pm \\ &Cl_2 \quad d = 199.1 \, pm \\ &Br_2 \quad d = 228.6 \, pm \\ &I_2 \quad d = 266.9 \, pm\end{aligned}$$

which corresponds to an increased valence shell size, hence increased electron-electron repulsion. An important result from experiment, which has been corroborated by theory, is that bond lengths tend not to vary much from molecule to molecule. Thus, a CH bond will have roughly the same value in methane, CH_4 as it will in aspirin, $C_9H_8O_4$.

Bond dissociation energies were discussed in the last lecture in the context of ionic bonds. There we used the symbol ΔE_d measured in kJ/mol. This measures the energy required to break a mole of a particular kind of bond. A similar periodic trend exists for bond dissociation energies. Consider the hydrogen halides:

$$\begin{aligned}&HF \quad \Delta E_d = 565 \ kJ/mol \quad d = 0.926 \ pm \\ &HCl \quad \Delta E_d = 429 \ kJ/mol \quad d = 128.4 \ pm \\ &HBr \quad \Delta E_d = 363 \ kJ/mol \quad d = 142.4 \ pm \\ &HI \quad \Delta E_d = 295 \ kJ/mol \quad d = 162.0 \ pm\end{aligned}$$

Thus, as bond lengths increase with increasing Z, there is a corresponding decrease in the bond dissociation energy.

CC bonds are an exception to the the rule of constancy of bond lengths across different molecules. Because CC bonds can be single, double, or triple bonds, some differences can occur. For example, consider the CC bond in the molecules ethane (C_2H_6), ethylene (C_2H_4) and acetylene (C_2H_2):

$$\begin{aligned}&C_2H_6 \quad (single) \quad d = 1.536 \ \mathring{A} \quad \Delta E_d = 345 \ kJ/mol \\ &C_2H_4 \quad (double) \quad d = 133.7 \, pm \quad \Delta E_d = 612 \ kJ/mol \\ &C_2H_2 \quad (tirple) \quad d = 126.4 \, pm \quad \Delta E_d = 809 \ kJ/mol\end{aligned}$$

The greater the *bond order*, i.e., number of shared electron pairs, the greater the dissociation energy. The same will be true for any kind of bond that can come in such different ``flavors", e.g., NN bonds, OO bonds, NO bonds, CO bonds, etc.

Polar covalent bonds

Most real chemical bonds in nature are neither truly covalent nor truly ionic. Only homonuclear bonds are truly covalent, and nearly perfect ionic bonds can form between group I and group VII elements, for example, KF. Generally, however, bonds are partially covalent and partially ionic, meaning that there is partial transfer of electrons between atoms and partial sharing of electrons.

In order to quantify how much ionic character (and how much covalent character) a bond possesses, electronegativity differences between the atoms in the bond can be used. We have already seen one method for estimating atomic electronegativities, the Mulliken method. In 1936, Linus Pauling came up with another method that forms the basis of our understanding of electronegativity today.

Pauling's method

Recall the Mulliken's method was based on the arithmetic average of the first ionization energy IE_1 and the electron affinity EA. Both of these energies are properties of individual atoms, hence this method is appealing in its simplicity. However, there is no information about bonding in the Mulliken method. Pauling's method includes such information, and hence is a more effective approach.

To see how the Pauling method works, consider a diatomic AB, which is polar covalent. Let ΔE_{AA} and ΔE_{BB} be the dissociation energies of the diatomics A_2 and B_2, respectively. Since A_2 and B_2 are purely covalent bonds, these two dissociation energies can be used to estimate the pure covalent contribution to the bond AB. Pauling proposed the geometric mean of ΔE_{AA} and ΔE_{BB}, this being more sensitive to large differences between these energies than the arithmetic average:

$$pure\ covalent\ contribution = \sqrt{\Delta E_{AA}\Delta E_{BB}}$$

If ΔE_{AB} is the true bond dissociation energy, then the difference

$$\Delta E_{AB} - \sqrt{\Delta E_{AA}\Delta E_{BB}}$$

is a measure of the ionic contribution. Let us define this difference to be Δ:

$$\Delta = \Delta E_{AB} - \sqrt{\Delta E_{AA}\Delta E_{BB}}$$

Then Pauling defined the electronegativity difference $\chi_A - \chi_B$ between atoms A and B to be

$$\chi_A - \chi_B = 0.102\sqrt{\Delta}$$

where Δ is measured in kJ/mol, and the constant 0.102 has units $mol^{1/2}/kJ^{1/2}$, so that the electronegativity difference is dimensionless. Thus, with some extra input information, he was able to generate a table of atomic electronegativities that are still used today (Table A2).

To use the electronegativities to estimate degree of ionic character, simply compute the absolute value of the difference for the two atoms in the bond. As an example, consider again the hydrogen halides:

$$\begin{array}{ll} HF & |\chi_F - \chi_H| = 1.78 \\ HCl & |\chi_{Cl} - \chi_H| = 0.96 \\ HBr & |\chi_{Br} - \chi_H| = 0.76 \\ HI & |\chi_I - \chi_H| = 0.46 \end{array}$$

As the electronegativity difference decreases, so does the ionic character of the bond. Hence its covalent character increases.

Electric dipole moment

In a nearly perfect ionic bond, such as KF, where electron transfer is almost complete, representing the molecule as

$$K^+F^-$$

is a very good approximation, since the charge on the potassium will be approximately $1e$ and the charge on the fluorine will be approximately $-1e$. For a polar covalent bond, such as HF, in which only partial charge transfer occurs, a more accurate representation would be

$$H^{+\delta}F^{-\delta}$$

where δ, expressed in units of \(e\), is known as a *partial charge*. It suggests that a fraction of an electron is transferred, although the reality is that there is simply a little more electron density on the more electronegative atom and a little less on the electropositive atom.

How much charge is actually transferred can be quantified by studying the *electric dipole moment* of the bond, which is a quantity that can be measured experimentally. The electric dipole moment of an assembly of charges $Q_1, Q_2, ..., Q_N$ having positions $r_1, r_2, ..., r_N$ is defined to be

$$\mu = Q_1 r_1 + Q_2 r_2 + ... + Q_N r_N = \sum_{i=1}^{N} Q_i r_i$$

Thus, for a diatomic with charges $Q_1 = Q = \delta e$ and $Q_2 = -Q = -\delta e$ on atoms 1 and 2, respectively, the dipole moment, according to the definition, would be

$$\begin{aligned} \mu &= Q_1 r_1 + Q_2 r_2 \\ &= Q r_1 - Q r_2 \\ &= Q(r_1 - r_2) \end{aligned}$$

Hence, the magnitude of the dipole moment is

$$\mu = |\mu| = Q|r_1 - r_2| = QR$$

where R is the bond length. As an example, consider HF, which has a partial charge on H of $0.41e$, which means $\delta = 0.41$, and a bond length of $0.926 \ \mathring{A}$. Thus, the magnitude of the dipole moment is

$$|\mu| = 0.41(1.602 \times 10^{-19} C)(0.926 \times 10^{-10} m) = 6.08 \times 10^{-30} C \cdot m$$

Thus, the units of the dipole moment are Coulomb$\cdot$ meters. However, as this example makes clear, this is a very large unit and awkward to work with for molecules. A more convenient unit is the Debye (D), defined to be

$$1D = 3.336 \times 10^{-30} \text{ Coulomb} \cdot \text{meters}$$

$1\ D$ is actually the dipole moment of two charges $+e$ and $-e$ separated by a distance of $0.208\ \mathring{A}$. Thus, for a diatomic with partial charges $+\delta$ and $-\delta$, the dipole moment in D is given by

$$\mu(D) = \frac{\delta * R(\mathring{A})}{0.2082 \ \mathring{A}\ D^{-1}}$$

and the percent ionic character is defined in terms of the partial charge δ by

$$percent\ ionic\ character = 100\% * \delta$$

As an example, consider HF again, for which $\delta = 0.41$. The bond length is $R = 0.926 \ \mathring{A}$. Thus, its dipole moment will be

$$\mu(D) = \frac{0.41 * 0.926\ \mathring{A}}{0.2082 \ \mathring{A}\ D^{-1}} = 1.82D$$

and its percent ionic character is 41%.

Experimental importance of the dipole moment

The electric dipole moment lies at the heart of a widely used experimental method for probing the vibrational dynamics of a system. If a system is exposed to a monochromatic electromagnetic field from a laser, then the electric dipole moment couples to the electric field component $E(r,t)$ in such a way that the energy is

$$\mathcal{E} = -\mu \cdot \mathbf{E}(\mathbf{r}, t)$$

In general, the electric field is a function of space and time having the general wave form

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t)$$

where ω is the frequency of the field $\omega = 2\pi c/\lambda$, with c the speed of light and λ the wavelength, and k is called the wave vector, $|k| = 2\pi/\lambda$, and the direction of k is the direction of wave propagation (this will be covered in more detail next semester). In most experiments, the wavelength is long enough compared to the size of the system studied that one can take the electric field to be spatially constant and consider only the time dependence. In this case,

$$\mathcal{E} \approx -\mu \cdot E_0 cos(\omega t)$$

Thus, the electric field varies as a simple cosine function at a single frequency ω.

The importance of the coupling between the dipole moment and the time-dependent electric field is that the frequency of the field can be varied over a range of natural frequencies in a given chemical system. Thus, chemical bonds vibrate at a particular natural frequency, three-atom bending modes have their characteristic frequency, etc. What one seeks in this experiment is a ``report" of the natural frequencies in the system, since from such a report, one can often tell one local chemical environment from another.

By sweeping through a range of frequencies, the coupling of the field to the dipole moment suggests that the local charge distribution will respond to the oscillations of the field at the field frequency. Thus, if the field frequency is ``tuned" to be that of a bond stretch, the charge distribution in the bond will be stimulated and report on the frequency of the bond, etc. At each frequency, the intensity I of the response can be measured, and a plot of I vs. ω is produced. Such a plot is called an *infrared spectrum*. The figure below shows the infrared spectrum for liquid water (left) and for 13 M (blue) and 1 M (red) KOH solutions (right).



In the left panel, the solid curve is the water spectrum obtained from a computer simulation, while the dashed curve is the experimentally obtained spectrum. On the right, the red and blue curves are from computer simulations, while the inset at the upper right is the experimentally measured spectrum. The peaks in the spectra occur at particular vibrational frequencies in the system. The water spectrum shows very distinct bands, while the spectrum of the KOH solutions shows both bands and continuum regions. The latter arise from the fact that protons can be transferred from water to hydroxide. As the proton moves across a hydrogen bond between water and the hydroxide ion, the vibrations in the bond sweep through a range of frequencies as the proton is transferred, giving rise to the continuum. This feature in the infrared spectra of solutions of strong acids and bases is known as *Zundel polarization*. More information on how we compute these spectra and how the computer simulation are performed can be found in the following research papers:

- H. S. Lee and M. E. Tuckerman, *J. Chem. Phys.* **126**, 164501 (2007)
- Z. W. Zhu and M. E. Tuckerman, *J. Phys. Chem. B* **106**, 8009 (2002).

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SECTION OVERVIEW

2.7: MO Theory - Heteronuclear Diatomic Molecules

Topic hierarchy

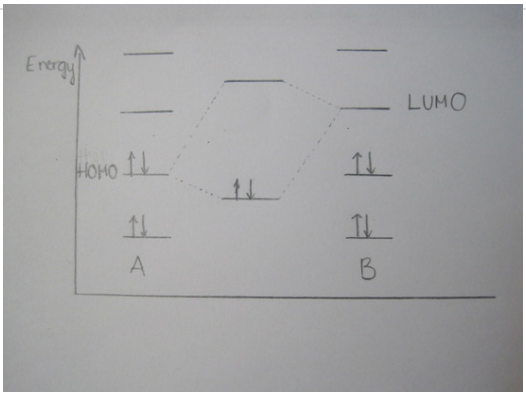
2.7A: MO Theory- Orbital Interactions

2.7B: Hydrogen Fluoride

2.7C: Carbon Monoxide

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2.7A: MO Theory- Orbital Interactions



picture 1

Factors affect the strength of orbital interaction:

References

1. Jean, Yvesand and Volatron, François. An Introduction to Molecular Orbitals. Oxford University Press. 11.03. 2005
2. McBride, J. M. “MO Interactions (HOMO/LUMO)”. 2001. 07 Oct 2010. <webspace.yale.edu/chem125_f0...o/homolumo.htm>
3. Housecroft, Catherine and Sharpe, Alan. Inorganic chemistry. 3rd edition. Prentice Hall. December 9, 2007

Outside Links

Problems

1, How do molecules orbitals form?

The formation of molecular orbitals is from the overlap of atomic orbitals; or more specific, from the wave interaction of atomic orbitals.

2, What are the factors that affect the orbital interaction?

There are some significant factors that affect the strength of orbital interaction

- Symmetry of the molecule orbital

- The difference between orbitals’ energies

- The orbitals' sizes

- The distance between orbitals

3, What are HOMO and LUMO? How do they interact in the molecule orbitals?

The highest energy occupied molecular orbital is called HOMO

The lowest energy unoccupied molecular orbital is called LUMO

These orbitals are a pair and they lie very close together in energy of two molecules. Therefore, the interaction between them is very strong.

4, What are the two types of electron waves interaction?

In-phase and out of phase interactions

5, How do the intensity of negative charge of electrons change in each types of of electron waves interaction?

The intensity of negative charge of electrons increases in the in-phase interaction and decreases in the out-of-phase interaction.

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2.7B: Hydrogen Fluoride

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SECTION OVERVIEW

2.8: Molecular Shape and the VSEPR Model

Topic hierarchy

2.8A: Valence-Shell Electron-Pair Repulsion Model

2.8B: Structures Derived from a Trigonal Bipyramid

2.8C: Limitations of the VSEPR Model

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2.8A: Valence-Shell Electron-Pair Repulsion Model

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2.8B: Structures Derived from a Trigonal Bipyramid

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2.8C: Limitations of the VSEPR Model

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SECTION OVERVIEW

2.9: Molecular Shape - Stereoisomerism

Topic hierarchy

2.9.1: Trigonal Bipyramidal Species

2.9.2: Trigonal Bipyramidal Structures

2.9A: Square Planar Species

2.9B: Octahedral Species

2.9D: High Coordination Numbers

2.9E: Double Bonds

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2.9.1: Trigonal Bipyramidal Species

Trigonal Bipyramidal Species are those that have a central p-block atom and are attached to 5 other atoms. It is classified as a EX5 molecule, where E stands for the central atom, and X stands for the atoms that are attached. It makes sense, then, to classify this molecule a 5-coordinate system. The VSEPR (valence shell electron pair repulsion) model is the what helps us identify how a molecule may or may not be trigonal bipyramidal.

Trigonal Bipyramidal Species

The central atom of the triognal bipyramidal species is bonded to 5 separate molecules. This means that the central atom must have an extended valence shell, in order to all for the 5 bonds to occur. The central atom is thus typically a p-block atom.

There are two different ways to classify the 5 X atoms, either as axial or equitorial. It is important to understand the difference between the two, so that we can reference them in future discussion.

The axial atoms are the ones above and below the central atom. These are the points of the 'pyramids' the molecule makes. (NOTE: Bipyramidal means two pyramids. If you look at a picture you should be able to see the pyramids relative to the top half and the bottom half of the central atom." The equatorial atoms are the ones that lie in the horizontal plane of the central atom. (Think of the equator relative to the Earth.)

Let us continue this discussion with the assumption that the EX5 is composed of just atoms (and *not* lone pairs). The bond angles between the equatorial atoms is 120 degrees. The bond angles between the axial and equitorial atoms is 90 degrees. The bond angles between the two axial atoms is 180 degrees. The angles formed by these atoms is the most stable conformation that can be maintained by the trigonal bipyramidal species.

Other Common Shapes for 5 Coordinate Molecules

As we have already discussed, when the central atom has 5 bonding pairs of electrons (those electrons being shared between two atoms), the shape of the molecule is trigonal bipyramidal. This section gives a little bit of information about how the shape of a molecule is affected when not all of the pairs of electrons are nonbonding.

Before that, however, it is important to discuss how bond angles are affected by lone pairs. According to VSEPR, electron-electron repulsion decreases in the following manner:

lone pair - lone pair > lone pair - bonding pair > bonding pair - bonding pair.

This means that presence of lone pairs will increase electron-electron repulsion, causing a change in the bond angles.

The first alternate shape for a 5 coordinate molecule, then, is where one of the bonding pairs of electrons is replaced with a lone pair. The best place for the lone pair to be is equatorial to the central atom. This allows for the least amount of electron-electron repulsion possible. This shape is called Seesaw.

The next possible shape is where there are two lone pairs on the central atom. Once again, the best place for these two molecules is equatorial to the central atom, for the least amount of electron repulsion to occur. This molecule is called T-shaped.

The last alternate shape for a 5 coordinate system is when there are three lone pairs. These are all equatorial to the central atom to establish the lowest energy conformation. This molecule is considered to be Linear.

Stereoisomers

Due to the fact that there are two possible types of X atoms (axial or equatorial) stereoisomers of trigonal bipyramidal species (with more than one type of A atom) are possible. If there are two different X atoms, then those atoms have the option of being *cis* or *trans* to each other. Meaning if one is axial, then the other can be equatorial (cis) or also axial (trans). Stereoisomers occur when two (or more) molecules with the same molecular formula have different molecular shapes.

References

1. Housecroft, Catherine E., and Alan G. Sharpe. *Inorganic Chemistry*. London: Pearson Education, 2008. Print.

2. Petrucci, Ralph H., et al. *General Chemistry: Principles and Modern Applications*. Upper Saddle River, NJ: Pearson Education, 2007. Print.

Outside Links

1. The Relationship Between the Number of Regions of Valence Electrons and the Molecular Geometry Around an Atom. Tutor-Page.com. 05 Nov. 2010. <www.tutor-pages.com/Chemistry..._Nonpolar.html>
2. Trigonal Bipyramidal Molecular Geometry. Wikipedia. 05 Nov. 2010. <http://en.Wikipedia.org/wiki/Trigona...cular_geometry>
3. Molecular Shape. Spark Notes. 05 Nov. 2010. <http://img.sparknotes.com/content/te...17002_0423.gif>

Problems

1. Explain why a trigonal bipyramidal molecule takes on the shape that it does.
2. What are the other possible shapes a 5-coordinate molecule can have? Give examples if possible.
3. What is a stereoisomer? Give an example using a trigonal bipyramidal molecule.

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2.9.2: Trigonal Bipyramidal Structures

Trigonal Bipyramidal electron configuration is part of the VSEPR model of an atom with 5 electron pairs.

Introduction

Trigonal Bipyramidal structures are electronic configurations of molecules. VSEPR gives us a handful of parent shapes. The one with 5 sets of bonded or non-bonded electrons.

Molecular Geometry of the Trigonal Bipyramidal Structures

Number of Lone pairs	Geometry	Bond Angles
0	Trigonal Bipyramidal	90 and 120
1	Seesaw	90 and 120
2	T-Shaped	90
3	Linear	180

The order of most repulsion to least repulsion among bonding and lone pair electrons are:

Lone pair-Lone pair > Lone pair-Bond pair > Bond pair-Bond pair

To decide where to place lone pairs on the parent Trigonal Bipyramidal structure, we must place lone pairs far away from each other and bond pairs. The seesaw shape maximizes the bond angles of the single lone pair and the other atoms in the molecule. The lone pair is in an equatorial position offering 120 and 90 degree bond angles, compared to only 90 degree bond angles if placed at the axial position.

The T shaped structure minimizes the remaining bond pair-bond pair angles at 90 degrees and maximizes the lone pair-lone pair bond angle at 120.

The linear structure does the same by making sure that the lone pairs are kept at a maximum of 120 degree bond angles. As a result, all are placed in the equatorial position, leaving room at the axial postion for the atoms. Thus, the bond angles of the atoms are 180 degrees from each other.

Stereoisomers

Since there are two types of atoms on a Trigonal Bipyramidal structure, axial and equatorial, there are different Stereoisomers that could arise depending on the substituents attached. For example, if there is 4 X atoms and 1 Y atom attached to the central atom, Y could either be in an equatorial position or in an axial position. If there are 3 X atoms and 2 Y atoms, then one Y atom could be placed in a equatorial position and the other in an axial position, or both Y atoms could be placed in the same position.

References

1. Housecroft, C.E., & Sharpe, A.G. (2008). *Inorganic chemistry*. Essex England: Pearson Education.
2. Petrucci, R.H., Harwood, W.S., Herring, F.G, & Madura, J.D. (2007). *General chemistry: principles and modern application*. Upper Saddle River, New Jersey: Pearson Education.

Problems

1. How would you arrange $SeCl4$?
2. How would you arrange $ArCl_2$?
3. How would you arrange $ICl_{3?}$

Contributors and Attributions

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2.9A: Square Planar Species

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2.9B: Octahedral Species

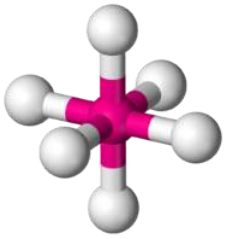
In inorganic chemistry, an octahedron is classified by its molecular geometry in which its distict shape is described as having six atoms, groups of atoms or electron pairs symmetrically arranged around one central atom, defining the vertices of an octahedron. The prefix *octa*, which means eight, comes from the fact that the molecule has eight symmetrical faces. All atoms are 90 degrees apart from one another, and 180 degrees apart from the atom, directly across and opposite from it. In regards to identifying each species, we will be looking at three separate unique shapes with different numbers of bond pairs and lone pairs. This allows us to distinguish and classifiy the octahedrals based on the following shapes: octahedral, square pyramidal, and square planar.

1. Introduction
2. Heading #2
3. References
4. Outside Links
5. Problems
6. Answers
7. Contributors and Attributions

Introduction

To be able to understand and distinguish the difference between the three types of octahedral species and how they differ from one molecule to the next, it is essential to try to visualize shapes geometrically and in 3D. A simple comprehension of geometry is required to be able to imagine molecules in 3D, as well as having basic background knowledge of the concept of bonding pairs and lone pairs. This allows one to recognize and see the difference in the molecular design for each individual molecule. We will begin by describing the design of an octahedral and then continue on to the next two molecules.

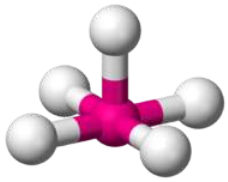
An octahedral is best described as a central atom symmetrically arranged by six other atoms. What makes this molecule different from other species is the fact that it is surrounded by six, either the same or different, atoms. There are six bonding pairs in this molecule and no lone electron pairs. The molecule below has no lone pairs of electrons surrounding it, thus allowing it to have a distinct shape. In a three dimensional sense, we may think of a x, y, and z coordinate plane having both its positive and negative coordinate systems. Another way of looking at it would be in the sense that all the faces of the molecule are present; through this reference, it resembles what would be a three dimensional prism. All the atoms are spread apart 90 degrees from each other and 180 from the atom directly across and opposite from it. The reson for the spacing is due to the molecule arranging itself in the most stable form possible, limiting the bond-pair to bond-pair interaction. Here is basic, but clear example of what an octahedral looks like:



Octahedral (6 bond pairs and 0 electron pairs)

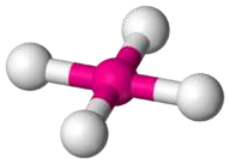
The next molecule that we will examine is known as a square pyramidal. This molecule has a lot of the same characteristics as that of an octahedral in the sense it consist of a central atom that is still symmetrically surrounded by six other atoms. What makes this molecule different from the previous molecule is the fact that this molecule does not consist of only bond-pair atoms surrounding it. There is one pair of electrons that has taken the place of one of the atoms and because these electrons are now present, it gives the molecule a distict new look. There are five bonding pairs and one electron pair. The atoms have to arrange themselves in the most stable form possible, not only limiting the bond-pair to bond-pair interaction, but also limiting the bond-pair to electron-pair interaction. The easiest way to visualize what this molecule looks like to visualize the x, y, and z coordinate plane again, but this time remove what would be considered the negative y coordinate axis and put a pair of lone pair electrons in its place. The

molecule is still considered apart of the octahedral species because it still satisfies the 6 atom requirement, but in terms of its shape, the electrons effect the shape. This allows it to have its new shape. If you actually exclude those electrons and lay the molecule on the surface, you can see that it looks like a three dimensional pyramid with a square base. Again all the atoms and electron pair are 90 degrees apart from each other and 180 from the atom directly across and opposite from it. Here is what a square pyramidal would look like:



Square Pyramidal (5 bond pairs and 1 electron pair)

The last of the octahedral species is known as a square planar. This molecule resembles both of the previous molecules, but more similarly resembles a square pyramidal. It still has many of the characteristics of a square pyramidal, but what makes it different is that rather than having only one pair of electrons replacing the position of an atom, there are two pairs of electrons that are replacing the position of two atoms. To visualize what this molecule looks like, we refer back to the x, y, and z coordinate system, the only difference is this time we are taking away the entire y coordinate, and replacing it with electrons on what would be the positive y coordinate axis as well as placing a pair of electrons in what would be considered the negative y coordinate axis. The reason for this arrangement goes back to having the molecule arrange itself in the most stable form possible limiting interactions between bond-pair to bond-pair, bond-pair to electron-pair, and electron-pair to electron-pair. If you try visualizing what this would look like, it almost resembles a three-dimensional "X" with two pairs of lone electrons. Because the lone pairs of electrons are still present, that allows this molecule to still be considered an octahedral due to the fact that it still meets the requirements of being surrounded by 6 atoms or groups. In regards to its shape the electron pairs cause repulsion, thus allowing it to have its new shape. The atoms and electrons are still 90 degrees apart from eachother and 180 degrees from the atom directly across and opposite from it. Here is what a square planar would look like:



Square Planar (4 bond pairs and 2 electron pairs)

Heading #2

Rename to desired sub-topic. You can delete the header for this section and place your own related to the topic. Remember to hyperlink your module to other modules via the link button on the editor toolbar.

References

1. Brown, Theodore L. *Chemistry: the Central Science.* 10th ed. Upper Saddle River, NJ: Pearson Prentice Hall, 2006. Print.
2. Housecroft, Catherine E., and Alan G. Sharpe. *Inorganic Chemistry*. 3rd ed. Harlow: Pearson Education, 2008. Print. (Pgs 51-52)

Outside Links

- Sample octahedral image adapted from Wikipedia key word octahedral geometry:*en.Wikipedia.org/wiki/**Octahedral**_molecular_**geometry***
- Sample square planar image adapted from Wikipedia key word square planar geometry:*en.Wikipedia.org/wiki/**Square_planar**_molecular_**geometry***
- Sample square pyramidal image adapted from Wikipedia key word square pyramidal geometry:*en.Wikipedia.org/.../**Square_pyramidal**_molecular_**geometry***

Problems

1. What causes the three different octahedral species to arrange the way they do? What conditions must be met?

2. Can two seperate electron-pair stand at 90 degrees apart from eachother? Why?

3. Give one example of a molecules that would fall into the category of a octehedral, square pyramidal, and square planar.

Answers

1. The molecules take the arrangment they do due to trying to arrange themselves in the most stable structure possible limiting the interaction between bond-pair and electron-pair interaction. As long as these conditions can be met, it is possible for the structure to not only exist, but remain stable.

2. This again goes back to satisfying the conditions of keeping the molecule as stable as possible by limiting lone-pair to lone -pair interaction as well as same sign interaction. Because electrons hold the same kind of charge, they can not be near eachother due to same charge repulsion and so they need to be as far away as possible from eachother so that the molecule may be stable.

3. Molecules that would fall into the category of triganol planar based on their molecular geometry would be SF6, a molecule that falls into the category of a square pyramidal would be BrF5 and one molecule that would fall into a category of a square planar would be [AuCl2]-.

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2.9D: High Coordination Numbers

Coordination numbers from 2 to 6 and the associated coordination complexes are very common, especially in transition metal chemistry. These complexes can take on a variety of geometries and each individual complex will have unique properties based on its substituents and their arrangement spatially. Though there is no set number of ligands, ions, or bound atoms required for a species to be considered "highly coordinated" versus general coordination, when the coordination number exceeds seven it is generally considered a high coordination number. High coordination numbers are of particular interest in solution phase and inorganic chemistry.

Introduction

The coordination number of a specified atom in a chemical species is the "number of other atoms directly linked to that specified atom."[1] Coordination itself is "the formation of a covalent bond, the two shared electrons of which have come from only one of the two parts of the molecular entity linked by it, as in the reaction of a Lewis acid and a Lewis base to form a Lewis adduct; alternatively, the bonding formed in this way."[2] Coordination number is a measure of one of two things:

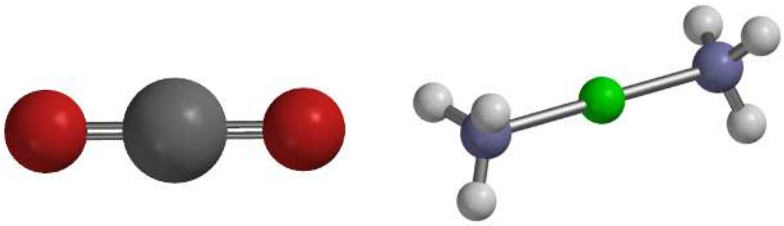
1. In a molecule, the coordination number is simply the number of bound atoms to that molecule.
2. For an ion the coordination number is the number of ions that are either associated to, or can associate with a given ionic species.
3. Coordination requires a sigma bond be present or available to be present, and so a pi bond does not contribute to the coordination number of a species.

Lower Coordination Numbers

Following are a few examples of more commonly encountered coordination numbers

Coordination Number 2

Coordination numbers of two are more common in organic molecules, or in non transition-metal containing species and relatively rare in transition metal containing species. Coordination numbers of two result in a linear or collinear spacial arrangement.

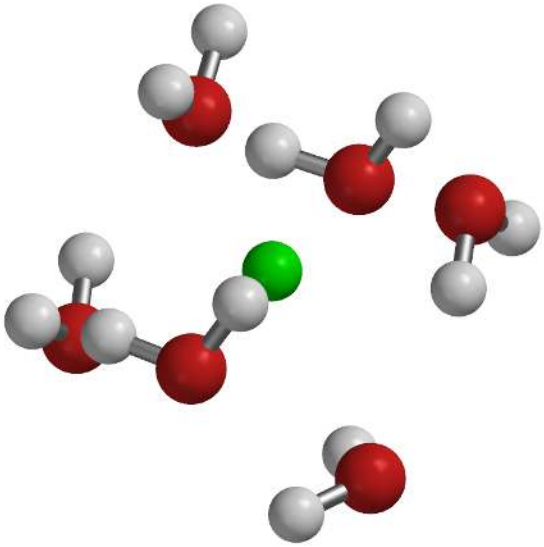


Carbon Dioxide, Coordination Number 2 $[Ag(NH_3)_2]^+$, Coordination Number 2

Coordination Number 6

Coordination number 6 is the most common coordination number, especially among transition metal containing species.[4]

Generally, the octahedron is the preferred coordination geometry. Other possible coordination geometries exist for coordination number six, such as trigonal prismatic.



$[Co(H_2O)_6)]^{3+}$, Coordination number 6

Higher Coordination

Higher coordination numbers; 7,8, 9, and above exist though they are less common.

Coordination Number 7

Seven coordinated atoms or molecules results in three main geometries:

- Pentagonal bipyramid
- Capped octahedron
- Capped trigonal prism

Coordination Number 8

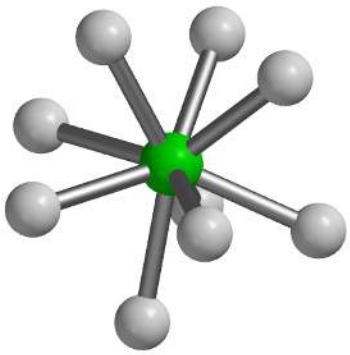
Eight coordinated atoms or molecules results in two main geometries:

- Square antiprism
- Dodecahedron

Coordination Number 9

The only structure yet identified for coordination number 9 systems is the tricrapt trigonal prism.

Two examples of these structures are $[ReH_9]^{2-}$ and $[TcH_9]^{2-}$ with the representative geometry shown below.



$[TcH_9]^{2-}$, Coordination number 9

Higher Coordination Numbers

Species exist with 10, 11, and 12 coordination numbers.

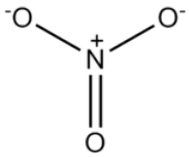
- Coordination numbers 10 and 11 are unique to complexes involving lanthanides and actinides. [4]
- Coordination number 12 has a structure that is involved in boron chemistry, the icosahedron.
- Coordination number 15 is the highest reported coordination number currently, being described for $[PbHe_{15}]^{2+}$[3]

References

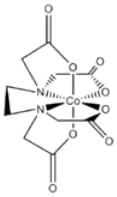
1. International Union of Pure and Applied Chemistry. "Coordination Number". *Compendium of Chemical Terminology* Internet edition.
2. International Union of Pure and Applied Chemistry. "Coordination". *Compendium of Chemical Terminology* Internet edition.
3. Hermann, A., Lein, M. and Schwerdtfeger, P. (2007), The Search for the Species with the Highest Coordination Number. Angewandte Chemie International Edition, 46: 2444–2447. doi: 10.1002/anie.200604148
4. Housecroft, Catherine E.; Sharpe, Alan G., *Inorganic Chemistry,* 3rd Ed. Pearson Education Limited 2008

Problems

1. What is the coordination number of the nitrate ion NO_3^-?



2. What is the coordination number around Co in this complex? How many different ligands are around Cobalt?



3. What coordination number do you expect $[Th(NO_3)_6]^{2-}$ to have? (Draw out a rough structure, remember lone pairs are required for coordination. What is the likely geometry for this?

Answers

1. Coordination number 3. Pi Bonds do not contribute to coordination number.
2. Coordination number 6. There is one ligand around Cobalt; EDTA is hexadentate.
3. Coordination number 12; Each NO_3^- ligand is bidentate. The likely geometry is icosahedral like other 12 coordination number species.

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- Brian Atwood (UC Davis)

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2.9E: Double Bonds

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CHAPTER OVERVIEW

3: Introduction to Molecular Symmetry

Topic hierarchy

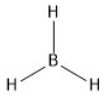
3.1: Introduction
3.2: Symmetry Operations and Elements
3.3: Successive Operations
3.4: Point Groups
3.5: Character Tables - An Introduction
3.6: Significance of Recognizing Symmetry Elements
3.7: Vibrational Spectroscopy
3.7A: Vibrational Spectroscopy
3.7C: Vibrational Spectroscopy of Linear and Bent triatomic Molecules
3.8: Chiral Molecules

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3.1: Introduction

Symmetry is important in the study of chemistry. It can be studied on both the molecular level and the crystalline level, of which the former will be discussed in this book.

A molecule is symmetrical if it stays in an indistinguishable configuration after some movement. For example, the molecule BH_3 in **3.1** can be rotated about an axis perpendicular to the screen and passes through the boron atom. If the rotation angle is 120°, the new configuration is indistinguishable from the original form.



3.1

The study of symmetry has many applications, some of which will be introduced in this chapter. Also in this chapter, some of the terminology and definitions used in group theory, the mathematical representation of symmetry, will be introduced.

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3.2: Symmetry Operations and Elements

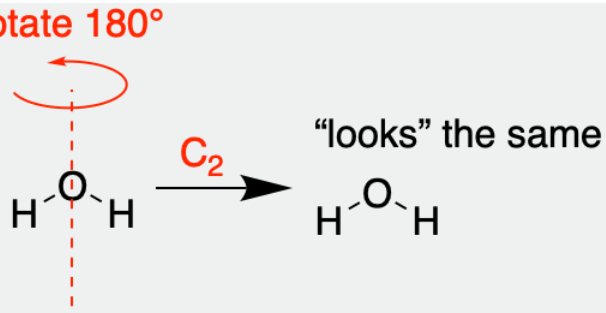


Figure 3.2.1: An example of a symmetry operation is a 180° rotation where the resulting position is indistinguishable from the original. A 180° rotation is called a C_2 operation; the axis of rotation is the symmetry element. (CC-BY-NC-SA; Kathryn Haas)

Introduction

The symmetry of a molecule consists of **symmetry operations** and **symmetry elements**. A symmetry operation is an operation that is performed to a molecule which leaves it indistinguishable and superimposable on the original position. Symmetry operations are performed with respect to symmetry elements (points, lines, or planes).

An example of a symmetry operation is a 180° rotation of a water molecule in which the resulting position of the molecule is indistinguishable from the original position (see Figure 3.2.1). In this example, the symmetry operation is the rotation and the symmetry element is the axis of rotation.

There are five types of symmetry operations including **identity**, **reflection**, **inversion**, **proper rotation**, and **improper rotation**. The improper rotation is the sum of a rotation followed by a reflection. The symmetry elements that correspond to the five types of symmetry operations are listed in Table 3.2.1.

Table 3.2.1: Table of elements and operations

Element	Operation	Symbol
Identity	identity	E
Proper axis	rotation by (360/n)°	C_n
Symmetry plane	reflection in the plane	σ
Inversion center	inversion of a point at (x,y,z) to (-x,-y,-z)	*i*
Improper axis	rotation by (360/n)°, followed by reflection in the plane perpendicular to the rotation axis	S_n

Symmetry Operations and Elements

Identity (E)

All molecules have the identity element. The identity operation is doing nothing to the molecule (it doesn't rotate, reflect, or invert...it just is).

Proper Rotation and Proper Axis (C_n)

A "proper" rotation is just a simple rotation operation about an axis. The symbol for any proper rotation or proper axis is $C_{(360/n)}$, where n is the degree of rotation. Thus, a 180° rotation is a C_2 rotation around a C_2 axis, and a 120° rotation is a C_3 rotation about a C_3 axis.

> **PRINCIPLE AXIS**: The principle axis of a molecule is the highest order proper rotation axis. For example, if a molecule had C_2 and C_4 axes, the C_4 is the principle axis.

Reflection and Symmetry Planes (σ)

Symmetry planes are mirror planes within the molecule. A reflection operation occurs with respect to a plane of symmetry. There are three classes of symmetry elements:

1. σ_h (horizontal): horizontal planes are perpendicular to principal axis
2. σ_v (vertical): vertical planes are parallel to the principal axis
3. σ_d (dihedral): dihedral planes are parallel to the principle axis and bisecting two C_2' axes

Inversion and Inversion Center (i)

The inversion operation requires a point of symmetry (a center of symmetry within a molecule). In other words, a point at the center of the molecule that can transform (x,y,z) into (-x,-y,-z) coordinate. Structures of tetrahedron, triangles, and pentagons lack an inversion center.

Improper rotation (S_n)

Improper rotation is a combination of a rotation with respect to an axis of rotation (C_n), followed by a reflection through a plane perpendicular to that C_n axis. In short, and S_n operation is equivalent to C_n followed by σ_h.

References

1. Introduction to Molecular Symmetry by J. S Ogden
2. Inorganic Chemistry by Catherine Housecroft And Alan G. Sharpe.

Problems

1. Water molecule H_2O was used as an example and was mentioned that water was rotated 180 degree around an axis bisecting the oxygen, then the molecule was superimposable on the original water molecule, how about CO_2? Is it going to be like the water molecule since CO_2 also has 2 atoms of oxygen.

Of course not, because every molecule has different molecular shape. To recognize the symmetry of any molecule the structure and the molecular shape of that molecule should be defined. The water molecule is bent but CO_2 is not, and if CO_2 is rotated 360 degree around the axis bisecting the C atom then it can be superimposed on the original molecule. We then see the symmetry for the CO_2.

2. Why should all of the five symmetry elements be done on a molecule in order to find the point group the molecule belongs to, why is performing only one or two of the symmetry elements not enough for recognizing the point group?

One or two of the symmetry elements will not be able to tell us everything about the molecule's symmetry since those one or two properties do not tell us everything about the molecule. Also, while different molecules may have one or two symmetrical properties in common, the five properties will not be the same for all molecules.

3. What does the symbol C_n stand for and what does n represent? Why is it important to identify n?

C is the axis of rotation and n is the order of the axis.

4. How are the character tables helpful?

The character table tells us about all the operational elements performed on the molecule and indicates if we have forgotten to perform any of the symmetry elements. The tables serve as a checklist because all the operational elements should be done on the molecule in order to find the point group of the molecule.

5. Why is important to find symmetry in molecules?

Symmetry tells us about bounding for that molecular bonding.

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3.3: Successive Operations

Sometimes, new symmetry operations form by carrying out two or more simpler operations successively to result in an indistinguishable configuration. For example, the improper rotation axis that was introduced in the last section results from rotation about an axis of rotation (C_n) followed by reflection about a plane perpendicular to that axis (σ_h).

$$S_n = C_n \times \sigma_h$$

Note also that C_n in this case need not be a symmetry element for the molecule. For example, staggered ethane has an S_6 symmetry element although it does not have a C_6. Another example of a symmetry element that results from a combination of two different elements is the inversion center (i), which results from a C_2 rotation followed by a reflection about a plane perpendicular to that axis (σ_h).

$$i = C_2 \times \sigma_h$$

Note that an inversion center is a special case of an improper rotation axis because it results when, in the first equation, $n = 2$. That is,

$$i = S_2$$

In fact, any symmetry operation can be carried out multiple time in a row. For example, when BH_3 is rotated twice by 120°, the two-step operation can be symboled by C_3^2. When the C_3 operation is performed a third time, the molecule returns to its original configuration; i.e,

$$C_3^3 = E$$

In general,

$$C_n^n = E$$

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3.4: Point Groups

Point groups are used to describe molecular symmetries and are a condensed representation of the symmetry elements a molecule may posses. This includes both bond and orbital symmetry. Knowing molecular symmetry allows for a greater understanding of molecular structure and can help to predict many molecular properties.

Introduction

Point groups are a quick and easy way to gain knowledge of a molecule. They not only contain a molecule's symmetry elements, but also give rise to a character table, which is a complete set of irreducible representations for a point group. A molecule's point group can be determined by either elucidating each symmetry element contained in a molecule or by properly using the Schreiber chart (see below).

Point groups usually consist of (but are not limited to) the following elements:

- E - The identity operator. This operation leaves a molecule completely unchanged and exists for mathematical purposes.
- C_n - The C_n proper axis of rotation is a 360/n° rotation that when performed leaves a molecule the same. A proper rotation with the highest value of n is known as the major axis of rotation.
- σ - The mirror plane. The mirror plane can be described as a plane which produces a reflection of part of a molecule that is unnoticeable and can be labeled as either σ_h , σ_v , σ_d.
- i - The inversion center. A molecule has a center of inversion if, when inverted, the molecule is unchanged.

See the section on symmetry elements for a more thorough explanation of each.

Each point group is associated with a specific combination of symmetry elements

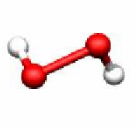
Each point group has it's own combination of symmetry elements. Listed below are some of the many point groups and their respective symmetry elements, according to category, followed by a representative example.

Non axial groups

C_1: E C_1: E, i

C_n groups

C_2: E, C_2 (notice the major axis of rotation is the point group) C_3: E, C_3, C_3^2



H_2O_2 C_2

D_n groups

D_2: E $C_2(z)$, $C_2(y)$, $C_2(x)$ D_3: E, $2C_3$, $3C_2$

C_{nv} groups

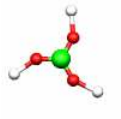
C_{2v}: E, C_2, $\sigma_v(xz)$, $\sigma_v'(yz)$ C_{3v}: E, $2C_3$, $3\sigma_v$



H_2O C_{2v}

C_{nh} groups

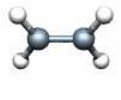
C_{2h}: E, C_2, i, σ_h C_{3h}: E, C_3, C_3^2, σ_h, S_3, S_3^3



$B(OH)_3$

D_{nh} groups

D_{2h}: E



C_2H_4 D_{2h}

How to determine a molecules point group

A molecule's point group can be determined by calculating all the symmetry elements of a molecule and matching them to a respective point group. This process, however, is greatly simplified when the Schreiber chart is used:

References

1. Housecroft, Catherine E.; Sharpe, Alan G., *Inorganic Chemistry*, 3rd Ed. Pearson Education Limited 2008, Chapter 4
2. Koster, George F.; Wheeler, Robert G.; Dimmock, John O., The Properties of Thirty-Two Point Groups, The MIT Press 1963
3. Bertolucci, Michael D.; Harris, Daniel C., Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy, Dover Publications 1989

Outside Links

- Point groups in 3-D

Problems

1. Determine the point group of BH_3 by calculating all it's symmetry elements then use the chart and determine which method is faster.
2. Determine the point groups of BH_3 and NH_3. Why is there a difference?
3. What is the point group of PPh_3?
4. Determine the point groups of CO_2 and H_2O and then compare them.
5. Propose a molecule with no symmetry. What is it's point group?

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3.5: Character Tables - An Introduction

Although the method of assigning a point group to a molecule depends on some knowledge of the symmetry elements the molecule has, it does not require the consideration of all elements. For example, the molecule CO_2 can be assigned the point group $D_{\infty h}$ using the scheme in section 3.4 by merely knowing that the molecule is linear and that it has the a center io inversion i. The point group assignment in this case did not require knowing that the molecule also has σ_h, for example. This type of knowledge is gained by examining character tables.

Definition

A character table is a table that contains the symmetry information of the molecule. This information can be used to analyze the molecule's behavior in many application, among which is spectroscopy. Each point group has its own character table. The following table is the character table of the point group C_{2v}:

Table 1: *The character table of the point group* C_{2v}.

C_{2v}	E	C_2 (z)	σ_v(xz)	σ_v(yz)	h = 4	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Understanding Character Tables

Symbols under the first column of the character tables

A (Mulliken Symbol)	(singly degenerate or one dimensional) symmetric with respect to rotation of the principle axis
B (Mulliken Symbol)	(singly degenerate or one dimensional) anti-symmetric with respect to rotation of the principle axis
E (Mulliken Symbol)	(doubly degenerate or two dimensional)
T (Mulliken Symbol)	(thirdly degenerate or three dimensional)
Subscript 1	symmetric with respect to the $C_n$principle axis, if no perpendicular axis, then it is with respect to σ_V
Subscript 2	anti-symmetric with respect to the $C_n$principle axis, if no perpendicular axis, then it is with respect to σ_V
Subscript g	symmetric with respect to the inverse
subscript u	anti-symmetric with respect to the inverse
prime	symmetric with respect to σ_h (reflection in horizontal plane)
double prime	anti-symmetric with respect to σ_h (opposite reflection in horizontal plane)

Symbols in the first row of the character tables

E	describes the degeneracy of the row (A and B= 1) (E=2) (T=3)
C_n	2pi/n= number of turns in one circle on the main axis without changing the look of a molecule (rotation of the molecule)
C_n'	2π/n= number of turns in one circle perpendicular to the main axis, without changing the structure of the molecule
C_n''	2π/n= number of turns in one circle perpendicular to the C_n' and the main axis, without changing the structure
σ'	reflection of the molecule perpendicular to the other sigma
σ_v (vertical)	reflection of the molecule vertically compared to the horizontal highest fold axis.
σ_h or $_d$ (horizontal)	reflection of the molecule horizontally compared to the horizontal highest fold axis.
i	Inversion of the molecule from the center
S_n	rotation of 2π/n and then reflected in a plane perpendicular to rotation axis.
#C_n	the # stands for the number of irreducible representation for the C_n
#σ	the # stands for the number irreducible representations for the sigmas.
the number in superscript	in the same rotation there is another rotation, for instance O_h has $3C_2=C_4^2$
other useful definitions	
(R_x,R_y)	the (,) means they are the same and can be counted once.
x^2+y^2, z^2	without (,) means they are different and can be counted twice.

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3.6: Significance of Recognizing Symmetry Elements

In the forgoing sections of this chapter, the necessary tools to assign a point group to a molecule and to be able to read a character table were introduced. A good question at this point is: What is the importance of these tools in inorganic chemistry?

In fact, there are many applications in the study of inorganic chemistry where these symmetry tools become handy. In general, these applications belong to one of the following categories:

- Understanding the spectroscopic properties of moelcules (introduced in section 3.7);
- Determining the chirality of molecular species (introduced in section 3.8);
- Constructing molecular and hybrid orbitals (Chapter 5).

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SECTION OVERVIEW

3.7: Vibrational Spectroscopy

Topic hierarchy

3.7A: Vibrational Spectroscopy

3.7C: Vibrational Spectroscopy of Linear and Bent triatomic Molecules

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3.7A: Vibrational Spectroscopy

All molecules are constantly vibrating, and can absorb energy from an incoming photon to increase their vibrations. The two types of vibrational spectroscopy are infrared spectroscopy and Raman spectroscopy. Vibrational spectroscopy is the science of measuring exactly which wavelengths of light are absorbed by a molecule. This technique could be used identify an unknown molecule by comparing its absorption to that of other molecules. Or vibrational spectroscopy could be used to gain further understanding of the physical properties of a known molecule.

Introduction

Molecular vibration can be modeled by balls attached by springs. Displacing an atom from its most stable position requires energy proportional to the displacement. IR spectroscopy can be used to characterize a molecule is the energy of its vibrations falls in the infrared range. Alternatively, higher energy light can be absorbed, the re-emitted at a different wavelength and/or in a different direction; this leads to Raman spectroscopy. So a molecule can absorb radiation to change bond lengths or positions with respect to the other atoms in the molecule.[3]

From the number, frequency, and intensity of these absorptions or emissions we can gain insight into the composition of the sample being measured. The number of different absorptions is indicative of the number of different atoms and shape of the molecule. The frequency or wavelength absorbed is indicative of the energy of the bonds and vibrations. And the intensity of the absorptions is related to the concentration of the analyte.[1]

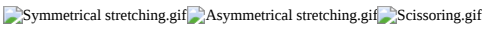
Vibrational Modes

The different possible vibrations are called vibrational modes. Vibrational modes are determined by all the different ways the atoms in the molecule can move with respect to eachother, called the vibrational degrees of freedom. Vibrational degrees of freedom differ from the total degrees of freedom in that translation (movement through space) and rotation do not contribute to the vibrational degrees of freedom.[4]

To find the number of vibrational modes one must first know the point group of the molecule. From there, the point group's character table will list all of the possible symmetry operations for the molecule. Each symmetry operation will leave some atoms in the molecule in place and/or move other atoms in the molecule. Count up the number of atoms that do not move for each symmetry operation, and multiply that number by the symmetry operation's contribution. This gives the total representation of atomic motion. From there, the vibrational modes can be found by reducing the total representation, according to the equation:

$$n=1/h*\Sigma XR*XI*N$$

where n is the number of modes with that symmetry, h is the total number of symmetry operations, X_I is the number of irreducible representations (the value calculated above), X_R is the number of reducible representations (the entry in the character table), and N is the number of identical symmetry operations. Finally, subtracting the rotational modes and translational modes from the reduced representation gives the number of vibrational modes.[6]



Three of the vibrational modes for the C_{2V} point group. Used with permission from http://en.Wikipedia.org/wiki/Infrared_spectroscopy

Infrared Spectroscopy

A vibrational mode will be observed in an infrared spectrum if it leads to a change in the molecular dipole moment. Compared to Raman spectroscopy, the infrared photon is completely absorbed and its energy is transfered to the vibration of the molecule, not re-emitted.[4]

Different bonds have different energies associated with them, and require different amounts of energy to stretch or bend. In general, the stronger the bond, the more energy required to deform it. So very weak bonds will only be deformed by low energy radiation, and strong bonds will only be deformed by high energy radiation. This leads to characteristic frequencies where only certain vibrations are absorbed. For example, C-H bonds are typically the only bonds observed in the range from 2960-2850 cm^{-1}. So if an absorption is present at that frequency, it can be assumed that it is due to a C-H bond.[1]

Raman Spectroscopy

A vibrational mode will be observed in Raman spectroscopy if it leads to a change in the polarizability of the electron cloud of a molecule.[4]

If a photon has energy that is significantly higher than the energy of the vibrational states, it may either be deflected without any change in energy, or it may interact with the molecule and either take energy from it or give energy to it.[2]

When the photon is absorbed and re-emitted in a different direction, it is called Rayleigh scattering, and this is strongly dependent on the wavelength of the incoming light. When there is a change in the energy of the photon, it is called Stokes scattering or anti-Stokes scattering, depending on whether energy is absorbed or lost by the molecule. This change in the behavior of the incoming photons can be measured, and will provide information about the concentration and chemical properties of the analyte.[3]

Diagram used with permission from http://en.Wikipedia.org/wiki/Raman_spectroscopy

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1. Jones, Llewellyn. *Inorganic Vibrational Spectroscopy*. 1. Los Alamos, New Mexico: Marcel Dekker, 1971. Print.
2. Steele, Derek. *Theory of Vibrational Spectroscopy*. Philadelphia: W. B. Saunders Company, 1971. Print.
3. Skoog, Douglas, James Holler, and Stanley Crouch.*Principles of Instrumental Analysis*. 6th. Belmont, California: Brooks/Cole, 2007. Print.
4. Housecroft, Catherine, and Alan Sharpe. *Inorganic Chemistry*. 3rd. New York: Pearson Prentice Hall, 2008. Print.
5. Ogden, J. S. *Introduction to Molecular Symmetry*. New York: Oxford University Press, Print.

Outside Links

- http://www2.ess.ucla.edu/~schauble/m...vibrations.htm
- http://www.webqc.org/symmetry.php
- www.ch.embnet.org/MD_tutorial/
- http://en.Wikipedia.org/wiki/Molecular_vibration
- http://en.Wikipedia.org/wiki/Raman_spectroscopy

Problems

1. Why is it that the symmetric stretch of carbon dioxide (CO_2) is IR inactive, while the symmetric stretch of carbonyl sulfide (COS) is IR active?

A: Because the symmetric stretch of CO_2 does not lead to a change in the dipole moment of the molecule, but the symmetric stretch of COS does.

2. How many vibrational modes are IR and Raman active for C_{20}?

A: 17 IR active modes, 29 Raman Active modes.

3. Are there any differences between the vibrational spectrums of H_2O, H_2S, and H_2Se?

A: Although they have the same number of atoms, the same point group, and the same number of vibrational modes, the frequencies at which the vibrational modes occur will be different.

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3.7C: Vibrational Spectroscopy of Linear and Bent triatomic Molecules

Vibrational spectroscopy, AKA Infrared (IR) Spectroscopy, is a highly useful and beneficial tool for determining structures and functional groups contained in compounds. Although used for many different structure types of polyatomic molecules, this particular Module is dedicated to triatomic molecules with bent and linear spacial molecular geometry.

Introduction

Triatomic molecules are molecules that contain three atoms. The atoms in triatomic molecules can all be the same, as in I_{3^-} all be different, as in HCN, or can be a mix like CO_2. Examples include H_2O, which is a bent and has a bond angle of 109º, and a linear triatomic molecule such as CO_2. All bent tri-atomic molecules belong to the point group C_{2v}, while all the liner tri-atomic molecules with an inversion center belong to the $D_{infinity\text{-}h}$ point group; Those without an inversion center belong to the point group $C_{infinity\text{-}v}$. This gives these two structures very different infrared spectrum even though they have the same number of atoms.

Linear molecules

Using VESPR theory there are several ways to achieve a linear structure. Tri-atomic molecules where the central atom is using ALL of its electrons in the bonds with the surrounding molecules, or in other words the central atom does not have any lone pairs surrounding it, will give rise to a linear molecule. Examples include CO_2 and BeH_3. This electronic configuration gives the central atom a sp hybridization. Triatomic molecules where the central atom does not use all of its electron pairs in the bonds between the other two atoms will, under certain circumstances, also give rise to a linear species. When the central atom is surrounded by three, or four lone pairs in addition to the two elements already attached will also give rise to a linear molecule. Examples include KrF_2.

Bent Molecules

There are also several ways to give rise to bent molecules using VESPR theory. A tri-atomic molecule with one, or two lone pair on the central atom will also give rise to bent species. One lone pair examples include SO_2, and two lone pair examples include H_2O

References

1. Volhardt and Schore. " Organic Chemistry: Structure and Function." 5th edition
2. Bruice, Paula, and Yukanis. "organic chemistry." 5th edition.

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3.8: Chiral Molecules

Introduction

Around the year 1847, the French scientist Louis Pasteur provided an explanation for the optical activity of tartaric acid salts. when he carried out a particular reaction, Pasteur observed that two types of crystals precipitated. Patiently and carefully using tweezers, Pasteur was able to separate the two types of crystals. Pasteur noticed that the types rotated the plane polarized by the same amount but in different directions. These two compounds are called enantiomers.

What are Enantiomers?

Two compounds are enantiomers if they are non-superimposable mirror images of each other. As was mentioned, enantiomers are characterized by their ability to rotate plane-polarized light. They also have the same physical properties (e.g., melting point, etc.) relative to each other. As a result, they are also referred to as being optically active. When it comes to symmetry, there are some general rules of thumb that help determine whether a molecule is chiral or achiral. This can be very useful because sometimes molecules can have relatively complicated structures and geometries that knowing whether or not they are chiral becomes a daunting task. The goal, as a result, is to determine the point group of the molecule and the symmetry elements associated with it, then inferring the chirality of the molecule.

Using Symmetry to Determine Chirality

For a molecule to be chiral, it must lack:

1. Center of inversion i and a plane of symmetry σ.
2. An improper rotation axis (rotation-reflection axis) S_n.

However, since, by definition, an improper rotation axis is a rotation about an certain axis followed by reflection about a plane perpendicular to that axis, and an inversion center is simply S_2, the absence of an improper axis requires, in most cases, that absence of both a plane of symmetry and an inversion center. As a result, it suffices, in most cases, to check for improper rotation axes to determine whether a molecule is chiral or not.

As a result of the previous discussion, there are a few classes of point groups that lack an improper axis. Those classes are C_1, C_n, and D_n. Cis-dichlorobis(ethylenediamine)cobalt (III) has two enantiomers that are chiral (figure 1), but the trans compound is achiral.

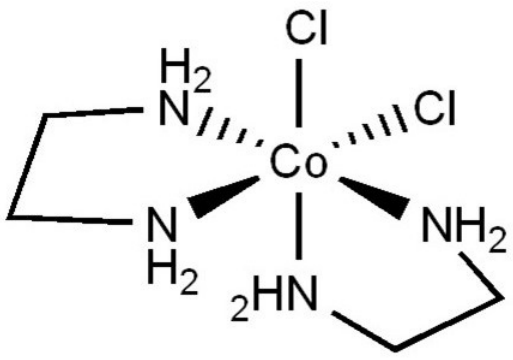


Figure 1: One of the chiral enantiomers of Cis-dichlorobis(ethylenediamine)cobalt (III).

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CHAPTER OVERVIEW

4: Experimental Techniques

Topic hierarchy

4.1: Introduction
4.2: Separation and Purification Techniques
4.2A: Gas Chromatography (GC)
4.2B: Liquid Chromatography (LC)
4.2C: High-Performance Liquid Chromatography (HPLC)
4.2D: Recrystallization
4.3: Elemental Analysis
4.3A: CHN Analysis by Combustion
4.3B: Atomic Absorption Spectroscopy (AAS)
4.4: Computational Analysis - Thermogravimetry (TG)
4.5: Mass Spectrometry
4.5A: Electron Ionization (EI)
4.5B: Fast Atom Bombardment (FAB)
4.5C: Matrix-Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF)
4.5D: Electrospray Ionization (ESI)
4.6: Infrared and Raman Spectroscopies
4.6A: Energies and Wavenumbers of Molecular Vibrations
4.6B: The Fourier Transform Infrared (FT-IR) Spectrometer and Sample Preparation
4.6C: Diagnostic Absorptions
4.6D: Deuterium/Hydrogen Exchange
4.6E: Raman Spectroscopy
4.7: Electronic Spectroscopy
4.7A: UV-VIS Absorption Spectroscopy
4.7B: Types of Absorption
4.7C: Absorbance and the Beer-Lambert Law
4.7D: Emission Spectroscopy
4.8: Nuclear Magnetic Resonance (NMR) Spectroscopy
4.8A: NMR Active Nuclei and Isotope Abundance
4.8B: Which Nuclei are Suitable for NMR Spectroscopic Studies
4.8C: Resonance Frequencies and Chemical Shifts
4.8D: Chemical Shift Ranges
4.8E: Solvents for Solution Studies
4.8F: Integration of Signals and Signal Broadening
4.8G: Homonuclear spin-spin coupling - \(^1H-^1H\)
4.8H: Heteronuclear spin-spin coupling - \(^{13}C-^1H\)
4.8I: Case Studies
4.8J: Stereochemically Non-Rigid Species

4.8K: Exchange Processes in Solution
4.9: Electron Paramagnetic Resonance (EPR) Spectroscopy
4.9A: What is EPR Spectroscopy?
4.9B: The Zeeman Electronic Effect
4.9C: EPR Spectra
4.10: Mossbauer Spectroscopy
4.10A: The Technique of Mossbauer Spectroscopy
4.10B: What Can Isomer Shift Data Tell Us?
4.11: Structure Determination - Diffraction Methods
4.11A: X-Ray Diffraction (XRD)
4.11B: Single Crystal X-Ray Diffraction
4.11C: Powder X-Ray Diffraction
4.11D: Single Crystal Neutron Diffraction
4.11E: Electron Diffraction
4.11F: Low-Energy Electron Diffraction (LEED)
4.11G: Structural Databases
4.12: Photoelectron Spectroscopy (PES, UPS, XPS, ESCA)
4.13: Computational Methods
4.13A: Hartree-Fock Theory
4.13B: Density Functional Theory
4.13C: Hückel MO Theory
4.13D: Molecular Mechanisms (MM)
4.14: Magnetism
4.14.1: example magnetic moment data and their interpretation
4.14.2: Magnetic Moments
4.14.3: Magnetic Moments 1
4.14.4: Magnetic Susceptibility Measurements
4.14.5: Magnetism

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SECTION OVERVIEW

4.2: Separation and Purification Techniques

Topic hierarchy

4.2A: Gas Chromatography (GC)

4.2B: Liquid Chromatography (LC)

4.2C: High-Performance Liquid Chromatography (HPLC)

4.2D: Recrystallization

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4.2A: Gas Chromatography (GC)

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4.2D: Recrystallization

Recrystallization

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SECTION OVERVIEW

4.3: Elemental Analysis

Topic hierarchy

4.3A: CHN Analysis by Combustion

4.3B: Atomic Absorption Spectroscopy (AAS)

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27.4A: Electronic Spectra and Magnetic Moments - Lanthanoids

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27.4C: Electronic Spectra and Magnetic Moments - Actinoids

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27.5A: Occurrence and Separation of the Lanthanoids

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27.5B: The Actinoids

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27.7A: Halides

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4.3A: CHN Analysis by Combustion

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27.7C: Complexes of Ln(III)

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27.8A: σ -Bonded Complexes

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27.8B: Cyclopentadienyl Complexes

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27.8C: Bis(arene) Derivatives

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27.8D: Complexes Containing the η 8 -cyclooctatetraenyl Ligand

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27.9: The Actinoid Metals

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27.10A: Thorium

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4.3B: Atomic Absorption Spectroscopy (AAS)

Guystav Kirchoff and Robert Bunsen first used atomic absorption spectroscopy—along with atomic emission—in 1859 and 1860 as a means for identify atoms in flames and hot gases. Although atomic emission continued to develop as an analytical technique, progress in atomic absorption languished for almost a century. Modern atomic absorption spectroscopy has its beginnings in 1955 as a result of the independent work of A. C. Walsh and C. T. J. Alkemade.[13] Commercial instruments were in place by the early 1960s, and the importance of atomic absorption as an analytical technique was soon evident.

10.4.1 Instrumentation

Atomic absorption spectrophotometers use the same single-beam or double-beam optics described earlier for molecular absorption spectrophotometers (see Figure 10.26 and Figure 10.27). There is, however, an important additional need in atomic absorption spectroscopy—we must covert the analyte into free atoms. In most cases our analyte is in solution form. If our sample is a solid, then we must bring it into solution before the analysis. When analyzing a lake sediment for Cu, Zn, and Fe, for example, we bring the analytes into solution as Cu^{2+}, Zn^{2+}, and Fe^{3+} by extracting them with a suitable reagent. For this reason, only the introduction of solution samples is considered in this text.

> What reagent we choose to use depends on our research goals. If we need to know the total amount of metal in the sediment, then we might use a microwave digestion using a mixture of concentrated acids, such as HNO_3, HCl, and HF. This destroys the sediment's matrix and brings everything into solution. On the other hand, if our interest is biologically available metals, we might extract the sample under milder conditions, such as a dilute solution of HCl or CH_3COOH at room temperature.

Atomization

The process of converting an analyte to a free gaseous atom is called **atomization**. Converting an aqueous analyte into a free atom requires that we strip away the solvent, volatilize the analytes, and, if necessary, dissociate the analyte into free atoms. Desolvating an aqueous solution of $CuCl_2$, for example, leaves us with solid particulates of $CuCl_2$. Converting the particulate $CuCl_2$ to gas phases atoms of Cu and Cl requires thermal energy.

$$\mathrm{CuCl_{2(aq)} \rightarrow CuCl_{2(s)} \rightarrow Cu_{(g)} + 2\,Cl_{(g)}} \tag{4.3B.1}$$

There are two common atomization methods: flame atomization and electrothermal atomization, although a few elements are atomized using other methods.

Flame Atomizer

Figure 10.42 shows a typical flame atomization assembly with close-up views of several key components. In the unit shown here, the aqueous sample is drawn into the assembly by passing a high-pressure stream of compressed air past the end of a capillary tube immersed in the sample. When the sample exits the nebulizer it strikes a glass impact bead, converting it into a fine aerosol mist within the spray chamber. The aerosol mist is swept through the spray chamber by the combustion gases—compressed air and acetylene in this case—to the burner head where the flame's thermal energy desolvates the aerosol mist to a dry aerosol of small, solid particles. The flame's thermal energy then volatilizes the particles, producing a vapor consisting of molecular species, ionic species, and free atoms.

> Compressed air is one of the two gases whose combustion produces the flame.

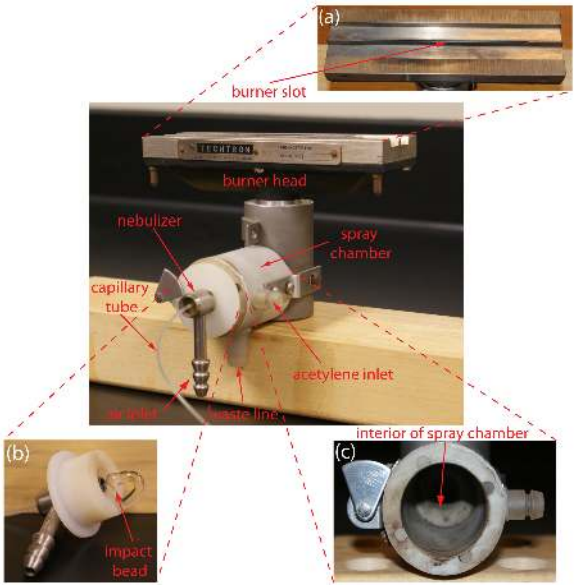


Figure 10.42 *Flame atomization assembly with expanded views of (a) the burner head showing the burner slot where the flame is located; (b) the nebulizer's impact bead; and (c) the interior of the spray chamber. Although the unit shown here is from an older instrument, the basic components of a modern flame AA spectrometer are the same.*

Burner. The slot burner in Figure 10.42a provides a long optical pathlength and a stable flame. Because absorbance increases linearly with the path length, a long path length provides greater sensitivity. A stable flame minimizes uncertainty due to fluctuations in the flame.

The burner is mounted on an adjustable stage that allows the entire assembly to move horizontally and vertically. Horizontal adjustments ensure that the flame is aligned with the instrument's optical path. Vertical adjustments adjust the height within the flame from which absorbance is monitored. This is important because two competing processes affect the concentration of free atoms in the flame. The more time the analyte spends in the flame the greater the atomization efficiency; thus, the production of free atoms increases with height. On the other hand, a longer residence time allows more opportunity for the free atoms to combine with oxygen to form a molecular oxide. For an easily oxidized metal, such as Cr, the concentration of free atoms is greatest just above the burner head. For metals, such as Ag, which are difficult to oxidize, the concentration of free atoms increases steadily with height (Figure 10.43). Other atoms show concentration profiles that maximize at a characteristic height.

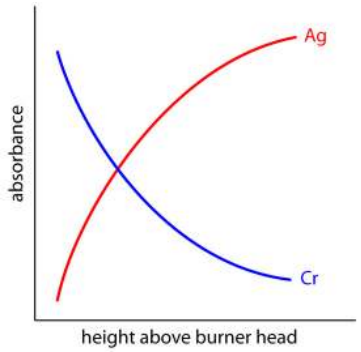


Figure 10.43 *Absorbance versus height profiles for Ag and Cr in flame atomic absorption spectroscopy.*

Flame. The flame's temperature, which affects the efficiency of atomization, depends on the fuel–oxidant mixture, several examples of which are listed in Table 10.9. Of these, the air–acetylene and the nitrous oxide–acetylene flames are the most popular. Normally the fuel and oxidant are mixed in an approximately stoichiometric ratio; however, a fuel-rich mixture may be necessary for easily oxidized analytes.

Table 10.9 *Fuels and Oxidants Used for Flame Combustion*

fuel	oxidant	temperature range (°C)
natural gas	air	1700–1900
hydrogen	air	2000–2100
acetylene	air	2100–2400
acetylene	nitrous oxide	2600–2800
acetylene	oxygen	3050–3150

Figure 10.44 shows a cross-section through the flame, looking down the source radiation's optical path. The primary combustion zone is usually rich in gas combustion products that emit radiation, limiting is usefulness for atomic absorption. The interzonal region generally is rich in free atoms and provides the best location for measuring atomic absorption. The hottest part of the flame is typically 2–3 cm above the primary combustion zone. As atoms approach the flame's secondary combustion zone, the decrease in temperature allows for formation of stable molecular species.

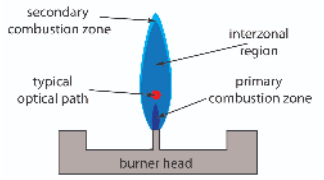


Figure 10.44 *Profile of typical flame using a slot burner. The relative size of each zone depends on many factors, including the choice of fuel and oxidant, and their relative proportions.*

Sample Introduction. The most common means for introducing samples into a flame atomizer is a continuous aspiration in which the sample flows through the burner while we monitor the absorbance. Continuous aspiration is sample intensive, typically requiring from 2–5 mL of sample.

Flame microsampling allows us to introduce a discrete sample of fixed volume, and is useful when we have a limited amount of sample or when the sample's matrix is incompatible with the flame atomizer. For example, continuously aspirating a sample that has a high concentration of dissolved solids—sea water, for example, comes to mind—may build-up a solid deposit on the burner head that obstructs the flame and that lowers the absorbance. Flame microsampling is accomplished using a micropipet to place 50–250 µL of sample in a Teflon funnel connected to the nebulizer, or by dipping the nebulizer tubing into the sample for a short time. Dip sampling is usually accomplished with an automatic sampler. The signal for flame microsampling is a transitory peak whose height or area is proportional to the amount of analyte that is injected.

Advantages and Disadvantages of Flame Atomization. The principal advantage of flame atomization is the reproducibility with which the sample is introduced into the spectrophotometer. A significant disadvantage to flame atomizers is that the efficiency of atomization may be quite poor. There are two reasons for poor atomization efficiency. First, the majority of the aerosol droplets produced during nebulization are too large to be carried to the flame by the combustion gases. Consequently, as much as 95% of the sample never reaches the flame. A second reason for poor atomization efficiency is that the large volume of combustion gases significantly dilutes the sample. Together, these contributions to the efficiency of atomization reduce sensitivity because the analyte's concentration in the flame may be a factor of 2.5×10^{-6} less than that in solution.[14] This is the reason for the waste line shown at the bottom of the spray chamber in Figure 10.42.

Electrothermal Atomizers

A significant improvement in sensitivity is achieved by using the resistive heating of a graphite tube in place of a flame. A typical electrothermal atomizer, also known as a **graphite furnace**, consists of a cylindrical graphite tube approximately 1–3 cm in length and 3–8 mm in diameter. As shown in Figure 10.45, the graphite tube is housed in an sealed assembly that has optically transparent windows at each end. A continuous stream of an inert gas is passed through the furnace, protecting the graphite tube from oxidation and removing the gaseous products produced during atomization. A power supply is used to pass a current through the graphite tube, resulting in resistive heating.

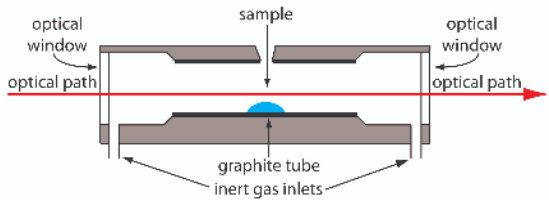


***Figure 10.45**: Diagram showing a cross-section of an electrothermal analyzer.*

Samples of between 5–50 μL are injected into the graphite tube through a small hole at the top of the tube. Atomization is achieved in three stages. In the first stage the sample is dried to a solid residue using a current that raises the temperature of the graphite tube to about 110°C. In the second stage, which is called ashing, the temperature is increased to between 350–1200°C. At these temperatures any organic material in the sample is converted to CO_2 and H_2O, and volatile inorganic materials are vaporized. These gases are removed by the inert gas flow. In the final stage the sample is atomized by rapidly increasing the temperature to between 2000–3000°C. The result is a transient absorbance peak whose height or area is proportional to the absolute amount of analyte injected into the graphite tube. Together, the three stages take approximately 45–90 s, with most of this time used for drying and ashing the sample.

Electrothermal atomization provides a significant improvement in sensitivity by trapping the gaseous analyte in the small volume within the graphite tube. The analyte's concentration in the resulting vapor phase may be as much as 1000× greater than in a flame atomization.[15] This improvement in sensitivity—and the resulting improvement in detection limits—is offset by a significant decrease in precision. Atomization efficiency is strongly influenced by the sample's contact with the graphite tube, which is difficult to control reproducibly.

Miscellaneous Atomization Methods

A few elements may be atomized by a chemical reaction that produces a volatile product. Elements such as As, Se, Sb, Bi, Ge, Sn, Te, and Pb, for example, form volatile hydrides when reacted with $NaBH_4$ in acid. An inert gas carries the volatile hydrides to either a flame or to a heated quartz observation tube situated in the optical path. Mercury is determined by the cold-vapor method in which it is reduced to elemental mercury with $SnCl_2$. The volatile Hg is carried by an inert gas to an unheated observation tube situated in the instrument's optical path.

10.4.2 Quantitative Applications

Atomic absorption is widely used for the analysis of trace metals in a variety of sample matrices. Using Zn as an example, atomic absorption methods have been developed for its determination in samples as diverse as water and wastewater, air, blood, urine, muscle tissue, hair, milk, breakfast cereals, shampoos, alloys, industrial plating baths, gasoline, oil, sediments, and rocks.

Developing a quantitative atomic absorption method requires several considerations, including choosing a method of atomization, selecting the wavelength and slit width, preparing the sample for analysis, minimizing spectral and chemical interferences, and selecting a method of standardization. Each of these topics is considered in this section.

Developing a Quantitative Method

Flame or Electrothermal Atomization? The most important factor in choosing a method of atomization is the analyte's concentration. Because of its greater sensitivity, it takes less analyte to achieve a given absorbance when using electrothermal atomization. Table 10.10, which compares the amount of analyte needed to achieve an absorbance of 0.20 when using flame atomization and electrothermal atomization, is useful when selecting an atomization method. For example, flame atomization is the method of choice if our samples contain 1–10 mg Zn^{2+}/L, but electrothermal atomization is the best choice for samples containing 1–10 μg Zn^{2+}/L.

***Table 10.10:** Concentration of Analyte Yielding an Absorbance of 0.20*

	Concentration (mg/L)[a]

	Concentration (mg/L)[a]	
element	flame atomization	electrothermal atomization
Ag	1.5	0.0035
Al	40	0.015
As	40[b]	0.050
Ca	0.8	0.003
Cd	0.6	0.001
Co	2.5	0.021
Cr	2.5	0.0075
Cu	1.5	0.012
Fe	2.5	0.006
Hg	70[b]	0.52
Mg	0.15	0.00075
Mn	1	0.003
Na	0.3	0.00023
Ni	2	0.024
Pb	5	0.080
Pt	70	0.29
Sn	50[b]	0.023
Zn	0.3	0.00071

[a] Source: Varian Cookbook, SpectraAA Software Version 4.00 Pro.

[b] As: 10 mg/L by hydride vaporization; Hg: 11.5 mg/L by cold-vapor; and Sn:18 mg/L by hydride vaporization

Selecting the Wavelength and Slit Width. The source for atomic absorption is a hollow cathode lamp consisting of a cathode and anode enclosed within a glass tube filled with a low pressure of Ne or Ar (Figure 10.46). Applying a potential across the electrodes ionizes the filler gas. The positively charged gas ions collide with the negatively charged cathode, sputtering atoms from the cathode's surface. Some of the sputtered atoms are in the excited state and emit radiation characteristic of the metal(s) from which the cathode was manufactured. By fashioning the cathode from the metallic analyte, a hollow cathode lamp provides emission lines that correspond to the analyte's absorption spectrum.

Because atomic absorption lines are narrow, we need to use a line source instead of a continuum source (compare, for example, Figure 10.18 with Figure 10.20). The effective bandwidth when using a continuum source is roughly 1000^× larger than an atomic absorption line; thus, $P_T \approx P_0$, $\%T \approx 100$, and $A \approx 0$. Because a hollow cathode lamp is a line source, P_T and P_0 have different values giving a $\%T < 100$ and $A > 0$.

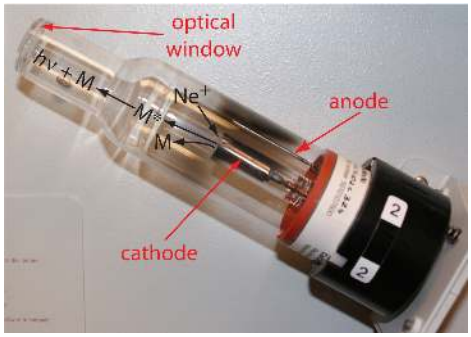


Figure 10.46: *Photo of a typical multielemental hollow cathode lamp. The cathode in this lamp is fashioned from an alloy containing Co, Cr, Cu, Fe, Mn, and Ni, and is surrounded by a glass shield to isolate it from the anode. The lamp is filled with Ne gas. Also shown is the process leading to atomic emission. See the text for an explanation.*

Each element in a hollow cathode lamp provides several atomic emission lines that we can use for atomic absorption. Usually the wavelength that provides the best sensitivity is the one we choose to use, although a less sensitive wavelength may be more appropriate for a larger concentration of analyte. For the Cr hollow cathode lamp in Table 10.11, for example, the best sensitivity is obtained using a wavelength of 357.9 nm.

Another consideration is the intensity of the emission line. If several emission lines meet our need for sensitivity, we may wish to use the emission line with the largest relative P_0 because there is less uncertainty in measuring P_0 and P_T. When analyzing samples containing ≈10 mg Cr/L, for example, the first three wavelengths in Table 10.11 provide an appropriate sensitivity. The wavelengths of 425.5 nm and 429.0 nm, however, have a greater P_0 and will provide less uncertainty in the measured absorbance.

Table 10.11 *Atomic Emission Lines for a Cr Hollow Cathode Lamp*

wavelength (nm)	slit width (nm)	mg Cr/L giving A = 0.20	P_0 (relative)
357.9	0.2	2.5	40
425.4	0.2	12	85
429.0	0.5	20	100
520.5	0.2	1500	15
520.8	0.2	500	20

The emission spectrum from a hollow cathode lamp includes, besides emission lines for the analyte, additional emission lines for impurities present in the metallic cathode and from the filler gas. These additional lines are a source of stray radiation that leads to an instrumental deviation from Beer's law. The monochromator's slit width is set as wide as possible, improving the throughput of radiation, while, at the same time, being narrow enough to eliminate the stray radiation.

Preparing the Sample. Flame and electrothermal atomization require that the sample be in solution. Solid samples are brought into solution by dissolving in an appropriate solvent. If the sample is not soluble it may be digested, either on a hot-plate or by microwave, using HNO_3, H_2SO_4, or $HClO_4$. Alternatively, we can extract the analyte using a Soxhlet extractor. Liquid samples may be analyzed directly or extracted if the matrix is incompatible with the method of atomization. A serum sample, for instance, is difficult to aspirate when using flame atomization and may produce an unacceptably high background absorbance when using electrothermal atomization. A liquid–liquid extraction using an organic solvent and a chelating agent is frequently used to concentrate analytes. Dilute solutions of Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Ni^{2+}, and Zn^{2+}, for example, can be concentrated by extracting with a solution of ammonium pyrrolidine dithiocarbamate in methyl isobutyl ketone.See Chapter 7 to review different methods for preparing samples for analysis.

Minimizing Spectral Interference. A spectral interference occurs when an analyte's absorption line overlaps with an interferent's absorption line or band. Because they are so narrow, the overlap of two atomic absorption lines is seldom a problem. On the other hand, a molecule's broad absorption band or the scattering of source radiation is a potentially serious spectral interference.

An important consideration when using a flame as an atomization source is its effect on the measured absorbance. Among the products of combustion are molecular species that exhibit broad absorption bands and particulates that scatter radiation from the source. If we fail to compensate for these spectral interference, then the intensity of transmitted radiation decreases. The result is an apparent increase in the sample's absorbance. Fortunately, absorption and scattering of radiation by the flame are corrected by analyzing a blank.

Spectral interferences also occur when components of the sample's matrix other than the analyte react to form molecular species, such as oxides and hydroxides. The resulting absorption and scattering constitutes the sample's background and may present a significant problem, particularly at wavelengths below 300 nm where the scattering of radiation becomes more important. If we know the composition of the sample's matrix, then we can prepare our samples using an identical matrix. In this case the background absorption is the same for both the samples and standards. Alternatively, if the background is due to a known matrix component, then we can add that component in excess to all samples and standards so that the contribution of the naturally occurring interferent is insignificant. Finally, many interferences due to the sample's matrix can be eliminated by increasing the atomization temperature. For example, by switching to a higher temperature flame it may be possible to prevent the formation of interfering oxides and hydroxides.

If the identity of the matrix interference is unknown, or if it is not possible to adjust the flame or furnace conditions to eliminate the interference, then we must find another method to compensate for the background interference. Several methods have been developed to compensate for matrix interferences, and most atomic absorption spectrophotometers include one or more of these methods.

One of the most common methods for **background correction** is to use a continuum source, such as a D_2 lamp. Because a D_2 lamp is a continuum source, absorbance of its radiation by the analyte's narrow absorption line is negligible. Only the background, therefore, absorbs radiation from the D_2 lamp. Both the analyte and the background, on the other hand, absorb the hollow cathode's radiation. Subtracting the absorbance for the D_2 lamp from that for the hollow cathode lamp gives a corrected absorbance that compensates for the background interference. Although this method of background correction may be quite effective, it does assume that the background absorbance is constant over the range of wavelengths passed by the monochromator. If this is not true, subtracting the two absorbances may underestimate or overestimate the background.

> Other methods of background correction have been developed, including Zeeman effect background correction and Smith–Hieftje background correction, both of which are included in some commercially available atomic absorption spectrophotometers. Consult the chapter's additional resources for additional information.

Minimizing Chemical Interferences. The quantitative analysis of some elements is complicated by chemical interferences occurring during atomization. The two most common chemical interferences are the formation of nonvolatile compounds containing the analyte and ionization of the analyte.

One example of the formation of nonvolatile compounds is the effect of PO_4^{3-} or Al^{3+} on the flame atomic absorption analysis of Ca^{2+}. In one study, for example, adding 100 ppm Al^{3+} to a solution of 5 ppm Ca^{2+} decreased the calcium ion's absorbance from 0.50 to 0.14, while adding 500 ppm PO_4^{3-} to a similar solution of Ca^{2+} decreased the absorbance from 0.50 to 0.38. These interferences were attributed to the formation of nonvolatile particles of $Ca_3(PO_4)_2$ and an Al–Ca–O oxide.[16]

When using flame atomization, we can minimize the formation of nonvolatile compounds by increasing the flame's temperature, either by changing the fuel-to-oxidant ratio or by switching to a different combination of fuel and oxidant. Another approach is to add a releasing agent or a protecting agent to the samples. A **releasing agent** is a species that reacts with the interferent, releasing the analyte during atomization. Adding Sr^{2+} or La^{3+} to solutions of Ca^{2+}, for example, minimizes the effect of PO_4^{3-} and Al^{3+} by reacting in place of the analyte. Thus, adding 2000 ppm $SrCl_2$ to the Ca^{2+}/PO_4^{3-} and Ca^{2+}/Al^{3+} mixtures described in the previous paragraph increased the absorbance to 0.48. A **protecting agent** reacts with the analyte to form a stable volatile complex. Adding 1% w/w EDTA to the Ca^{2+}/PO_4^{3-} solution described in the previous paragraph increased the absorbance to 0.52.

Ionization interferences occur when thermal energy from the flame or the electrothermal atomizer is sufficient to ionize the analyte

$$M_{(g)} \overset{\Delta}{\rightleftharpoons} M^+_{(g)} + e^- \tag{10.24}$$

where M is the analyte. Because the absorption spectra for M and M^+ are different, the position of the equilibrium in reaction 10.24 affects absorbance at wavelengths where M absorbs. To limit ionization we add a high concentration of an **ionization suppressor**, which is simply a species that ionizes more easily than the analyte. If the concentration of the ionization suppressor is sufficient, then the increased concentration of electrons in the flame pushes reaction 10.24 to the left, preventing the analyte's ionization. Potassium and cesium are frequently used as an ionization suppressor because of their low ionization energy.

Standardizing the Method. Because Beer's law also applies to atomic absorption, we might expect atomic absorption calibration curves to be linear. In practice, however, most atomic absorption calibration curves are nonlinear, or linear for only a limited range of concentrations. Nonlinearity in atomic absorption is a consequence of instrumental limitations, including stray radiation from the hollow cathode lamp and the variation in molar absorptivity across the absorption line. Accurate quantitative work, therefore, often requires a suitable means for computing the calibration curve from a set of standards.

Most instruments include several different algorithms for computing the calibration curve. The instrument in my lab, for example, includes five algorithms. Three of the algorithms fit absorbance data using linear, quadratic, or cubic polynomial functions of the analyte's concentration. It also includes two algorithms that fit the concentrations of the standards to quadratic functions of the absorbance.

When possible, a quantitative analysis is best conducted using external standards. Unfortunately, matrix interferences are a frequent problem, particularly when using electrothermal atomization. For this reason the method of standard additions is often used. One limitation to this method of standardization, however, is the requirement that there be a linear relationship between absorbance and concentration.

The best way to appreciate the theoretical and practical details discussed in this section is to carefully examine a typical analytical method. Although each method is unique, the following description of the determination of Cu and Zn in biological tissues provides an instructive example of a typical procedure. The description here is based on Bhattacharya, S. K.; Goodwin, T. G.; Crawford, A. J. *Anal. Lett.* **1984**, *17*, 1567–1593, and Crawford, A. J.; Bhattacharya, S. K. Varian Instruments at Work, Number AA–46, April 1985.

Representative Method 10.2: Determination of Cu and Zn in Tissue Samples

Description of Method

Copper and zinc are isolated from tissue samples by digesting the sample with HNO_3 after first removing any fatty tissue. The concentration of copper and zinc in the supernatant are determined by atomic absorption using an air-acetylene flame.

Procedure

Tissue samples are obtained by a muscle needle biopsy and dried for 24–30 h at 105°C to remove all traces of moisture. The fatty tissue in the dried samples is removed by extracting overnight with anhydrous ether. After removing the ether, the sample is dried to obtain the fat-free dry tissue weight (FFDT). The sample is digested at 68°C for 20–24 h using 3 mL of 0.75 M HNO_3. After centrifuging at 2500 rpm for 10 minutes, the supernatant is transferred to a 5-mL volumetric flask. The digestion is repeated two more times, for 2–4 hours each, using 0.9-mL aliquots of 0.75 M HNO_3. These supernatants are added to the 5-mL volumetric flask, which is diluted to volume with 0.75 M HNO_3. The concentrations of Cu and Zn in the diluted supernatant are determined by flame atomic absorption spectroscopy using an air-acetylene flame and external standards. Copper is analyzed at a wavelength of 324.8 nm with a slit width of 0.5 nm, and zinc is analyzed at 213.9 nm with a slit width of 1.0 nm. Background correction using a D_2 lamp is necessary for zinc. Results are reported as mg of Cu or Zn per gram of FFDT.

Questions

1. Describe the appropriate matrix for the external standards and for the blank?

The matrix for the standards and the blank should match the matrix of the samples; thus, an appropriate matrix is 0.75 M HNO_3. Any interferences from other components of the sample matrix are minimized by background correction.

2. Why is a background correction necessary for the analysis of Zn, but not for the analysis of Cu?

Background correction compensates for background absorption and scattering due to interferents in the sample. Such interferences are most severe when using a wavelength less than 300 nm. This is the case for Zn, but not for Cu.

3. A Cu hollow cathode lamp has several emission lines. Explain why this method uses the line at 324.8 nm.

wavelength (nm)	slit width (nm)	mg Cu/L for A = 0.20	P_0 (relative)
217.9	0.2	15	3
218.2	0.2	15	3
222.6	0.2	60	5
244.2	0.2	400	15
249.2	0.5	200	24
324.8	0.5	1.5	100
327.4	0.5	3	87

With 1.5 mg Cu/L giving an absorbance of 0.20, the emission line at 324.8 nm has the best sensitivity. In addition, it is the most intense emission line, which decreases the uncertainty in the measured absorbance.

Example 10.10

To evaluate the method described in Representative Method 10.2, a series of external standard is prepared and analyzed, providing the results shown here.[17]

µg Cu/mL	absorbance	µg Cu/mL	absorbance
0.000	0.000	0.500	0.033
0.100	0.006	0.600	0.039
0.200	0.013	0.700	0.046
0.300	0.020	1.000	0.066
0.400	0.026		

A bovine liver standard reference material was used to evaluate the method's accuracy. After drying and extracting the sample, a 11.23-mg FFDT tissue sample gives an absorbance of 0.023. Report the amount of copper in the sample as µg Cu/g FFDT.

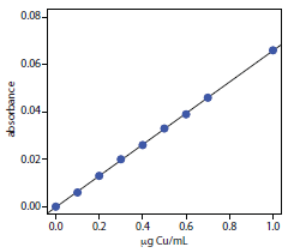
Solution

Linear regression of absorbance versus the concentration of Cu in the standards gives a calibration curve with the following equation.

$$A = -0.0002 + 0.0661 \times \frac{\text{g Cu}}{\text{mL}} \qquad (4.3B.2)$$

Substituting the sample's absorbance into the calibration equation gives the concentration of copper as 0.351 µg/mL. The concentration of copper in the tissue sample, therefore, is

$$\frac{\frac{0.351\ \text{g Cu}}{\text{mL}} \times 5.000\ \text{mL}}{0.01123\ \text{g sample}} = 156\ \text{g Cu/g FFDT} \tag{4.3B.3}$$



10.4.3 - Evaluation of Atomic Absorption Spectroscopy

Scale of Operation

Atomic absorption spectroscopy is ideally suited for the analysis of trace and ultratrace analytes, particularly when using electrothermal atomization. For minor and major analyte, sample can be diluted before the analysis. Most analyses use a macro or a meso sample. The small volume requirement for electrothermal atomization or flame microsampling, however, makes practical the analysis micro and ultramicro samples.

> See Figure 3.5 to review the meaning of macro and meso for describing samples, and the meaning of major, minor, and ultratrace for describing analytes.

Accuracy

If spectral and chemical interferences are minimized, an accuracy of 0.5–5% is routinely attainable. When the calibration curve is nonlinear, accuracy may be improved by using a pair of standards whose absorbances closely bracket the sample's absorbance and assuming that the change in absorbance is linear over this limited concentration range. Determinate errors for electrothermal atomization are often greater than that obtained with flame atomization due to more serious matrix interferences.

Precision

For absorbance values greater than 0.1–0.2, the relative standard deviation for atomic absorption is 0.3–1% for flame atomization and 1–5% for electrothermal atomization. The principle limitation is the variation in the concentration of free analyte atoms resulting from variations in the rate of aspiration, nebulization, and atomization when using a flame atomizer, and the consistency of injecting samples when using electrothermal atomization.

Sensitivity

The sensitivity of a flame atomic absorption analysis is influenced strongly by the flame's composition and by the position in the flame from which we monitor the absorbance. Normally the sensitivity of an analysis is optimized by aspirating a standard solution of the analyte and adjusting operating conditions, such as the fuel-to-oxidant ratio, the nebulizer flow rate, and the height of the burner, to give the greatest absorbance. With electrothermal atomization, sensitivity is influenced by the drying and ashing stages that precede atomization. The temperature and time used for each stage must be optimized for each type of sample.

> See Chapter 14 for several strategies for optimizing experiments.

Sensitivity is also influenced by the sample's matrix. We have already noted, for example, that sensitivity can be decreased by chemical interferences. An increase in sensitivity may be realized by adding a low molecular weight alcohol, ester, or ketone to the solution, or by using an organic solvent.

Selectivity

Due to the narrow width of absorption lines, atomic absorption provides excellent selectivity. Atomic absorption can be used for the analysis of over 60 elements at concentrations at or below the level of µg/L.

Time, Cost, and Equipment

The analysis time when using flame atomization is short, with sample throughputs of 250–350 determinations per hour when using a fully automated system. Electrothermal atomization requires substantially more time per analysis, with maximum sample throughputs of 20–30 determinations per hour. The cost of a new instrument ranges from between $10,000–$50,000 for flame atomization, and from $18,000–$70,000 for electrothermal atomization. The more expensive instruments in each price range include double-beam optics, automatic samplers, and can be programmed for multielemental analysis by allowing the wavelength and hollow cathode lamp to be changed automatically.

Contributors

David Harvey (DePauw University)

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27.10C: Plutonium

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27.11A: (\sigma\)-Bonded Complexes

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27.11B: Cyclopentadienyl Derivatives

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27.11C: Complexes Containing the η 8 -cyclooctatetraenyl Ligand

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CHAPTER OVERVIEW

28: Inorganic materials and nanotechnology

Topic hierarchy

28.1: Introduction
28.2: Electrical Conductivity in Ionic Solids
28.2A: Sodium and Lithium Ion Conductors
28.2B: d-Block Metal(II) Oxides
28.3: Transparent Conducting Oxides and their Applications in Devices
28.3A: Sn-doped \(In_2O_3\) (ITO) and F-doped \(SnO_2\) (FTO)
28.3B: Dye-Sensitized Solar Cells (DSCs)
28.3C: Solid State Lighting - OLEDs
28.3D: Solid State Lighting - LECs
28.4: Superconductivity
28.4A: Superconductors - Early Examples and Basic Theory
28.4B: High-temperature Superconductors
28.4C: Iron-based Superconductors
28.4D: Chevrel Phases
28.4E: Superconducting Properties of \(MgB_2\)
28.4F: Applications of Superconductors
28.5: Ceramic Materials - Color Pigments
28.5A: White Pigments (Opacifiers)
28.5B: Adding Color
28.6: Chemical Vapour Deposition (CVD)
28.6A: High-purity Silicon for Semiconductors
28.6B: \(\alpha\)-Boron Nitride
28.6C: Silicon Nitride and Carbide
28.6D: III-V Semiconductors
28.6E: Metal Deposition
28.6F: Ceramic Coatings
28.6G: Perovskites and Cuprate Superconductors
28.7: Inorganic Fibres
28.7A: Boron Fibres
28.7B: Carbon Fibres
28.7C: Silicon Carbide Fibres
28.7D: Alumina Fibres
28.8: Graphene
28.9: Carbon Nanotubes

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28.1: Introduction

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28.2A: Sodium and Lithium Ion Conductors

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28.2B: d-Block Metal(II) Oxides

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SECTION OVERVIEW

4.4: Computational Analysis - Thermogravimetry (TG)

Topic hierarchy

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28.3: Transparent Conducting Oxides and their Applications in Devices

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28.3A: Sn-doped $I\ \ n\ 2\ \ O\ 3$ (ITO) and F-doped $S\ \ n\ \ O\ 2$ (FTO)

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28.3B: Dye-Sensitized Solar Cells (DSCs)

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28.3C: Solid State Lighting - OLEDs

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28.3D: Solid State Lighting - LECs

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28.4: Superconductivity

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28.4A: Superconductors - Early Examples and Basic Theory

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28.4B: High-temperature Superconductors

Learning Objectives

- To become familiar with the properties of superconductors.

Contributors

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Video from Wisconsin MRSEC @ YouTube

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28.4C: Iron-based Superconductors

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28.4D: Chevrel Phases

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SECTION OVERVIEW

4.5: Mass Spectrometry

Topic hierarchy

4.5A: Electron Ionization (EI)

4.5B: Fast Atom Bombardment (FAB)

4.5C: Matrix-Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF)

4.5D: Electrospray Ionization (ESI)

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28.4E: Superconducting Properties of $M\ g\ B\ 2$

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28.4F: Applications of Superconductors

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SECTION OVERVIEW

28.5: Ceramic Materials - Color Pigments

Topic hierarchy

28.5A: White Pigments (Opacifiers)

28.5B: Adding Color

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28.5A: White Pigments (Opacifiers)

An opacifier is a substance added to a material in order to make the ensuing system opaque. An example of a chemical opacifier is titanium dioxide (TiO_2), which is used to opacify ceramic glazes and milk glass. Opacifiers must have a refractive index substantially different from the system. Conversely, clarity may be achieved in a system by choosing components with very similar refractive indices.

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28.5B: Adding Color

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28.6A: High-purity Silicon for Semiconductors

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28.6B: α -Boron Nitride

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28.6C: Silicon Nitride and Carbide

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28.6D: III-V Semiconductors

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4.5A: Electron Ionization (EI)

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28.6E: Metal Deposition

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28.6F: Ceramic Coatings

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28.6G: Perovskites and Cuprate Superconductors

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28.7: Inorganic Fibres

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28.7A: Boron Fibres

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28.7B: Carbon Fibres

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28.7C: Silicon Carbide Fibres

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28.7D: Alumina Fibres

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28.8: Graphene

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28.9: Carbon Nanotubes

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4.5B: Fast Atom Bombardment (FAB)

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29.2A: Iron Storage and Transport

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29.2B: Metallothioneins - Transporting Some Toxic Metals

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29.3: Dealing with O_2

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29.3A: Haemoglobin and Myoglobin

29.3B: Hemocyanin

29.3C: Hemerythrin

29.3D: Cytochromes P-450

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29.3A: Haemoglobin and Myoglobin

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29.3A: Haemoglobin and Myoglobin is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

29.3B: Hemocyanin

Hemocyanin is used for oxygen transport in many arthropods (spiders, crabs, lobsters, and centipedes) and in mollusks (shellfish, octopi, and squid); it is responsible for the bluish-green color of their blood. The protein is a polymer of subunits that each contain two copper atoms (rather than iron), with an aggregate molecular mass of greater than 1,000,000 amu. Deoxyhemocyanin contains two Cu^{+} ions per subunit and is colorless, whereas oxyhemocyanin contains two Cu^{2+} ions and is bright blue. As with hemerythrin, the binding and release of O_2 correspond to a two-electron reaction:

$$2\,Cu^{+} + O_2 \rightleftharpoons Cu^{2+}{-}O_2{}^{2-}{-}Cu^{2+} \tag{29.3B.1}$$

Although hemocyanin and hemerythrin perform the same basic function as hemoglobin, these proteins are not interchangeable. In fact, hemocyanin is so foreign to humans that it is one of the major factors responsible for the common allergies to shellfish.

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29.3C: Hemerythrin

Hemerythrin is used to transport O_2 in a variety of marine invertebrates. It is an octamer (eight subunits), with each subunit containing two iron atoms and binding one molecule of O_2. Deoxyhemerythrin contains two Fe^{2+} ions per subunit and is colorless, whereas oxyhemerythrin contains two Fe^{3+} ions and is bright reddish violet. These invertebrates also contain a monomeric form of hemerythrin that is located in the tissues, analogous to myoglobin. The binding of oxygen to hemerythrin and its release can be described by the following reaction, where the HO_2^- ligand is the hydroperoxide anion derived by the deprotonation of hydrogen peroxide (H_2O_2):

$$2\,Fe^{2+} + O_2 + H^+ \rightleftharpoons 2\,Fe^{3+}{-}O_2H \tag{29.3C.1}$$

Thus O_2 binding is accompanied by the transfer of two electrons (one from each Fe^{2+}) and a proton to O_2.

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4.5C: Matrix-Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF)

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29.3D: Cytochromes P-450

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29.4A: Blue Copper Proteins

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29.4B: The Mitochondrial Electron-transfer Chain

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29.4C: Iron-Sulfur Proteins

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29.5: The Zn^{2+} Ion - Nature's Lewis Acid

Topic hierarchy

29.5A: Carbonic Anhydrase II

29.5B: Carboxypeptidase A

29.5C: Carboxypeptidase G2

29.5D: Cobalt-for-Zinc Ion Substitution

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29.5A: Carbonic Anhydrase II

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29.5B: Carboxypeptidase A

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4.5D: Electrospray Ionization (ESI)

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29.5D: Cobalt-for-Zinc Ion Substitution

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SECTION OVERVIEW

4.6: Infrared and Raman Spectroscopies

Topic hierarchy

4.6A: Energies and Wavenumbers of Molecular Vibrations

4.6B: The Fourier Transform Infrared (FT-IR) Spectrometer and Sample Preparation

4.6C: Diagnostic Absorptions

4.6D: Deuterium/Hydrogen Exchange

4.6E: Raman Spectroscopy

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4.6A: Energies and Wavenumbers of Molecular Vibrations

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4.6B: The Fourier Transform Infrared (FT-IR) Spectrometer and Sample Preparation

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4.6C: Diagnostic Absorptions

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4.6E: Raman Spectroscopy

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SECTION OVERVIEW

4.7: Electronic Spectroscopy

Topic hierarchy

4.7A: UV-VIS Absorption Spectroscopy

4.7B: Types of Absorption

4.7C: Absorbance and the Beer-Lambert Law

4.7D: Emission Spectroscopy

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4.7A: UV-VIS Absorption Spectroscopy

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4.7B: Types of Absorption

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4.7C: Absorbance and the Beer-Lambert Law

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4.7D: Emission Spectroscopy

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SECTION OVERVIEW

4.8: Nuclear Magnetic Resonance (NMR) Spectroscopy

Topic hierarchy

4.8A: NMR Active Nuclei and Isotope Abundance

4.8B: Which Nuclei are Suitable for NMR Spectroscopic Studies

4.8C: Resonance Frequencies and Chemical Shifts

4.8D: Chemical Shift Ranges

4.8E: Solvents for Solution Studies

4.8F: Integration of Signals and Signal Broadening

4.8G: Homonuclear spin-spin coupling - \(^1H-^1H\)

4.8H: Heteronuclear spin-spin coupling - \(^{13}C-^1H\)

4.8I: Case Studies

4.8J: Stereochemically Non-Rigid Species

4.8K: Exchange Processes in Solution

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4.8A: NMR Active Nuclei and Isotope Abundance

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4.8B: Which Nuclei are Suitable for NMR Spectroscopic Studies

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4.8C: Resonance Frequencies and Chemical Shifts

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4.8D: Chemical Shift Ranges

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4.8F: Integration of Signals and Signal Broadening

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4.8G: Homonuclear spin-spin coupling - 1 H − 1 H

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4.8H: Heteronuclear spin-spin coupling - 13 C − 1 H

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4.8J: Stereochemically Non-Rigid Species

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4.8K: Exchange Processes in Solution

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SECTION OVERVIEW

4.9: Electron Paramagnetic Resonance (EPR) Spectroscopy

Topic hierarchy

4.9A: What is EPR Spectroscopy?

4.9B: The Zeeman Electronic Effect

4.9C: EPR Spectra

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4.9A: What is EPR Spectroscopy?

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4.9B: The Zeeman Electronic Effect

Magnetism results from the circular motion of charged particles. This property is demonstrated on a macroscopic scale by making an electromagnet from a coil of wire and a battery. Electrons moving through the coil produce a magnetic field (Figure $4.9B.1$), which can be thought of as originating from a magnetic dipole or a bar magnet.

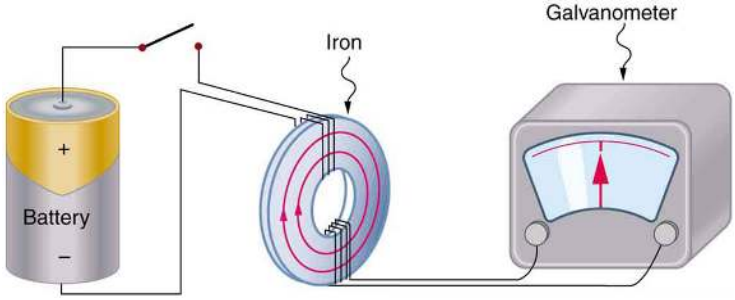


Figure $4.9B.1$: Faraday's apparatus for demonstrating that a magnetic field can produce a current. A change in the field produced by the top coil induces an emf and, hence, a current in the bottom coil. When the switch is opened and closed, the galvanometer registers currents in opposite directions. No current flows through the galvanometer when the switch remains closed or open. (CC BY 3.0; OpenStax).

> *Magnetism results from the circular motion of charged particles.*

Electrons in atoms also are moving charges with angular momentum so they too produce a magnetic dipole, which is why some materials are magnetic. A magnetic dipole interacts with an applied magnetic field, and the energy of this interaction is given by the scalar product of the magnetic dipole moment, and the magnetic field, $\vec{B}$.

$$E_B = -\vec{\mu}_m \cdot \vec{B} \tag{4.9B.1}$$

Magnets are acted on by forces and torques when placed within an external applied magnetic field (Figure $4.9B.2$). In a uniform external field, a magnet experiences no net force, but a net torque. The torque tries to align the magnetic moment ($\vec{\mu}_m$ of the magnet with the external field $\vec{B}$. The magnetic moment of a magnet points from its south pole to its north pole.

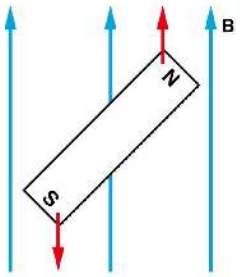


Figure $4.9B.2$: A magnet will feel a force to realign in an external field, i.e., go from a higher energy to a lower energy. The energy of this system is determined by Equation 4.9B.1 and classical can vary since the angle between $\vec{\mu}_m$ and $\vec{B}$ can vary continuously from 0 (low energy) to 180° (high energy).

In a non-uniform magnetic field a current loop, and therefore a magnet, experiences a net force, which tries to pull an aligned dipole into regions where the magnitude of the magnetic field is larger and push an anti-aligned dipole into regions where magnitude the magnetic field is smaller.

Quantum Effects

As expected, the quantum picture is different. Pieter Zeeman was one of the first to observe the splittings of spectral lines in a magnetic field caused by this interaction. Consequently, such splittings are known as the **Zeeman effect**. Let's now use our current knowledge to predict what the Zeeman effect for the 2p to 1s transition in hydrogen would look like, and then compare this prediction with a more complete theory. To understand the Zeeman effect, which uses a magnetic field to remove the degeneracy of different angular momentum states, we need to examine how an electron in a hydrogen atom interacts with an external magnetic

field, $\vec{B}$. Since magnetism results from the circular motion of charged particles, we should look for a relationship between the angular momentum $\vec{L}$ and the magnetic dipole moment $\vec{\mu}_m$.

The relationship between the magnetic dipole moment $\vec{\mu}_m$ (also referred to simply as the magnetic moment) and the angular momentum $\vec{L}$ of a particle with mass m and charge q is given by

$$\vec{\mu}_m = \frac{q}{2m}\vec{L} \tag{4.9B.2}$$

For an electron, this equation becomes

$$\vec{\mu}_m = -\frac{e}{2m_e}\vec{L} \tag{4.9B.3}$$

where the specific charge and mass of the electron have been substituted for q and m. The magnetic moment for the electron is a vector pointing in the direction opposite to $\vec{L}$, both of which classically are perpendicular to the plane of the rotational motion.

Exercise 4.9B.1

Will an electron in the ground state of hydrogen have a magnetic moment? Why or why not?

The relationship between the angular momentum of a particle and its magnetic moment is commonly expressed as a ratio, called the gyromagnetic ratio, γ. Gyro is Greek for turn so gyromagnetic simply relates turning (angular momentum) to magnetism. Now you also know why the Greek sandwiches made with meat cut from a spit turning over a fire are called gyros.

$$\gamma = \frac{\mu_m}{L} = \frac{q}{2m} \tag{4.9B.4}$$

In the specific case of an electron,

$$\gamma_e = -\frac{e}{2m_e} \tag{4.9B.5}$$

Exercise 4.9B.2

Calculate the magnitude of the gyromagnetic ratio for an electron.

To determine the energy of a hydrogen atom in a magnetic field we need to include the operator form of the hydrogen atom Hamiltonian. The Hamiltonian always consists of all the energy terms that are relevant to the problem at hand.

$$\hat{H} = \hat{H}^0 + \hat{H}_m \tag{4.9B.6}$$

where $\hat{H}^0$ is the Hamiltonian operator in the absence of the field and $\hat{H}_m$ is written using the operator forms of Equations 4.9B.1 and 4.9B.3),

$$\hat{H}_m = -\hat{\mu}\cdot\vec{B} = \frac{e}{2m_e}\hat{L}\cdot B \tag{4.9B.7}$$

The scalar product

$$\hat{L}\cdot\vec{B} = \hat{L}_x B_x + \hat{L}_y B_y + \hat{L}_z B_z \tag{4.9B.8}$$

simplifies if the z-axis is defined as the direction of the external field because then B_x and B_y are automatically 0, and Equation 4.9B.6 becomes

$$\hat{H} = \hat{H}^0 + \frac{eB_z}{2m_e}\hat{L}_z \tag{4.9B.9}$$

where B_z is the magnitude of the magnetic field, which is along the z-axis.

We now can ask, “What is the effect of a magnetic field on the energy of the hydrogen atom orbitals?” To answer this question, we will not solve the Schrödinger equation again; we simply calculate the expectation value of the energy, $\langle E\rangle$, using the existing hydrogen atom wavefunctions and the new Hamiltonian operator.

$$\langle E \rangle = \left\langle \hat{H}^0 \right\rangle + \frac{eB_z}{2m_e} \left\langle \hat{L}_z \right\rangle \tag{4.9B.10}$$

where

$$\left\langle \hat{H}^0 \right\rangle = \int \psi^*_{n,l,m_l} \hat{H}^0 \psi_{n,l,m_l} d\tau = E_n \tag{4.9B.11}$$

and

$$\left\langle \hat{L}_z \right\rangle = \int \psi^*_{n,l,m_l} \hat{L}_z \psi_{n,l,m_l} d\tau = m_l \hbar \tag{4.9B.12}$$

Exercise 4.9B.3

Show that the expectation value $\left\langle \hat{L}_z \right\rangle = m_l \hbar$.

The expectation value approach provides an exact result in this case because the hydrogen atom wavefunctions are eigenfunctions of both $\hat{H}^0$ and $\hat{L}_z$. If the wavefunctions were not eigenfunctions of the operator associated with the magnetic field, then this approach would provide a first-order estimate of the energy. First and higher order estimates of the energy are part of a general approach to developing approximate solutions to the Schrödinger equation. This approach, called perturbation theory, is discussed in the next chapter.

The expectation value calculated for the total energy in this case is the sum of the energy in the absence of the field, E_n, plus the Zeeman energy, $\frac{e\hbar B_z m_l}{2m_e}$

$$\langle E \rangle = E_n + \frac{e\hbar B_z m_l}{2m_e} \tag{4.9B.13}$$

$$= E_n + \mu_B B_z m_l \tag{4.9B.14}$$

The factor

$$\frac{e\hbar}{2m_e} = -\gamma_e \hbar = \mu_B \tag{4.9B.15}$$

defines the constant μ_B, called the **Bohr magneton**, which is taken to be the fundamental magnetic moment. It has units of 9.2732×10^{-21} erg/Gauss or 9.2732×10^{-24} Joule/Tesla. This factor will help you to relate magnetic fields, measured in Gauss or Tesla, to energies, measured in ergs or Joules, for any particle with a charge and mass the same as an electron.

Equation 4.9B.14 shows that the m_l quantum number degeneracy of the hydrogen atom is removed by the magnetic field. For example, the three states ψ_{211}, ψ_{21-1}, and ψ_{210}, which are degenerate in zero field, have different energies in a magnetic field, as shown in Figure 4.9B.3.

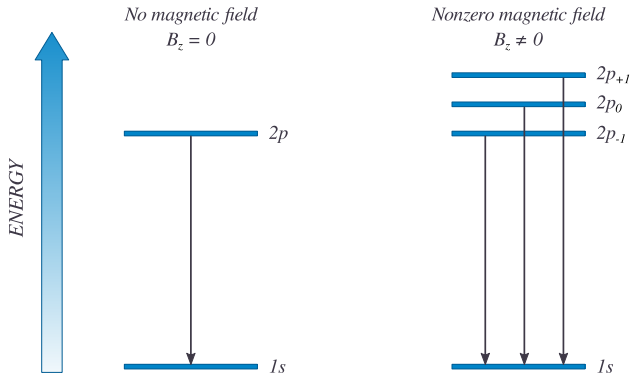


Figure 4.9B.3: The Zeeman effect. Emission when an electron switches from a 2p orbital to a 1s orbital occurs at only one energy in the absence of a magnetic field, but can occur at three different energies in the presence of a magnetic field.

The $m_l = 0$ state, for which the component of angular momentum and hence also the magnetic moment in the external field direction is zero, experiences no interaction with the magnetic field. The $m_l = +1$ state, for which the angular momentum in the z-direction is +ħ and the magnetic moment is in the opposite direction, against the field, experiences a raising of energy in the presence of a field. Maintaining the magnetic dipole against the external field direction is like holding a small bar magnet with its poles aligned exactly opposite to the poles of a large magnet (Figure $4.9B.5$). It is a higher energy situation than when the magnetic moments are aligned with each other.

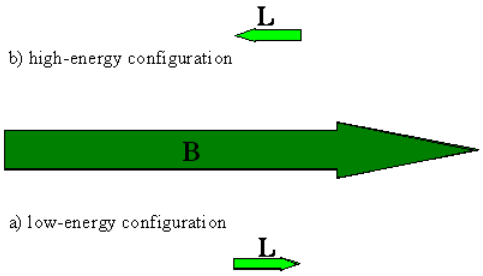


Figure $4.9B.4$: The effect of an external magnetic field (B) on the energy of a magnetic dipole (L) oriented a) with and b) against the applied magnetic field.

Exercise $4.9B.4$

Carry out the steps going from Equation 4.9B.10 to Equation 4.9B.14.

Exercise $4.9B.5$

Consider the effect of changing the magnetic field on the magnitude of the Zeeman splitting. Sketch a diagram where the magnetic field strength is on the x-axis and the energy of the three 2p orbitals is on the y-axis to show the trend in splitting magnitudes with increasing magnetic field. Be quantitative, calculate and plot the exact numerical values using a software package of your choice.

Exercise $4.9B.6$

Based on your calculations in Exercise $4.9B.2$ sketch a luminescence spectrum for the hydrogen atom in the n = 2 level in a magnetic field of 1 Tesla. Provide the numerical value for each of the transition energies. Use cm^{-1} or electron volts for the energy units.

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4.9C: EPR Spectra

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SECTION OVERVIEW

4.10: Mossbauer Spectroscopy

Topic hierarchy

4.10A: The Technique of Mossbauer Spectroscopy

4.10B: What Can Isomer Shift Data Tell Us?

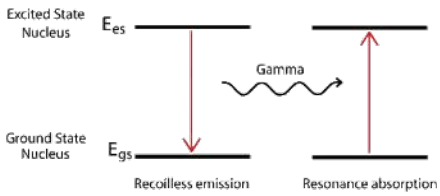
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4.10A: The Technique of Mossbauer Spectroscopy

Mössbauer spectroscopy is a versatile technique used to study nuclear structure with the absorption and re-emission of gamma rays, part of the electromagnetic spectrum. The technique uses a combination of the Mössbauer effect and Doppler shifts to probe the hyperfine transitions between the excited and ground states of the nucleus. Mössbauer spectroscopy requires the use of solids or crystals which have a probability to absorb the photon in a recoilless manner, many isotopes exhibit Mössbauer characteristics but the most commonly studied isotope is ^{57}Fe.

Introduction

Rudolf L. Mössbauer became a physics student at Technical University in Munich at the age of 20. After passing his intermediate exams Mössbauer began working on his thesis and doctorate work in 1955, while working as an assistant lecturer at Institute for Mathematics. In 1958 at the age of 28 Mössbauer graduated, and also showed experimental evidence for recoilless resonant absorption in the nucleus, later to be called the Mössbauer Effect. In 1961 Mössbauer was awarded the Nobel Prize in physics and, under the urging of Richard Feynman, accepted the position of Professor of Physics at the California Institute of Technology.



Mössbauer Effect

The recoil energy associated with absorption or emission of a photon can be described by the conservation of momentum. In it we find that the recoil energy depends inversely on the mass of the system. For a gas the mass of the single nucleus is small compared to a solid. The solid or crystal absorbs the energy as phonons, quantized vibration states of the solid, but there is a probability that no phonons are created and the whole lattice acts as the mass, resulting in a recoilless emission of the gamma ray. The new radiation is at the proper energy to excite the next ground state nucleus. The probability of recoilless events increases with decreasing transition energy.

$$P_R = P_\gamma$$

$$P_\gamma^2 = P_\gamma^2$$

$$2ME_R = \frac{E_\gamma^2}{c^2}$$

$$E_R = \frac{E_\gamma^2}{2Mc^2}$$

Doppler Effect

The Doppler shift describes the change in frequency due to a moving source and a moving observer. f is the frequency measured at the observer, v is the velocity of the wave so for our case this is the speed of light c, v_r is the velocity of the observer, v_s is the velocity of the source which is positive when heading away from the observer, and f_0 is the initial frequency.

$$f = \left(\frac{v + v_r}{v + v_s}\right) f_0$$

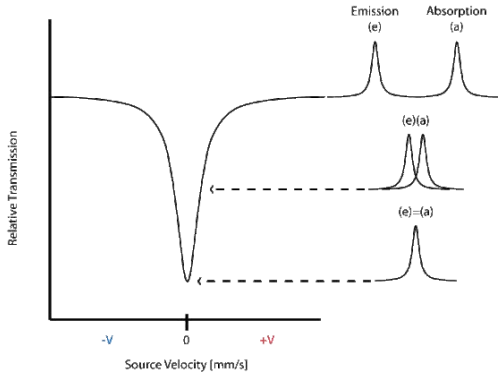
$$f = \left(\frac{c}{c + v_s}\right) f_0$$

In the case where the source is moving toward a stationary observer the perceived frequency is higher. For the opposite situation where the source travels away from the observer frequencies recorded at the observer will be of lower compared to the initial wave. The energy of a photon is related to the product of Planck's constant and the frequency of the electromagnetic radiation. Thus for

increasing frequencies the corresponding energy also increase, and the same is true in the reverse case where frequencies decrease and therefore energy decreases.

$$E = \frac{hc}{\lambda} = h\nu$$

The energy differences between hyperfine states are minimal (fractions of an eV) and the energy variation is achieved by the moving the source toward and away from the sample in an oscillating manner, commonly at a velocity of a few mm/s. The transmittance is then plotted against the velocity of the source and a peak is seen at the energy corresponding to the resonance energy.

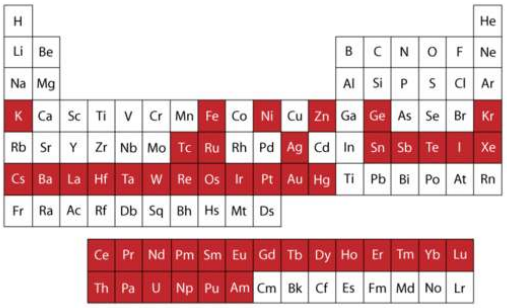


In the above spectrum the emission and absorption are both estimated by the Lorentzian distribution.

Mössbauer Isotopes

By far the most common isotopes studied using Mössbauer spectroscopy is ^{57}Fe, but many other isotopes have also displayed a Mössbauer spectrum. Two criteria for functionality are

1. The excited state is of very low energy, resulting in a small change in energy between ground and excited state. This is because gamma rays at higher energy are not absorbed in a recoil free manner, meaning resonance only occurs for gamma rays of low energy.
2. The resolution of Mössbauer spectroscopy depends upon the lifetime of the excited state. The longer the excited state lasts the better the image.



Both conditions are met by ^{57}Fe and it is thus used extensively in Mössbauer spectroscopy. In the figure to the right the red colored boxes of the periodic table of elements indicate all elements that have isotopes visible using the Mössbauer technique.

Hyperfine Interactions

Mössbauer spectroscopy allows the researcher to probe structural elements of the nucleus in several ways, termed isomer shift, quadrupole interactions, and magnetic splitting. These are each explained by the following sections as individual graphs, but in practice Mössbauer spectrum are likely to contain a combination of all effects.

Isomer Shift

An isomeric shift occurs when non identical atoms play the role of source and absorber, thus the radius of the source, R_s, is different that of the absorber, R_a, and the same holds that the electron density of each species is different. The Coulombic interactions affects the ground and excited state differently leading to a energy difference that is not the same for the two species. This is best illustrated with the equation:

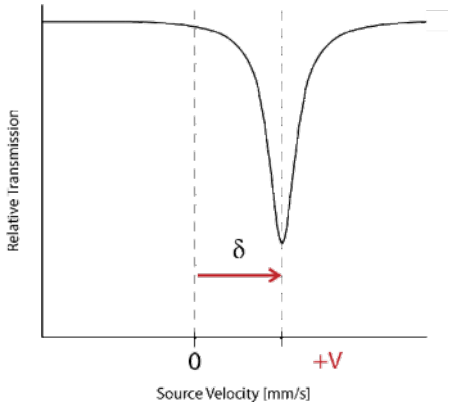
$$R_A \neq R_S$$

$$\rho_S \neq \rho_S$$

$$E_A \neq E_S$$

$$\delta = E_A - E_S = \frac{2}{3} nZe^2(\rho_A - \rho_S)(R_{es}^2 - R_{gs}^2)$$

Where delta represents the change in energy necessary to excite the absorber, which is seen as a shift from the Doppler speed 0 to V_1. The isomer shift depends directly on the s-electrons and can be influenced by the shielding p, d, f electrons. From the measured delta shift there is information about the valance state of the absorbing atom



The energy level diagram for δ shift shows the change in source velocity due to different sources used. The shift may be either positive or negative.

Quadrupole Interaction

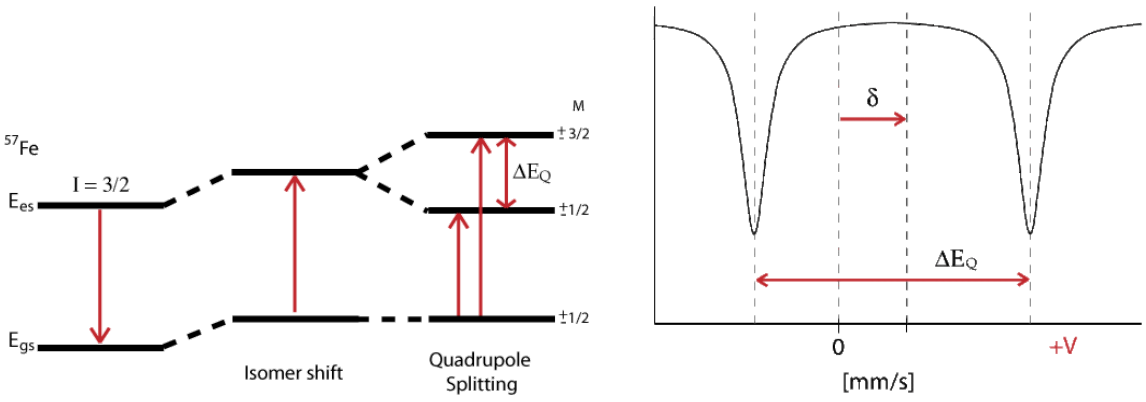
The Hamiltonian for quadrupole interaction using ^{57}Fe nuclear excited state is given by

$$H_Q = \frac{eQV_{ZZ}}{12}[3I_Z^2 - I(I+1) + \eta(I_X^2 - I_y^2)]$$

where the nuclear excited states are split into two degenerate doublets in the absence of magnetic interactions. For the asymmetry parameter $\eta = 0$ doublets are labeled with magnetic quantum numbers $m_{es} = \pm 3/2$ and $m_{es} = \pm 1/2$, where the $m_{es} = \pm 3/2$ doublet has the higher energy. The energy difference between the doublets is thus

$$\Delta EQ = \frac{eQV_{zz}}{2}\sqrt{1 + \frac{\eta^2}{3}}$$

The energy diagram and corresponding spectrum can be seen as

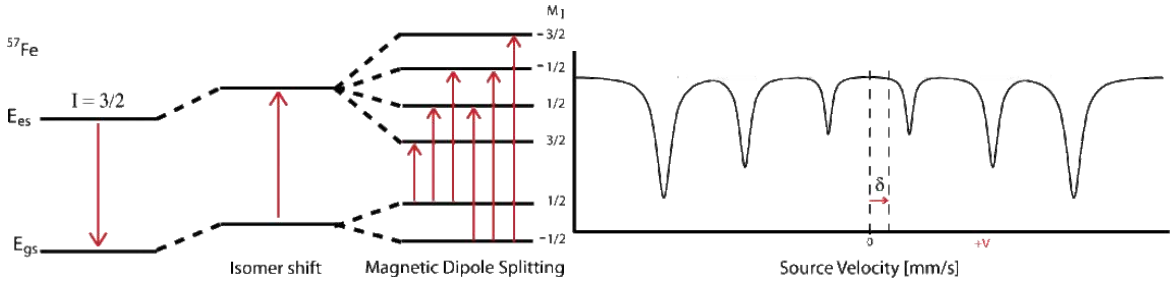


Magnetic Splitting

Magnetic splitting of seen in Mössbauer spectroscopy can be seen because the nuclear spin moment undergoes dipolar interactions with the magnetic field

$$E(m_I) = -g_n \beta_n B_{eff} m_I \tag{14}$$

where g_n is the nuclear g-factor and β_n is the nuclear magneton. In the absence of quadrupole interactions the Hamiltonian splits into equally spaced energy levels of



The allowed gamma stimulated transitions of nuclear excitation follows the magnetic dipole transition selection rule:

$$\Delta I = 1$$

and

$$\Delta m_I = 0, \pm 1$$

where m_I is the magnetic quantum number and the direction of β defines the nuclear quantization axis. If we assume g and A are *isotropic* (direction independent) where $g_x = g_y = g_z$ and B is actually a combination of the applied and internal magnetic fields:

$$H = g\beta S \cdot B + AS \cdot I - g_n\beta_n B \cdot I$$

The electronic Zeeman term is far larger then the nuclear Zeeman term, meaning the electronic term dominates the equation so S is approximated by $\langle S \rangle$ and

$$\langle S_z \rangle = m_s = \pm \frac{1}{2}$$

and

$$\langle S_x \rangle = \langle S_y \rangle \approx 0$$

$$H_n = A\langle S \rangle \cdot I - g_n\beta_n B \cdot I$$

Pulling out a $-g_n\beta_n$ followed by I leaves

$$H_n = -g_n\beta_n \left(-\frac{A\langle S \rangle}{g_n\beta_n} + B \right) I$$

Substituting the internal magnetic field with

$$B_{int} = -\frac{A\langle S \rangle}{g_n\beta_n}$$

results in a combined magnetic field term involving both the applied magnetic field and the internal magnetic field

$$H_n = -g_n\beta_n(B_{int} + B) \cdot I$$

which is simplified by using the effective magnetic field B_{eff}

$$H_n = -g_n\beta_n B_{eff} \cdot I$$

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Problems

1. The magnetic splitting of $m_I = 0$ intensity of transition is related to $sin^2(\theta)$ of the angle between the incoming gamma ray and the effective magnetic field. When is the intensity of transition at max?
2. Why is it important for the sample to be in solid or crystalline state?
3. What case will result in a delta shift of 0. 00 mm/s?
4. Why is the Doppler effect important to Mössbauer spectroscopy?
5. Why are both the emission and absorption distributions the same? (both estimated with Lorentzian functions)

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4.10B: What Can Isomer Shift Data Tell Us?

Among the drawbacks of the technique are the limited number of gamma ray sources and the requirement that samples be solid in order to eliminate the recoil of the nucleus. Mössbauer spectroscopy is unique in its sensitivity to subtle changes in the chemical environment of the nucleus including oxidation state changes, the effect of different ligands on a particular atom, and the magnetic environment of the sample.

As an analytical tool Mössbauer spectroscopy has been especially useful in the field of geology for identifying the composition of iron-containing specimens including meteors and moon rocks. In situ data collection of Mössbauer spectra has also been carried out on iron rich rocks on Mars.[10]

In another application, Mössbauer spectroscopy is used to characterize phase transformations in iron catalysts, e.g., those used for Fischer–Tropsch synthesis. While initially consisting of hematite (Fe_2O_3), these catalysts transform into a mixture of magnetite (Fe_3O_4) and several iron carbides. The formation of carbides appears to improve catalytic activity, however it can also lead to the mechanical break-up and attrition of the catalyst particles, which can cause difficulties in the final separation of catalyst from reaction products.[11]

Mössbauer spectroscopy has also been used to determine the relative concentration change in the oxidation state of antimony (Sb) during the selective oxidation of olefins. During calcination all the Sb ions in an antimony-containing tin dioxide catalyst transform into the +5 oxidation state. Following the catalytic reaction, almost all Sb ions revert from the +5 to the +3 oxidation state. A significant change in the chemical environment surrounding the antimony nucleus occurs during the oxidation state change which can easily be monitored as an isomer shift in the Mössbauer spectrum.[12]

This technique has also been used to observe the second-order transverse Doppler effect predicted by the theory of relativity, because of very high energy resolution.[13]

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SECTION OVERVIEW

4.11: Structure Determination - Diffraction Methods

Topic hierarchy

4.11A: X-Ray Diffraction (XRD)

4.11B: Single Crystal X-Ray Diffraction

4.11C: Powder X-Ray Diffraction

4.11D: Single Crystal Neutron Diffraction

4.11E: Electron Diffraction

4.11F: Low-Energy Electron Diffraction (LEED)

4.11G: Structural Databases

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4.11A: X-Ray Diffraction (XRD)

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4.11D: Single Crystal Neutron Diffraction

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4.11F: Low-Energy Electron Diffraction (LEED)

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4.12: Photoelectron Spectroscopy (PES, UPS, XPS, ESCA)

Learning Objectives

- Demonstrate how photoelectron spectroscopy can be used to resolve the absolute energies of molecular orbitals.

Photoelectron spectroscopy (PES) utilizes photo-ionization and analysis of the kinetic energy distribution of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample.

- **X-ray Photoelectron Spectroscopy** (XPS) uses soft x-rays (with a photon energy of 200-2000 eV) to examine electrons in *core*-levels.
- **Ultraviolet Photoelectron Spectroscopy** (UPS) using vacuum UV radiation (with a photon energy of 10-45 eV) to examine electrons in *valence* levels.

Both photoelectron spectroscopies are based upon a single photon in/electron out process. The energy of a photon of all types of electromagnetic radiation is given by the Planck–Einstein relation:

$$E = h\nu \tag{4.12.1}$$

where h is Planck constant and ν is the frequency (Hz) of the radiation. UPS is a powerful technique to exam molecular electron structure since we are interested in the molecular orbitals from polyatomic molecules (especially the valence orbitals) and is the topic of this page.

Photoelectron spectroscopy uses monochromatic sources of radiation (i.e. photons of fixed energy). In UPS the photon interacts with valence levels of the molecule or solid, leading to ionization by removal of one of these valence electrons. The kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted photoelectrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyzer and a photoelectron spectrum can thus be recorded.

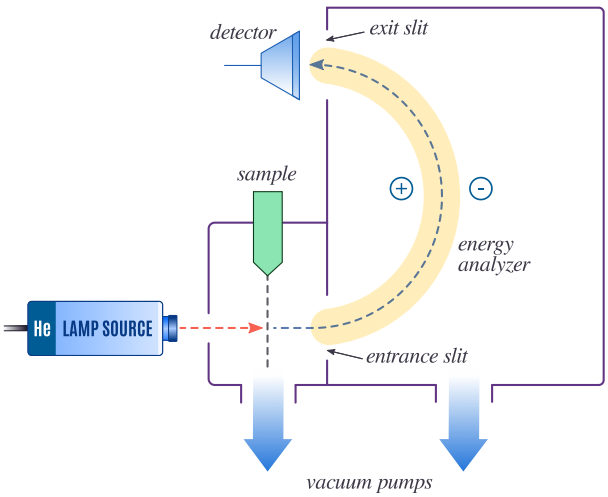


Figure 10.4.1: Diagram of a basic, typical PES instrument used in UPS, where the radiation source is an UV light source. When the sample is irradiated, the released photoelectrons pass through the lens system which slows them down before they enter the energy analyzer. The analyzer shown is a spherical deflection analyzer which the photoelectrons pass through before they are collected at the collector slit. (CC BY 4.0; Ümit Kaya via LibreTexts)

The process of photoionization can be considered in several ways. One way is to look at the overall process for a species A:

$$A + \text{photon} \rightarrow A^+ + e^- \tag{4.12.2}$$

Conservation of energy then requires that (after using Equation 4.12.1):

$$E(A) + h\nu = E(A^+) + E(e^-) \tag{4.12.3}$$

Since the free electron's energy is present solely as kinetic energy (KE) (i.e., there is no internal energy in a free electron)

$$E(e^-) = KE$$

Equation 4.12.3 can then be rearranged to give the following expression for the KE of the photoelectron:

$$KE = h\nu - [E(A^+) - E(A)] \tag{4.12.4}$$

The final term in brackets represents the difference in energy between the ionized and neutral species and is generally called the **vertical ionization energy** (IE) of the ejected electron; this then leads to the following commonly quoted equations:

$$KE = h\nu - IE \tag{4.12.5}$$

or

$$IE = h\nu - KE \tag{4.12.6}$$

The vertical ionization energy is a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level (i.e., a free electron). Photoelectron spectroscopy measures the relative energies of the ground and excited positive ion states that are obtained by removal of single electrons from the neutral molecule.

Note

Equation 4.12.5 may look familiar to you as it the same equation Einstein used to describe the photoelectric effect except the vertical ionization energy (IE) is substituted for workfunction Φ. Both vertical ionization energy and workfunctions are metrics for the binding energy of an electron in the sample.

At a fundamental level, ionization energies are well-defined thermodynamic quantities related to the heats of protonation, oxidation/reduction chemistry, and ionic and covalent bond energies. Ionization energies are closely related to the concepts of electronegativity, electron-richness, and the general reactivity of molecules. The energies and other characteristic features of the ionization bands observed in photoelectron spectroscopy provide some of the molecular orbitals detailed and specific quantitative information regarding the electronic structure and bonding in molecules.

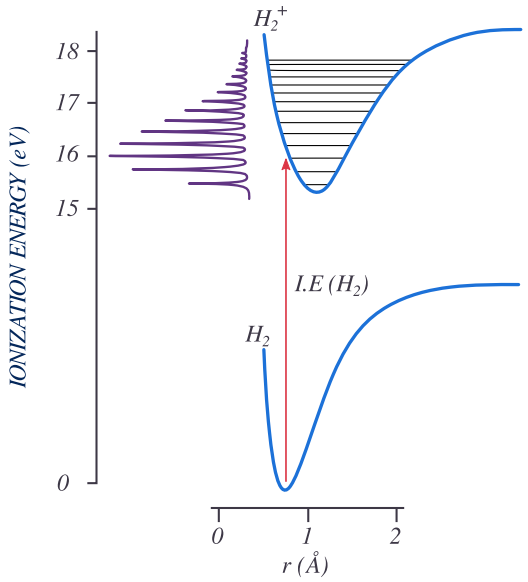


Figure 10.4.2: Vertical ionization process for molecular hydrogen. (CC BY 4.0; Ümit Kaya via LibreTexts)

Ionization is explicitly defined in terms of transitions between the ground state of a molecule and ion states as shown in Equation 4.12.6 and as illustrated in the Figure 10.4.2. Nonetheless, the information obtained from photoelectron spectroscopy is typically discussed in terms of the electronic structure and bonding in the ground states of neutral molecules, with ionization of electrons

occurring from bonding molecular orbitals, lone pairs, antibonding molecular orbitals, or atomic cores. These descriptions reflect the relationship of ionization energies to the molecular orbital model of electronic structure.

Ionization energies are directly related to the energies of molecular orbitals by Koopmans' theorem, which states that the negative of the eigenvalue of an occupied orbital from a Hartree-Fock calculation is equal to the *vertical ionization energy* to the ion state formed by removal of an electron from that orbital (Figure 10.4.3), provided the distributions of the remaining electrons do not change (i.e., frozen).

$$I_j = -\epsilon_j \tag{4.12.7}$$

There are many limitations to Koopmans' theorem, but in a first order approximation each ionization of a molecule can be considered as removal of an electron from an individual orbital. The ionization energies can then be considered as measures of orbital stabilities, and shifts can be interpreted in terms of orbital stabilizations or destabilizations due to electron distributions and bonding. Koopmans' theorem is implicated whenever an orbital picture is involved, but is not necessary when the focus is on the total electronic states of the positive ions.

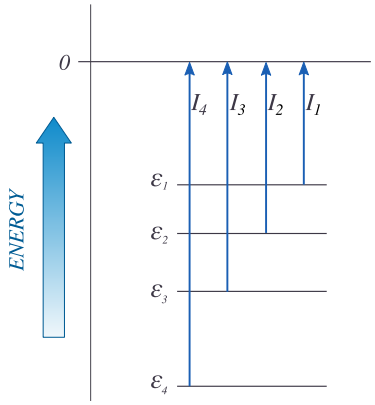


Figure 10.4.3: Within Koopmans' Theorem, the energies of the orbitals ϵ have an attractively simple physical interpretation: they give the amount of energy necessary to remove (ionize) the electron out of the molecular orbital, which corresponds to the negative of the experimentally observable ionization potential (I). (CC BY 4.0; Ümit Kaya via LibreTexts)

Koopmans' Theorem

Koopmans' theorem argues that the negative of the eigenvalue of an occupied orbital from a Hartree-Fock calculation is equal to the vertical ionization energy to the ion state formed by removal of an electron from that orbital.

Several different ionization energies can be defined, depending on the degree of vibrational excitation of the cations. In general, the following two types of ionization energies are considered (Figure 10.4.4):

- Adiabatic ionization energy corresponds to the ionization energy associated with this transition

  $$M(X, v''= 0) + h\nu \rightarrow M^+(x, v' = 0) + e^-$$

  Adiabatic ionization energy that is, the minimum energy required to eject an electron from a molecule in its ground vibrational state and transform it into a cation in the lowest vibrational level of an electronic state x of the cation.
- Vertical ionization energy corresponds to the ionization energy associated with this transition

  $$M(X, v''= 0) + h\nu \rightarrow M^+(x, v' = n) + e^-$$

  where, the value n of the vibrational quantum number v' corresponds to the vibrational level whose wavefunction gives the largest overlap with the v" = 0 wavefunction. This is the most probable transition and usually corresponds to the vertical transition where the internuclear separations of the ionic state are similar to those of the ground state.

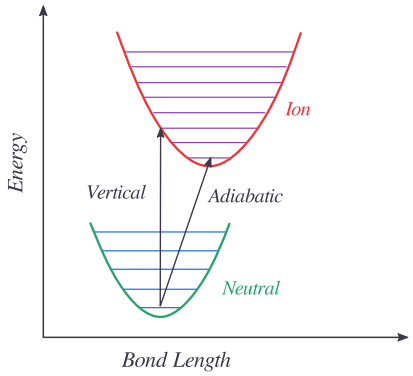


Figure 10.4.4: Difference between vertical and adiabatic ionization energies for a simple harmonic oscillator system. (CC BY 4.0; Ümit Kaya via LibreTexts)

The geometry of an ion may be different from the neutral molecule. The measured ionzation energy in a PES experiment can refer to the vertical ionization energy, in which case the ion is in the same geometry as the neutral, or to the adiabatic ionzaiton energy, in which case the ion is in its lowest energy, relaxed geometry (mostly the former though). This is illustrated in the Figure 10.4.4. For a diatomic the only geometry change possible is the bond length. The figure shows an ion with a slightly longer bond length than the neutral. The harmonic potential energy surfaces are shown in green (neutral) and red (ion) with vibrational energy levels. The vertical ionzation energy is **always greater** than the adiabatic ionzation energy.

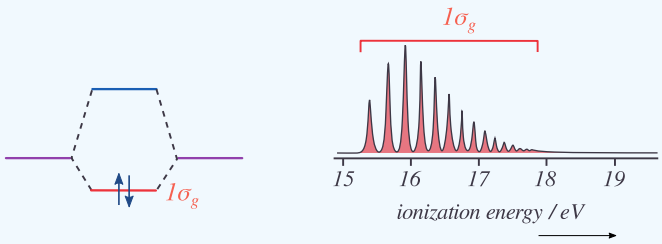
Differing Ionization Energies

You have been exposed to three metrics of ionization energies already, which are similar, but with distinct differences:

- The *ionization energy* (also called *adiabatic ionization energy*) is the lowest energy required to effect the removal of an electron from a molecule or atom, and corresponds to the transition from the lowest electronic, vibrational and rotational level of the isolated molecule to the lowest electronic, vibrational and rotational level of the isolated ion.
- The *binding energy* (also called *vertical ionization energy*) is the energy change corresponding to an ionization reaction leading to formation of the ion in a configuration which is the same as that of the equilibrium geometry of the ground state neutral molecule.
- The *workfunction* is the minimum energy needed to remove an electron from a (bulk) solid to a point in the vacuum.

Example 10.4.1: Molecular Hydrogen

As you remember, the molecular orbital description of molecular hydrogen involves two $|1s\rangle$ atomic orbitals generating a bonding $1\sigma_g$ and antibonding $2\sigma_u^*$ molecular orbitals. The two electrons that are responsible for the H_2 bond are occupied in the $1\sigma_g$.



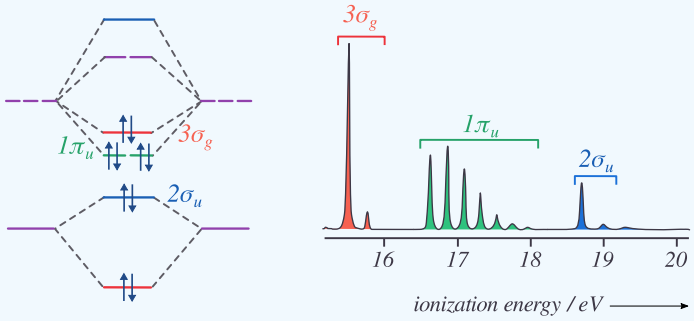
MO diagram and PES spectrum of H_2. (CC BY 4.0; Ümit Kaya via LibreTexts)

The PES spectrum has a single band that corresponds to the ionization of a $1\sigma_g$ electron. The multiple peaks are due to electrons ejecting from a range of stimulated vibrational energy levels. When extensive vibrational structure is resolved in a

PES molecular orbital, then the removal of an electron from that molecular orbital induces a significant change in the bonding (in this case an increase in the bond length since the bond order has been reduced).

Example 10.4.2: Molecular Nitrogen

Diatomic nitrogen is more complex than hydrogen since multiple molecular orbitals are occupied. Four molecular orbitals are occupied (the two $1\pi_u$ orbitals are both occupied). The UV photoelectron spectrum of N_2, has three bands corresponding to $3\sigma_g$, $1\pi_u$ and $2\sigma_u$ occupied molecular orbitals. Both $3\sigma_g$ and $2\sigma_u$ are weakly bonding and antibonding. The $1\sigma_g$ orbital is not resolved in this spectrum since the incident light $h\nu$ used did not have sufficient energy to ionize electrons in that deeply stabilized molecular orbital.



MO diagram and PES spectrum of N_2. (CC BY 4.0; Ümit Kaya via LibreTexts)

Note that extensive vibrational structure for the $1\pi_u$ band indicates that the removal of an electron from this molecular orbital causes a significant change in the bonding.

Hydrogen Chloride

The molecular energy level diagram for HCl is reproduced in Figure 10.4.5

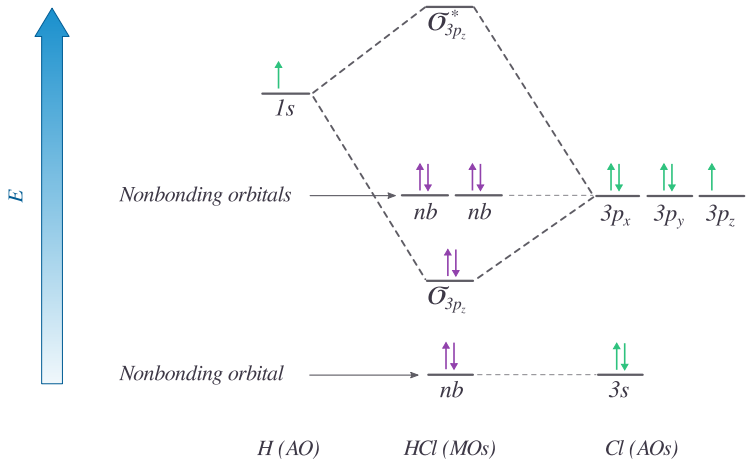


Figure 10.4.5: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts molecular orbitals strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1. (CC BY 4.0; Ümit Kaya via LibreTexts)

Important aspects of molecular orbital diagram in Figure 10.4.5:

- The H 1*s* energy lies well above the Cl 2*s* and 2*p* atomic orbitals;
- The valence electron configuration can be written $3\sigma^2 1\pi^4$;

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- The H 1*s* orbital contributes only to the σ molecular orbitals, as does one of the Cl 2*p* orbitals (hence the lines in Figure 10.4.5 connecting these atomic orbitals and the 3σ and 4σ molecular orbitals);
- The remaining Cl 2*p* orbitals (ie those perpendicular to the bond axis) are unaffected by bonding, and these form the 1π molecular orbitals;
- The 1π orbitals are nonbonding - they are not affected energetically by the interaction between the atoms, and are hence neither bonding nor antibonding;
- The 3σ orbital is weakly bonding, and largely Cl 2*p*;
- The 3σ* orbital is antibonding, and primarily of H 1*s* character;

Figure 10.4.6 shows the analogous MO diagram and photoelectron spectrum for HCl. The spectrum has two bands corresponding to non-bonding 1*p* (or 1π) molecular orbitals (with negligible vibrational structure) and the 3*s* bonding molecular orbital (vibrational structure).

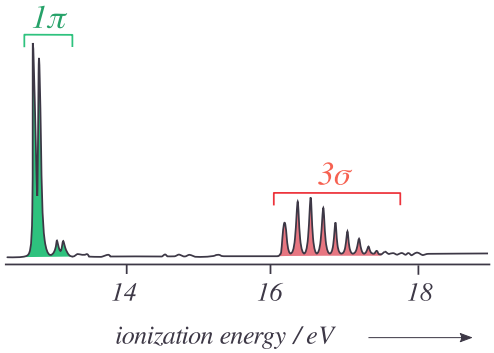


Figure 10.4.6: Photoelectron spectrum HCl. (CC BY 4.0; Ümit Kaya via LibreTexts)

The higher energy (more stabilized) core molecular orbitals are not observed since the incident photon energy $h\nu$ is below their ionization energies.

Water

In the simplified valence bond theory perspective of the water molecule, the oxygen atom form four sp^3 hybrid orbitals. Two of these are occupied by the two lone pairs on the oxygen atom, while the other two are used for bonding. Within the molecular orbital picture, the electronic configuration of the H_2O^+ molecule is $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$ where the symbols a_1, b_2 and b_1 are orbital labels based on molecular symmetry that will be discussed later (Figure 10.4.7). Within Koopmans' theorem:

- The energy of the $1b_1$ HOMO corresponds to the ionization energy to form the H_2O^+ ion in its ground state $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^1$.
- The energy of the second-highest molecular orbitals $3a_1$ refers to the ion in the excited state $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^2$.

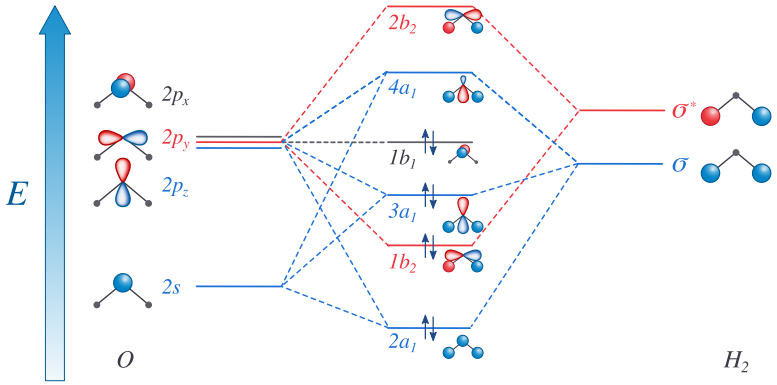


Figure 10.4.7: MO diagram for water. (CC BY 4.0; Ümit Kaya via LibreTexts)

The Hartree–Fock orbital energies (with sign changed) of these orbitals are tabulated below and compared to the experimental ionization energies.

Molecular orbital	Hartree–Fock orbital Energies (eV)	Experimental Ionization Energies (eV)
$2a_1$	36.7	32.2
$1b_2$	19.5	18.5
$3a_1$	15.9	14.7
$1b_1$	13.8	12.6

As explained above, the deviations between orbital energy and ionization energy is small and due to the effects of orbital relaxation as well as differences in electron correlation energy between the molecular and the various ionized states.

The molecular orbital perspective has the lone pair in different orbitals (one in a non-bonding orbital ($1b_1$ and one in the bonding orbitals). We tern to the photoelectron spectroscopy to help identify which theory is more accurate (i.e., describes reality better). The photoelectron spectrum of water in Figure 10.4.6 can be interpreted as having three major peaks with some fine structure arises from vibrational energy changes. The light source used in this experiment is not sufficiently energetic to ionize electrons from the lowest lying molecular orbitals.

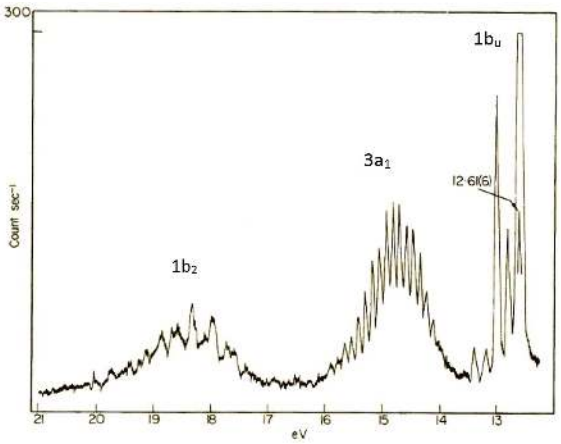


Figure 10.4.8: Photoelectron spectrum of water. Note the energy axes is flipped compared to other spectra on this page. This spectrum does not go to high enough energy to show the deep $2a_1$ molecular orbital.

If water was formed two identical O-H bonds and two lone pairs on the oxygen atom line valence bond theory predicts, then the PES in Figure 10.4.8 would have two (degenerate) peaks, one for the two bonds and one for the two lone pairs. The photoelectron spectrum clearly shows three peaks in the positions expected for the molecular orbitals in Figure 10.4.8.

If the molecular orbitals in Figure 10.4.7 represent the real electronic structure, how do we view the bonding? These molecular orbitals are delocalized and bare little relationship to the familiar 2-center bonds used in valence bond theory. For example, the $2a_1$ $1b_1$ and $3a_1$ molecular orbitals all have contributions from all three atoms, they are really 3-centered molecular orbitals. The bonds however can be thought of as representing a build up of the total electron density which loosely put is a total of all the orbital contributions. Despite this, we keep the ideas of hybridization and 2-center bonds because they are useful NOT because they represent reality

Summary

A photoelecton spectrum can show the relative energies of occupied molecular orbitals by ionization. (i.e. ejection of an electron). A photoelectron spectrum can also be used to determine energy spacing between vibrational levels of a given electronic state. Each orbital energy band has a structure showing ionization to different vibrational levels.

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SECTION OVERVIEW

4.13: Computational Methods

Topic hierarchy

4.13A: Hartree-Fock Theory

4.13B: Density Functional Theory

4.13C: Hückel MO Theory

4.13D: Molecular Mechanisms (MM)

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4.13A: Hartree-Fock Theory

In a modern *ab initio* electronic structure calculation on a closed shell molecule, the electronic Hamiltonian is used with a single determinant wavefunction. This wavefunction, ψ, is constructed from molecular orbitals, ψ that are written as linear combinations of contracted Gaussian basis functions, φ

$$\varphi_j = \sum_k c_{jk}\psi_k \tag{4.13A.1}$$

The contracted Gaussian functions are composed from primitive Gaussian functions to match Slater-type orbitals (STOs). The exponential parameters in the STOs are optimized by calculations on small molecules using the nonlinear variational method and then those values are used with other molecules. The problem is to calculate the electronic energy from

$$E = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} \tag{4.13A.2}$$

and find the optimum coefficients c_{jk} for each molecular orbital in Equation 4.13A.1 by using the Self Consistent Field Method and the Linear Variational Method to minimize the energy as was described in the previous chapter for the case of atoms.

To obtain the total energy of the molecule, we need to add the internuclear repulsion to the electronic energy calculated by this procedure. The total energy of the molecule can be calculated for different geometries (i.e. bond lengths and angles) to find the minimum energy configuration. Also, the total energies of possible transition states can be calculated to find the lowest energy pathway to products in chemical reactions.

$$V_{rs} = \sum_{r=1}^{N-1} \sum_{s=r+1}^{N} \frac{Z_r Z_s}{r_{rs}} \tag{4.13A.3}$$

Exercise 4.13A.1

For a molecule with three nuclei, show that the sums in Equation 4.13A.3 correctly include all the pairwise potential energy terms without including any twice.

As we improve the basis set used in calculations by adding more and better functions, we expect to get better and better energies. The variational principle says an approximate energy is an upper bound to the exact energy, so the lowest energy that we calculate is the most accurate. At some point, the improvements in the energy will be very slight. This limiting energy is the lowest that can be obtained with a single determinant wavefunction. This limit is called the *Hartree-Fock limit*, the energy is the *Hartree-Fock energy*, the molecular orbitals producing this limit are called *Hartree-Fock orbitals*, and the determinant is the *Hartree-Fock wavefunction*.

Exercise 4.13A.2

Write a one-sentence definition of the Hartree-Fock wavefunction that captures all the essential features of this function.

Restricted vs. Unrestricted Hartree-Fock

You may encounter the terms *restricted* and *unrestricted* Hartree-Fock. The above discussion pertains to a restricted HF calculation. In a restricted HF calculation, electrons with α spin are restricted or constrained to occupy the same spatial orbitals as electrons with β spin. This constraint is removed in an unrestricted calculation. For example, the spin orbital for electron 1 could be $\psi_A(r_1)\alpha(1)$, and the spin orbital for electron 2 in a molecule could be $\psi_B(r_2)\beta(2)$, where both the spatial molecular orbital and the spin function differ for the two electrons. Such spin orbitals are called *unrestricted*. If both electrons are constrained to have the same spatial orbital, e.g. $\psi_A(r_1)\alpha(1)$ and $\psi_A(r_2)\beta(2)$, then the spin orbital is said to be *restricted*. While unrestricted spin orbitals can provide a better description of the electrons, twice as many spatial orbitals are needed, so the demands of the calculation are much higher. Using unrestricted orbitals is particular beneficial when a molecule contains an odd number of electrons because there are more electrons in one spin state than in the other.

Carbon Dioxide

Now consider the results of a self-consistent field calculation for carbon monoxide, CO. It is well known that carbon monoxide is a poison that acts by binding to the iron in hemoglobin and preventing oxygen from binding. As a result, oxygen is not transported by the blood to cells. Which end of carbon monoxide, carbon or oxygen, do you think binds to iron by donating electrons? We all know that oxygen is more electron-rich than carbon (8 vs 6 electrons) and more electronegative. A reasonable answer to this question therefore is *oxygen*, but experimentally it is carbon that binds to iron.

A quantum mechanical calculation done by Winifred M. Huo, published in J. Chem. Phys. 43, 624 (1965), provides an explanation for this counter-intuitive result. The basis set used in the calculation consisted of 10 functions: the ls, 2s, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals of C and O. Ten molecular orbitals (mo's) were defined as linear combinations of the ten atomic orbitals, which are written as

$$\psi_k = \sum_{j=1}^{10} C_{kj}\varphi_j \tag{4.13A.4}$$

where k identifies the mo and j identifies the atomic orbital basis function. The ground state wavefunction ψ is written as the Slater Determinant of the five lowest energy molecular orbitals ψ_k. Equation 4.13A.5 gives the energy of the ground state,

$$E = \frac{\left\langle \psi | \hat{H} | \psi \right\rangle}{\langle \psi | \psi \rangle} \tag{4.13A.5}$$

where the denominator accounts for the normalization requirement. The coefficients C_{kj} in the linear combination are determined by the variational method to minimize the energy. The solution of this problem gives the following equations for the molecular orbitals. Only the largest terms have been retained here. These functions are listed and discussed in order of increasing energy.

- $1s \approx 0.941 s_o$. The 1 says this is the first σ orbital. The σ says it is symmetric with respect to reflection in the plane of the molecule. The large coefficient, 0.94, means this is essentially the 1s atomic orbital of oxygen. The oxygen 1s orbital should have a lower energy than that of carbon because the positive charge on the oxygen nucleus is greater.
- $2s \approx 0.921 s_c$. This orbital is essentially the 1s atomic orbital of carbon. Both the 1σ and 2σ are "nonbonding" orbitals since they are localized on a particular atom and do not directly determine the charge density between atoms.
- $3s \approx (0.722 s_o + 0.182 p_{zo}) + (0.282 s_c + 0.162 p_{zc})$. This orbital is a "bonding" molecular orbital because the electrons are delocalized over C and O in a way that enhances the charge density between the atoms. The 3 means this is the third σ orbital. This orbital also illustrates the concept of hybridization. One can say the 2s and 2p orbitals on each atom are hybridized and the molecular orbital is formed from these hybrids although the calculation just obtains the linear combination of the four orbitals directly without the *à priori* introduction of hybridization. In other words, hybridization just falls out of the calculation. The hybridization in this bonding LCAO increases the amplitude of the function in the region of space between the two atoms and decreases it in the region of space outside of the bonding region of the atoms.
- $4s \approx (0.372 s_c + 0.12 p_{zc}) + (0.542 p_{zo} - 0.432 s_0)$. This molecular orbital also can be thought of as being a hybrid formed from atomic orbitals. The hybridization of oxygen atomic orbitals, because of the negative coefficient with $2s_O$, decreases the electron density between the nuclei and enhances electron density on the side of oxygen facing away from the carbon atom. If we follow how this function varies along the internuclear axis, we see that near carbon the function is positive whereas near oxygen it is negative or possibly small and positive. This change means there must be a node between the two nuclei or at the oxygen nucleus. Because of the node, the electron density between the two nuclei is low so the electrons in this orbital do not serve to shield the two positive nuclei from each other. This orbital therefore is called an "antibonding" mo and the electrons assigned to it are called antibonding electrons. This orbital is the antibonding partner to the 3σ orbital.
- $1\pi \approx 0.322 p_{xc} + 0.442 p_{xo}$ and $2\pi \approx 0.322 p_{yc} + 0.442 p_{yo}$. These two orbitals are degenerate and correspond to bonding orbitals made up from the p_x and p_y atomic orbitals from each atom. These orbitals are degenerate because the x and y directions are equivalent in this molecule. π tells us that these orbitals are antisymmetric with respect to reflection in a plane containing the nuclei.
- $5\sigma \approx 0.382_{sC} - 0.382_{pC} - 0.292 p_{zO}$. This orbital is the sp hybrid of the carbon atomic orbitals. The negative coefficient for $2p_C$ puts the largest amplitude on the side of carbon away from oxygen. There is no node between the atoms. We conclude this is a nonbonding orbital with the nonbonding electrons on carbon. This is not a "bonding" orbital because the electron density

between the nuclei is lowered by hybridization. It also is not an antibonding orbital because there is no node between the nuclei. When carbon monoxide binds to Fe in hemoglobin, the bond is made between the C and the Fe. This bond involves the donation of the 5σ nonbonding electrons on C to empty d orbitals on Fe. Thus mo theory allows us to understand why the C end of the molecule is involved in this electron donation when we might naively expect O to be more electron-rich and capable of donating electrons to iron.

Exercise 4.13A.3

Summarize how Quantum Mechanics is used to describe bonding and the electronic structure of molecules.

Exercise 4.13A.4

Construct an energy level diagram for CO that shows both the atomic orbitals and the molecular orbitals. Show which atomic orbitals contribute to each molecular orbital by drawing lines to connect the mo's to the ao's. Label the molecular orbitals in a way that reveals their symmetry. Use this energy level diagram to explain why it is the carbon end of the molecule that binds to hemoglobin rather than the oxygen end.

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4.13B: Density Functional Theory

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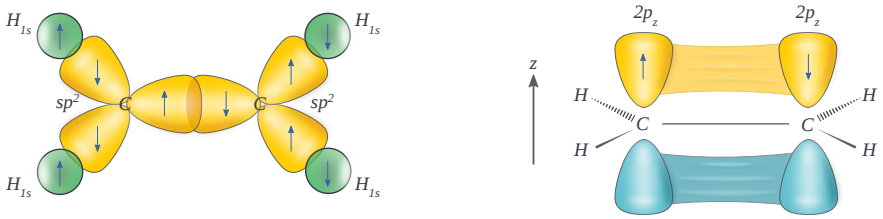
4.13C: Hückel MO Theory

Learning Objectives

- Demonstrate how Hückel's theory approximates the full molecular orbital picture of molecules by treating the σ-bonding and π-bonding networks independently.

Molecular orbital theory has been very successfully applied to large conjugated systems, especially those containing chains of carbon atoms with alternating single and double bonds. An approximation introduced by Hückel in 1931 considers only the delocalized *p* electrons moving in a framework of π-bonds. This is, in fact, a more sophisticated version of a free-electron model.

The simplest hydrocarbon to consider that exhibits π bonding is ethylene (ethene), which is made up of four hydrogen atoms and two carbon atoms. Experimentally, we know that the H−C−H and H−C−C angles in ethylene are approximately 120°. This angle suggests that the carbon atoms are sp^2 hybridized, which means that a singly occupied sp^2 orbital on one carbon overlaps with a singly occupied *s* orbital on each H and a singly occupied sp^2 lobe on the other C. Thus each carbon forms a set of three σ bonds: two C–H (sp^2 + *s*) and one C–C (sp^2 + sp^2) (part a of Figure 10.5.1).



(a) C_2H_4 σ - bonded framework *(b) C_2H_4 π bonding*

Figure 10.5.1 : (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1s orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C–H bonds and one C–C bond). (b) One singly occupied unhybridized $2p_z$ orbital remains on each carbon atom to form a carbon–carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the *z*-axis.) (CC BY-NC; Ümit Kaya via LibreTexts)

The Hückel approximation is used to determine the energies and shapes of the π molecular orbitals in conjugated systems. Within the Hückel approximation, the covalent bonding in these hydrocarbones can be separated into two independent "frameworks": the σ -bonding framework and the the σ-bonding framework. The wavefunctions used to describe the bonding orbitals in each framework results from different combinations of atomic orbitals. The method limits itself to addressing conjugated hydrocarbons and specifically only π electron molecular orbitals are included because these determine the general properties of these molecules; the sigma electrons are ignored. This is referred to as *sigma-pi separability* and is justified by the orthogonality of σ and π orbitals in planar molecules. For this reason, the Hückel method is limited to planar systems. Hückel approximation assumes that the electrons in the π bonds “feel” an electrostatic potential due to the entire σ-bonding framework in the molecule (i.e. it focuses only on the formation of π bonds, given that the σ bonding framework has already been formed).

Conjugated Systems

A conjugated system has a region of overlapping p-orbitals, bridging the interjacent single bonds, that allow a *delocalization* of π electrons across all the adjacent aligned p-orbitals. These π electrons do not belong to a single bond or atom, but rather to a group of atoms.

Ethylene

Before considering the Hückel treatment for ethylene (C_2H_4), it is beneficial to review the general bonding picture of the molecule. Bonding in ethylene involves the sp^2 hybridization of the $2s$, $2p_x$, and $2p_y$ atomic orbitals on each carbon atom; leaving the $2p_z$ orbitals untouched (Figure 10.5.2).

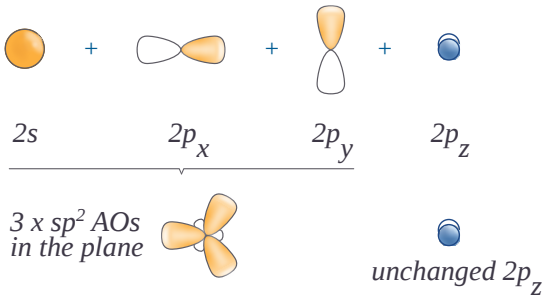


Figure 10.5.2 : Hybridizing of the carbon atomic orbitals to give sp^2 hybrid orbitals for bonding to hydrogen atoms in ethylene. (CC BY-NC; Ümit Kaya via LibreTexts)

The use of hybrid orbitals in the molecular orbital approach describe here is merely a convenience and not invoking valence bond theory (directly). An identical description can be extracted using exclusively atomic orbitals on carbon, but the interpretation of the resulting wavefunctions is less intuitive. For example, the i[th] molecular orbital can be described via hybrid orbitals

$$|\psi_1\rangle = c_1|sp_1^2\rangle + c_2|1s_a\rangle$$

or via atomic orbitals.

$$|\psi_1\rangle = a_1|2s\rangle + a_1|2p_x\rangle + a_1|2p_y\rangle + a_4|1s_a\rangle$$

where $\{a_i\}$ and $\{c_i\}$ are coefficients of the expansion. Either describe will work and both are identical approaches since

$$|sp_1^2\rangle = b_1|2s\rangle + b_1|2p_x\rangle + b_1|2p_y\rangle$$

where $\{c_i\}$ are coefficients describing the hybridized orbital.

The bonding occurs via the mixing of the electrons in the sp^2 hybrid orbitals on carbon and the electrons in the $1s$ atomic orbitals of the four hydrogen atoms (Figure 10.5.1 ; left) resulting in the σ-bonding framework. The π-bonding framework results from the unhybridized $2p_z$ orbitals (Figure 10.5.2 ; right). The independence of these two frameworks is demonstrated in the resulting molecular orbital diagram in Figure 10.5.3 ; Hückel theory is concerned only with describing the molecular orbitals and energies of the π bonding framework.

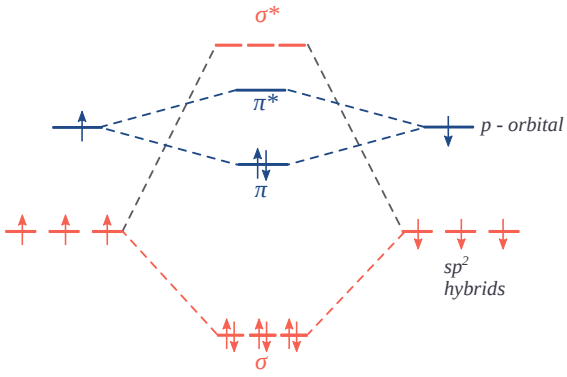


Figure 10.5.3 : Molecular orbitals demonstrating the sigma-pi separability of the π-bonding framework (blue) and the σ-bonding frameworks (red) of ethylene. (CC BY-NC; Ümit Kaya via LibreTexts)

> *Hückel treatment is concerned only with describing the molecular orbitals and energies of the π bonding framework.*

Since Hückel theory is a special consideration of molecular orbital theory, the molecular orbitals $|\psi_i\rangle$ can be described as a linear combination of the $2p_z$ atomic orbitals ϕ at carbon with their corresponding $\{c_i\}$ coefficients:

$$|\psi_i\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle \tag{4.13C.1}$$

This equation is substituted in the Schrödinger equation:

$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle$$

with $\hat{H}$ the Hamiltonian and E_i the energy corresponding to the molecular orbital to give:

$$\hat{H}c_1|\phi_1\rangle + \hat{H}c_2|\phi_2\rangle = Ec_1|\phi_1\rangle + Ec_2|\phi_2\rangle \tag{4.13C.2}$$

If Equation 4.13C.2 is multiplied by $\langle\phi_1|$ (and integrated), then

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \tag{4.13C.3}$$

where H_{ij} are the Hamiltonian matrix elements (see note below)

$$H_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle = \int \phi_i H \phi_j \mathrm{d}v$$

and S_{ij} are the overlap integrals.

$$S_{ij} = \langle\phi_i|\phi_j\rangle = \int \phi_i \phi_j \mathrm{d}v$$

If Equation 4.13C.2 is multiplied by $\langle\phi_2|$ (and integrated), then

$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0 \tag{4.13C.4}$$

Both Equations 4.13C.3 and 4.13C.4 can better represented in matrix notation,

$$\begin{bmatrix} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) \\ c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) \end{bmatrix} = 0$$

or more simply as a product of matrices.

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{4.13C.5}$$

All diagonal Hamiltonian integrals H_{ii} are called **Coulomb integrals** and those of type H_{ij} are called **resonance integrals**. Both integrals are negative and the resonance integrals determines the strength of the bonding interactions. The equations described by Equation 4.13C.5 are called the ***secular equations*** and will also have the trivial solution of

$$c_1 = c_2 = 0$$

Within linear algebra, the secular equations in Equation 4.13C.5 will also have a non-trivial solution, if and only if, the secular determinant is zero

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \tag{4.13C.6}$$

or in shorthand notation

$$\det(H - ES) = 0$$

Everything in Equation 4.13C.6 is a known number except E. Since the secular determinant for ethylene is a 2×2 matrix, finding E, requires solving a quadratic equation (after expanding the determinant)

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{21} - ES_{21})(H_{12} - ES_{12}) = 0$$

There will be two values of E which satisfy this equation and they are the molecular orbital energies. For ethylene, one will be the bonding energy and the other the antibonding energy for the π-orbitals formed by the combination of the two carbon $2p_z$ orbitals (Equation 4.13C.1). However, if more than two $|\phi\rangle$ atomic orbitals were used, e.g., in a bigger molecule, then more energies would be estimated by solving the secular determinant.

Solving the secular determinant is simplified within Hückel method via the following four assumptions:

1. All overlap integrals S_{ij} are set equal to zero. This is quite reasonable since the $\pi-$ orbitals are directed perpendicular to the direction of their bonds (Figure 10.5.1). This assumption is often call neglect of differential overlap (NDO).

2. All resonance integrals H_{ij} between non-neighboring atoms are set equal to zero.
3. All resonance integrals H_{ij} between neighboring atoms are equal and set to β.
4. All coulomb integrals H_{ii} are set equal to α.

These assumptions are mathematically expressed as

$$H_{11} = H_{22} = \alpha$$

$$H_{12} = H_{21} = \beta$$

Assumptions 1 means that the overlap integral between the two atomic orbitals is 0

$$S_{11} = S_{22} = 1$$

$$S_{12} = S_{21} = 0$$

Matrix Representation of the Hamiltonian

The Coulomb integrals

$$H_{ii} = \langle \phi_i | H | \phi_i \rangle$$

and resonance integrals.

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle \;\; (i \neq i)$$

are often described within the matrix representation of the Hamiltonian (specifically within the $|\phi\rangle$ basis):

$$\hat{H} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}$$

or within the Hückel assumptions

$$\hat{H} = \begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix}$$

The Hückel assumptions reduces Equation 4.13C.5 in two homogeneous equations:

$$\begin{bmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{4.13C.7}$$

if Equation 4.13C.7 is divided by β:

$$\begin{bmatrix} \dfrac{\alpha - E}{\beta} & 1 \\ 1 & \dfrac{\alpha - E}{\beta} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

and then a new variable x is defined

$$x = \frac{\alpha - E}{\beta} \tag{4.13C.8}$$

then Equation 4.13C.7 simplifies to

$$\begin{bmatrix} x & 1 \\ 1 & x \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{4.13C.9}$$

The trivial solution gives both wavefunction coefficients equal to zero and the other (non-trivial) solution is determined by solving the secular determinant

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

which when expanded is $x^2 - 1 = 0$ so $x = \pm 1$.

Knowing that $E = \alpha - x\beta$ from Equation 4.13C.8, the energy levels can be found to be

$$E = \alpha - \pm 1 \times \beta$$

or

$$E = \alpha \mp \beta$$

Since β is negative, the two energies are ordered (Figure 10.5.4)

- For π_1: $E_1 = \alpha + \beta$
- For π_2: $E_2 = \alpha - \beta$

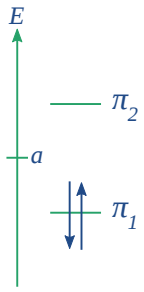


Figure 10.5.4 : π energies of ethylene with occupation. (CC BY-NC; Ümit Kaya via LibreTexts)

To extract the coefficients attributed to these energies, the corresponding x values can be substituted back into the Secular Equations (Equation 4.13C.9). For the lower energy state ($x = -1$)

$$\begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

This gives $c_1 = c_2$ and the molecular orbitals attributed to this energy is then (based off of Equation 4.13C.1):

$$|\psi_1\rangle = N_1(\phi_1\rangle + |\phi_2\rangle) \tag{4.13C.10}$$

where N_1 is the normalization constant for this molecular orbital; this is the **bonding** molecular orbital.

For the higher energy molecular orbital ($x = -1$) and then

$$\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

This gives $c_1 = -c_2$ and the molecular orbitals attributed to this energy is then (based off of Equation 4.13C.1):

$$\psi_2\rangle = N_2(\phi_1\rangle - |\phi_2\rangle) \tag{4.13C.11}$$

where N_2 is the normalization constant for this molecular orbital; this is the **anti-bonding** molecular orbital.

The normalization constants for both molecular orbitals can obtained via the standard normalization approach (i.e., $\langle\psi_i|\psi_i\rangle = 1$) to obtain

$$N_1 = N_2 = \frac{1}{\sqrt{2}}$$

These molecular orbitals form the π-bonding framework and since each carbon contributes one electron to this framework, only the lowest molecular orbital ($|\psi_1\rangle$) is occupied (Figure 10.5.5) in the ground state. The corresponding electron configuration is then π_1^2.

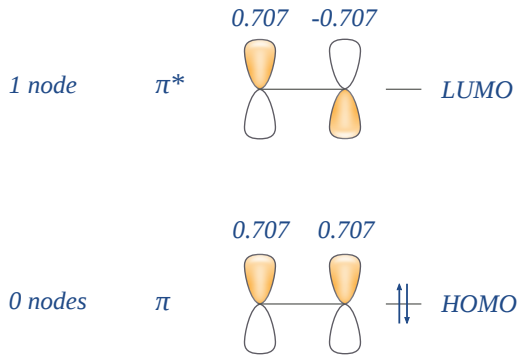


Figure 10.5.5 : Schemetic representation of the π molecular orbitals framework for ethylene . Notice that the antibonding molecular orbital has one more node than the bonding molecular orbital as expected since it is higher in energy. (CC BY-NC; Ümit Kaya via LibreTexts)

> *HOMO and LUMO are acronyms for highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively and are often referred to as frontier orbitals. The energy difference between the HOMO and LUMO is termed the HOMO–LUMO gap.*

The 3-D calculated π molecular orbitals are shown in Figure 10.5.6 .

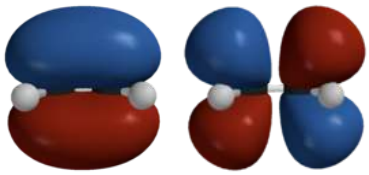


Figure 10.5.6 : Calculated π molecular orbitals for ethylene . (left) the bonding orbital (|\psi_1 \rangle\) and (right) the antibonding ($|\psi_2\rangle$ orbital.

Limitations of Hückel Theory

Hückel theory was developed in the 1930's when computers were unavailable and a simple mathematical approaches were very important for understanding experiment. Although the assumptions in Hückel theory are drastic they enabled the early calculations of molecular orbitals to be performed with mechanical calculators or by hand. Hückel Theory can be extended to address other types of atoms in conjugated molecules (e.g., nitrogen and oxygen). Moreover, it can be extended to also treat σ orbitals and this "Extended Hückel Theory" is still used today. Despite the utility of Hückel Theory, it is highly qualitative and we should remember the limitations of Hückel Theory:

- Hückel Theory is very approximate
- Hückel Theory cannot calculate energies accurately (electron-electron repulsion is not calculated)
- Hückel Theory typically overestimates predicted dipole moments

Hückel Theory is best used to provide simplified models for understanding chemistry and for a detailed understanding modern *ab initio* molecular methods discussed in Chapter 11 are needed.

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- **10.5: The pi-Electron Approximation of Conjugation (Hückel Theory)** by Seymour Blinder is licensed CC BY-NC-SA 4.0.

4.13D: Molecular Mechanisms (MM)

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SECTION OVERVIEW

4.14: Magnetism

Topic hierarchy

4.14.1: example magnetic moment data and their interpretation

4.14.2: Magnetic Moments

4.14.3: Magnetic Moments 1

4.14.4: Magnetic Susceptibility Measurements

4.14.5: Magnetism

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4.14.1: example magnetic moment data and their interpretation

Summary of applicable formulae

1) Spin-Only magnetic moment
$\mu_{s.o.} = \sqrt{\{4S(S+1)\}}$ B.M.

2) For A and E ground terms
$\mu_{eff} = \mu_{s.o.} (1-\alpha \lambda /\Delta)$ B.M.
Do not expect Temperature dependence.

3) For T ground terms with orbital angular momentum contribution
$\mu_{S+L} = \sqrt{\{4S(S+1) + L(L+1)\}}$ B.M.
T terms generally show marked Temperature dependence.

The examples that follow are arranged showing the experimentally observed values, the theoretical "spin-only" value and possible variations expected.

A number of the examples involve "alums" where the central Transition Metal ion can be considered to be octahedrally coordinated by water molecules.

---

d^1

VCl_4
V(IV) tetrahedral

80K	300K	$\mu_{s.o.}$ /B.M.
1.6	1.6	1.73

^2E ground term - hence don't expect Temperature dependence and small variation from spin-only value can be accounted for by equation 2) above. For less than a half-filled d shell, the sign of λ is positive so the effect on μ should be that $\mu_{eff} < \mu_{s.o.}$

VCl_6^{2-}
V(IV) octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
1.4	1.8	1.73

$^2T_{2g}$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.
Since there is a direct orbital angular momentum contribution we should calculate μ_{S+L} from equation 3) above.
For a full S+L contribution this would give μ_{S+L} = 3 B.M. which is clearly much higher than the 1.8 B.M. found at 300K. So, $\mu_{s.o.} < \mu_{obs} < \mu_{S+L}$
showing that the magnetic moment is partially quenched.

d^2

V^{3+} in $(NH_4)V(SO_4)_2.12H_2O$ (an alum)
V(III) octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
2.7	2.7	2.83

$^3T_{1g}$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.
Since there is a direct orbital angular momentum contribution we should calculate μ_{S+L} from equation 3) above.
For a full S+L contribution this would give $\mu_{S+L} = \sqrt{(20)} = 4.47$ B.M. which is clearly much higher than the 2.7 B.M. found at 300K.
So, $\mu_{obs} < \mu_{s.o.} < \mu_{S+L}$
showing that the magnetic moment is significantly quenched.
In this case, there is no observed Temperature variation between 80 and 300K and it may require much lower temperatures to see the effect?

d^3

Cr^{3+} in $KCr(SO_4)_2.12H_2O$ (an alum)
Cr(III) octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
3.8	3.8	3.87

$^4A_{2g}$ ground term - hence don't expect Temperature dependence and small variation from spin-only value can be accounted for by equation 2) above. For less than a half-filled d shell the sign of λ is positive so the effect on μ should be that $\mu_{eff} < \mu_{s.o.}$

d^4

$CrSO_4.6H_2O$
Cr(II) octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
4.8	4.8	4.9

^5E_g ground term - hence don't expect Temperature dependence and small variation from spin-only value can be accounted for by equation 2) above. For less than a half-filled d shell the sign of λ is positive so the effect on μ should be that $\mu_{eff} < \mu_{s.o.}$

$K_3Mn(CN)_6$
Mn(III) low-spin octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
3.1	3.2	2.83

$^3T_{1g}$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.
Since there is a direct orbital angular momentum contribution we should calculate μ_{S+L} from equation 3) above.
For a full S+L contribution this would give $\mu_{S+L} = \sqrt{(20)} = 4.47$ B.M. which is clearly much higher than the 3.2 B.M. found at 300K.
So, $\mu_{s.o.} < \mu_{obs} < \mu_{S+L}$
showing that the magnetic moment is partially quenched.
In this case, there is a small Temperature variation observed between 80 and 300K.

d^5

$K_2Mn(SO_4)_2.6H_2O$ (an alum)
Mn(II) high-spin octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
5.9	5.9	5.92

$^6A_{1g}$ ground term - hence do not expect Temperature dependence and L=0 so no orbital contribution possible.
Expect $\mu_{eff} = \mu_{s.o.}$

$K_3Fe(CN)_6$
Fe(III) low-spin octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
2.2	2.4	1.73

$^2T_{2g}$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.
Since there is a direct orbital angular momentum contribution we should calculate μ_{S+L} from equation 3) above.
For a full S+L contribution this would give $\mu_{S+L} = \sqrt{(9)} = 3$ B.M. which is clearly much higher than the 2.4 B.M. found at 300K.
So, $\mu_{s.o.} < \mu_{obs} < \mu_{S+L}$
showing that the magnetic moment is partially quenched.

d^6

Fe^{2+} in $(NH_4)_2Fe(SO_4)_2.6H_2O$ (an alum)
Fe(II) high-spin octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
5.4	5.5	4.9

$^5T_{2g}$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.
Since there is a direct orbital angular momentum contribution we should calculate μ_{S+L} from equation 3) above.
For a full S+L contribution this would give $\mu_{S+L} = \sqrt{(30)} = 5.48$ B.M. which is close to the 5.5 B.M. found at 300K.
So, $\mu_{s.o.} < \mu_{obs} \sim \mu_{S+L}$
showing that the magnetic moment is not showing much quenching.

d^7

Cs_2CoCl_4
Co(II) tetrahedral

80K	300K	$\mu_{s.o.}$ /B.M.
4.5	4.6	3.87

$^4A_2$ ground term - hence don't expect Temperature dependence and small variation from spin-only value can be accounted for by equation 2) above. For more than a half-filled d shell the sign of λ is negative so the effect on μ should be that $\mu_{eff} > \mu_{s.o.}$
The observed values are somewhat bigger than expected for the small (0.2 B.M.) variation due to equation 2) so other factors must be affecting the magnetic moment. These effects will not be covered in this course!

Co^{2+} in $(NH_4)_2Co(SO_4)_2.6H_2O$ (an alum)
Co(II) high-spin octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
4.6	5.1	3.88

$^4T_{1g}$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.
Since there is a direct orbital angular momentum contribution we should calculate μ_{S+L} from equation 3) above.
For a full S+L contribution this would give $\mu_{S+L} = \sqrt{(27)} = 5.2$ B.M. which is close to the 5.1 B.M. found at 300K.
So, $\mu_{s.o.} < \mu_{obs} \sim \mu_{S+L}$
showing that the magnetic moment is not showing much quenching.

d^8

Ni^{2+} in $(NH_4)_2Ni(SO_4)_2.6H_2O$ (an alum)
Ni(II) octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
3.3	3.3	2.83

$^3A_{2g}$ ground term - hence don't expect Temperature dependence and small variation from spin-only value can be accounted for by equation 2) above. For more than a half-filled d shell the sign of λ is negative so the effect on μ should be that $\mu_{eff} > \mu_{s.o.}$
The observed values are somewhat bigger than expected for the small (0.2 B.M.) variation due to equation 2) so other factors must be affecting the magnetic moment. These effects will not be covered in this course!

$(Et_4N)_2NiCl_4$
Ni(II) tetrahedral

80K	300K	$\mu_{s.o.}$ /B.M.
3.2	3.8	2.83

$^3T_2$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.
Since there is a direct orbital angular momentum contribution we should calculate μ_{S+L} from equation 3) above.
For a full S+L contribution this would give $\mu_{S+L} = \sqrt{(20)} = 4.47$ B.M. which is higher than the 3.8 B.M. found at 300K.
So, $\mu_{s.o.} < \mu_{obs} < \mu_{S+L}$
showing that the magnetic moment is partially quenched.

d^9

Cu^{2+} in $(NH_4)_2Cu(SO_4)_2.6H_2O$ (an alum)
Cu(II) octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
1.9	1.9	1.73

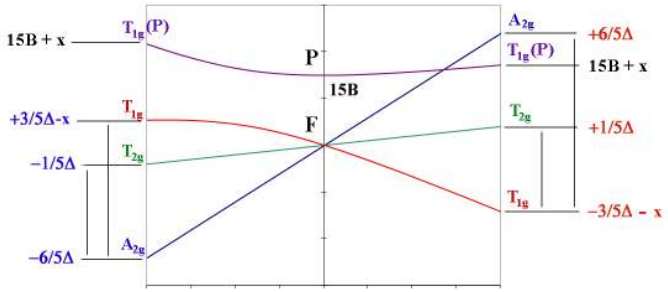
^2E_g ground term - hence don't expect Temperature dependence and small variation from spin-only value can be accounted for by equation 2) above. For more than a half-filled d shell the sign of λ is negative so the effect on μ should be that $\mu_{eff} > \mu_{s.o.}$

Contributors and Attributions

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4.14.2: Magnetic Moments



oct d^3,d^8 tet d^2,d^7 ←----------→ oct d^2,d^7 tet d^3,d^8

Three peaks are predicted in their electronic spectra, namely:

- $^4T_2 \leftarrow {}^4A_2$ ν1
- $^4T_1(F) \leftarrow {}^4A_2$ ν2
- $^4T_1(P) \leftarrow {}^4A_2$ ν3 ** the band observed in the visible region

The energy of the third transitions is approximately $\nu_3 = 6/5\ \Delta + 15B$ (where B is the Racah parameter and ignoring configuration interactions). For Co(II) tetrahedral complexes B has generally been found to be about 750 cm^{-1}. Hence Δ for the three complexes above can be calculated to be roughly, $\Delta = (\nu_3 - 15x750) \times 5/6$, or:

$Copyr_2Cl_2$ (16260-15x750) x 5/6 = 4175 cm^{-1}
$Copyr_2Br_2$ (15870-15x750) x 5/6 = 3850 cm^{-1}
$Copyr_2I_2$ (14925-15x750) x 5/6 = 3063 cm^{-1}

For three unpaired electrons the spin only magnetic moment is predicted to be 3.87 BM. Using a value for the free ion spin orbit coupling constant (λ) of -172 cm^{-1} then a better approximation of the magnetic moment can be obtained by using the third formula above. This would give a value of:

- $Copyr_2Cl_2$ 3.87*(1+ 688/4175) = 4.49 B.M. found 4.42 BM
- $Copyr_2Br_2$ 3.87*(1+ 688/3850) = 4.57 B.M. found 4.50 BM
- $Copyr_2I_2$ 3.87*(1+ 688/3063) = 4.76 B.M. found 4.48 BM

In the case of the series;

$$CoI_4^{2-},\ CoBr_4^{2-},\ CoCl_4^{2-},\ Co(NCS)_4^{2-}$$

the magnetic moments have been recorded as

4.77, 4.65, 4.59, 4.40 BM

showing even more clearly the inverse effect of the spectrochemical series on the magnetic moment.

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4.14.3: Magnetic Moments 1

Magnetic Moments

Lecture 4. CHEM1902 Coordination Chemistry

Magnetic moments are often used in conjunction with electronic spectra to gain information about the oxidation number and stereochemistry of the central metal ion in coordination complexes.

A common laboratory procedure for the determination of the magnetic moment for a complex is the Gouy method which involves weighing a sample of the complex in the presence and absence of a magnetic field and observing the difference in weight. A template is provided for the calculations involved.

For first row transition metal ions in the free ion state, i.e. isolated ions in a vacuum, all 5 of the 3d orbitals are degenerate.

A simple crystal field theory approach to the bonding in these ions assumes that when they form octahedral complexes, the energy of the d orbitals are no longer degenerate but are split such that two orbitals, the d_{x2-y2} and the d_{z2} (e_g subset) are at higher energy than the d_{xy}, d_{xz}, d_{yz} orbitals (the t_{2g} subset).

For octahedral ions with between 4 and 7 d electrons, this gives rise to 2 possible arrangements called either high spin/weak field or low spin/strong field respectively. The energy gap is dependent on the position of the coordinated ligands in the SPECTROCHEMICAL SERIES.

See an interactive JAVA applet for examples.

Note: For CHEM1902, we assume that all Co(III), d^6 complexes are octahedral and LOW spin, i.e. t_{2g}^6.

In tetrahedral complexes, the energy levels of the orbitals are again split, such that the energy of two orbitals, the d_{x2-y2} and the d_{z2} (e subset) are now at lower energy (more favoured) than the remaining three d_{xy}, d_{xz}, d_{yz} (the t2 subset) which are destabilised.

Tetrahedral complexes are ALL high spin since the difference between the 2 subsets of energies of the orbitals is much smaller than is found in octahedral complexes.

The usual relationship quoted between them is: $\Delta_{tet} \approx 4/9\ \Delta_{oct}$.

Square planar complexes are less commmon than tetrahedral and **for CHEM1902 we will assume that the only ions forming square planar complexes are d^8 e.g. Ni(II), Pd(II), Pt(II), etc.** *d^8 can therefore be either square planar or tetrahedral.* As with octahedral complexes, the energy gap between the dxy and dx^2-y^2 is Δoct and these d^8 systems are all considered strong field / low spin complexes hence they are all diamagnetic, μ=0 Bohr Magneton (B.M.).

The formula used to calculate the spin-only magnetic moment can be written in two forms; the first based on the number of **unpaired** electrons, n, and the second based on the **total** electron spin quantum number, S. Since for each unpaired electron, n=1 and S=1/2 then the two formulae are clearly related and the answer obtained must be identical.

Return to Coordination Chemistry Course Outline.

Return to Chemistry, UWI-Mona, Home Page

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Created Dec 1995. Links checked and/or last modified 23rd March 2015.

URL **http://wwwchem.uwimona.edu.jm/spectra/MagMom.html**

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4.14.4: Magnetic Susceptibility Measurements

The Gouy Method

Perhaps the simplest technique for measuring the magnetic susceptibility of metal complexes is the Gouy Method.

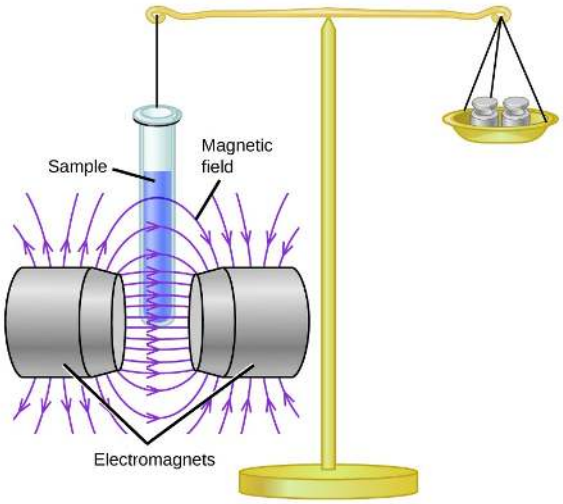


Figure 4.14.4.1: A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample. (CC BY-SA 3.0; OpenStax).

From a classical description of magnetism, Lenz's Law (around 1834) can be written as

$$\frac{B}{H} = 1 + 4\pi\frac{I}{H} \tag{4.14.4.1}$$

or

$$\frac{B}{H} = 1 + 4\pi\kappa \tag{4.14.4.2}$$

where

- B/H is called the **magnetic permeability** of the material and
- κ is the magnetic susceptibility per unit volume (I/H).

The determination of a **magnetic susceptibility** depends on the measurement of B/H. Experimentally, the Gouy method involves measuring the force on the sample by a magnetic field and is dependent on the tendency of a sample to concentrate a magnetic field within itself.

At any given point, dx, of the sample, the force is given by:

$$dF = \mu\backslash\text{circH}\ \kappa\ dV\left(\frac{dH}{dx}\right) \tag{4.14.4.3}$$

where

- μ° is the permeability of a vacuum (=1 when using c.g.s. units)
- H is the magnitude of the magnetic field at point, dx,
- dV is the volume of the sample at point dx,
- κ is the magnetic susceptibility per unit volume.

The sample is uniformly packed into a glass tube (Gouy tube) each end of which is at a constant field strength. This is attained by using a tube that is packed to a certain height (say 10 cm) and the tube is suspended between the poles of a magnet such that the bottom of the sample is in the center of the field (a region where a uniform field strength can be readily obtained) whilst the top of the sample is out of the field, i.e. $H = 0$. By integrating the above equation, the total force on the sample can be given as:

$$F = \frac{1}{2}\mu^{\circ} A\kappa(H^2 - H^{\circ 2}) \tag{4.14.4.4}$$

and since $H^o = 0$ at the top of the sample then

$$F = \frac{1}{2}\mu^{\circ} A\kappa H^2 \tag{4.14.4.5}$$

where A is the cross sectional area of the sample.

The force is measured by the apparent change in mass when the magnetic field is switched on, or

$$F = g\ \delta w = \frac{1}{2}\mu^{\circ} A\kappa H^2 \tag{4.14.4.6}$$

where δw is the apparent change in mass, and g is the acceleration due to gravity.

An allowance needs to be made for the tube, since it will have its own magnetic properties as a result of the air within the tube (which is displaced from the tube when the sample is introduced) and also from the materials used in its construction. Equation 4.14.4.6 becomes:

$$g\delta w' = 1/2A\mu^{o}(\kappa - \kappa')H^2$$

where

- $\delta w' = \delta w + \delta$
- δ is a constant allowing for the magnetic properties of the empty tube
- κ' is the volume susceptibility of the displaced air.

This leads to:

$$\kappa = \frac{2g\delta w'}{\mu^{\circ} AH^2} + \kappa'$$

Converting from volume susceptibility to gram susceptibility (χ_g) leads to:

$$\chi_g = \frac{\kappa}{\rho} = \frac{\kappa\ V}{W}$$

where ρ is the density of the sample so that

$$\chi_g = \frac{\beta\delta w'}{W} + \frac{\kappa' V}{W}$$

or

$$\chi_g = \frac{\alpha + \beta\delta w'}{W}$$

where

- α is a constant allowing for the air displaced by the sample,
- β is a constant that is dependent on the field strength, = $\frac{2gV}{\mu^{\circ} AH^2}$
- W is the weight of the sample used.

Written more simply then:

$$\chi_g\ (cal) = \frac{\beta\delta w'}{W\ (cal)} + \cancelto{\approx 0}{\frac{\alpha}{W\ (cal)}}$$

the last expression is usually negligible.

β is then obtained and from this

$$\chi_g\ (sample) = \frac{\beta\delta w'}{W\ (sample)} + \cancelto{\approx 0}{\frac{\alpha}{W\ (sample)}}$$

the χ_g sample can be obtained, again the factor for the susceptibility of air is usually negligible.

To accurately determine the gram magnetic susceptibility of a sample, it is necessary to predetermine the value of the constants α, β and δ. Since these constants are dependent on the amount of sample placed in the tube, the tube itself and the magnetic field strength, it should be emphasized that each experimenter **must** determine these constants for their particular configuration. That is, results obtained with one tube are **not transferable** to other Gouy tubes.

The field strength is determined by the current supplied to the electromagnet. In order to ensure a constant magnetic field strength from one measurement to the next, always set the current to the same value. Note that the magnet may display hysteresis effects so that if you do go beyond the 5 Amp value it may take some time to reestablish itself, after you have decreased the power.

Determination of the Constants

Select a tube and piece of nichrome wire to make an assembly which will allow the tube to be suspended from the analytical balance so that the bottom of the tube is aligned halfway between the polefaces of the magnet and the top of the sample is above the magnet and hence subject to essentially zero field, H=0.



1: Determining δ

Adjust the zero setting on the balance, then suspend the empty tube from the balance and weigh it (W1). Set the field to the required strength and reweigh the tube (W2). The force on the tube, δ, therefore is:

$$\delta = W2 - W1 \tag{4.14.4.7}$$

this will normally be negative since the tubes are generally diamagnetic and pushed out of the field, ie. weigh less.

2: Determining α

Fill the tube to the required height with water and weigh it (check the zero first), this will give W3. Assuming the density of water at this temperature is 1.00 g cm^{-3} this gives the volume of water (and also that of the sample).

vol. =(W3-W1)/1.00 where the weight changes should be expressed in g.

$$\alpha = \kappa'.V \tag{4.14.4.8}$$

α= 0.029 x (W3-W1) in 10^{-6} c.g.s. units,

where 0.029 is the volume susceptibility of air /cm^3. For strongly paramagnetic samples this correction is generally insignificant.

3: Determining β

The determination of β requires the use of a compound whose magnetic properties have been well established. Common calibrants include $HgCo(SCN)_4$ and $[Ni(en)_3]S_2O_3$. Since the magnetic properties are often temperature dependent, the susceptibility of the calibrant must be calculated for the temperature at which the sample is measured.

Record the temperature, T1. Fill the tube to the required height with the calibrant (in this case either $HgCo(SCN)_4$ or $[Nien_3]S_2O_3$ and weigh it with the field off (W4) and with the field on (W5).

For $HgCo(SCN)_4$ the following relationship can be used:

χ_g = 4985 / (T+10) in 10^{-6} c.g.s units at temperature T, while the corresponding relationship for $[Ni(en)_3]S_2O_3$ is:

$$\chi_g = 3172 / T \text{ in } 10^{-6} \text{ c.g.s units at temperature T}$$

Using this χ_g then

$$\beta = \frac{\chi_g W - \alpha}{\delta w'}$$

where $\delta w' = (W5 - W4) - \delta$ in mg and $W = (W4 - W1)$ in g

Determination of the Magnetic Susceptibility of your sample

Once α and β are known, then $\chi_{m'}$ can be determined for the sample in question. Fill the tube to the required height with your sample and weigh it with the field off (W6) and with the field on (W7). From this calculate:

$$\chi_g = \frac{\alpha + \beta\delta w'}{W}$$

where δw' = (W7 - W6) - δ in mg and W = (W6 - W1) in g

To convert from χ_g to χ_m the molar mass must be accurately known, since:

$$\chi_m = \chi_g x R.M.M.$$

The final correction is for the diamagnetism of the sample

$$\chi'_m = \chi_m + \chi_m(dia)$$

where $\chi_m(dia)$ is the susceptibility arising from the diamagnetic properties of the electron pairs (and therefore not a property of the unpaired electrons) and must be allowed for. The values for $\chi_m(dia)$ have been well documented (Pascal's constants) for different atoms and ions and a selection of them are tabulated.

To summarize, the overall procedure is:

```
Weigh the empty tube              - magnet off/on   W1/W2
Weigh the tube with water         - magnet off      W3
Weigh the tube with calibrant     - magnet off/on   W4/W5
Weigh the tube with your sample   - magnet off/on   W6/W7
Record the temperature(s) of calibrant/sample       T1/T2 in K
Calculate the Molar Mass of your sample             M.M.
Estimate the total diamagnetic correction for your sample D.C.
```

Calculate the magnetic moment using:

&delta = (W2 - W1) in mg
α = 0.029 x (W3 - W1) in 10^{-6} c.g.s. units
β = [(χ_m{Calibrant}) (W4 - W1) - α]/ [(W5 - W4) - δ] at temperature T1

χ_m {Sample} = [α + β {(W7 - W6) - δ}]/(W6 - W1) at temperature T2

χ'_m = (χ_m x R.M.M.) + χ_m dia

also $\chi'_m = \mu \circ \mu_b^2$ N/3k. $\mu eff^2/T$

where μ_b is the Bohr Magneton, N is Avogadro's number and k is the Boltzmann constant. Hence,

$\mu_{eff} = \sqrt{(3k/\mu^\circ \mu_b{}^2 N)}. \sqrt{(\chi'_m T2)}$ B.M.

or $\mu_{eff} = 2.828 \sqrt{(\chi'_m T2 \times 10^{-6})}$ at temperature T2

where the 10^{-6} that has been ignored in these expressions is finally included.

(Determination of the magnetic moment using the Gouy method has been simplified by the use of an on-line template or spreadsheet.)

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4.14.5: Magnetism

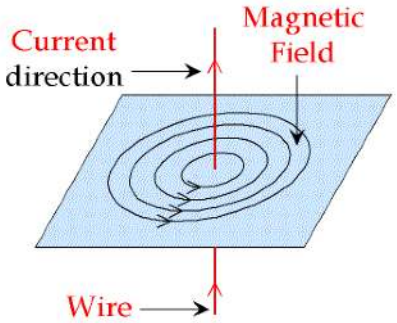


***Figure 1**: The "Right Hand Rule" for an induced magnetic field*

In an atom, the magnetic field is due to the coupled spin and orbital magnetic moments associated with the motion of electrons. The spin magnetic moment is due to the precession of the electrons about their own axes where as the orbital magnetic moment is due to the motion of electrons around the nucleus. The resultant combination of the spin and orbital magnetic moments of the constituent atoms of a material gives rise to the observed magnetic properties.

Historically, magnetism has been recognized for thousands of years. An account, that is probably apochryphal, tells of a shepherd called Magnes in Crete who around 900 B.C discovered the naturally occurring magnet lodestone (a form of the the spinel magnetite, Fe_3O_4) in a region later named Magnesia. Supposedly while he was walking over a deposit, the lodestone pulled the nails out of his sandals and the metal tip from his staff.

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CHAPTER OVERVIEW

5: Bonding in Polyatomic Molecules

Topic hierarchy

5.1: Introduction

5.2: Valence Bond Theory - Hybridization of Atomic Orbitals

- 5.2A: What is Orbital Hybridization?
- 5.2B: sp Hybridization
- 5.2C: sp^2 Hybridization
- 5.2D: sp3 Hybridization
- 5.2E: Other Hybridization Schemes

5.3: Valence Bond Theory - Multiple Bonding in Polyatomic Molecules

- 5.3A: Introduction
- 5.3B: C_2H_4
- 5.3C: HCN
- 5.3D: BF_3

5.4: MO Theory - The Ligand Group Orbital (LGO) Approach and Application to Triatomic Molecules

- 5.4A: MO Diagrams - Moving from Diatomic to Polyatomic Species
- 5.4B: MO Approach to Bonding in Linear XH_2 - Symmetry Matching by Inspection
- 5.4C: MO Approach to Bonding in Linear XH_2 - Working from Molecular Symmetry
- 5.4D: A Bent Triatomic - H_2O

5.5: MO Theory Applied to Polyatomic Molecules BH_3, NH_3, and CH_4

- 5.5A: BH_3
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- 5.5D: A Comparison of MO and VB Bonding Models

5.6: MO Theory - Bonding Analyses Soon Become Complicated

5.7: MO Theory - Learning to Use the Theory Objectively

- 5.7A: π-Bonding in CO_2
- 5.7B: $[NO_3]^-$
- 5.7C: SF_6
- 5.7D: Three-Center Two-Electron Interactions
- 5.7E: A More Advanced Problem - B_2H_6

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5.2A: What is Orbital Hybridization?

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5.2B: sp Hybridization

The geometrical shape and the inherent physical/chemical properties seen in molecules can be attributed to atomic and molecular orbitals. Features of molecular structure can be explained by taking into consideration (1) how orbitals interact within a single atom to form hybrid atomic orbitals and (2) how atomic orbitals between different atoms interact, giving rise to molecular orbitals. This module will serve as a reminder of the fundamental concepts of bonding as they relate to molecular structure, as well as an investigation into the complexities of hybridized atomic orbitals

1. The Localized Electron Bonding Model
2. The Heisenberg Uncertainty Principle
3. Orbitals and Hybridization
4. References
5. Outside Links
6. Problems
7. Contributors and Attributions

The Localized Electron Bonding Model

What is a chemical bond? The most elementary way to understand the bonding between two or more atoms is to make use of Lewis dot structures; a structure drawn where each valence electron surrounding an atom is symbolized by a dot and each bonding electron is symbolized by a pair of dots or a dash (Wade p.7). In accordance with the observations of G. N. Lewis, atoms having or sharing 8 valence electrons will tend to be in an arrangement of lowest energy (ACS p.11). A more sophisticated approach to understanding bonding is to consider how atomic orbitals within individual atoms interact with one another forming molecular orbitals and subsequent covalent bonding. A complete understanding of the subject involves knowledge of quantum mechanics, wave functions and molecular symmetry. This module will focus on how atomic orbitals on an individual atom can give rise to hybrid atomic orbitals, which define the geometry of the bond, and how hybrid atomic atoms of different atoms come together to form molecular orbitals, which define the geometry of the molecule.

Why do chemical bonds form? The stability of a covalent bond, the bond formed when atomic orbitals of separate atoms interact to form molecular orbitals, results from there being a large amount of electron density in the region of space between the two nuclei (Wade p.44). This region is known as the bonding region and here the electrons are close to both nuclei, subsequently lowering the overall energy.

The Heisenberg Uncertainty Principle

The Heisenberg Uncertainty Principle rationalizes the inability of chemists and physicists alike to simultaneously determine both the position and momentum of an atomic particle in space. In lieu of this, theoretical chemists had to develop methods of calculating the position of an electron in terms of probabilities rather than assigning electrons fixed location about a nucleus (Barret p.2). These calculations are collectively known as quantum mechanics, with the Schrödinger wave equation ($\hat{H}\Psi = i\hbar\, d/dt\Psi$) being the quantum mechanic calculation of greatest interest to orbital symmetry. Solving the Schrödinger wave equation gives the shapes of atomic orbitals represented graphically as the probability of finding an electron residing in a region of space about an atom.

Orbitals and Hybridization

Valence Bond theory describes the formation of a chemical bond in terms of overlapping between atomic orbitals. The 1*s* orbital of hydrogen, for example, can overlap in-phase and combine constructively to form a molecular orbital called a sigma bond.

Furthermore, a 1s orbital is analogous to the fundamental vibration of a guitar string. The wave function is seemingly positive and negative simultaneously. The effect of squaring the wave function gives the distribution of electron density, which can be used to graphically represent the spherical symmetry of an *s* orbital.

Atomic orbitals can interact to form new molecular orbitals but let us first consider that orbitals within an individual atom can interact amongst themselves giving rise to hybridized atomic orbitals. Yielding a *sp* hybrid orbital with an electron density predominately concentrated toward one side of the atom. Molecular orbital theory dictates that the number of hybrid orbitals

produced must equal the sum of the orbitals that underwent hybridization and be it that we started with one *s* orbital and one *p* orbital (for a total of two orbitals) we must finish with a total of two hybrid *sp* orbitals.

The final result of this hybridization is a pair of directional *sp* hybrid orbitals pointed in opposite directions, providing enough electron density in the bonding regions to provoke a sigma bond to both the left and the right of the atom. These 2 *sp* hybrid orbitals generate a bond angle of 180˚, creating a bond formation with linear geometry. Lastly, the degree of orbital hybridization is governed by the number of attachments (ligands) found on a central atom, lone pairs of electrons included. Table 1.1 provides a summary of orbital hybridization wherein the number of ligands attached to a central molecule correlates to the molecules geometry.

Table 1.1 Summary of hybridization

# of attachments	Hybridization	Geometry	angle(s)
2	sp	Linear	180°
3	sp^2	Trigonal planar	120°
4	sp^3	Tetrahedral	109.5°
5	sp^3d	Trigonal bipyramidal	120° and 90°
6	sp^3d^2	Octahedral	90°

sp Hybridization

As discussed, molecular orbitals form as a result of constructive & destructive wave overlap of atomic orbitals between different atoms as well as the potential for atomic orbitals contained within an atom can combine amongst themselves giving rise to hybrid atomic orbitals. It becomes prudent then to consider the spatial orientation of atomic orbitals during the interaction of orbitals on different atoms in the formation of chemical bonds.

The chemical bonding of compounds with triple bonds, such as alkynes, can be expounded by sp hybridization. Inspection of the electron configuration of carbon reveals that the electrons in the 2s orbital mix with only one of the three available p orbitals. This results in two hybrid sp orbitals and two unaltered p orbitals. C_2H_2, for instance, is held together then by the overlap of adjacent/approaching sp-sp hybrid orbitals on each carbon atom. The bond that ultimately forms is a sigma bond complemented by additional pi bonds formed by p-p orbital overlap; triple bonds are actually composed of two different types of bonds, sigma and pi. Each carbon also bonds to a hydrogen by means of a sigma bond formed this time by s-sp orbital overlap.

References

1. Wade, L.G. *Organic Chemistry* 5th Edition. Pearson Education, INC. New Jersey 2003
2. Barrett, Jack *Structure and Bonding.* Published by The Royal Society of Chemistry Cambridge, UK 2001
3. Preparing for Your ACS Examination in Organic Chemistry10 Printing; American Chemical Society Division of Chemical Education Examinations Institute. Washington D.C. 2009
4. Zumdahl, Steven S., Zumdahl, Susan A. *Chemistry* 7th Edition. Houghton Mifflin Company, Boston 2007

Outside Links

- Interactive Molecular Structure & Bonding at www2.chemistry.msu.edu:80/fac...Jml/intro3.htm

Problems

1. Using the space provided please draw a) an *s* orbital & all three appropriately labeled *p* orbitals and b) the product(s) of their hybridization.

a)
b)

2. The constructive overlap between orbitals of Hydrogen forming sigma bonds was discussed. Please describe the sigma* anti-bonding orbital that results from destructive overlap.

3. Please a) draw both the Lewis Dot and VSEPR structure of CO2 labeling the hybridization and bond angle b) draw the orbitals that overlap during bond formation of CO2 c) identify all the symmetry elements.

a) Structure of CO_2
b) Orbitals
c) Symmetry Elements

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5.2C: sp^2 Hybridization

The sp^2 hybridization is the mixing of one s and two p atomic orbitals, which involves the promotion of one electron in the s orbital to one of the 2p atomic orbitals. The combination of these atomic orbitals creates three new hybrid orbitals equal in energy-level. The hybrid orbitals are higher in energy than the s orbital but lower in energy than the p orbitals, but they are closer in energy to the p orbitals. The new set of formed hybrid orbitals creates trigonal structures, creating a molecular geometry of 120 degrees.

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5.2D: sp3 Hybridization

Introduction

The term "sp^3 hybridization" refers to the mixing character of one 2s-orbital and three 2p-orbitals to create four hybrid orbitals with similar characteristics. In order for an atom to be sp^3 hybridized, it must have an s orbital and three p orbitals.

From wave function to the visual representation:

Four equivalent sp3 hybrid orbitals, resulting from the combination of one s atomic orbital and three p atomic orbitals, can then describe by four new wave functions (equations 1 – 4)

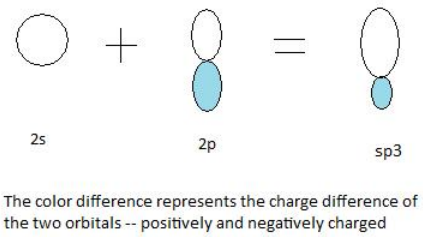
$\psi(sp^3) = 0.5 (\psi_{2s} + \psi_{2px} + \psi_{2py} + \psi_{2pz})$ (1)

$\psi(sp^3) = 0.5 (\psi_{2s} + \psi_{2px} - \psi_{2py} - \psi_{2pz})$ (2)

$\psi(sp^3) = 0.5 (\psi_{2s} - \psi_{2px} - \psi_{2py} + \psi_{2pz})$ (3)

$\psi(sp^3) = 0.5 (\psi_{2s} - \psi_{2px} + \psi_{2py} - \psi_{2pz})$ (4)

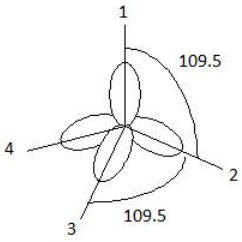
Plotting any of these four wave functions gives a picture representation of a sp^3 orbital. Each hybrid orbital consists of a large lobe and a small lobe, pointing in two opposite direction (figure 1).



The color difference represents the charge difference of the two orbitals -- positively and negatively charged

The Bond Angle is 109.5°:

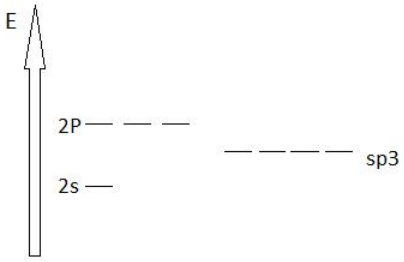
When the graphs of the four wave functions are combined, the resulting picture shows the tetrahedral arrangement of the four sp^3 hybrid orbitals around the central atom. Because of the tetrahedral molecular geometry, the calculate bond angles between 1 and 2, 1 and 3, 1 and 4, 2 and 3, 2 and 4, and 3 and 4 approximately equal 109.5° (figure 2).



The Energy level and election population:

All four sp3 hybrid orbitals are delocalized—they occupy the same energy level; however, they are higher in energy than the 2s orbital and lower in energy than the 2p orbital (figure 3).

Just like any other atomic orbital, each sp3 hybrid orbital can house 2 elections.



S-character and the stability of the anion:

Each sp3 orbital has 1 part of s-character to 3 parts of p-character. In other words, it has 25% s-character and 75% p-character. Since the s orbital is closer to the nucleus and thus lower in energy than the p orbital, the electrons of sp^3 hybridized species are held farther from the nucleus than those in sp^2 (33% s-character) and sp (50% s-character) hybridized species. The closer the electrons are to the nucleus, the more stable they are. Therefore, when bearing the negative charge, sp^3 species are less stable than sp^2 and sp species. Put differently, sp^3 species are less likely to get deprotonated (leaving a pair of electron behind).

Hybridization and bond length/bond strength:

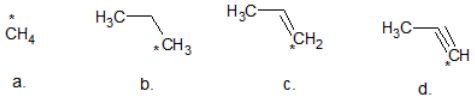
The greater the s-character, the closer the electrons are held to the nucleus, the shorter the bond, and the stronger the bond. Thus, sp^3 hybridized atoms form longer and weaker bonds than those of sp^2 and sp hybridized.

References

1. Brown W H, Foote C S, Iverson B L, Anslyn E V. Organic Chemistry, 5th Ed. Brooks/Cole Cengage Learning 2009, 2005.

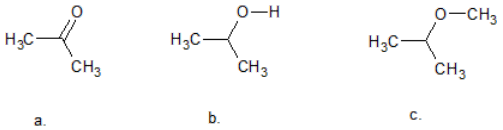
Problems

1. Which of the (*) carbons is/are sp^3 hybridized

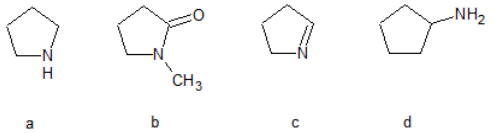


2. Draw the energy diagram for the orbitals of sp^3 hybridzied carbon and nitrogen. Then fill in the correct number of electron.

3. Indicate the hybridization of oxygen in each molecule



4. Which nitrogen atom(s) is/are sp^3 hybridized



5. Describe the bonding scheme of CH_4.

Answers:

1. a and b

2. Just like the energy diagram in fig.3.
For carbon, each sp^3 orbital has 1 electron. For nitrogen, the first sp^3 orbital has 2 electrons, then one electron for each of the remaining three

3. All of them (Don't for get the elctron pairs)

4. a and d

5. Carbon has four half-filled sp3 hybrid orbitals. Each orbital overlaps with a partially filled 1s atomic orbital of hydrogen to form 4 sigma bonds. To visualize, hydrogen atoms are placed at the four corner of the tetrahedron.

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5.2E: Other Hybridization Schemes

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5.3A: Introduction

When Valence Bond Theory is applied to the multiple bonding in polyatomic molecules, there are two types of bonds that can form: homonuclear and heteronuclear. Homonuclear bonds occur between multiples of the same element and heteronuclear bonds occur between different elements. Homonuclear bonds can occur on a diatomic scale all the way up to large polymers made completely of carbon atoms. However, most polyatomic atoms involve heteronuclear bonds. When considering bonding in polyatomic molecules for VB theory, it is easiest to use a mixture of Lewis structures and Atomic Orbital Hybridization to explain.

1. Bonding In Molecules
2. Example: Ethyne
3. References
4. Outside Links
5. Problems
6. Answers

Bonding In Molecules

When trying to figure out the bonding of a molecule, it is a good idea to look at the electronic configuration of the atoms (Housecroft, 120). This allows you to know how many valence electrons you have to work with. Then the number of bonds attached to each atom should be determined using the lewis structure of the molecule. After the lewis structure has been determined, find the hybridization of each atom in the molecule. With the determined hybridization, a picture of the molecule should be easy to create.

Example: Ethyne

Ethyne, or acetylene as it is commonly referred to as, has a lewis structure that shows that there is a triple bond between the two carbon atoms. Using valence orbital hybridization, sp hybridization is determined for triple bonded molecules, which means that carbon has two free 2p orbitals that form 2 pi bonds. Using this info you would draw the two carbon atoms with sp bonds connecting them and the two pi orbitals from each atom bonding with each other. Each hydrogen atom has its s orbital is overlapped with each carbon atom's second sp bond . The molecule overall would have a linear structure.

References

1. Housecroft, Catherine E. and Sharpe, Alan G. *Inorganic Chemistry.* 3rd Edition. Harlow: Pearson Education, 2008
2. Petrucci et al. *General Chemistry: Principles and Modern Applications*. 9th Edition. Upper Saddle River: Pearson Education, 2007

Outside Links

- This is not meant for references used for constructing the module, but as secondary and unvetted information available at other site
- Link to outside sources. Wikipedia entries should probably be referenced here.

Problems

1. Provide the lewis structure and hybridization of the carbonyl carbon in formaldehyde.

2. Provide the hybridization of S in SH_2 and a picture of the hybrid orbitals.

3. Provide the lewis structure and a drawing of the hybrid orbitals in CHF_3.

4. Provide the electronic configuration, hybridization, and lewis structure of PF_3.

5. Provide the electronic configuration and a drawing of the hybrid orbitals of CO_2.

Answers

1. sp^2 

2. sp^3 

3.  

4. P=[Ne] $3s^2$ $3p^3$; F=[He] $2s^2$ $2p^5$; sp^3 

5. C= [He] $2s^2$ $2p^2$; O=[He] $2s^2$ $2p^4$; 

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5.3B: C_2H_4

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5.3C: $H\ \ C\ \ N$

HCN, hydrogen cyanide, is a volatile and poisnous compound with distinguished bitter odor. It is linear molecule with a triple bond between C and N atom and has bond angle of 180 degrees. It can be found in fruits that have pits due to the fact that they contain small amounts of cyanohydrins which slowly releases hydrogen cyanide. Also it can be found in exhaust of vehicles and burning nitrogen-containig plastics.

Introduction

The valence bond theory can be explained by overlapping of atomic orbitals which electrons are localized in the reigion to form chemical bonds. However, when you utilize this approach to explain chemical structure of the molecule, you must aware that there are various atomic orbitals for bonding which will significantly influence the structure of the molecule.

Definition of Valence Bond Theory

The Valence Bond thoery simply explains the bond formation just like lewis dot structure, but instead it explains the bonding in terms of covalent bond by quantum mechanics. According to this theory, bond will form when

1) An orbital of one atom occupy another atom's orbital, known as overlap.

2) number of electrons in both orbital is adds up to no more than two.

Just like forming a molecule with lewis dot structure, bonds between atoms complete when two electrons share same orbital together.

Bond strength depends on the the amount of overlap since electrons are attracted to nuclei of both atoms, more electrons will pull more nuceli thus increase bond strength. However, two orbitals can not contian more than two atoms due to the maximum capacity it can hold.

Also, because known atomic geometry can not be able to have effective overlap, atomic orbitals combine with each other and reconfigure themselves into a different configuration. This process is called hybrdization.

This formation of new hybrid orbital is possible by combining several types of orbitals (s,p,d and etc).

Describe HCN molecular bond by using Valence Bond Theory

In HCN molecule, the C atom includes *sp*-hybridized orbital, since it will combine with only two other atoms to form HCN. One of the *sp*-hybrid orbitals of carbon atom overlaps with the 1*s* orbital of H atom, while the other sp-hybrid orabital mixes with one of the nitrogen's atom's three atomic *p* orbitals which were unhybridized. Because px orbital of C and N will form sigma bond, this leaves with two N atom *p*-orbitals which form two mutually perpendicular pi bonds to the two atomic *p* orbitals on the C atom. HCN thus has one single and one triple bond. The latter consists of a sigma bond from the overlap of a C *atom sp* hybrid orbital with a N atom *p* orbital, and two mutually perpendicular pi bonds are formed from parallel atomic *p* orbitals of carbon and nitrogen atoms.

References

1. Winter, Mark J. *Chemical Bonding*. Oxford: Oxford UP, 2005. Print.
2. Roger L. Dekock and Harry B. Gray. *Chemical Structure and Bonding*. University Science Books. 1989.

Outside Links

1. Shaik, Sason S., and Philippe C. Hiberty. *A Chemist's Guide to Valence Bond Theory*. Hoboken, NJ: Wiley-Interscience, 2008. Print.

2. "Bonding and Hybridization." *Department of Chemistry & Biochemistry @ Boise State University*. Web. 05 Nov. 2010. <chemistry.boisestate.edu/peop...rganic/bonding and hybridization/bonding_hybridization.htm>.

Problems

1. What type of bond is present in the HCN molecular orbitals?

2. What theory is necessary to explain the formation of hybridized orbitals?

3. Explain why HCN is linear.

Answers

1. 1 sigma bond between H and C atoms. 1 sigma bond and 2 pi bond is present between C and N atoms.

2. Valence bond thoery as wells as hybridization. Lewis dot structure can be used to get the basic idea of the structure.

3. Because of the 2 pi bonds and 1 sigma bond formed by the hybridization of $2p_x$, $2p_y$, and $2p_z$ between C and N atoms, this 2p overlap makes the bond stronger and shorter therefore the bond between C and N is linear. Also, based on the property of atoms to be on the position at smallest strichinderance as possible, H atom will be as far away from C atom, which will result in the linear structure.

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5.3D: BF_3

The Valence Bond Theory is usually represented by the Lewis dot models. Boron is an unusual molecule because it does not follow the octet rule by having eight valence electrons around the boron atom. BF_3 has single bonds between the boron atom and the fluorine atoms and contains no double bonds and an empty p orbital (figure 3). This is not predicted by the valence bond theory because it does not allow for any empty orbitals.

Valence bond theory and how it fails

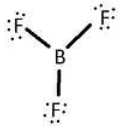


figure 1

Valence Bond Theory states that when a half filled orbital, in contact with another half filled orbital, will hybridize to form a more stable bonding orbital. According to the Valence Bond Theory, the lone pair of one of the fluorine atoms should overlap to form a pi bond with the boron atom through a double bond in order to complete an octet on the boron atom (figure 2), but this does not occur.

There are two major reasons why there is no pi bond between any of the F atoms and B atoms: electronegativity and separation of charge. If one were to write out formal charges of the molecule without the pi bond, they will find that the formal charges on all of the atoms are 0. The boron shares it's 3 valence electrons with the fluorine creating a total of 6 electrons shared with the fluorine, making it's formal charge 0. Each fluorine shares one of it's valence electrons creating a total of 2 shared electrons with boron and has 6 more electrons to themselves, making their formal charges also 0 (figure 1).

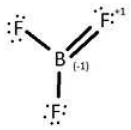


figure 2

If one of the fluorines were to form a pi bond with the boron, then the fluorine, which is the most electronegative element, will have an oxidized state and a formal charge of +1 and, consequently the boron atom would have a formal charge of -1. Although this still leaves the BF_3 molecule to have an overall formal charge of 0, the most stable form would be BF_3 with no pi bonds because each of the atom's formal charge is 0. The most stable state is to leave the boron with an empty p orbital.

The empty p orbital

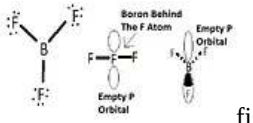


figure 3

BF_3 is a planar molecule because it does not have a lone pair, which makes it have a trigonal planar geometry. BF_3 is considered a Lewis acid because it accepts electrons at its empty p orbital.

Examples of reactivity of the empty p orbital

The most common reactions with involving BF_3 is to form complexes with ethers.

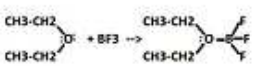


figure 4

Other molecules like BF3

Carbenes are molecules that are used for different organic synthesis reactions. They typically involve a carbon with a lone pair and 2 bonded halides (like bromide). It also includes this empty p orbital and is fairly reactive.

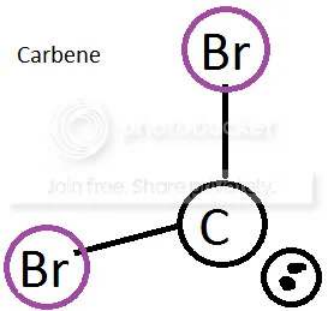


figure 5

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5.4D: A Bent Triatomic - H_2O

Water is a triatomic species, with one oxygen atom for every two hydrogen atoms per molecule. Through a combination of polarized bonds between the oxygen and hydrogen atoms, and a bent molecular geometry that gives the molecule an overall dipole moment, water posesses several unique chemical and physical properties that are unlike any other species of its size.

Molecular Structure

The classic model for the water molecule (H_2O) is a central oxygen atom bonded to two hydrogen atoms on either side. Unlike other triatomic species that have a linear shape, the bonds on a water molecule are tilted at a slight angle, due to the presence of lone-pair electrons on the oxygen atom. Through VSEPR theory, it is shown that H_2O has a steric number of 4, with two lone pairs and two bond pairs, making its molecular geometry "bent". As a result, the angle between the two oxygen-hydrogen bonds are approximately 104.5°, which is slightly smaller than the angle typically found in tetrahadral-shaped molecules (see above image). This is due to the particularly strong repulsions by the lone-pair electrons on the oxygen atom, which pushes the hydrogens closer together than usual. Each of the oxygen-hydrogen bonds measure approximately 95.84pm in length. This bent geometry due to the presence of lone pair electrons makes water different from typical linear triatomic species, both on an atomic and a macroscopic level.

Physical and Chemical Properties

Through its combination of bent geometry and polarized bonds, H_2O has unique physical properties that are uncharacteristic of most other small molecules. As a result of oxygen being more eletronegative than hydrogen, the oxygen-hydrogen bonds have an unequal sharing of electrons, with a majority of the negative charge going to the oxygen atom, and leaving the positive chage to the hydrogens. With the bent structure of H_2O, this creates a dipole on the overall molecule, with the oxygen end being negatively charged, and the hydrogen end being positively charged. As a polar molecule with hydrogen atoms, H_2O can undergo hydrogen bonding with neighboring H_2O atoms, in which the oxygen atoms are weakly bonded to hydrogen atoms from other molecules, due to the differences in electrical charge (see image above). This intermolecular attraction makes water a relatively stable substance, and gives it physical properties such as a relatively high boiling point (100°C) and melting point (0°C). Compare this to other molecules of this size, but are nonpolar, such as methane (CH_4), with a boiling point of -161.6 °C and melting point of -182.5 °C.

References

1. Housecroft, Catherine E. & Sharpe, Alan G. (2008). *Inorganic Chemisty* (3rd ed.). United Kingdom: Pearson Education Limited.
2. Petrucci, Ralph H., Harwood, William S., Herring, Geoffrey F., & Madura, Jeffry D. (2007). *General Chemistry: Principles & Modern Applications* (9th ed.). New Jersey: Pearson Education, Inc.

Outside Links

- http://en.Wikipedia.org/wiki/Water
- http://en.Wikipedia.org/wiki/Water_model

Problems

1) Would you expect BeH_2 to also be a bent triatomic molecule?
- No, because Be lacks the presence of lone pair electrons, which would give the molecule a linear geometry.

2) What makes water highly unusual in its solid phase, compared to its liquid phase?
- Unlike most substances, wherein the solid state is denser than the liquid state, water is less dense in the solid state, meaning its volume expands when freezing.

3) Would you expect ethanol to mix with water? Why or why not?
- Yes, because both substances are polar, the two liquids are miscible, and will mix to form a single homogeneous solution.

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SECTION OVERVIEW

5.5: MO Theory Applied to Polyatomic Molecules $B\ H\ 3$, $N\ H\ 3$, and $C\ H\ 4$

Topic hierarchy

5.5A: \(BH_3\)

5.5B: \(NH_3\)

5.5C: \(CH_4\)

5.5D: A Comparison of MO and VB Bonding Models

5.5: MO Theory Applied to Polyatomic Molecules BH_3, NH_3, and CH_4 is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

5.5A: $B\ H\ 3$

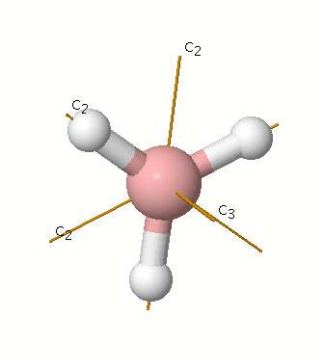


Figure 1: Molecule structure of BH_3 (Used with permission from Dean.H Johnston)

Symmetry Labels

E''	2	-1	0	-2	1	0	(R_x,R_y)	(xz,yz)

FIGURE2: Character table for the the point group D3h

B atom in BH3:

+s-orbital: with the shape of the sphere, its function is $x^2+y^2+z^2$. Therefore, 2s orbital hasa_1' symmetry

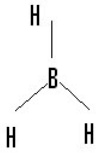
+p-orbital: has 3 orbitals , p_x, p_y, p_z. Therefore, $2p_z$ orbital has a_2'' symmetry

$2p_x$ and $2p_y$ orbital are degenerate and have e' symmetry

3 Hydrogen atoms in BH3: (Ligand group orbitals)

a. Symmetry labels of LGOs:

-With the symmetry operations of BH3 above, we can determine how many LGO unmoved by creating the following table:



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
LGO	3	0	1	3	0	1

-Next, with these values we can apply the following formula to identify the symmetry labels of the Ligan group orbitals

a= 1/h ∑[(N).Xr(R).Xi(R)]

h: the total number of coeficients of symmetry operation

N: the coeficient of the each symmetry operation

Xr(R): the character of the reducible representation corresponding to the R (values that just found in the LGO row

Xi(R): the character of the irreducible representation corresponding to the R (from the character table)

Calculation:

A1'= 1/12 [(1)(3)(1)+(2)(0)(1)+(3)(1)(1)+(1)(3)(1)+(2)(0)(1)+(3)(1)(1)] = 1 A1'

A2'= 1/12 [(1)(3)(1)+(2)(0)(1)+(3)(1)(-1)+(1)(3)(1)+(2)(0)(1)+(3)(1)(-1)]= 0 A2'

E'= 1/12 [(1)(3)(2)+(2)(0)(-1)+(3)(1)(0)+(1)(3)(2)+(2)(0)(-1)+(3)(1)(0)]= 1E'

A1"= 1/12 [(1)(3)(1)+(2)(0)(1)+(3)(1)(1)+(1)(3)(-1)+(2)(0)(-1)+(3)(1)(-1)]= 0 A1"

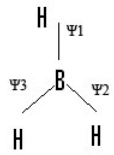
A2"= 1/12 [(1)(3)(1)+(2)(0)(1)+(3)(1)(-1)+(1)(3)(-1)+(2)(0)(-1)+(3)(1)(1)] = 0 A2"

E"= 1/12 [(1)(3)(2)+(2)(0)(-1)+(3)(1)(0)+(1)(3)(-2)+(2)(0)(1)+(3)(1)(0)] = 0 E "

Thus, LGO's symmetry labels are a1' + e'

b. How to determine the shapes of the LGOS?

-LGO's symmetry labels are a1' + e'. There are 3 LGOs that can be made out of these symmetry labels,one LGO is from a1' and two LGOs are from e' due to doubly degenerate. In order to determine the shape of each LGO, we would use the wavefunctions.



-Three hydrogens in BH3 are assigned with Ψ1, Ψ2, Ψ3. Now lets look at how each Ψ is affected by the symmetry operations of the D3h and their results are completed in the following table:

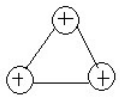
D_{3h}	E	C_3	C^2_3	C_2	C_2'	C_2''	σ_h	S_3	S^2_3	σ_v	σ_v'	σ_v''
Ψ1	Ψ1	Ψ2	Ψ3	Ψ1	Ψ3	Ψ2	Ψ1	Ψ2	Ψ3	Ψ1	Ψ3	Ψ2
a1'	1	1	1	1	1	1	1	1	1	1	1	1
LGO1	Ψ1	Ψ2	Ψ3	Ψ1	Ψ3	Ψ2	Ψ1	Ψ2	Ψ3	Ψ1	Ψ3	Ψ2

Ψ (a1') = 4Ψ1+4Ψ2+4Ψ3

= 4(Ψ1+Ψ2+Ψ3)

Ψ(a1')= 1/√3 (Ψ1+Ψ2+Ψ3)

-The shape of the LGO1 is



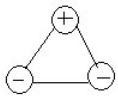
D_{3h}	E	C_3	C^2_3	C_2	C_2'	C_2''	σ_h	S_3	S^2_3	σ_v	σ_v'	σ_v''
Ψ1	Ψ1	Ψ2	Ψ3	Ψ1	Ψ3	Ψ2	Ψ1	Ψ2	Ψ3	Ψ1	Ψ3	Ψ2
e'	2	-1	-1	0	0	0	2	-1	-1	0	0	0
LGO1	2Ψ1	-Ψ2	-Ψ3	0	0	0	2Ψ1	-Ψ2	-Ψ3	0	0	0

Ψ(e') = 4 (Ψ1)-2 (Ψ2)-2 (Ψ3)

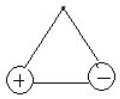
= 2[2(Ψ1)-Ψ2-Ψ3]

Ψ(e') = 1/ √6 (2 Ψ1-Ψ2-Ψ3)

-The shape of the LGO2 is



-Noticed that in the LGO2, we have 1 nodal plane which is the horizonal line between the positive charge and negative charge. Therefore, the LGO3 (doubly degenerate with e') would also 1 nodal plane and its wavefunction would be Ψ(e') = 1/√2 (Ψ2-Ψ3). The shape of the LGO3 is



MO diagram

-As we can see in this diagram, the energy level of 3 LGOs are higher than the 2s orbital and below the 2 p orbital dued to the electronegativy of both Boron and Hydrogen. Hydrogen has higher electronegativity than boron, therefore hydrogen would have lower energy level in the MO diagram.

-In addition, B has 3 electrons in the valence electrons and 3 hydrogens have total 3 electrons. Therefore, the total number of electrons filled in orbitals are 6. With all of the informations above about symmetry labels of B atom and the 3 LGOs, we now construct the MO diagram of BH3. Noticed that, the bonding formation only happens to atoms that have the same symmetry labels. 2s orbital and LGO(1) would contribute 1 electron to give 2 spin pairs electrons at the a_1' energy level. $2p_x$ and $2p_y$ orbitals would bond to the LGO(2) and LGO(3), which give 2 spin pairs electrons at the e' energy level.

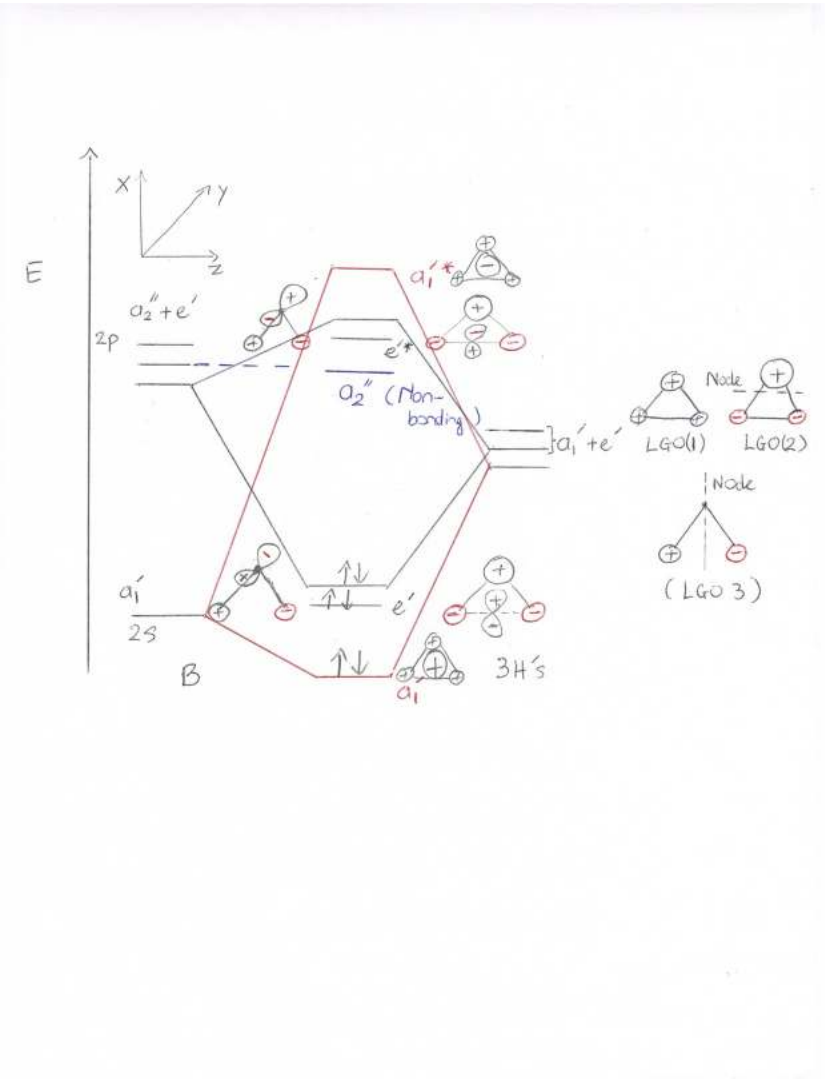
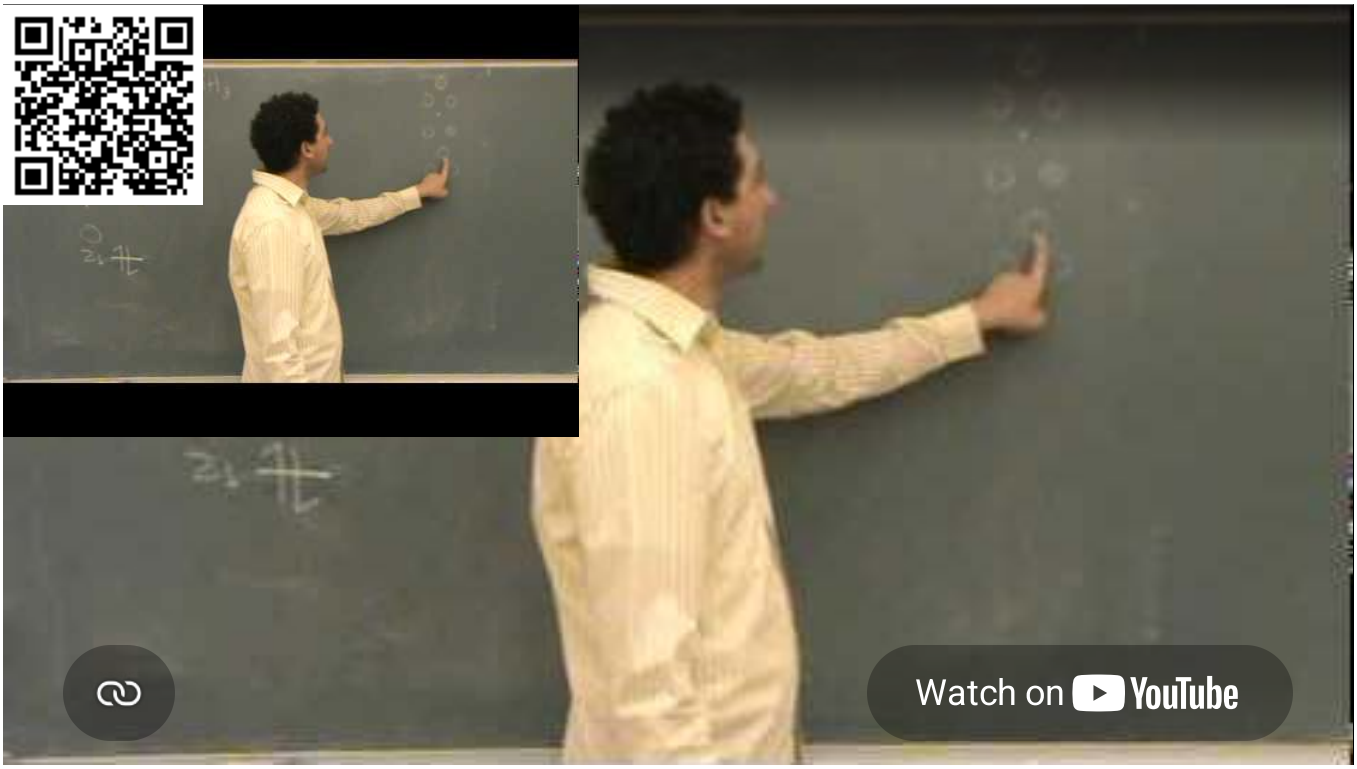


FIGURE 3: MO diagram for the formation of BH3

-there is a detailed explaination that performed in this video

https://chem.libretexts.org/@go/page/2550



References

1. Pople, John A.. *Approximate Molecular Orbital Theory (Advanced Chemistry)*. New York: Mcgraw-Hill (Tx), 1970. Print., Phy Sci Engr Library QD461. P66
2. Noebe, Guillermo (EDT)/, Ronald D. (EDT)/ Abel, and Phillip B. (EDT) Bozzolo. *Applied Computational Materials Modeling*. Berlin and Heidelberg: Springer Verlag, 2007. Print. Phy Sci Engr Library TA 404.23.A66
3. Housecroft, Catherine, and Alan G. Sharpe. *Housecroft Inorganic Chemistry 3e (3rd Edition)*. 3 ed. Alexandria, VA: Prentice Hall, 2008. 128

Outside Links

- symmetry.otterbein.edu/gallery/index.html
- http://www.youtube.com/watch?v=82u4v...ext=1&index=25

Problems

1. What are the non-bonding orbital in this BH_3? '
2. In the above MO diagram, why does e' have 2 lines energy levels compared to a1' has only 1 line energy level?
3. What is the bond order of BH3 in this MO diagram?
4. Assume that we have d orbitals in this BH_3, what are symmetry labels that d-orbitals have based on the character table?
5. Explain why a1' has the lowest energy level in the MO diagram.

Answers

1. a2"
2. because e' is doubly degenerate molecule orbital.
3. B.O = 3
4. a1' + e' + e"
5. a1' has no node, so it is stable and has lowest energy compare to e'.

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5.5B: $N \quad H$ 3

C_{3v}	E	$2C_3$	$3\sigma_v$	Linear Rotations	Quadratic
A_1	1	1	1	z	x^2+y^2,z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x,y)(R_x, R_y)$	$(x^2-y^2, xy)(xz,yz)$

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5.5C: CH_4

This module seeks to explain the bonding of the 4 Hydrogen atoms to the 1 Carbon atom in the molecule CH4 (methane),using the molecular orbital theory. Molecular orbital theory describes orbitals that are formed with the interaction of the atomic orbitals of given atoms. These orbitals are spread out over the entire molecule and electrons fill these orbitals in accordance with the aufbau principle.

1. Introduction
2. The Symmetry of CH4
3. Character Table for Td Point group
4. Molecular Orbital Diagram for CH4
5. References
6. Outside Links
7. Problems
8. Contributors and Attributions

Introduction

Various concepts explain the molecular orbital theory in the bonding in methane, including character tables, symmetry, LGOs (ligand group orbital approach), and a qualitative MO diagram.

The Symmetry of CH_4

- CH_4 belongs to the T_d point group and contains: $8C_3$ axes, $3C_2$ axes, $6S_4$ axes, and a dihedral plane of symmetry. Using the character table for the T_d point group,

Character Table for T_d Point group

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

Molecular Orbital Diagram for CH4

Rename to desired sub-topic. You can delete the header for this section and place your own related to the topic. Remember to hyperlink your module to other modules via the link button on the editor toolbar.

References

1. Housecroft, C; Sharpe, A. (2008). Bonding in Polyatomic Molecules. In: Pearson Education Limited *Inorganic Chemistry*. Edinburgh Gate: Pearson Education Limited. pgs. 33, 130-131.

Outside Links

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Problems

What are ligand group orbitals, and how are they used in MO theory in polyatomic molecules?

How many Vibrational modes and IR/Ramen stretches are there in CH_4?

What are the major differences between VB theory and MO theory applied to polyatomic molecules?

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5.5D: A Comparison of MO and VB Bonding Models

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5.6: MO Theory - Bonding Analyses Soon Become Complicated

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5.7: MO Theory - Learning to Use the Theory Objectively

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5.7A: π -Bonding in $C\ \ O\ 2$

Molecular Orbital (MO) theory is used by scientists to understand bonding in molecules. Carbon dioxide is a linear, centrosymmetric molecule with $D_{\infty h}$ symmetry. Surrounded by two oxygens, carbon is the central atom. MO therory predicts π bond formation resulting from the interaction of C $2P_{x \text{ and } y}$ atomic orbitals with O fragment LGO(Ligand Group Orbitals).

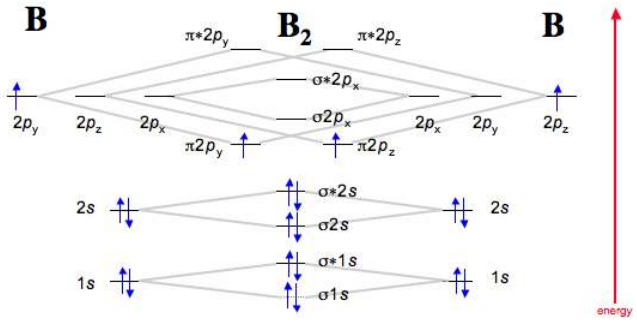
1. Introduction
2. MO Theory
3. Carbon Dioxide MO diagram
4. References
5. Outside Links
6. Problems
7. Contributors and Attributions

Introduction

Carbon dioxide is a well studied molecule. Carbon dioxide is a covalent compound comprised of three atoms, carbon surrounded by two oxygens. Both carbon and oxygen contain p orbitals that are able to interact based on symmetry compatability. Valence bond (VB) theory predicts four bonds for carbon and two for each oxygen. The bond order of each carbon-oxygen bond is 2. Carbon dioxide contains two double bonds. Each double bond is comprised of one sigma bond and one π bond. Carbon dioxide is an important reagent used in industry, is a cental aspect of our global carbon cycle and is the basis for climate change. Lastly, Molecular Orbital (MO) theory is a better tool to use than VB theory because it does not assume localization of electrons. MO theory is based on Linear Combinations of Atomic Orbitals (LCAO).

MO Theory

Mo theory is used to predict bonding, anti-bonding and non-bonding orbitals. Anti-bonding orbitals are always higher in energy than corresonding bonding orbitals. Anti-bonding orbitals are usually indicated with an *. For example, σ*=sigma anti-bonding and σ=sigma bonding. Bonding can be thought of as atomic orbitals being in phase (constructive) and anti-bonding as being out of phase (destructive). Mo diagrams are graphical representations of orbital interactions based on symmetry compatability. Mo diagrams are based on individual atom electron configurations. For example, $B=1s^2 2s^2 2p^1$. Boron has three valence electrons (highest n=principle quantum number in nS or nP) and 2 core electrons. Diatomic Boron (B_2) has an MO diagram:



http://www.meta-synthesis.com/webbook/39_diatomics/diatomics.html

Notice that each individual B atom has 3 valence(n=2) electrons. When combined to form molecular orbitals the bond order is 1: BO=1/2(Bonding-Anti).

Carbon Dioxide MO diagram

The carbon dioxide MO diagram is based on a C atom and an O--O ligand fragment. Carbon has 2S and $2P_{x,y,z}$ orbitals and the O--O fragment has 2S and $2P_{x,y,z}$ orbitals that are involved in the formation of molecular orbitals. Since CO_2 has $D_{\infty h}$ symmetry the central atom's orbital symmetry lables can be obtained from the corresponding point group table: $2S=\sigma_g$, $2P_z=\sigma_u$ and $2P_{x,y}=\pi_u$. The LGO symmetry lables can be calculated using the point group table as well: $\Gamma_\sigma=2\sigma_g + 2\sigma_u$ and $\Gamma_\pi=2\pi_g + 2\pi_u$. The MO diagram for CO_2 is more complicated than the diagram for B_2. The follwing diagram fails to label orbital symmetries but the LGO $2P_{x,y}$

particpate in the formation of π double bonds. The $2\pi_g$ orbiatls are nonbonding because the C $2P_{x,y}$ atomic orbitals are π_u. The LGO $2P_z$ orbitals are involved in σ bonds.



http://cnx.org/content/m32935/latest/

Ater the formation of σ bonds resulting from C 2S and $2P_z$ electrons with O 2S and $2P_z$ orbitals the remaining C $2P_x$ and $2P_y$ orbitals interact with the O LGO fragment. Qualitatively, $\pi_u(2P_{x,y})$ is dipected by the MO diagram as dumbbells overlaping in phase and $\pi_g(2P_{x,y})^*$ as overlapping out of phase.

References

1. Housecroft, C.E., and Sharpe, A.G., *Inorganic Chemistry*, 3rd edition, Pearson Education Limited, Edinburgh, 2008.
2. McQuarrie D.A., and Simon, J.D., *Physical Chemistry A Molecular Approach*, University Science Books, 1997.

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Problems

What does the g subscipt stand for in σ_g?

answer: The g implies symmetric with respect to inversion throught the center of the molecule.

Is carbon dioxide centrosymmetric? Does it have an inversion center?

answer: Yes carbon dioxide in centrosymmetric and includes an inversion center.

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5.7B: [N O 3] −

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5.7C: $S \quad F$ 6

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5.7D: Three-Center Two-Electron Interactions

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5.7E: A More Advanced Problem - $B\ 2\ \ H\ 6$

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CHAPTER OVERVIEW

6: Structures and Energetics of Metallic and Ionic solids

- 6.1: Introduction
- 6.2: Packing of Spheres
  - 6.2A: Cubic and Hexagonal Closed Packing
  - 6.2B: The Unit Cell of HPC and CCP
    - 1.1: The Unit Cell
  - 6.2C: Interstitial Holes in HCP and CCP
  - 6.2D: Non-closed Packing- Simple Cubic and Body Centered Cubic
- 6.3: The Packing of Spheres Model Applied to the Structures of Elements
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6.17A: Schottky Defect
6.17B: Frenkel Defect
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6.17F: Thermodynamic Effects of Crystal Defects

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6.1: Introduction

Crystalline solids

- The atoms, molecules or ions pack together in an ordered arrangement
- Such solids typically have flat surfaces, with unique angles between faces and unique
- 3-dimensional shape
- Examples of crystalline solids include diamonds, and quartz crystals

Amorphous solids

- No ordered structure to the particles of the solid
- No well defined faces, angles or shapes
- Often are mixtures of molecules which do not stack together well, or large flexible molecules
- Examples would include glass and rubber

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SECTION OVERVIEW

6.2: Packing of Spheres

Topic hierarchy

6.2A: Cubic and Hexagonal Closed Packing

6.2B: The Unit Cell of HPC and CCP

1.1: The Unit Cell

6.2C: Interstitial Holes in HCP and CCP

6.2D: Non-closed Packing- Simple Cubic and Body Centered Cubic

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6.2A: Cubic and Hexagonal Closed Packing

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6.2B: The Unit Cell of HPC and CCP

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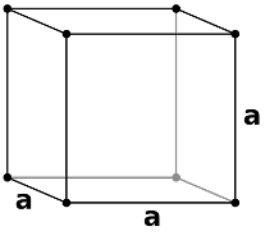
1.1: The Unit Cell

The Unit Cell refers to a part of a simple crystal lattice, a repetitive unit of solid, brick-like structures with opposite faces, and equivalent edge points. In 1850, Auguste Bravais proved that crystals could be split into fourteen unit cells. Although there are several types of unit cells found in cubic lattices, we will be discussing the basic ones: Simple Cubic, Body-centered Cubic, and Face-centered Cubic. If any atom recrystalizes, it will eventually become the original lattice. Crystallization refers the purification processes of molecular or structures;.

Introduction

The Unit Cell contains seven crystal systems and fourteen crystal lattices. These unit cells are given types and titles of symmetries, but we will be focusing on cubic unit cells. One of the most commonly known unit cells is rock salt NaCl (Sodium Chloride), an octahedral geometric unit cell. The whole lattice can be reproduced when the unit cell is duplicated in a three dimensional structure. These unit cells are imperative for quite a few metals and ionic solids crystallize into these cubic structures. Calculating with unit cells is a simple task because edge-lengths of the cell are equal along with all 90° angles.

Simple Cubic Unit Cells



Simple Cubic unit cells indicate when lattice points are only at the corners. They are the simplest (hence the title) repetitive unit cell. The lattice points at the corners make it easier for metals, ions, or molecules to be found within the crystalline structure. This phenomena is rare due to the low packing of density, but the closed packed directions give the cube shape.

Since the edges of each unit cell are equidistant, each unit cell is identical. In order to be labeled as a "Simple Cubic" unit cell, each eight cornered same particle must at each of the eight corners. This unit cell only contains one atom. Its packing efficiency is about 52%.

To packing efficiency, we multiply eight corners by one-eighth (for only one-eighth of the atom is part of each unit cell), giving us one atom.

8 Corners of a given atom x 1/8 of the given atom's unit cell = 1 atom

To calculate edge length in terms of *r* the equation is as follows:

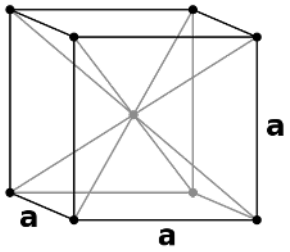
$$2r$$

An example of a Simple Cubic unit cell is Polonium.

Body-centered Cubic Unit Cells

Body-centered Cubic (BCC) unit cells indicate where the lattice points appear not only at the corners but in the center of the unit cell as well. The atoms touch one another along the cube's diagonal crossing, but the atoms don't touch the edge of the cube. All atoms are identical. This type of unit cell is more common than that of the Simple Cubic unit cell due to tightly packed atoms. Its packing efficiency is about 68% compared to the Simple Cubic unit cell's 52%.

This unit cells contains two atoms.



To determine this, we multiply the previous eight corners by one-eighth and *add* one for the additional lattice point in the center.

(8 Corners of a given atom x 1/8 of the given atom's unit cell) + 1 additional lattice point = 2 atoms)

To calculate edge length in terms of *r* the equation is as follows:

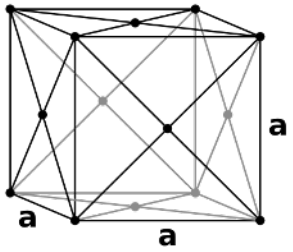
$$\frac{4r}{\sqrt{3}} \tag{1.1.1}$$

Some examples of BCCs are Iron, Chromium, and Potassium.

It is a common mistake for CsCl to be considered bcc, but it is not. Instead, it is non-closed packed.

Face-centered Cubic Unit Cells

Face-centered Cubic (FCC) unit cells indicate where the lattice points are at both corners and on each face of the cell.



This is a more common type of unit cell since the atoms are more tightly packed than that of a Simple Cubic unit cell. Like the BCC, the atoms don't touch the edge of the cube, but rather the atoms touch diagonal to each face. Its packing efficiency is the highest with a percentage of 74%. Atoms touch one another along the face diagonals. All atoms are identical.

This unit cell contains four atoms.

To determine this, we take the equation from the aforementioned Simple Cubic unit cell and *add* to the parenthesized six faces of the unit cell multiplied by one-half (due to the lattice points on each face of the cubic cell).

(8 corners of a given atom x 1/8 of the given atom's unit cell) + (6 faces x 1/2 contribution) = 4 atoms)

To calculate edge length in terms of *r* the equation is as follows:

$$2\sqrt{2}r \tag{1.1.2}$$

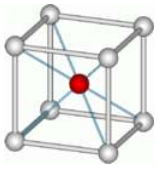
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1. Brown, Theodore L. *Chemistry: the Central Science.* 10th ed. Upper Saddle River, NJ: Pearson Prentice Hall, 2006. Print. (Pgs 466-467)
2. Housecroft, Catherine E., and Alan G. Sharpe. *Inorganic Chemistry*. 3rd ed. Harlow: Pearson Education, 2008. Print. (Pgs 149-151)
3. Tro, Nivaldo J. *Chemistry: a Molecular Approach.* 1st ed. Upper Saddle River, NJ: Pearson/Prentice Hall, 2008. Print. (Pgs 498-500)

Outside Links

- Simple Cubic Unit Cell image adapted from the Wikimedia Commons file "Image: http://en.Wikipedia.org/wiki/File:La...mple_cubic.svg"
- Body-centered Cubic Unit Cell image adapted from the Wikimedia Commons file "http://en.Wikipedia.org/wiki/File:La...ered_cubic.svg"
- Face-centered Cubic Unit Cell image adapted from the Wikimedia Commons file "Image: http://en.Wikipedia.org/wiki/File:La...ered_cubic.svg"
- Image from Problem 3 adapted from the Wikimedia Commons file "Image: http://upload.wikimedia.org/wikipedi...Cl_crystal.png"

Problems



1. What is the edge length of the atom Polonium if its radius is 167 pm?
2. What type of unit cell is Caesium Chloride as seen in the picture. Briefly explain your answer. Diagram---------->
3. Give two other examples (none of which is shown above) of a Face-Centered Cubic Structure metal. Briefly explain your reasonings.
4. Silver crystallizes with a FCC; the raidus of the atom is 160 pm. What is the density of the solid silver in grams per cubic centimeters?

Answers

1. Polonium is a Simple Cubic unit cell, so the equation for the edge length is *2r*. Therefore, 2(167pm) = 334pm
2. Caesium Chloride is a non-closed packed unit cell. It is common for one to mistake this as a body-centered cubic, but it is not. The reason for this is because the ions do not touch one another. Also, in order to be considered BCC, all the atoms must be the same. Since the middle atome is different than the corner atoms, this is not a BCC.

3. Two examples of a FCC cubic structure metals are Lead and Aluminum. Each contains four atoms, six of which run diagonally on each face.
4. We approach this problem by first finding the mass of the unit cell. Mass of Silver is 107.87 g/mol, thus we divide by Avagadro's number 6.022 x $10^{-22.}$

We end up with 1.79 x 10^{-22} g/atom. Next we find the mass of the unit cell by multiplying the number of atoms in the unit cell by the mass of each atom (1.79 x 10^{-22} g/atom)(4) = 7.167 x 10^{-22} grams.

Next we find the edge length by:

$$2\sqrt{2} * 160pm \tag{1.1.3}$$

Which equals 4.525 x 10^{-10} meters.

Now we find the volume which equals the edge length to the third power. We convert meters into centimeters by dividing the edge length by 1 cm/10^{-2}m to the third power. (4.525 x 10^{-10} m x 1cm/10^{-2}m = 9.265 x 10^{-23} cubic centimeters.)

Finally, we find the density by mass divided by volume. So, 7.167 x 10^{-22} grams/9.265 x 10^{-23} cubic centimeters = 7.74 g/cm^3

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- Sonika Sidher--UC Davis

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6.2C: Interstitial Holes in HCP and CCP

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6.2D: Non-closed Packing- Simple Cubic and Body Centered Cubic

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SECTION OVERVIEW

6.3: The Packing of Spheres Model Applied to the Structures of Elements

Topic hierarchy

6.3A: Group 18 Elements in the Solid State

6.3B: H_2 and F_2 Solids

6.3C: Solid Metallic Elements

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6.3A: Group 18 Elements in the Solid State

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6.3B: H_2 and F_2 Solids

Hydrogen and Fluorine, as well as Chlorine, Bromine and Iodine, exist as diatomic molecules. Both diatomic Hydrogen and diatomic Florine exist as gasses at room temperature and exhibit extremely low melting and boiling points. If the temperature of the system is lowered below the respective melting points of Hydrogen or Fluorine, molecular motion is reduced and a crystalline lattice is formed, creating a solid.

Solid State Hydrogen and Fluorine

Elemental Hydrogen and Elemental Fluorine, H_2 and F_2 respectively, exist as gases at room temperature. Though the melting point of H_2 is 20.4 K (-252.75 °C), a temperature of 14.0 K (-259.15 °C) is required for the solidification of H_2.[3,4] As the solid structure is formed, the diatomic Hydrogen molecules adopt a hexagonal close packing (hcp) structure.[4] Fluorine exhibits similar behaviour. The melting point of Fluorine is 53.54K (-219.61 °C), at which point the diatomic Fluorine adopts a cubic close packed crystalline arrangement (ccp), instead of a hexagonal close packed arrangement.[3,4]

Ability to use the sphere model of Crystalline structure for H_2 and F_2 solids

When solid, both dihydrogen and difluorine are small enough to allow for rotation within the solid structure (the radius of Fluorine is about equivalent to that of Hydrogen). This rotation occurs about a central axis midway between the two distal atoms of the molecule, creating two equal radii from the middle of the H-H or F-F bond to the outer boundary of each H or F atom. This rotation occurs 360° in the x, y and z directions of the central axis, as well as all manner of combinations of these three variables. The rotation of the molecule in all directions creates what can be though of as a spherical shell, the boundary of which is created by the distal atoms.[4]

Some common uses for solid hydrogen include gamma-ray ablation cages for elemental analysis, and a solid state cage in which to look at hydrogen bonding within molecules. [1,2]

References

1. Palaszewski, B. (2002) "Solid Hydrogen Experiments for Atomic Propellants: Particle Formation Energy and Imaging Analysis" Retrieved from gltrs.grc.nasa.gov/reports/20...002-211915.pdf
2. Wang, X., Andrews, L. *J. Phys. Chem. A*, 2004, 108 (7), pp 1103–1106 **DOI:** 10.1021/jp037382q
3. Merck Index. 14th ed. Merck: Whitehouse Station, NJ, 2007; 4896
4. Sharpe, Housecroft "Inorganic Chemistry" 3 ed.

Outside Links

- This is not meant for references used for constructing the module, but as secondary and unvetted information available at other site
- Link to outside sources. Wikipedia entries should probably be referenced here.

Problems

1. Why can F_2 and H_2 be considered similar molecules and thus exhibit similar behaviour in rotation?

2. What is the different between a cubic close packing structure and hexagonal close packing?

3. Why do difluorine and dihydrogen exhibit different packing structures.

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6.3C: Solid Metallic Elements

A metal (from Greek μέταλλον métallon, "mine, quarry, metal") is a material (an element, compound, or alloy) that is typically hard, opaque, shiny, and has good electrical and thermal conductivity. Metals are generally *malleable* - that is, they can be hammered or pressed permanently out of shape without breaking or cracking - as well as *fusible* (able to be fused or melted) and *ductile* (able to be drawn out into a thin wire). About 91 of the 118 elements in the periodic table are metals (some elements appear in both metallic and non-metallic forms).

Atoms of metals readily lose their outer shell electrons, resulting in a free flowing cloud of electrons within their otherwise solid arrangement. This provides the ability of metallic substances to easily transmit heat and electricity. While this flow of electrons occurs, the solid characteristic of the metal is produced by electrostatic interactions between each atom and the electron cloud. This type of bond is called a metallic bond.

Cubic and hexagonal close packing.

Crystalline solids consist of repeating patterns of its components in three dimensions (a crystal lattice) and can be represented by drawing the structure of the smallest identical units that, when stacked together, form the crystal. This basic repeating unit is called a *unit cell*.

Many metals adopt close packed structures i.e. cubic close packed (face centred cubic) and hexagonal close packed structures. A simple model for both of these is to assume that the metal atoms are spherical and are packed together in the most efficient way (close packing or closest packing). For closest packing, every atom has 12 equidistant nearest neighbours, and therefore a coordination number of 12. If the close packed structures are considered as being built of layers of spheres then the difference between hexagonal close packing and cubic close packed is how each layer is positioned relative to others. It can be envisaged that for a regular buildup of layers:

- hexagonal close packing has alternate layers positioned directly above/below each other, A,B,A,B,...
- cubic close packed (face centered cubic) has every third layer directly above/below each other, A,B,C,A,B,C,...

Body centred cubic

This is not a close packed structure. Here each metal atom is at the centre of a cube with 8 nearest neighbors, however the 6 atoms at the centres of the adjacent cubes are only approximately 15% further away so the coordination number can therefore be considered to be 14 when these are included. Note that if the body centered cubic unit cell is compressed along one 4 fold axis the structure becomes cubic close packed (face centred cubic).

cubic close packing (ccp)
packing efficiency =74%
CN=12

hexagonal close packing (hcp)
packing efficiency =74%
CN=12

body-centred cubic packing (bcc)
packing efficiency =68%

CN=8

Trends in melting point

Melting points are chosen as a simple measure of the stability or strength of the metallic lattice. Some simple trends can be noted. The transition metals have generally higher melting points than the others. In the alkali metals (Group 1) and alkaline earth metals (Group 2) the melting point decreases as atomic number increases, but in transition metal groups with incomplete d-orbital subshells, the heavier elements have higher melting points. For a given period, the melting points reach a maximum at around Group 6 and then fall with increasing atomic number.

Mercury, caesium and gallium have melting points below 30 °C whereas all the other metals have sufficiently high melting points to be solids at "room temperature". The structures of the metals can be summarised by the table below which shows that most metals crystallise in roughly equal amounts of bcc, hcp and ccp lattices.

Crystal structure of metallic elements in the periodic table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
453.69 Li bcc	1560 Be hcp					MP (K) At. Symbol Lattice type						B	C	N	O	F	Ne
370.87 Na bcc	923 Mg hcp											933.47 Al ccp	Si	P	S	Cl	Ar
336.53 K bcc	1115 Ca ccp	1814 Sc hcp	1941 Ti hcp	2183 V bcc	2180 Cr bcc	1519 Mn	1811 Fe bcc	1768 Co hcp	1728 Ni ccp	1357.8 Cu ccp	692.68 Zn hcp	302.91 Ga	Ge	As	Se	Br	Kr
312.46 Rb bcc	1050 Sr ccp	1799 Y hcp	2128 Zr hcp	2750 Nb bcc	2896 Mo bcc	2430 Tc hcp	2607 Ru hcp	2237 Rh ccp	1828 Pd ccp	1235 Ag ccp	594 Cd	430 In	505 Sn	904 Sb	Te	I	Xe
301.59 Cs bcc	1000 Ba bcc		2506 Hf hcp	3290 Ta bcc	3695 W bcc	3459 Re hcp	3306 Os hcp	2719 Ir ccp	2041.4 Pt ccp	1337.33 Au ccp	234.32 Hg	577 Tl hcp	600.61 Pb ccp	544.7 Bi	527 Po	At	Rn

Group 1: Alkali metals

The alkali metals have their outermost electron in an s-orbital and this electronic configuration results in their characteristic properties. The alkali metals provide the best example of group trends in properties in the periodic table, with elements exhibiting well-characterized homologous behaviour.

The alkali metals have very similar properties: they are all shiny, soft, highly reactive metals at standard temperature and pressure and readily lose their outermost electron to form cations with charge +1. They can all be cut easily with a knife due to their softness, exposing a shiny surface that tarnishes rapidly in air due to oxidation by atmospheric moisture and oxygen. Because of their high reactivity, they must be stored under oil to prevent reaction with air, and are found naturally only in salts and never as the

free element. In the modern IUPAC nomenclature, the alkali metals comprise the group 1 elements, excluding hydrogen (H), which is only nominally considered a group 1 element.

extended structures of Li, Mg, Ca

Lithium -bcc

Magnesium -hcp

Spacefill

UnitCell

All Layers

A

B

A

B

A layers

Calcium -ccp

Spacefill

UnitCell

All Layers

A

B

C

A

B

C layers

Note that Housecroft and Sharpe has Ca and Sr both listed as hexagonal and not cubic (face) close packed lattices. Calcium and Strontium exist in several allotropic forms and the lowest temperature forms (for Ca < 450 °C) are ccp. At high temperatures phase transitions occur to give hexagonal.

Return to the course outline or move on to Lecture 5: Structure of the elements Boron, Carbon and Phosphorus, Sulfur.

References

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'Inorganic Chemistry' - C. Housecroft and A.G. Sharpe, Prentice Hall, 4th Ed., 2012, ISBN13: 978-0273742753, pps 24-27, 43-50, 172-176, 552-558, 299-301, 207-212
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SECTION OVERVIEW

6.4: Polymorphism in Metals

Polymorphism is the ability of a solid material to exist in more than one form or crystal structure.

Topic hierarchy

6.4A: Polymorphism - Phase Changes in the Solid State

6.4B: Phase Diagrams

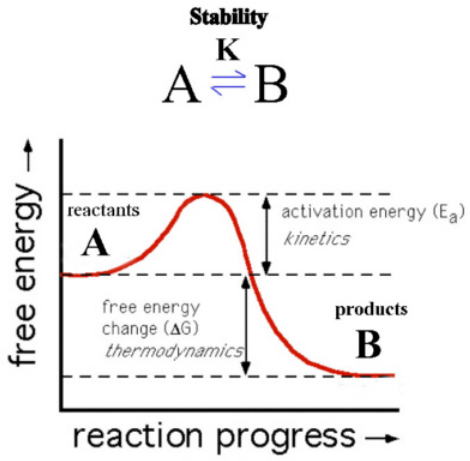
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6.4A: Polymorphism - Phase Changes in the Solid State

Polymorphism is when a solid material can exist in more than one form or crystal structure. Polymorphism is very similar to Allotropy, but they should not be confused, polymorphism describes molecules, while Allotropy is used to describe atoms. Polymorphism has many uses whether it was in pharmaceutical, explosives or even food. This process was discovered by Eilhard Mitscherlich in 1821.

Kinetic vs. Thermodynamic Stability

When discussing the concept of Stability it is necessary to distinguish between thermodynamic and kinetic stability.



Here B is at lower energy than A so that ΔG is negative. The reaction should therefore proceed spontaneously and B is the more thermodynamically stable species.

The reaction as shown though has a barrier to the progress of the reaction called the Activation Barrier (Ea) and so the reaction may proceed very slowly. The thermodynamics describes only the starting and ending position of the reaction and not the intermediate or transition state. If the kinetics is slow, A is described as being **inert** while if it proceeds quickly then A is described as being **labile**.

The conditions that distinguish them are:
if the reaction takes longer than 1 minute under the conditions of concentration 0.1 M, temperature 25°C, then it is INERT,
if under the same conditions the reaction time < 1 minute, then it is LABILE.

In the lecture on isomerism, we depend on the samples being kinetically stable i.e. inert.

In the lecture on Chelation and Stability we concentrate on thermodynamic stability and look at the changes in free energy, enthalpy and entropy during the reaction. When we consider thermodynamic stability we need to be familiar with 2 formulae:

$\Delta G^{\ominus}$ = - RT ln(K) or alternatively $\Delta G^{\ominus}$ = - 2.303RT $\log_{10}$(K) ---(1)
$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ ---(2)

The first relates the free energy to the stability constant and the second shows the breakdown into the component enthalpy and entropy terms.

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6.4B: Phase Diagrams

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6.5: Metallic Radii

Atomic radius is the radius of an atom which measures the distant from its nucleus to the electron. And metallic radii are the radii of the metallic atoms. It is the size of a metallic atom. However the actually measurement of the radius is very vague because electrons don’t stay at one point, they orbits around.

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6.6: Melting Points and Standard Enthalpies of Atomization of Metals

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SECTION OVERVIEW

6.7: Alloys and Intermetallic Compounds

Alloys are mixtures of metals or a mixture of a metal and another element. An alloy may be a *solid solution* of metal elements (a homogeneous mixture) or a mixture of metallic phases (a heterogeneous mixture of two or more solutions).

Topic hierarchy

6.7A: Substitutional Alloys

6.7B: Interstitial Alloys

6.7C: Intermetallic Compounds

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6.7A: Substitutional Alloys

When a molten metal is mixed with another substance, there are two mechanisms that can cause an alloy to form: (1) *atom exchange* or (2) *interstitial mechanism*. The relative size of each element in the mix plays a primary role in determining which mechanism will occur.

When the atoms are relatively similar in size, the atom exchange method usually happens, where some of the atoms composing the metallic crystals are substituted with atoms of the other constituent. This is called a *substitutional alloy*. Examples of substitutional alloys include bronze and brass, in which some of the copper atoms are substituted with either tin or zinc atoms.

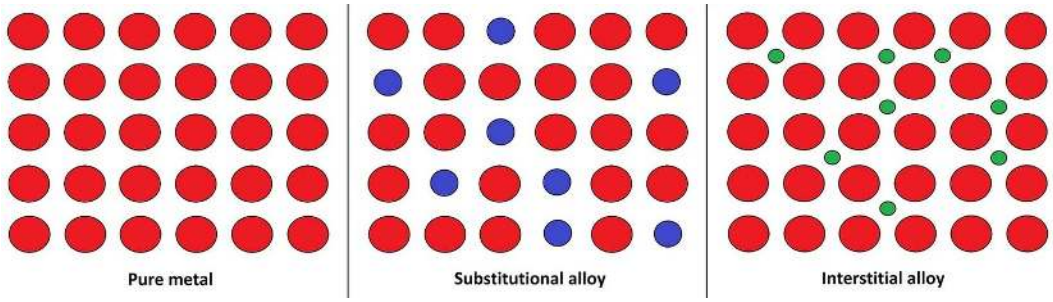


Figure 6.7A.1: Different atomic mechanisms of alloy formation, showing pure metal, substitutional, and interstitial structures. (CCO; Hbf878 via Wikipedia)

Why Substitutional Alloys Occur: Bonding

The bonding between two metals is best described as a combination of metallic electron "sharing" and covalent bonding, one can't occur without the other and the proportion of one to the other changes depending on the constituents involved. Metals share there electrons throughout there structure, this flow of electrons is the reason behind many of the characteristics associated with metals, including their ability to act as conductors. The different amount and strength of covalent bonds can change depending on the different specific metals involved and how they are mixed. The covalent bonding is what is responsible for the crystal structure as well as the melting point and various other physical properties.

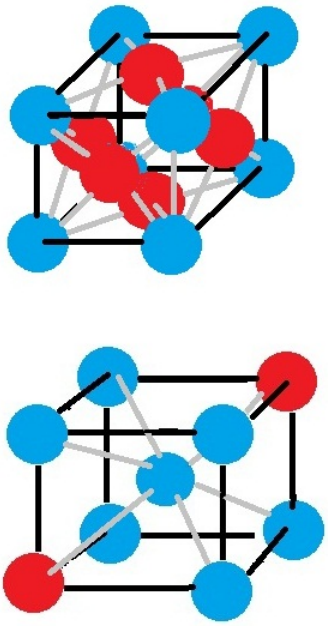


Figure 6.7A.2: Examples of Substitutional Metal Alloys. Depending on the specific type of substitutional alloy they can have multiple crystal structures. Two of the possible structures include Face Center Cubic (left), and Cubic Center Cubic (right). The structure of the metal alloy is not limited to these two structures, but combined they represent a large portion of the common alloys.

As the similarities between the electron structure of the metals involved in the alloy increase, the metallic characteristics of the alloy decrease. Pure metals are useful but their applications are often limited to each individual metal's properties. Alloys allow metal mixtures that have increased resistance to oxidation, increased strength, conductivity, and melting point; Essentially any property can be manipulated by adjusting alloy concentrations. An example could be Brass Door fixtures, they are strong and resist corrosion better then pure zinc or copper, the two major metals that constitute a brass alloy. The combination also has a low melting point allowing it to be easily cast into many different shapes and sizes.(1) There are many other aspects of substitutional alloys that could be explored in depth, but the basic concept is the idea that each individual metal in an alloy give the final product its chemical and physical properties.

Substitutional alloys played an important role in the development of human society and culture as we know it today. The Bronze age itself is named after the Substitutional alloy consisting of tin in a metallic solution of copper. Ancient bronzes are very impure, or even mislabeled, containing large amounts of zinc and arsenic as well as lots of impurities. These many substitutional alloys allowed for stronger tools and weapons, they allowed for increased productivity in the workshop as well as on the battlefield. The need for raw materials like tin and copper for the production of bronze also spurred an increase in trade, since their ores are rarely found together. The current chemical understanding of substitutional alloys would not be so in depth if it weren't for the usefulness of the alloys to humans.

Summary

An alloy is a mixture of metals that has bulk metallic properties different from those of its constituent elements. Alloys can be formed by substituting one metal atom for another of similar size in the lattice (substitutional alloys), by inserting smaller atoms into holes in the metal lattice (interstitial alloys), or by a combination of both. Although the elemental composition of most alloys can vary over wide ranges, certain metals combine in only fixed proportions to form intermetallic compo

References

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2. Wang, F. E.. (2005). *Bonding theory for metals and alloys*. Amsterdam: Elsevier.
3. Dickinson, O. T. P. K. (1994). *The Aegean Bronze age*. Cambridge world archeology. Cambridge: Cambridge University Press.

Problems

1. Are substitutional metal alloys naturally occurring on earths surface?
2. What are two characteristics of a metal required for a substitutional alloy to form?
3. Can Oxygen or Nitrogen be a part of the crystal structure of a substitutional alloy?

Solutions

1. No, the oxidizing nature of the earths atmosphere, as well as the need for specific and concentrated metals keeps these from being found naturally occurring.
2. Similar radii and similar electronegativity.
3. Only metallic elements can form the necessary metallic bonds that allow alloys to form.

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6.7B: Interstitial Alloys

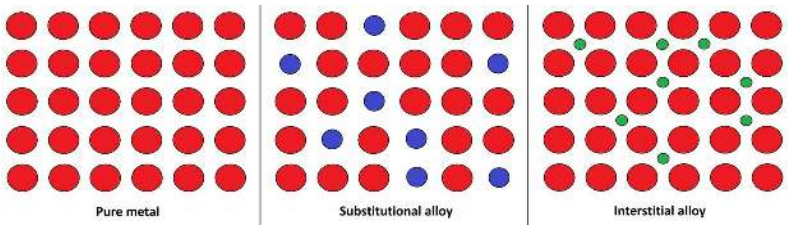


***Figure 6.7B.1**: Different atomic mechanisms of alloy formation, showing pure metal, substitutional, and interstitial structures. from Wikipedia.*

With the interstitial mechanism, one atom is usually much smaller than the other, so cannot successfully replace an atom in the crystals of the base metal. The smaller atoms become trapped in the spaces between the atoms in the crystal matrix, called the *interstices*. This is referred to as an *interstitial alloy*. Steel is an example of an interstitial alloy, because the very small carbon atoms fit into interstices of the iron matrix. Stainless steel is an example of a combination of interstitial and substitutional alloys, because the carbon atoms fit into the interstices, but some of the iron atoms are replaced with nickel and chromium atoms.

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6.7C: Intermetallic Compounds

Intermetallic compounds are solid phases containing two or more metallic elements, with optionally one or more non-metallic elements, whose crystal structure differs from that of the other constituents. Under this definition the following are included

- The definition of a metal is taken to include:
  - the so-called post-transition metals, i.e. aluminium, gallium, indium, thallium, tin and lead
  - some, if not all, of the metalloids, e.g. silicon, germanium, arsenic, antimony and tellurium.

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SECTION OVERVIEW

6.8: Bonding in Metals and Semicondoctors

6.8A: Electrical Conductivity and Resistivity

6.8B: Band Theory of Metals and Insulators

6.8C: The Fermi Level

6.8D: Band Theory of Semiconductors

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6.8A: Electrical Conductivity and Resistivity

Electrical resistivity and conductivity is an important property for materials. Different materials have different conductivity and resistivity. Electrical conductivity is based on electrical transport properties. These can be measured with multiple techniques by using a variety of instruments. If electricity easily flows through a material, that material has high conductivity. Some materials that have high conductivity include copper and aluminum. Electrical conductivity is the measure of how easily electricity flows through a material.

Conductivity vs Resistivity

Conductivity and resistivity are inversely proportional to each other. When conductivity is low, resistivity is high. When resistivity is low, conductivity is high. The equation is as follows:

$$\rho = \frac{1}{\sigma} \tag{6.8A.1}$$

where

- Resistivity is represented by ρ and is measured in **Ohm-meters** (Ωm),
- Conductivity is represented by σ and is measured in **Siemens** ($1/\Omega m$).

Since conductivity is the measure of how easily electricity flows, electrical resistivity measures how much a material resists the flow of electricity.

Electrical Transport Properties

Simply put, electricity is the movement of electrons through a material. As electrons move through a material, it comes into contact with atoms in the material. Collisions slow the electrons down. Each collision increases the resistivity of the material. The easier the electrons continue through a material, the fewer collisions that take place and the higher the conductivity.

When temperature increases, the conductivity of metals usually decreases, while the conductivity of semiconductors increases. This of course assumes that the material is homogenous, which is not always the case. You can calculate resistivity using the following equation

$$\frac{E}{J} = \rho \tag{6.8A.2}$$

As you already read, ρ is the symbol for resistivity. E is the electric field and has units of Volts per meter (V/m). J is the current density and has units of amps per meter squared (A/m2). The electric field is calculated by dividing the Voltage by the length, l, that voltage is applied.

$$E = \frac{V}{l} \tag{6.8A.3}$$

The current density is calculated by the equation below

$$J = \frac{I}{A} \tag{6.8A.4}$$

I is the current and is divided by the cross sectional area, A, over which the current flows.

Resistivity vs Resistance

Resistivity and resistance are two different things. Resistivity does not depend on size or shape. Resistance, however, does. You can calculate resistance with the equation below.

$$R = \frac{V}{I} \tag{6.8A.5}$$

R refers to resistance and is measured in Ω. V is the voltage and is measured in volts. I measures the current and its unit is amps (A).

References

1. Electrical Conductivity and Resistivity, Heaney, Michael, Electrical Measurement, Signal Processing, and Displays. Jul 2003
2. Levy, Peter M., and Shufeng Zhang. "Electrical Conductivity of Magnetic Multilayered Structures." *Physical Review Letters* 65.13 (1990): 1643-646. Print.

Problems

1. What is the current density of a material with a resistivity of 12.Ωm and an electric field of 64.V/m?
2. If the voltage of 6V is passed through a substance with a radius of 2m and a length of 3m, what is the electric field?
3. What is the electric field of a material when the current is equal to 25A, the resistance is measured to be 78Ω, the current density equals 24A/m2, and the length the current flows is 100m?
4. A material has a voltage of 150V and width of 24m. The material also has a current of 62A and travels a distance of 5m. What is the conductivity?
5. A metal originally has an electron colliding with every fifth atom and increases from a temperature of 6K to 100K. A semiconductor originally has an electron colliding with every fifth atom and increases from a temperature of 6K to 100K. What material will have a greater resistivity? Why?

Answers to Problems:

1. $E/J = \rho$ ---> $J=E/\rho = 64V/m / 12\Omega m = 5.33A/m^2$

2. $E=V/l = 6V/3m = 2V/m$

3. $E=V/l$

$V=IR$ ---> $E=IR/l = 25A \times 78\Omega/100m = 19.5V/m$

4. $E/J = \rho$

$E=V/l$

$J=I/A$ ---> $\rho=(V/l)/(I/A) = (150V/5m)/(62A/(24m \times 5m) = 58\Omega m$

$\rho = 1/\sigma$ ---> $1/\rho = \sigma = 1/58\Omega m$

5. The material that has the greatest resistivity is the metal because as temperature increases metals are more likely to increase in resistivity and semiconductors usually decrease in resistivity as temperature increase.

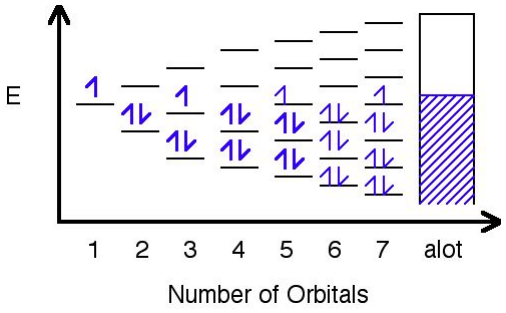
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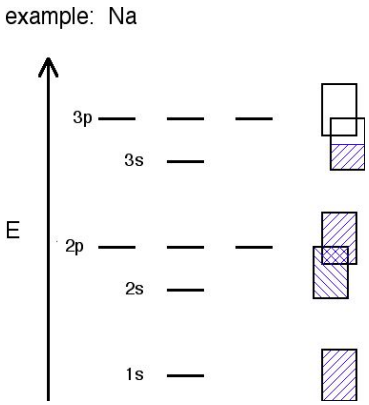
6.8B: Band Theory of Metals and Insulators

Band Theory was developed with some help from the knowledge gained during the quantum revolution in science. In 1928, Felix Bloch had the idea to take the quantum theory and apply it to solids. In 1927, Walter Heitler and Fritz London discovered bands- very closely spaced orbitals with not much difference in energy.



In this image, orbitals are represented by the black horizontal lines, and they are being filled with an increasing number of electrons as their amount increases. Eventually, as more orbitals are added, the space in between them decreases to hardly anything, and as a result, a band is formed where the orbitals have been filled.

Different metals will produce different combinations of filled and half filled bands.



Sodium's bands are shown with the rectangles. Filled bands are colored in blue. As you can see, bands may overlap each other (the bands are shown askew to be able to tell the difference between different bands). The lowest unoccupied band is called the conduction band, and the highest occupied band is called the valence band.

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- In Na, the 3s band is 1/2 full.
- In Mg, the 3s band is full.
- In Al, the 3s band is full and the 3p ban is 1/2 full... and so on.

The probability of finding an electron in the conduction band is shown by the equation:

$$P = \frac{1}{e^{\Delta E/RT} + 1} \tag{6.8B.1}$$

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ELEMENT	ΔE(kJ/mol) of energy gap	# of electrons/cm^3 in conduction band	insulator, or conductor?
C (diamond)	524 (big band gap)	10^{-27}	insulator
Si	117 (smaller band gap, but not a full conductor)	10^{9}	semiconductor
Ge	66 (smaller band gap, but still not a full conductor)	10^{13}	semiconductor

Conductors, Insulators and Semiconductors

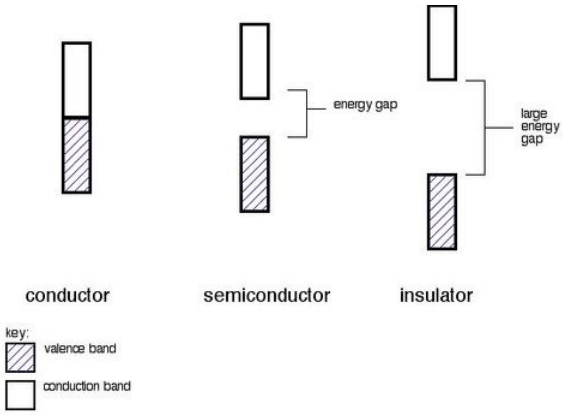


Diagram comparing conductor, semiconductor, and insulator energy bands. Conductor has overlapping bands; semiconductor has small gap; insulator has large gap. Key: valence and conduction bands.

A. Conductors

Metals are conductors. There is no band gap between their valence and conduction bands, since they overlap. There is a continuous availability of electrons in these closely spaced orbitals.

B. Insulators

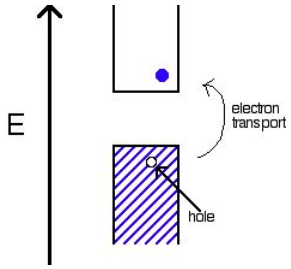
In insulators, the band gap between the valence band the the conduction band is so large that electrons cannot make the energy jump from the valence band to the conduction band.

C. Semiconductors

Semiconductors have a small energy gap between the valence band and the conduction band. Electrons can make the jump up to the conduction band, but not with the same ease as they do in conductors. There are two different kinds of semiconductors: **intrinsic** and **extrinsic**.

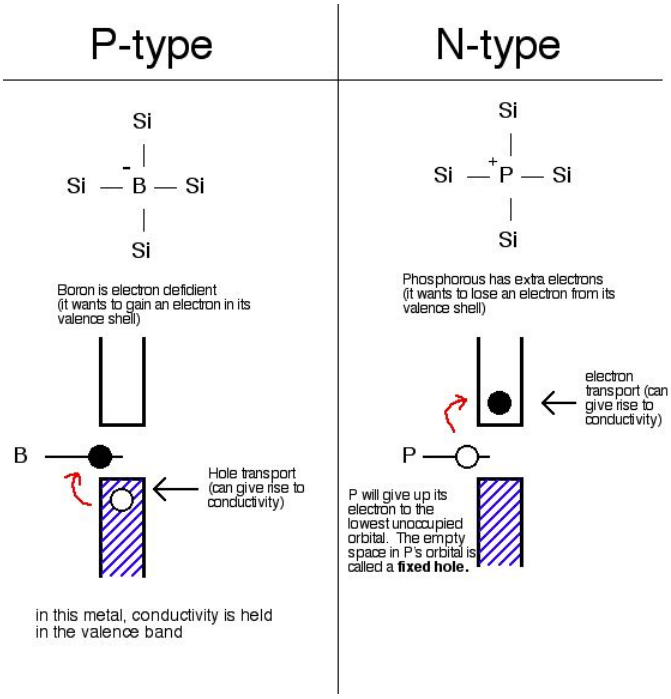
i. Intrinsic Semiconductors

An intrinsic semiconductor is a semiconductor in its pure state. For every electron that jumps into the conduction band, the missing electron will generate a hole that can move freely in the valence band. The number of holes will equal the number of electrons that have jumped.



ii. Extrinsic Semiconductors

In extrinsic semiconductors, the band gap is controlled by purposefully adding small impurities to the material. This process is called **doping**. Doping, or adding impurities to the lattice can change the electrical conductivity of the lattice and therefore vary the efficiency of the semiconductor. In extrinsic semiconductors, the number of holes will not equal the number of electrons jumped. There are two different kinds of extrinsic semiconductors, p-type (positive charge doped) and n-type (negative charge doped).



? Exercise 6.8B.1

How do you distinguish between a valence band and a conduction band?

Answer

The valence band is the highest band with electrons in it, and the conduction band is the highest band with no electrons in it.

? Exercise 6.8B.2

Is the energy gap between an insulator smaller or larger than the energy gap between a semiconductor?

Answer

Larger

Exercise 6.8B.3

What two methods bring conductivity to semiconductors?

Answer

Electron transport and hole transport

Exercise 6.8B.4

You are more likely to find electrons in a conduction band if the energy gap is smaller/larger?

Answer

Smaller

References

1. Petrucci, Harwood, Herring, Madura. GENERAL CHEMISTRY Principles and Modern Applications 9th Edition. Macmillan Publishing Co: New Jersey. 1989.
2. Moore, John T. Chemistry Made Simple. Random House Inc: New York. 2004.

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6.8C: The Fermi Level

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Fermi level

The Fermi Level is the energy level which is occupied by the electron orbital at temperature equals 0 K. The level of occupancy determines the conductivity of different materials. For solid materials such as metals, the orbital occupancy can be calculated by making an approximation based on the crystalline structure. These orbitals, combined with the energy level, determine whether the material is an insulator, semi-conductor, or conductor. The orbitals are categorized according to its energy. The lower energy orbitals combine and form a band called the valence electron band, and the higher energy orbitals combine to form a band called the conduction band. There is a gap between the valence and conduction band called the energy gap; the larger the energy gap, the more energy it is required to transfer the electron from the valence band to the conduction band.

Energy Band Diagram

The diagram below is an example of an energy band diagram. The upper box represents the conduction band, the lower box represents the valence band, and the yellow is the occupancy level of electrons. The conductivity of a material can be determined by the energy diagram. In order to conduct electricity, an electron must make a transition into another state since electrons cannot occupy the same quantum states. When the electron cannot make that transition, it will be not be able to conduct electricity. When the band is completely filled, the closest state an electron to transfer to will be the states in the conduction band, and that would require the electron to jump over the band gap, thus making it more difficult to conduct electricity. With this rule, it is easy to tell the difference between insulator, semi-conductor, and conductors. The energy band on the left side is an insulator because if an electron wants to go into a higher energy state, it will need to jump through that huge energy gap. Since it requires a large amount of energy to move the electron, the material will have a difficult time conducting electricity. The energy band in the middle is a semi-conductor because although the electrons have to jump across the energy gap, the energy gap is small. If an electron wants to make a transition, it will require very little energy since they are all int he same energy band. Thus, for the material in the middle, although it will have difficulty conducting electricity, it is not impossible. The energy

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band in the right is a conductor. Although the valence band is filled just like the insulator and semi-conductor, the conduction band overlaps the valence band. If an electron wants to make a transition, it will require very little amount of energy. Which means the material on the right can conduct electricity very easily.

Fermi Level

The electrons that occupies the orbits are described by Fermi-Dirac distribution as the figure below, the distribution takes on the form of:

$$\frac{1}{1 + \exp[(E-u)/KT]} \quad (1)$$

http://upload.wikimedia.org/wikipedi...irac_distr.svg

Where E is the energy of the system, u is the fermi level, K is the Boltzmann constant, and T is the temperature. The Fermi-Dirac distribution accounts for the population level at different energies. The Fermi level is at $e/u = 1$ and $KT = u$. Whenever the system is at the Fermi level, the population n is equal to 1/2. The tail part in the exponential is very important for the conductivity of semi-conductors. If you can bring the Fermi level high enough, then part of the tail will go over to the conduction band. Thus, the electron will have an easier time making a

transition to the conduction band and the conductivity will increase. The conductivity can also be affect by factors such as temperature and purity. From the distribution, the temperature has a direct effect on how the energy states are populated. When temperature increases the tail of the exponential gets longer and wider, thus making the conduction band level population more accessible. For Semi-conductor materials, having an access to the conduction band level means it can conduct electricity with energy, which means the conductivity of the material is increased. The purity also affects the Fermi level. Purity defects with atoms that have excess electrons would bring the Fermi level up, and making it easier for electrons to jump into the conduction band.

References

1. Kittel, Charles. Introduction to Solid State Physics. Eighth edition. New Jersey: John wiley & Sons, Inc, 2005.
2. Griffiths, Davis. Introduction to Quantum Mechanics. Second edition. New Jersey: Pearson Education, Inc, 2005.
3. Band energies.jpg

Problems

1. Besides the Fermi Level, what other factor determines the population in different energy levels?

answer: Temperature

2. What is the difference between a semi-conductor and an insulator?

answer: A semi-conductor has a smaller band gap and therefore, while more difficulty than a conductor, is able to conduct electricity if you put in enough energy.

3. What does the Fermi level determines?

answer: The Fermi level determines several factors. It determines the population at different energy levels. It also determines how easily can the material conductor electricity. As your Fermi level approaches your conduction band energy, it will be easier for the electrons from the valence band to travel to the conduction band.

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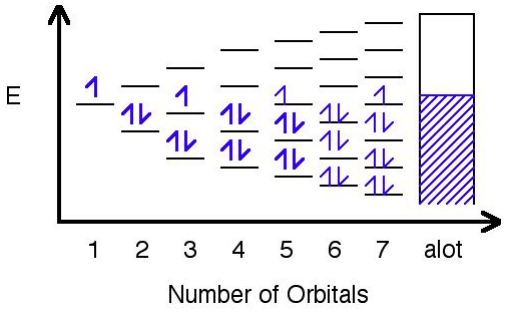
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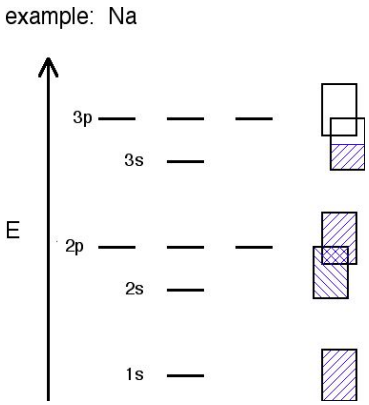
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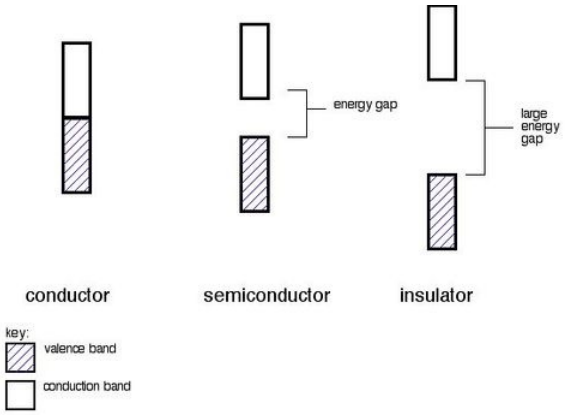


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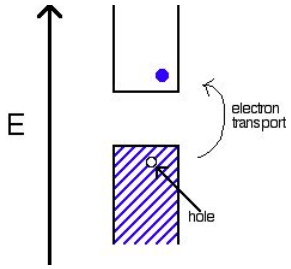
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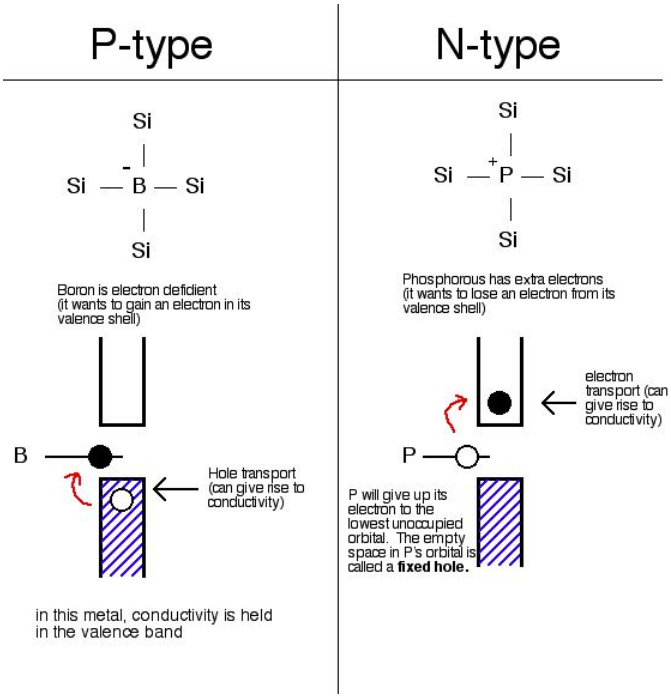
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? Exercise 6.8D.2

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Answer

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Exercise 6.8D.3

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Answer

Electron transport and hole transport

Exercise 6.8D.4

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Answer

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2. Moore, John T. Chemistry Made Simple. Random House Inc: New York. 2004.

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SECTION OVERVIEW

6.9: Semiconductors

Topic hierarchy

6.9A: Intrinsic Semiconductors

6.9B: Extrinsic (n-type and p-type) Semiconductors

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6.9A: Intrinsic Semiconductors

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6.9B: Extrinsic (n-type and p-type) Semiconductors

Extrinsic Semiconductors

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SECTION OVERVIEW

6.10: Size of Ions

Topic hierarchy

6.10A: Ionic Radii

6.10B: Periodic Trends in Ionic Radii

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6.10A: Ionic Radii

In a crystal lattice, the ionic radius is a measure of the size of the atom's ion.[6] When formed, ionic atoms change in size with respect to their orginal atom. Cation radii will decrease and the anion radii will increase in size compared to their neutral atoms. Questions such as: "What methodology is used by chemists to measure ionic radii?" and "Are there any non-experimental ways to estimate the size of ionic radii?" will be answered in this module. Accordingly, there are many ways to determine ionic radii.

1. Introduction
2. Hard-Sphere model
3. Periodic Trends
4. References
5. Outside Links
6. Problems
7. Answers

Introduction

In the past, after an atom is ionized, X-ray diffraction is used to measure how much the radius of the atom increased or decreased. However, scientists wanted to use another technique, due to the fact, that X-ray diffraction is difficult to distinguish a boundary between two ions. As a result, the *hard sphere model* can be used.

Hard-Sphere model

The Hard-Sphere model are impenetrable spheres that do not overlap in space.[5] The Hard-Sphere model has been tested by well-known scientists; Lande', Pauling and Goldsmidt. The ion radii measured under crystal state of ionic compound which cations and anions are stacking in pattern as shown below.

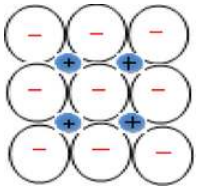


Figure 1: Schematic of the hard-sphere model

The Hard-Sphere model can be applied to metallic and ionic compounds such as NaCl, which is shown below.

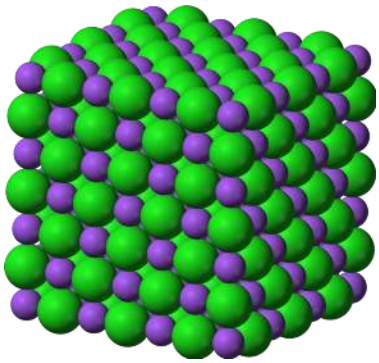


Figure 2: 3-D hard sphere model of Sodium Chloride, taken with permission from en.Wikipedia.org/wiki/File:So...e-3D-ionic.png

In general, scientists uses formula of Internuclear distance to test out the radii of ion then compared with the ion radii had done on X-ray diffraction:

$$\text{Internuclear distance (d)} = r_{cation} + r_{anion}\ ^{2}$$

*To calculate ion radii, Lande used ionic compound under solid state (ex: NaCl). This will minize the distribution of electrons.

1. Find the radii of anion (r^-) atom.
2. Find internuclear distance (d) between anion and cation.

3. Use Internuclear distance formula to find the r^+.

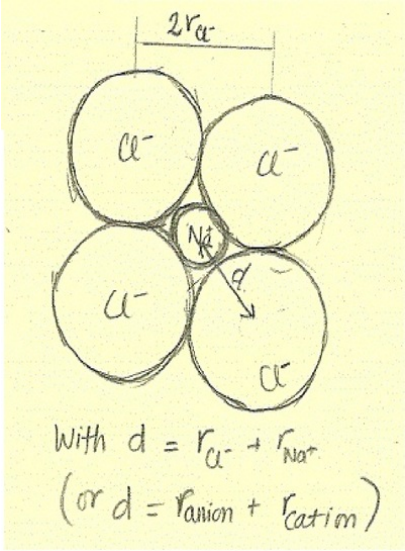


Figure 3: The Hard sphere model can roughly determine the ion radii.

Periodic Trends

As described earlier, cations are smaller in size compared to their neutral atoms while anions are larger in size.Cations are smaller than its neutral atoms because the positive nuclear charge, which holds the electrons in closer, exceeds the negative charge when a metal atom loses an electron. On the contrary, anions are larger because the electrons are not held as tightly, repulsions of electrons increase, and the electrons spread out more due to nonmetal atoms gaining an electron. Refer to the outside link to learn more about the periodic trends for ionic radii (http://abulafia.mt.ic.ac.uk/shannon/ptable.php).

References

1. Kotz, Treichel, Weaver,2006, *Chemistry and Chemical Reactivity*, Thomson Brooks/Cole, Mason, OH, p.358-364
2. Housecroft C., and Shappe A., 2008, *Inorganic Chemistry 3rd edition*, Pearson Education Limited, England, p.162-164
3. Barrera, M, and FZuloagat. "*Determination of the ionic radii by means of the Kohn-Sham potential: Identification of the chemical potential.*" International journal of quantum chemistry 106.9 (2006):2044-2053.
4. "*Ionic radii for Group 1 and Group 2 halide, hydride, fluoride, oxide, sulfide, selenide and telluride crystals*." Dalton transactions 39.33 (2010):7786-.
5. http://en.Wikipedia.org/wiki/Hard_spheres
6. http://en.Wikipedia.org/wiki/Ionic_radius

Outside Links

- http://abulafia.mt.ic.ac.uk/shannon/ptable.php

Problems

1. What is the most general formula that used to determine the ion radii for hard sphere model?
2. Find radius for Cacium ion in Calcium Chloride ($CaCl_2$). List out all the steps (numbers are not necessary)
3. Determine which is larger:

a) K^+ or Cs^+?

b) La^{3+} or Lu^{3+}?

c) Ca^{2+} or Zn^{2+}?

Answers

1. Internuclear distance (d) = $r_{cation} + r_{anion}$

2. Find the radii of anion (r^-) *atom; Find internuclear distance (d) between anion and cation; Use Internuclear distance formula to find the* r^+.

3. a.) Cs^+ b.) La^{3+} c.) Ca^{2+}

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6.10B: Periodic Trends in Ionic Radii

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SECTION OVERVIEW

6.11: Ionic Lattices

Topic hierarchy

6.11A: Structure - Rock Salt (NaCl)

6.11B: Structure - Caesium Chloride (CsCl)

6.11C: Structure - Fluorite (CaF_2)

6.11D: Structure - Antifluorite

6.11E: Structure - Zinc Blende (ZnS)

6.11F: Structure - β-Cristobalite (SiO_2)

6.11H: Structure - Rutile (TiO_2)

6.11I: Structure - Layers (\(CdI_2\) and \(CdCl_2\))

6.11J: Structure - Perovskite (\(CaTiO_3\))

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6.11A: Structure - Rock Salt (NaCl)

Rock salt also known as NaCl is an ionic compound. It occurs naturally as white cubic crystals. The structure of NaCl is formed by repeating the unit cell. It has an organized structure and has a 1:1 ratio of Na:Cl.

Introduction

Rock salt (NaCl) is an ionic compound that occurs naturally as white crystals. It is extracted from the mineral form halite or evaporation of seawater. The structure of NaCl is formed by repeating the face centered cubic unit cell. It has 1:1 stoichiometry ratio of Na:Cl with a molar mass of 58.4 g/mol. Compounds with the sodium chloride structure include alikali halides and metal oxides and transition-metal compounds. An important role to many important applications is structure and dynamics of water. Some applications include crystallization of proteins and conformational behavior of peptides and nucleic acids.

Structure

Figure $6.11A.1$ shows how the Na^+ and Cl^- ions occupy the space. The smaller ions are the Na^+ with has an atomic radius of 102 pm, and the larger ions are the Cl^- with an atomic radium of 181 pm. Since NaCl are one to one ratio as a compound, the coordination numbers of Na and Cl are equal. The larger green ions represent Cl^- and the smaller purple ions represent Na^+. However, the structure of this molecule allows their positions to be switched since the coordination numbers are equivalent.

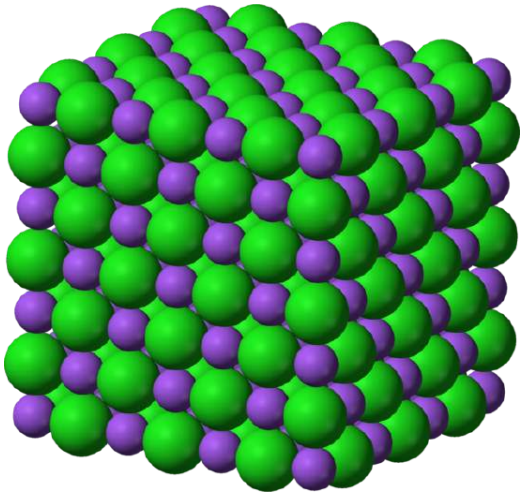


Figure $6.11A.1$: The crystal structure of sodium chloride, NaCl, a typical ionic compound. The smaller purple spheres represent sodium cations, $\mathrm{Na^+}$, and the larger green spheres represent chloride anions, $\mathrm{Cl^-}$. (Public Domain; Benjah-bmm27 via Wikipedia)

A Unit Cell

The unit cell of NaCl consists of $\mathrm{Na^+}$ ions and $\mathrm{Cl^-}$ ions. There are four types of site: unique central position, face site, edge sites and corner site, which are used to determine the number of Na^+ ions and Cl^- ions in the unit cell of NaCl. When counting the number of ions, a corner site would be shared by 7 other unit cells. Therefore, 1 corner would be 1/8 of an ion. A similar occurrence happens with the face site and the edge sites. For a face site, it is shared by 1 other unit cell and for an edge site, the ion is shared by 3 other unit cells. NaCl is a face centered cubic unit cell which has four cations and four anions. This can be shown by counting the number of ions and multiplying them in relation to their position.

- $\mathrm{Na^+}$:

$$1_{center} + 12_{edge} \times \frac{1}{4} = 4 \,\text{sodium ions total per cell}$$

- $\mathrm{Cl^-}$:

$$4_{face} \times \frac{1}{2} + 8_{corner} \times \frac{1}{8} = 4 \,\text{chloride ions total per cell}$$

Each ion in this lattice has six of the other kind of ion as its nearest neighbors, and twelve of the same kind of ions as its second nearest neighbors. There are many ionic compounds that assume this structure including all other halides of Na, Li, K and Rb. CsF, AgF, AgCl, BaO, CoO, and SrS are also among many that will form similar structures to NaCl.

Outside Links

- Video about structure of NaCl: http://www.youtube.com/watch?v=csfOBynrF8E
- Unit Cell. http://www.case.edu/artsci/chem/chim...ids/xtal1.html

References

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6.11B: Structure - Caesium Chloride (CsCl)

This page is going to discuss the structure of the molecule cesium chloride ($CsCl$), which is a white hydroscopic solid with a mass of 168.36 g/mol. Cesium Chloride is a type of unit cell that is commonly mistaken as Body-Centered Cubic. This misconception is easy to make, since there is a center atom in the unit cell, but CsCl is really a **non-closed packed structure** type.

Introduction

CsCl has a boiling point of 1303 degrees Celsius, a melting point of 646 degrees Celsius, and is very soluble in water. For the most part this molecule is stable, but is not compatible with strong oxidizing agents and strong acids. Although it is not hazardous, one should not prolong their exposure to CsCl. CsCl is an ionic compound that can be prepared by the reaction:

$$Cs_2CO_3 + 2\,HCl \longrightarrow 2\,CsCl + H_2O + CO_2 \tag{6.11B.1}$$

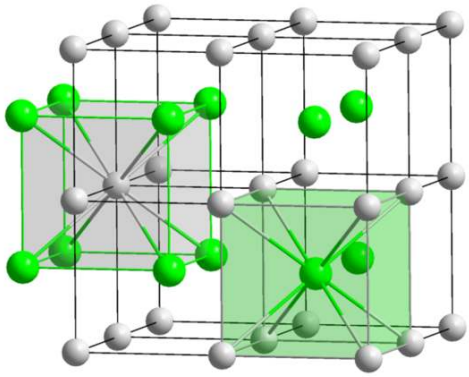


Figure $6.11B.1$: $CsCl$ Coordination Cubes. (Public Domain; Solid State via Wikipedia)

CsCl crystallize in a primitive cubic lattice which means the cubic unit cell has nodes only at its corners. The structure of CsCl can be seen as two interpenetrating cubes, one of Cs^+ and one of Cl^-. The ions are not touching one another. Touching would cause repulsion between the anion and cation. Some may mistake the structure type of CsCl with NaCl, but really the two are different. CsCl is more stable than NaCl, for it produces a more stable crystal and more energy is released.

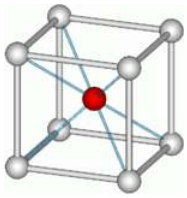


Figure $6.11B.2$: Unit Cell of CsCl (en.Wikipedia.org/wiki/Caesium_chloride

Anions and cations have similar sizes. Each Cs^+ is surrounded by 8 Cl^- at the corners of its cube and each Cl^- is also surrounded by 8 Cs^+ at the corners of its cube. The cations are located at the center of the anions cube and the anions are located at the center of the cations cube. There is one atom in CsCl. To determine this, the following equation is given:

8 Corners of a given atom x 1/8 of the given atom's unit cell = 1 atom

Applications

Cesium chloride is used in centrifugation, a process that uses the centrifugal force to separate mixtures based on their molecular density. It is also used in the preparation of electrically conducting glasses. Radioactive CsCl is used in some types of radiation therapy for cancer patients, although it is blamed for some deaths.

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6.11C: Structure - Fluorite (CaF_2)

Calcium Fluoride is a solid and forms a cube like structure that is centralized around the calcium molecules. The crystal lattice structure that Calcium Fluoride is also known as the fluorite structure (Figure $6.11C.1$) where the Ca^{2+} ions are eight-coordinate, being centered in a cube of eight F^- ions. Each F^- is coordinated to four Ca^{2+} in the shape of a tetrahedron.

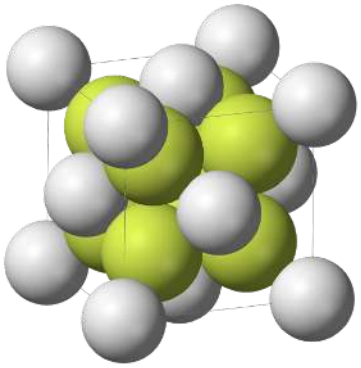


Figure $6.11C.1$: Fluorite unit cell. (Public Domain; Benjah-bmm27 via Wikipedia)

Calcium Fluoride is Quasilinear

When Calcium Fluoride is in a single molecule it forms a Quasilinear structure. Quasilinear means the molecule resonates between a linear shape and a bent shape.Calcium Fluoride is a polyatomic molecule that contains one calcium molecule and two fluoride molecules. Calcium Fluoride is a quasilinear molecule the bonds are created from the single electrons of calcium and the single electron from fluoride. CaF_2 has its electrons contained with in the 3d orbitals and are able to move between d_{yz} and d_z^2 squared. The molecule in linear when they are in the d_z^2 orbitals the molecule is also the most stable in this shape. When the electrons are in the d_{yz} orbitals the molecule becomes bent. The molecule resonates between these two shapes making it quasilinear. Figures two and three show how the d-orbitals cause the molecule to bend.

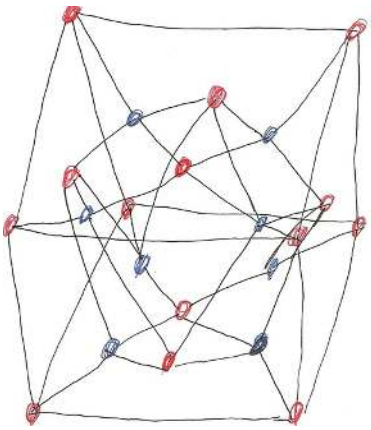


Fig # 1

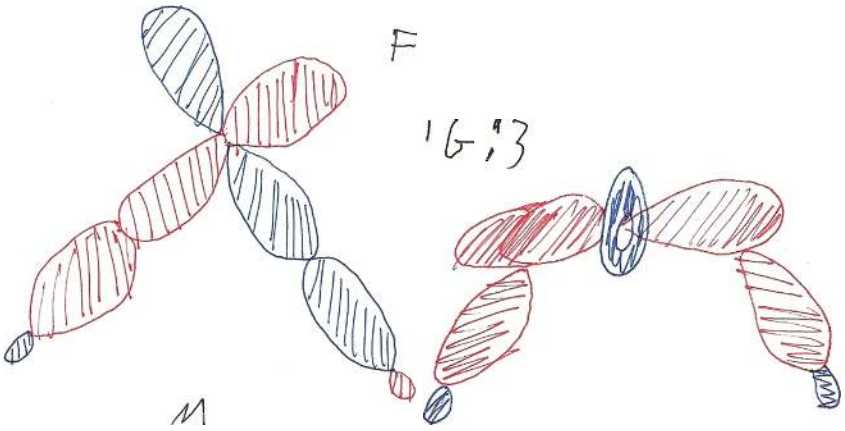


Fig # 2 Fig # 3

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6.11D: Structure - Antifluorite

Antifluorite is a mineral with a crystal structure identical with that of fluorite but with the positions of the cations and anions reversed (Figure 6.11*D*.1).

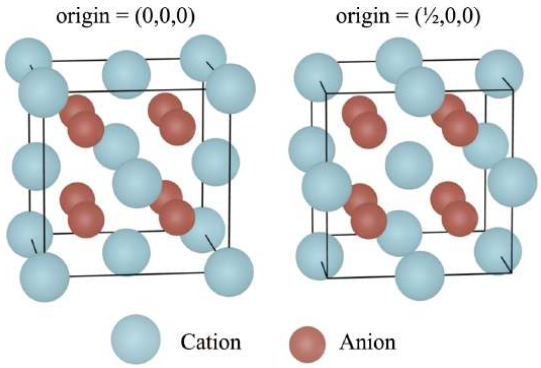


Figure 6.11*D*.1: Unit cell of the fluorite structure, from two equivalent perspectives. In the antifluorite structure, the blue positions are taken by the anion, the red positions by the cation. (CC BY-SA 4.0; Paburr via source)

The same crystal structure is found in numerous ionic compounds with formula AB2, such as ceria (CeO2), zirconia (cubic ZrO2), uranium dioxide (UO2). In the corresponding anti-structure, called the antifluorite structure, anions and cations are swapped, such as beryllium carbide (Be2C) or lithium oxide (Li2O), potassium sulfate (K2SO4).

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- en.Wikipedia.org/wiki/Anti-structure

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6.11E: Structure - Zinc Blende (ZnS)

ZnS has a unique structure type compared to other molecules, having different types of unique structures. ZnS can have a zinc blende structure which is a "diamond-type network" and at a different temperature, ZnS can become the wurtzite structure type which has a hexagonal type symmetry. Structure-wise, the zinc blende structure is more thermodynamically favored, however, because of the wurtzite structures slow construction, both forms of ZnS can be found.

Summary: Zinc blend is a compound that comes in two forms: sphalerite and wurtzite. These are characterized by a 1:1 stoichiometric ratio of Zinc to Sulfur. It maintains a tetrahedral arrangement in both forms.

Introduction

Zinc sulfide (ZnS) is a unique compound that forms two types of crystalline structures. These two polymorphs are wurtzite and zincblende (also known as sphalerite). Wurtzite has a hexagonal structure, while zincblende is cubic. It is characterized by single bonds between each atom and maintenance of a 1:1 zinc to sulfur ratio.

sphalerite:

Site	Zn	S
Central	4	0
Face	0	6(1/2) = 3
Corner	0	8(1/8) = 1
Total	4	4

Since the number of atoms in a single unit cell of Zn and S is the same, it is consistent with the formula ZnS.

The ionic radius for Zn^{2+} is 74pm and for S^{2-} is 190pm. Therefore the ratio between cationic and anionic radii in zinc blend is 0.39 (74pm/190 pm) .This suggests a tetrahedral ion arrangement and four nearest neighbors from standard crystal structure prediction tables. Therefore, four sulfur atoms surround each zinc atom and four zinc atoms surround each sulfur atom.$_2$ The coordination number, the number of of electron pairs donated to a metal by its ligands, for both zinc an sulfur is four.[1,2] The difference between wurtzite and zincblende lies in the different arrangements of layers of ions.[2]

Zincblende (Sphalerite)

Zincblende is characterized as a **cubic closet packing** (ccp), also known as face-centered cubic, structure.[1,4] This crystal lattice structure is shown in Figures 1 & 2 below.

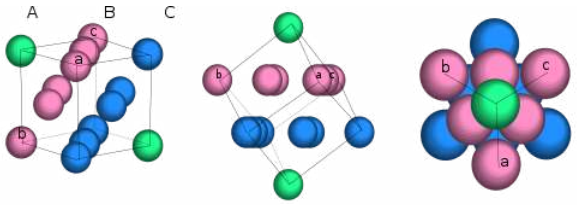


Fig. 1. A break down of cubic closest packing. (Author: Maghémite Date: May 5, 2008. Licensed under the Creative Commons Attribution-Share Alike 3.0 Unported, 2.5 Generic, 2.0 Generic and 1.0 Generic license.)

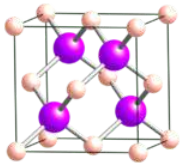


Fig. 2. A representation of ccp structure. (from Public Domain)

Notice how only half of the tetrahedral sites are occupied.

Thermal stability

Density tends to decrease as temperature increases. In this case, since ccp structures are more dense than hcp structures, so a conversion from sphalerite to wurtzite occurs naturally over time at a rate similar to that of diamond to graphite. The sphalerite structure is favored at 298k by 13kJ/mol, but at 1296K the transition to wurtzite occurs.[3]

Wurtzite

Wurtzite has a hexagonal closest packing structure (hcp), which is characterized by 12 ions in the corners of each unit that create a hexagonal prism (seen in Fig. 3).[2] As discussed previously, zincblende slowly transforms to wurtzite due to thermodynamic stability.

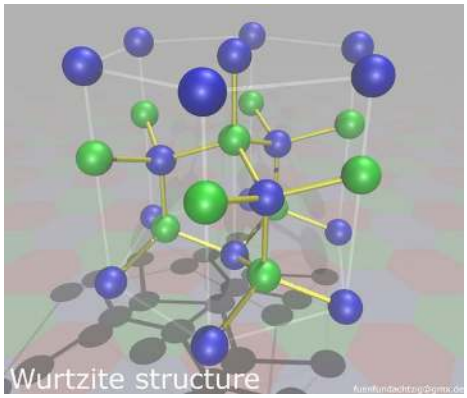


Fig 3. HCP structure of wurtzite. (Creator: Alexander Mann Date: 01/14/2006 Licensed under the Creative Commons Attribution-Share Alike 2.0 Germany license)

Calculating density of a crystal structure

Density = Mass of unit cell / volume of unit cell.

where:

Mass of unit cell = Number of atoms in a unit cell x the mass of each atom

volume of unit cell = $a^3 \times 10^{-30}$

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6.11F: Structure - β-Cristobalite (SiO_2)

Silicon dioxide, SiO_2, also known as silica is a linear molecule that is formed by one silicon atom and two oxygen atoms with two sets of doubles bonds and 4 single bonds. Because of its main component: glass, silicon dioxide is a very common and important molecule in the construction industry. One of the forms of silicon dioxide is quartz, which is found in sand.

The Structure of Silica

SiO_2 is a 3 dimensional structure and comes from the tetrahedral structure, SiO_4. Each of the Silicon atoms are connected to each other with an oxygen atom, which creates a "diamond type network". All forms of SiO_2 possess a 3 dimensional shape and has a diamond structure. The bonding angle of Si-O-Si, which is the building block of the SiO_2 molecule, is 144 degrees. These are called polymorph and in order to be stable, 3 of these polymorph are suppose to exist. This stable unit creates a a temperature for each of the different forms of SiO_2. Forms that have (alpha) are at low temperature, while forms with (beta) are at high temperature. The structure of the different forms of SiO_2 is important because it gives each of the different forms of SiO_2 different characteristics and functions. Commercially, SiO_2 is very important in steel, electronic, and semiconductor industries because of its structure, SiO_2 is able to undergo rapid temperature changes and still maintain its shape and structure.

Different Forms of Silica **and Their Uses**

There are many different forms of SiO_2, which mainly derived quartz glass. One form that is derived from quartz is beta-cristobalite, which is found in high temperature. Some other forms are beta-quartz, alpha-quartz, beta-tridymite, alpha-tridymite, alpha=cristobalite, and many more. The alpha and beta stands for the temperature range. Alpha molecules have low temperature while beta molecules have high temperature.

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2. Pacific Rim Conference on Ceramic and Glass Technology. 2006. Advances in Glass and Optical Materials II. American Ceramic Society. Westerville, Ohio.
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6.11H: Structure - Rutile (TiO_2)

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6.11I: Structure - Layers (\(CdI_2\) and \(CdCl_2\))

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2. Heading #1
3. Heading #2
4. References
5. Outside Links
6. Problems
7. Contributors and Attributions

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6.11J: Structure - Perovskite ($CaTiO_3$)

Figure 2: Superconducting Sr_2RuO_4 (wikis.lib.ncsu.edu/index.php/Perovskite)

Some other unique properties that sets perovskites apart and makes them ideal for technological applications include: it is the only crystal structure that is ferroelectric (spontaneous alignment of the electric dipoles caused by interactions between them) not because of an external magnetic field but due to its crystal structure, its ferro-, pyro-, and piezo-electric properties, and structural properties such as durability and chemical flexibility.

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- Matthew Ibbotson: Undergraduate in Chemical Engineering, Senior

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SECTION OVERVIEW

6.12: Crystal Structure of Semiconductors

Topic hierarchy

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SECTION OVERVIEW

6.13: Lattice Energy - Estimates from an Electrostatic Model

Topic hierarchy

6.13A: Coulombic Attraction Within an Isolated Ion-Pair

6.13B: Coulombic Interactions in an Ionic Lattice

6.13C: Born Forces

6.13D: The Born-Landé Equation

6.13E: Madelung Constants

6.13F: Refinements to the Born-Lande Equation

6.13G: Overview

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6.13A: Coulombic Attraction Within an Isolated Ion-Pair

Coulombic Forces

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6.13B: Coulombic Interactions in an Ionic Lattice

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6.13C: Born Forces

Born forces are one type of force that acts upon atoms in an ionic lattice. In simplest terms, because ions have some finite size, electron-electron and nucleus-nucleus interactions occur and give rise to repulsion forces and electrostatic potential, both called Born forces.

Introduction

Lattice energy is the energy released when gaseous cations and anions bond to form a solid ionic compound. With the Born-Lande equation one can calculate the lattice energy of a crystalline ionic compound. Born and Lande theorized around the turn of the century, that lattice energy of a crystalline ionic compound could be found by calculating terms of electrostatic potential and a repulsive potential.

$$\Delta U = \frac{-LA|Z_+||Z_-|e^2}{4\pi\epsilon_o r} \tag{1}$$

with

- L is the avagadro's constant (6.022 \times 10^{23}\) and
- 'A is the Madelung Constant

The first potential is the force of attraction. It is a negative value because it pulls the two atoms closer together, and the forming of a bond is energetically favorable. The negative value of Avogadro's number (6.022×10^{23}) times a Madelung Constant (varies) times the absolute value of the charge of the cation times the absolute value of the charge of the anion, times the charge of an electron (1.6022×10^{-19} C) all over four times pi times the emissivity of space times the ion radius.

$$\Delta U = \frac{-LB}{r^n} \tag{2}$$

with

- B is the repulsion coefficient and
- 'N is the Born exponent

The second equation is the repulsive force. It found by multiplying Avogadro's number (6.022×10^{23}) by a repulsion coefficient, and dividing that by the ionic radius raised to the power of a Born exponent (some number between 5 and 12).

Implications of Born Forces

Attractive forces are affected by the charge of the ions and their radii. Ions with large charges (like Mg^{7+} or O^{2-}) have greater attractive potential than those with smaller charges (like Na^{1+} or F^{1-}). Smaller ions (like Li^+ or Cl^-) also have greater electrostatic potential than larger ions (like I^- or Cs^+). The Madelung constant is dependent on the crystal structure type. This value is found in tables online or in a text, but in general can be thought of as large with larger cation-cation distances and anion-anion distances. A structure with fluorite geometry has a relatively large A value, whereas rock salt crystals have a much lower A value.

Repulsive forces are mainly determined by the born exponent. The Born exponent is dictated by the electronic configuration of the noble gas in the row above it on the periodic table (a closed shell).

Max Born

Max Born was a German physicist and mathematician who was instrumental in the development of quantum mechanics. He also made contributions to solid-state physics and optics and supervised the work of a number of notable physicists in the 1920s and 30s.



Figure: Max Born (1882–1970)

Born won the 1954 Nobel Prize in Physics for his "fundamental research in Quantum Mechanics, especially in the statistical interpretation of the wave function".

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Problems

Plug in and cancel SI units to the Born-Lande equation to find the units of lattice energy, electrostatic potential, and repulsion forces. All energies are in units of kJ/mol

1. Looking at the equations for Born forces and a periodic table what do you expect to have a higher lattice energy (most negative enthalpy): NaCl, LiF, or KCl?
2. Looking at the equations for Born forces and a periodic table what do you expect to have a higher lattice energy (most negative enthalpy): NaOH, Al_2O_3, or $Mg(OH)_2$?
3. What lattice structure type Rutile or CsCl has the greater relative Madelung constant? (You need not look in a table if you know the shapes of these crystal geometries)
4. What are the oxidation states of Barium and Oxygen in the crystalline lattice BaO?
5. Calculate the lattice energy of Sodium Chloride using the Born-Lande equation (find all needed information from tables). Compare this calculated value to experimentally found value of -787kJ/mol.

Solutions

1. LiF
2. Al_2O_3
3. Rutile
4. Ba^{2+} and O^{2-}
5. The calculated value is -756kJ/mol.

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6.13D: The Born-Landé Equation

The Born-Landé equation is a concept originally formulated in 1918 by the scientists Born and Landé and is used to calculate the lattice energy (measure of the strength of bonds) of a compound. This expression takes into account both the Born interactions as well as the Coulomb attractions.

Introduction

Due to its high simplicity and ease, the Born-Landé equation is commonly used by chemists when solving for lattice energy. This equation proposed by Max Born and Alfred Landé states that lattice energy can be derived from ionic lattice based on electrostatic potential and the potential energy due to repulsion. To solve for the Born-Landé equation, you must have a basic understanding of lattice energy:

- Lattice energy decreases as you go down a group (as atomic radii goes up, lattice energy goes down).
- Going across the periodic table, atomic radii decreases, therefore lattice energy increases.

The Born-Landé equation was derived from these two following equations. the first is the electrostatic potential energy:

$$\Delta U = -\frac{N_A M \left|Z^+\right| \left|Z^-\right| e^2}{4\pi\epsilon_o r} \tag{6.13D.1}$$

with

- M_A is Avogadro's constant (6.022×10^{23})
- M is the Madelung Constant (a constant that varies for different structures)
- e is the charge of an electron (1.6022×10^{-19} C)
- Z^+ is the cation charge
- Z^- is the anion charge
- ϵ_o is the permittivity of free space

The second equation is the repulsive interaction:

$$\Delta U = \frac{N_A B}{r^n} \tag{6.13D.2}$$

with

- B is the repulsion coefficient and
- n is the Born Exponent (typically ranges between 5-12) that is used to measure how much a solid compresses

These equations combine to form:

$$\Delta U(0K) = \frac{N_A M \left|Z^+\right| \left|Z^-\right| e^2}{4\pi\epsilon_o r_o}\left(1 - \frac{1}{n}\right) \tag{6.13D.3}$$

with

- r_0 is the closest ion distance

Calculate Lattice Energy

Lattice energy, based on the equation from above, is dependent on multiple factors. We see that the charge of ions is proportional to the increase in lattice energy. In addition, as ions come into closer contact, lattice energy also increases.

Example $6.13D.1$

Which compound has the greatest lattice energy?

- AlF_3
- NACl
- LiF

- $CaCl_2$

Solution

This question requires basic knowledge of lattice energy. Since F_3 gives the compound a +3 positive charge and the Al gives the compound a -1 negative charge, the compound has large electrostatic attraction. The bigger the electrostatic attraction, the greater the lattice energy.

Example $6.13D.2$

What is the lattice energy of NaCl? (Hint: you must look up the values for the constants for this compound)

Solution

-756 kJ/mol (again, this value is found in a table of constants)

Example $6.13D.3$

Calculate the lattice energy of NaCl.

Solution

$$Lattice\ Energy\ of\ NaCl = -\frac{\frac{6.022\ x\ 10^{23}}{mole}(1.6022^{-19})\times 1.747}{4\pi \times 8.85\ x\ 10^{-12}\frac{c^2}{m}\times 282\ x\ 10^{-12} m}\left(1-\frac{1}{9}\right) \approx -756\ \frac{kJ}{mol}$$

References

1. Johnson, D. A. *Metals and Chemical Change*. Cambridge: Royal Society of Chemistry, 2002.
2. Cotton, F. Albert, and F. Albert Cotton. *Advanced Inorganic Chemistry.* New York: Wiley, 1999.

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6.13E: Madelung Constants

There are many factors to be considered such as covalent character and electron-electron interactions in ionic solids. But for simplicity, let us consider the ionic solids as a collection of positive and negative ions. In this simple view, appropriate number of cations and anions come together to form a solid. The positive ions experience both attraction and repulsion from ions of opposite charge and ions of the same charge. The Madelung constant is a property of the crystal structure and depends on the lattice parameters, anion-cation distances, and molecular volume of the crystal.

1D Crystal

Before considering a three-dimensional crystal lattice, we shall discuss the calculation of the energetics of a linear chain of ions of alternate signs (Figure 6.13E.1).

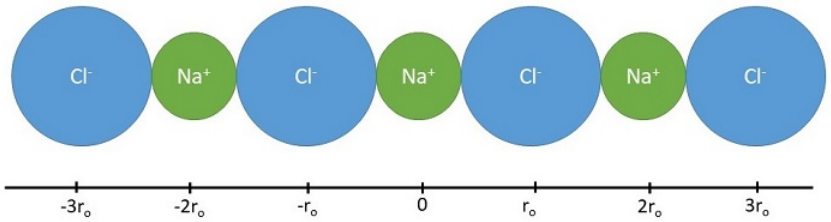


Figure 6.13E.1: A hypothetical one-dimensional NaCl lattice.

Let us select the positive sodium ion in the middle (at $x = 0$) as a reference and let r_0 be the shortest distance between adjacent ions (the sum of ionic radii). The Coulomb energy of the other ions in this 1D lattice on this sodium atom can be decomposed by proximity (or "shells").

- **Nearest Neighbors (first shell):** This reference sodium ion has two negative chloride ions as its neighbors on either side at $\pm r_0$ so the Coulombic energy of these interactions is

$$\underbrace{\frac{-e^2}{4\pi\epsilon_o r_o}}_{\text{left chloride ion}} + \underbrace{\frac{-e^2}{4\pi\epsilon_o r_o}}_{\text{right chloride ion}} = -\frac{2e^2}{4\pi\epsilon_o r_o} \tag{6.13E.1}$$

- **Next Nearest Neighbors (second shell)**: Similarly the repulsive energy due to the next two positive sodium ions at a distance of $2r_0$ is

$$\underbrace{\frac{+e^2}{4\pi\epsilon_o (2r_o)}}_{\text{left sodium ion}} + \underbrace{\frac{+e^2}{4\pi\epsilon_o (2r_o)}}_{\text{right sodium ion}} = +\frac{2e^2}{4\pi\epsilon_o (2r_o)} \tag{6.13E.2}$$

- **Next Next Nearest Neighbors (third shell)**: The attractive Coulomb energy due to the next two chloride ions neighbors at a distance $3r_0$ is

$$\underbrace{\frac{-e^2}{4\pi\epsilon_o (3r_o)}}_{\text{left chloride ion}} + \underbrace{\frac{-e^2}{4\pi\epsilon_o (3r_o)}}_{\text{right chloride ion}} = -\frac{2e^2}{4\pi\epsilon_o (3r_o)} \tag{6.13E.3}$$

and so on. Thus the total energy due to all the ions in the linear array is

$$E = -\frac{2e^2}{4\pi\epsilon_o r_o} + \frac{2e^2}{4\pi\epsilon_o (2r_o)} - \frac{2e^2}{4\pi\epsilon_o (3r_o)} - \ldots \tag{6.13E.4}$$

or

$$E = \frac{e^2}{4\pi\epsilon_o r_o}\left[2\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \ldots\right)\right] \tag{6.13E.5}$$

We can use the following Maclaurin expansion

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^3}{4} + \cdots \tag{6.13E.6}$$

to simplify the sum in the parenthesis of Equation 6.13E.5 as $\ln(1+1)$ to obtain

$$E = \frac{e^2}{4\pi\epsilon_o r_o}[2\ln 2] \tag{6.13E.7}$$

$$= \frac{e^2}{4\pi\epsilon_o} M \tag{6.13E.8}$$

The first factor of Equation 6.13E.7 is the Coulomb energy for a single pair of sodium and chloride ions, while the $2\ln 2$ factor is the *Madelung constant* ($M \approx 1.38$) per molecule. The Madelung constant is named after Erwin Medelung and is a geometrical factor that depends on the arrangement of ions in the solid. If the lattice were different (when considering 2D or 3D crystals), then this constant would naturally differ.

3D Crystal

In three dimensions the series does present greater difficulty and it is not possible to sum the series conveniently as in the case of one-dimensional lattice. As an example, let us consider the the $NaCl$ crystal. In the following discussion, assume r be the distance between Na^+ and Cl^- ions. The nearest neighbors of Na^+ are six Cl^- ions at a distance 1*r*, 12 Na^+ ions at a distance 2*r*, eight Cl^- ions at 3*r*, six Na^+ ions at 4*r*, 24 Na^+ ions at 5*r*, and so on. Thus, the electrostatic potential of a single ion in a crystal by approximating the ions by point charges of the surrounding ions:

$$E_{ion-lattice} = \frac{Z^2 e^2}{4\pi\epsilon_o r} M \tag{6.13E.9}$$

For NaCl is a poorly converging series of interaction energies:

$$M = \frac{6}{1} - \frac{12}{2} + \frac{8}{3} - \frac{6}{4} + \frac{24}{5} \ldots \tag{6.13E.10}$$

with

- Z is the number of charges of the ions, (e.g., 1 for NaCl),
- e is the charge of an electron ($1.6022 \times 10^{-19}\ C$),
- $4\pi\epsilon_o$ is 1.11265x10^{-10} C^2/(J m).

The Madelung constant depends on the structure type and Equation 6.13E.10 is applicable only for the sodium chloride (ei.g, rock salt) lattice geometry. Other values for other structural types are given in Table $6.13E.2$. A is the number of anions coordinated to cation and C is the numbers of cations coordinated to anion.

Table $6.13E.2$: Madelung Constants

Compound	*Crystal Lattice*	*M*	*A : C*	*Type*
NaCl	NaCl	1.74756	6 : 6	Rock salt
CsCl	CsCl	1.76267	6 : 6	CsCl type
CaF_2	Cubic	2.51939	8 : 4	Fluorite
$CdCl_2$	Hexagonal	2.244		
MgF_2	Tetragonal	2.381		
ZnS (wurtzite)	Hexagonal	1.64132		
TiO_2 (rutile)	Tetragonal	2.408	6 : 3	Rutile
$bSiO_2$	Hexagonal	2.2197		
Al_2O_3	Rhombohedral	4.1719	6 : 4	Corundum

A is the number of anions coordinated to cation and *C* is the numbers of cations coordinated to anion.

There are other factors to consider for the evaluation of lattice energy and the treatment by Max Born and Alfred Lande led to the formula for the evaluation of lattice energy for a mole of **crystalline solid**. The Born–Landé equation (Equation 6.13E.11) is a means of calculating the lattice energy of a crystalline ionic compound and derived from the electrostatic potential of the ionic lattice and a repulsive potential energy term

$$U = \frac{N_A M Z^2 e^2}{4\pi\epsilon_o r}\left(1 - \frac{1}{n}\right) \tag{6.13E.11}$$

where

- N_A is Avogadro constant;
- M is the Madelung constant for the lattice
- z^+ is the charge number of cation
- z^- is the charge number of anion
- e is elementary charge, 1.6022×10^{-19} C
- ε_0 is the permittivity of free space
- r_0 is the distance to closest ion
- n is the **Born exponent** that is typically between 5 and 12 and is determined experimentally. n is a number related to the electronic configurations of the ions involved (Table $6.13E.3$).

Table $6.13E.1$: n values for select solids

Atom/Molecule	*n*
He	5
Ne	7
Ar	9
Kr	10
Xe	12
LiF	5.9
LiCl	8.0
LiBr	8.7
NaCl	9.1
NaBr	9.5

Example $6.13E.1$: NaCl

Estimate the lattice energy for NaCl.

Solution

Using the values giving in the discussion above, the estimation is given by

$$U_{NaCl} = \frac{(6.022 \times 10^{23}/mol)(1.74756)(1.6022 \times 10^{-19})^2(1.747558)}{4\pi\,(8.854 \times 10^{-12} C^2/m)(282 \times 10^{-12}\ m)}\left(1 - \frac{1}{9.1}\right)$$
$$= -756\,kJ/mol$$

Much more should be considered in order to evaluate the lattice energy accurately, but the above calculation leads you to a good start. When methods to evaluate the energy of crystallization or lattice energy lead to reliable values, these values can be used in the Born-Hable cycle to evaluate other chemical properties, for example the electron affinity, which is really difficult to determine directly by experiment.

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6.13F: Refinements to the Born-Lande Equation

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6.13G: Overview

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6.14: Lattice Energy - The Born-Haber Cycle

Ionic solids tend to be very stable compounds. The enthalpies of formation of the ionic molecules cannot alone account for this stability. These compounds have an additional stability due to the lattice energy of the solid structure. However, lattice energy cannot be directly measured. The Born-Haber cycle allows us to understand and determine the lattice energies of ionic solids.

Introduction

This module will introduce the idea of lattice energy, as well as one process that allows us to calculate it: the Born-Haber Cycle. In order to use the Born-Haber Cycle, there are several concepts that we must understand first.

Lattice Energy

Lattice Energy is a type of potential energy that may be defined in two ways. In one definition, the lattice energy is the energy required to break apart an ionic solid and convert its component atoms into gaseous ions. This definition causes the value for the lattice energy to always be positive, since this will always be an endothermic reaction. The other definition says that lattice energy is the reverse process, meaning it is the energy released when gaseous ions bind to form an ionic solid. As implied in the definition, this process will always be exothermic, and thus the value for lattice energy will be negative. Its values are usually expressed with the units kJ/mol.

Lattice Energy is used to explain the stability of ionic solids. Some might expect such an ordered structure to be less stable because the entropy of the system would be low. However, the crystalline structure allows each ion to interact with multiple oppositely charge ions, which causes a highly favorable change in the enthalpy of the system. A lot of energy is released as the oppositely charged ions interact. It is this that causes ionic solids to have such high melting and boiling points. Some require such high temperatures that they decompose before they can reach a melting and/or boiling point.

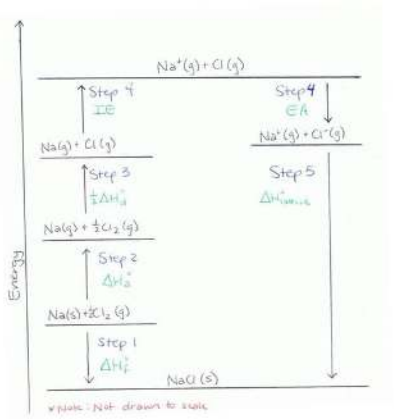
Born-Haber Cycle

There are several important concept to understand before the Born-Haber Cycle can be applied to determine the lattice energy of an ionic solid; ionization energy, electron affinity, dissociation energy, sublimation energy, heat of formation, and Hess's Law.

- **Ionization Energy** is the energy required to remove an electron from a neutral atom or an ion. This process always requires an input of energy, and thus will always have a positive value. In general, ionization energy increases across the periodic table from left to right, and decreases from top to bottom. There are some excepts, usually due to the stability of half-filled and completely filled orbitals.
- **Electron Affinity** is the energy released when an electron is added to a neutral atom or an ion. Usually, energy released would have a negative value, but due to the definition of electron affinity, it is written as a positive value in most tables. Therefore, when used in calculating the lattice energy, we must remember to subtract the electron affinity, not add it. In general, electron affinity increases from left to right across the periodic table and decreases from top to bottom.
- **Dissociation energy** is the energy required to break apart a compound. The dissociation of a compound is always an endothermic process, meaning it will always require an input of energy. Therefore, the change in energy is always positive. The magnitude of the dissociation energy depends on the electronegativity of the atoms involved.
- Sublimation energy is the energy required to cause a change of phase from solid to gas, bypassing the liquid phase. This is an input of energy, and thus has a positive value. It may also be referred to as the energy of atomization.
- **The heat of formation** is the change in energy when forming a compound from its elements. This may be positive or negative, depending on the atoms involved and how they interact.
- **Hess's Law** states that the overall change in energy of a process can be determined by breaking the process down into steps, then adding the changes in energy of each step. The Born-Haber Cycle is essentially Hess's Law applied to an ionic solid.

Using the Born-Haber Cycle

The values used in the Born-Haber Cycle are all predetermined changes in enthalpy for the processes described in the section above. Hess' Law allows us to add or subtract these values, which allows us to determine the lattice energy.



Step 1

Determine the energy of the metal and nonmetal in their elemental forms. (Elements in their natural state have an energy level of zero.) Subtract from this the heat of formation of the ionic solid that would be formed from combining these elements in the appropriate ration. This is the energy of the ionic solid, and will be used at the end of the process to determine the lattice energy.

Step 2

The Born-Haber Cycle requires that the elements involved in the reaction are in their gaseous forms. Add the changes in enthalpy to turn one of the elements into its gaseous state, and then do the same for the other element.

Step 3

Metals exist in nature as single atoms and thus no dissociation energy needs to be added for this element. However, many nonmetals will exist as polyatomic species. For example, Cl exists as Cl_2 in its elemental state. The energy required to change Cl_2 into 2Cl atoms must be added to the value obtained in Step 2.

Step 4

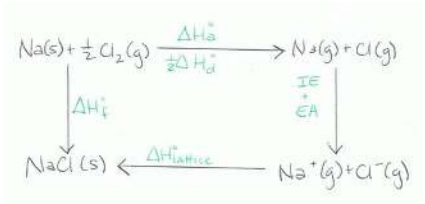
Both the metal and nonmetal now need to be changed into their ionic forms, as they would exist in the ionic solid. To do this, the ionization energy of the metal will be added to the value from Step 3. Next, the electron affinity of the nonmetal will be subtracted from the previous value. It is subtracted because it is a release of energy associated with the addition of an electron.

*This is a common error due to confusion caused by the definition of electron affinity, so be careful when doing this calculation.

Step 5

Now the metal and nonmetal will be combined to form the ionic solid. This will cause a release of energy, which is called the lattice energy. The value for the lattice energy is the difference between the value from Step 1 and the value from Step 4.

The diagram below is another representation of the Born-Haber Cycle.



Equation

The Born-Haber Cycle can be reduced to a single equation:

Heat of formation= Heat of atomization+ Dissociation energy+ (sum of Ionization energies)+ (sum of Electron affinities)+ Lattice energy

*Note: In this general equation, the electron affinity is added. However, when plugging in a value, determine whether energy is released (exothermic reaction) or absorbed (endothermic reaction) for each electron affinity. If energy is released, put a negative sign in front of the value; if energy is absorbed, the value should be positive.

Rearrangement to solve for lattice energy gives the equation:

Lattice energy= Heat of formation- Heat of atomization- Dissociation energy- (sum of Ionization energies)- (sum of Electron Affinities)

References

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3. Ladd, Mark. Crystal Structures: Lattices and Solids in Stereoview. Chichester: Horwood, 1999.
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Problems

1. Define lattice energy, ionization energy, and electron affinity.
2. What is Hess' Law?
3. Find the lattice energy of KF(s).
   Note: Values can be found in standard tables.
4. Find the lattice energy of $MgCl_2$(s).
5. Which one of the following has the greatest lattice energy?
   a. A) MgO
   b. B) NaC
   c. C) LiCl
   d. D) $MgCl_2$
6. Which one of the following has the greatest Lattice Energy?
   a. NaCl
   b. $CaCl_2$
   c. $AlCl_3$
   d. KCl

Solutions

1. Lattice energy: The difference in energy between the expected experimental value for the energy of the ionic solid and the actual value observed. More specifically, this is the energy gap between the energy of the separate gaseous ions and the energy of the ionic solid.
   Ionization energy: The energy change associated with the removal of an electron from a neutral atom or ion.
   Electron affinity: The release of energy associated with the addition of an electron to a neutral atom or ion.
2. Hess' Law states that the overall energy of a reaction may be determined by breaking down the process into several steps, then adding together the changes in energy of each step.
3. Lattice Energy= [-436.68-89-(0.5*158)-418.8-(-328)] kJ/mol= **-695.48 kJ/mol**
4. Lattice Energy= [-641.8-146-243-(737.7+1450.6)-(2*-349)] kJ/mol= **-2521.1 kJ/mol**
5. MgO. It has ions with the largest charge.
6. $AlCl_3$. According to the periodic trends, as the radius of the ion increases, lattice energy decreases.

References

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6.15: Lattice Energy - Calculated vs. Experimental Values

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SECTION OVERVIEW

6.16: Application of Lattice Energies

Topic hierarchy

6.16A: Estimation of Electron Affinities

6.16B: Fluoride Affinities

6.16C: Estimation of Standard Enthalpies of Formation and Disproportionation

6.16D: The Kapustinskii Equation

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6.16A: Estimation of Electron Affinities

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6.16B: Fluoride Affinities

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6.16C: Estimation of Standard Enthalpies of Formation and Disproportionation

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6.16D: The Kapustinskii Equation

9.05: Kapustinskii equation

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SECTION OVERVIEW

6.17: Defects in Solid State Lattices

Topic hierarchy

6.17.E: Defects in Solid State Lattices (Exercises)

6.17A: Schottky Defect

6.17B: Frenkel Defect

6.17C: Experimental Observations of Schottky and Frenkel Defects

6.17D: Non-Stoichiometric Compounds

6.17E: Color Centers (F-Centers)

6.17F: Thermodynamic Effects of Crystal Defects

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6.17.E: Defects in Solid State Lattices (Exercises)

Crystal Defects and Solids

Problems

All diagrams must be hand drawn, no photocopies or computer images will be accepted.

1. Nonstoichiometric compounds
2. Stoichiometric titanium (II) oxide and magnesium oxides have densities of 4.93 and 3.58 g cm^{-3} respectively. X-ray diffraction studies have shown that both have the NaCl structure, with unit cell edges of 416.2 and 421.2 pm respectively. Assume that the presence of vacancies does not affect the cell edge lengths. Estimate the percentage of vacancies in these solids.
3. Explain the Pilling-Bedworth principle regarding the protective behaviour of oxide films of metal (Swaddle: p103-104). From the following densities (d), evaluate the molar volumes (V^o = molar mass/d) of the metals and of the oxides. Suggest which oxides forms protective layers?

Metal	d(metal)	Oxide	d(oxide)	V^o(metal)	V^o(oxide)	Protective?
Be	1.85	BeO	3.01			
Ca	1.54	CaO	3.25-3.38			
Al	2.70	Al_2O_3	3.97			
Fe	7.86	FeO	5.7			
		Fe_2O_3	5.24			
		Fe_3O_4	5.18			
Ti	4.50	TiO_2	4.26			

FeO, wuestite; Fe_2O_3, hematite; Fe_3O_4, magnetite;
TiO_2, rutile.

What advantages and disadvantages do Al and Ti have in their application as material for tableware? This is an open ended question, and give a common-sense type discussion.

4. y = 1.6 nm after 1 day
   y = 3.5 nm after 1 year Estimate *c* and *k*. What are the thickness of the oxide layer at *t* = 5, 10, and 20 years?

   What effect does moisture have on the oxidation of iron?

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6.17A: Schottky Defect

Lattice structures are not perfect; in fact most of the time they experience defects. Lattice structures (or crystals) are prone to defects especially when their temperature is greater than 0 K [1]. One of these defects is known as the Schottky defect, which occurs when oppositely charged ions vacant their sites [1].

Introduction

Like the human body, lattice structures (most commonly known as crystals) are far from perfection. Our body works hard to keep things proportional but occasionally our right foot is bigger than our left; similarly, crystals may try to arrange it's ions under a strict layout, but occasionally an ion slips to another spot or simply goes missing. Realistically speaking, it should be expected that crystals will depart itself from order (not surprising considering defects occurs at temperature greater than 0 K). There are many ways a crystal can depart itself from order (thus experiences defects); these defects can be grouped in different categories such as Point Defects, Line Defects, Planar Defects, or Volume or Bulk Defects [2]. We will focus on Point Defects, specifically the defect that occurs in ionic crystal structures (i.e. NaCl) called the Schottky Defect.

Point Defects

Lattice structures (or crystals) undergoing point defects experience one of two types:

1. atoms or ions leaving their spot (thus creating vacancies).
2. atoms or ions slipping into the little gaps in between other atoms or ions; those little gaps are known as interstitials--since atoms or ions in the crystals are occupying interstitials, they inherently become (create) interstitials.

By the simplest definition, the Schottky defect is defined by type one, while type two defects are known as the Frenkel defect. The Schottky defect is often visually demonstrated using the following layout of anions and cations:

+	-	+	-	+	-	+	-	+	-	+
-	+	-	+	-	+	-	+	(vacant)	+	-
+	-	+	-	+	-	+	-	+	-	+
-	+	-	(vacant)	-	+	-	+	-	+	-
+	-	+	-	+	-	+	-	+	-	+
-	+	-	+	-	+	-	+	-	+	-

Figure 6.17A.1*: The positive symbols represents cations (i.e. Na^+) and the negative symbol represents anions (i.e. Cl^-).*

In addition, this layout is applicable only for ionic crystal compounds of the formula MX--layout for ionic crystals with formula MX_2 and M_2X_3 will be discussed later--where M is metal and X is nonmetal. Notice the figure has exactly one cation and one anion vacating their sites; that is what defines a (one) Schottky Defect for a crystal of MX formula--for every cation that vacant its site, the same number of anion will follow suit; essentially the vacant sites come in pairs. This also means the crystal will neither be too positive or too negative because the crystal will always be in equilibrium in respect to the number of anions and cations.

It is possible to approximate the number of Schottky defects (n_s) in a MX ionic crystal compound by using the equation:

$$N = \exp^{-\frac{\Delta H}{2RT}} \tag{6.17A.1}$$

where

- ΔH is the enthalpy of defect formation,
- R is the gas constant,
- T is the absolute temperature (in K), and

N can be calculated by:

$$N = \frac{\text{density of the ionic crystal compound} \times N_A}{\text{molar mass of the ionic crystal compound}} \tag{6.17A.2}$$

From Equation 6.17A.1, it is also possible to calculate the fraction of vacant sites by using the equation:

$$\frac{n_s}{N} = \exp^{-\frac{\Delta H}{2RT}} \tag{6.17A.3}$$

Schottky defects for MX_2 and M_2X_3

As mentioned earlier, a Schottky defect will always result a crystal structure in equilibrium--where no crystal is going to be too positive or too negative; thus in the case of:

- MX_2: one Schottky defect equals one cation and two anion vacancy.
- M_2X_3: one Schottky defect equals two cation and three anion vacancy.

References

1. Housecroft, Catherine. Inorganic Chemistry. Pearson Prentice Hall 2008.
2. Sólyom, J.(Jenö). Fundamentals of the Physics of Solids. Translated by Attila Piróth. New York : Springer, c2007.
3. Tilley, Richard. Understanding Solids. John Wiley & Sons, LTD. 2004.

Problems

1. How does an ionic crystal structure maintain electrical neutrality despite undergoing a Schottky defect?
2. How is a Schottky defect defined for a compound with a MX formula? MX_2? M_2X_3?
3. Given that the enthalpy of defect formation for LiCl is 3.39 x 10^{-19} J and the density of LiCl is 2.068 g/cm^{-3}. Calculate the number of Schottky defect at 873 K.
4. Using the number of Schottky defect solved for question 3, determine the fraction of vacant site for LiCl.
5. If a anion and a cation vacant its site and occupies a space between other anions and cations, is it still a Schottky defect?

Answers

1. For a MX compound: one anion and one cation vacant their sites, so the overall charge will remain balanced. This is the same for MX_2 and M_2X_3 because appropriate numbers of anions and cations vacant their site thus leaving the overall charge neutral.
2. MX compound: one Schottky defect is when one anion and one cation leave their sites. MX_2 compound: one Schottky defect is when one anion and two cations leave their sites. M_2X_3 is when two anions and three cations leave their sites.

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6.17B: Frenkel Defect

The **Frenkel defect** (also known as the Frenkel pair/disorder) is a defect in the lattice crystal where an atom or ion occupies a normally vacant site other than its own. As a result the atom or ion leaves its own lattice site vacant.

The Frenkel Defect in a Molecule

The Frenkel Defect explains a defect in the molecule where an atom or ion (normally the cation) leaves its own lattice site vacant and instead occupies a normally vacant site (Figure $6.17B.1$). The cation leaves its own lattice site open and places itself between the area of all the other cations and anions. This defect is only possible if the cations are smaller in size when compared to the anions.

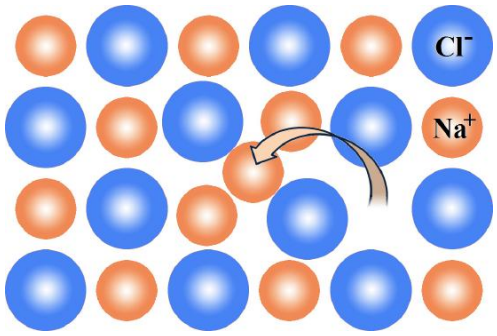


Figure $6.17B.1$: The Frenkel defect within the NaCl structure. (CC BY-SA 3.0; VladVD via Wikipedia)

The number of Frenkel Defects can be calculated using the equation:

$$\sqrt{NN^*}\, e^{\frac{\Delta H}{2RT}}$$

where N is the number of normally occupied positions, N^* is the number of available positions for the moving ion, the ΔH of formation is the enthalpy formation of one Frenkel defect, and R is the gas constant. Frenkel defects are intrinsic defects because the existence causes the Gibbs energy of a crystal to decrease, which means it is favorable to occur.

Solids Found with a Frenkel Defect

The crystal lattices are relatively open and the coordination number is low.

References

1. Housecroft, Catherine E., and Alan G. Sharpe. *Inorganic Chemistry*. 3rd ed. Harlow: Pearson Education, 2008. Print.
2. Tilley, Richard. *Understanding Solids.* John Wiley & Sons, LTD. 2004.

Problems

1. What requirements are needed in order for the Frenkel defect to occur in an atom?
2. What are the differences between the Schottky defect and the Frenkel defect?

Answers

1. A low coordination number as well as having the crystal lattices open for the molecule.
2. The Frenkel defect causes an cation to leave its own lattice and go to another, while Sckhotty defect depicts that an equal number of cations and anions must be absent to maintain charge neutraility.

Contributors and Attributions

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6.17C: Experimental Observations of Schottky and Frenkel Defects

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6.17D: Non-Stoichiometric Compounds

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6.17E: Color Centers (F-Centers)

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6.17F: Thermodynamic Effects of Crystal Defects

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CHAPTER OVERVIEW

7: Acids, bases and ions in aqueous solution

Topic hierarchy

7.1: Introduction
- 7.1A: Acid-Base Theories and Concepts

7.2: Properties of Water
- 7.2A: Structure and Hydrogen Bonding
- 7.2B: The Self Ionization of Water
- 7.2C: Water as a Brønstead Acid or Base

7.3: Definitions and Units in Aqueous Solution
- 7.3A: Molarity and Molality
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7.4: Some Bronstead Acids and Bases
- 7.4A: Carboxylic Acids - Examples of Mono-, Di-, and Polybasic Acids
- 7.4B: Inorganic Acids
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7.5: The Energetics of Acid Dissociation in Aqueous Solution
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7.6: Trends within a Series of Oxoacids \(EO_n(OH)_m\)

7.7: Aquated Cations - Formation and Acidic Properties
- 7.7A: Water as a Lewis Base
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7.8: Amphoteric Oxides and Hydroxides
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7.9: Solubilities of Ionic Salts
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7.10: Common-Ion Effect

7.11: Coordination Complexes - An Introduction
- 7.11A: Definitions and Terminology
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7.12: Stability Constants of Coordination Complexes

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7.13A: Ionic Size and Charge
7.13B: Hard and Soft Metal Centers and Ligands

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7.1: Introduction

Acids

An acid (from the Greek *oxein* then Latin *acidus/acére* meaning sour) is a chemical substance whose aqueous solutions were characterized by a sour taste, the ability to turn blue litmus red, and the ability to react with bases and certain metals (like calcium) to form salts. Aqueous solutions of acids have a pH smaller than 7. The lower the pH, the higher the acidity and thus the higher the concentration of hydrogen ions in the solution (using the Arrhenius or Brønsted-Lowry definition).

Some notes on acids-bases, pH and the use of logarithms in calculations are available.

There are a number of common definitions for acids, for example, the **Arrhenius**, **Brønsted-Lowry**, and the **Lewis** definition. The Arrhenius definition defines acids as substances which increase the concentration of hydrogen ions (H^+), when dissolved in water. The Brønsted-Lowry definition is an expansion of this and defines an acid as a substance which can act as an H^+ donor. By this definition, any compound which can be easily deprotonated can be considered an acid. Examples include alcohols and amines which contain O-H or N-H fragments. A Lewis acid is a substance which can accept a pair of electrons to form a covalent bond. Examples of Lewis acids include all metal cations, and electron-deficient molecules such as boron trifluoride and aluminium trichloride.

Common examples of acids include hydrochloric acid (a solution of hydrogen chloride gas in water, this is the acid found in the stomach that activates digestive enzymes), acetic acid (vinegar is a dilute solution, generally under 5%), sulfuric acid (used in wet-cell car batteries), and tartaric acid (a solid used in baking). As these examples show, acids can be solutions or pure substances, and can be derived from solids, liquids, or gases.

$HCl(aq) + NaOH(aq) \rightleftarrows NaCl + H_2O$
$HOAc(aq) + NaOH(aq) \rightleftarrows NaOAc + H_2O$
$H_2SO_4(aq) + 2NaOH(aq) \rightleftarrows Na_2SO_4 + 2H_2O$
$HO_2CCH(OH)CH(OH)CO_2H(aq) + 2NaOH(aq) \rightleftarrows Na_2Tartrate + 2H_2O$

Bases

The "modern" concept of a base in chemistry, stems from Guillaume-François Rouelle who in 1754 suggested that a base was a substance which reacted with acids "by giving it a concrete base or solid form" (as a salt). In addition they gave aqueous solutions which were characterized as slippery to the touch, tasted bitter, changed the colour of indicators (e.g., turned red litmus paper blue), and promoted certain chemical reactions (base catalysis). Examples of bases are the hydroxides of the alkali and alkaline earth metals (NaOH, $Ca(OH)_2$, etc.).

For a substance to be classified as an Arrhenius base, it must produce hydroxide ions in solution. In order to do so, Arrhenius believed the base must contain hydroxide in the formula. This made the Arrhenius model limited, as it did not readily explain the basic properties of aqueous solutions of ammonia (NH_3.aq, often written as NH_4OH to better fit the Arrhenius model) or its organic derivatives (amines). In the more general Brønsted-Lowry acid-base theory, a base is a substance that can accept hydrogen ions (H^+). In the Lewis model, a base is an electron pair donor.

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7.1A: Acid-Base Theories and Concepts

There are three primary theories of acid-base chemistry that are often taught together: Arrhenius theory, Brønsted-Lowry theory, and Lewis acid-base theory. Each theory is introduced below.

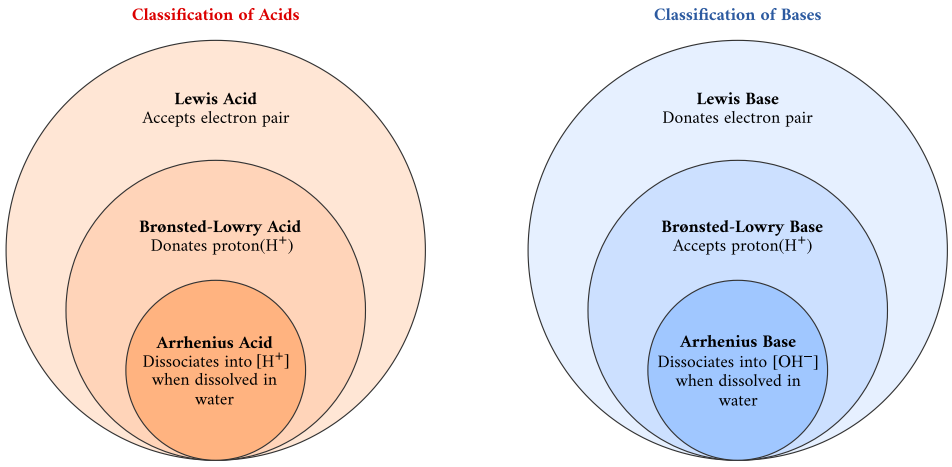


Figure 7.1A.1: Hierarchal definitions of acids and bases via the three primary theories. These theories are designed to be "superset" of the previous classification. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Arrhenius Definition of Acids and Bases

The Swedish chemist Svante Arrhenius attributed the properties of acidity to hydrogen ions (H^+) in 1884. An Arrhenius acid is a substance that, when added to water, increases the concentration of H^+ ions in the water. Note that chemists often write $H^+(aq)$ and refer to the hydrogen ion when describing acid-base reactions, but the free hydrogen nucleus does not exist alone in water. It exists in a hydrated form which for simplicity is often written as the hydronium (hydroxonium) ion, H_3O^+. Thus, an Arrhenius acid can also be described as a substance that increases the concentration of hydronium ions when added to water. This definition stems from the equilibrium dissociation (self-ionization) of water into hydronium and hydroxide (OH^-) ions:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

with K_w defined as $[H^+][OH^-]$.

The value of K_w varies with temperature, as shown in the table below where at 25 °C K_w is approximately 1.0×10^{-14}, i.e. $pK_w = 14$.

Water temperature	K_w / 10^{-14}	pK_w
0 °C	0.112	14.95
25 °C	1.023	13.99
50 °C	5.495	13.26
75 °C	19.95	12.70
100 °C	56.23	12.25

In pure water the majority of molecules are H_2O, but the molecules are constantly dissociating and re-associating, and at any time a small number of the molecules (about 1 in 10^7) are hydronium and an equal number are hydroxide. Because the numbers are equal, pure water is neutral (not acidic or basic) and has an electrical conductivity of 5.5 microSiemen, µS/m. For comparison, sea water's conductivity is about one million times higher, 5 S/m (due to the dissolved salt).

Proton vs. Hydron

Although the term proton is often used for H^+, this should really be reserved for H (protium) not D (deuterium) or T (tritium). The more general term, hydron covers all isotopes of hydrogen.

An Arrhenius base, on the other hand, is a substance which increases the concentration of hydroxide ions when dissolved in water, hence decreasing the concentration of hydronium ions.

Upshot

To qualify as an Arrhenius acid, upon the introduction to water, the chemical must either cause, directly or otherwise:

- an increase in the aqueous hydronium concentration, or
- a decrease in the aqueous hydroxide concentration.

Conversely, to qualify as an Arrhenius base, upon the introduction to water, the chemical must either cause, directly or otherwise:

- a decrease in the aqueous hydronium concentration, or
- an increase in the aqueous hydroxide concentration.

The definition is expressed in terms of an equilibrium expression:

$$\text{acid} + \text{base} \rightleftharpoons \text{conjugate base} + \text{conjugate acid}.$$

With an acid, HA, the equation can be written symbolically as:

$$HA + B \rightleftharpoons A^- + HB^+$$

The double harpoons sign, $\rightleftharpoons$, is used because the reaction can occur in both forward and backward directions. The acid, HA, can lose a hydron to become its conjugate base, A^-. The base, B, can accept a hydron to become its conjugate acid, HB^+. Most acid-base reactions are fast so that the components of the reaction are usually in dynamic equilibrium with each other.

Brønsted-Lowry Definition of Acids and Bases

While the Arrhenius concept is useful for describing many reactions, it has limitations. In 1923, chemists Johannes Nicolaus Brønsted and Thomas Martin Lowry independently recognized that acid-base reactions involve the transfer of a hydron. A Brønsted-Lowry acid (or simply Brønsted acid) is a species that donates a hydron to a Brønsted-Lowry base. The Brønsted-Lowry acid-base theory has several advantages over the Arrhenius theory. Consider the following reactions of acetic acid (CH_3COOH):

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4{}^+$$

Both theories easily describe the first reaction: CH_3COOH acts as an Arrhenius acid because it acts as a source of H_3O^+ when dissolved in water, and it acts as a Brønsted acid by donating a hydron to water. In the second example CH_3COOH undergoes the same transformation, in this case donating a hydron to ammonia (NH_3), but it cannot be described using the Arrhenius definition of an acid because the reaction does not produce hydronium ions.

Upshot

To qualify as an Brønsted-Lowry acid, the chemical must either cause, directly or otherwise:

- donate a proton.

Conversely, to qualify as an Brønsted-Lowry base, the chemical must either cause, directly or otherwise:

- accept a proton.

Lewis Definition of Acids and Bases

A third concept was proposed in 1923 by Gilbert N. Lewis which includes reactions with acid-base characteristics that do not involve a hydron transfer. A Lewis acid is a species that reacts with a Lewis base to form a Lewis adduct. The Lewis acid accepts a pair of electrons from another species; in other words, it is an electron pair acceptor. Brønsted acid-base reactions involve hydron

transfer reactions while Lewis acid-base reactions involve electron pair transfers. All Brønsted acids are Lewis acids, but not all Lewis acids are Brønsted acids.

$$BF_3 + F^- \rightleftharpoons BF_4^-$$

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

In the first example BF_3 is a Lewis acid since it accepts an electron pair from the fluoride ion. This reaction cannot be described in terms of the Brønsted theory because there is no hydron transfer. The second reaction can be described using either theory. A hydron is transferred from an unspecified Brønsted acid to ammonia, a Brønsted base; alternatively, ammonia acts as a Lewis base and transfers a lone pair of electrons to form a bond with a hydrogen ion.

Upshot

To qualify as an Lewis acid, the chemical must

- accept an electron pair

Conversely, to qualify as an Lewis base, the chemical must:

- donate an electron pair

Other Acid-Base Definitions

Lux-Flood acid-base definition

This acid-base theory was a revival of the oxygen theory of acids and bases, proposed by German chemist Hermann Lux in 1939 and further improved by Håkon Flood circa 1947. It is still used in modern geochemistry and for the electrochemistry of molten salts. This definition describes an acid as an oxide ion (O^{2-}) acceptor and a base as an oxide ion donor. For example:

$$MgO\ (\text{base}) + CO_2\ (\text{acid}) \rightleftharpoons MgCO_3$$

$$CaO\ (\text{base}) + SiO_2\ (\text{acid}) \rightleftharpoons CaSiO_3$$

$$NO_3^-\ (\text{base}) + S_2O_7^{2-}\ (\text{acid}) \rightleftharpoons NO_2^+ + 2\,SO_4^{2-}$$

Usanovich acid-base definition

Mikhail Usanovich developed a general theory that does not restrict acidity to hydrogen-containing compounds, and his approach, published in 1938, was even more general than the Lewis theory. Usanovich's theory can be summarized as defining an acid as anything that *accepts negative species, anions or electrons* or *donates positive ones, cations*, and a base as the reverse. This definition could even be applied to the concept of redox reactions (oxidation-reduction) as a special case of acid-base reactions. Some examples of Usanovich acid-base reactions include:

- species exchanged: anion O^{2-}

$$Na_2O\ (\text{base}) + SO_3\ (\text{acid}) \longrightarrow 2\,Na^+ + SO_4^{2-}$$

- species exchanged: anion S^{2-}

$$3\,(NH_4)_2S\ (\text{base}) + Sb_2S_5\ (\text{acid}) \longrightarrow 6\,NH_4^+ + 2\,SbS_4^{3-}$$

- species exchanged: electron

$$2\,Na\ (\text{base}) + Cl_2\ (\text{acid}) \longrightarrow 2\,Na^+ + 2\,Cl^-$$

A comparison of the above definitions of Acids and Bases shows that the Usanovich concept encompasses all of the others but some feel that because of this it is too general to be useful.

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SECTION OVERVIEW

7.2: Properties of Water

Water covers 71% of the Earth's surface and is vital for all known forms of life. On Earth, 96.5% of the planet's water is found in seas and oceans, 1.7% in groundwater, 1.7% in glaciers and the ice caps of Antarctica and Greenland, a small fraction in other large water bodies, and 0.001% in the air as vapour, clouds (formed from solid and liquid water particles suspended in air), and precipitation.

Only 2.5% of the Earth's water is freshwater, and 98.8% of that water is in ice and groundwater. Less than 0.3% of all freshwater is in rivers, lakes, and the atmosphere, and an even smaller amount of the Earth's freshwater (0.003%) is contained within biological bodies and manufactured products.

The major chemical and physical properties of water are:

- Water is a liquid at standard temperature and pressure. It is tasteless and odourless. The intrinsic colour of water and ice is a very slight blue hue, although both appear colourless in small quantities. Water vapour is essentially invisible as a gas.
- Water is the only substance occurring naturally in all three phases as solid, liquid, and gas on the Earth's surface
- Water is transparent in the visible electromagnetic spectrum. Thus aquatic plants can live in water because sunlight can reach them. Infrared light is strongly absorbed by the hydrogen-oxygen or OH bonds.
- Since the water molecule is not linear and the oxygen atom has a higher electronegativity than hydrogen atoms, the oxygen atom carries a partial negative charge, whereas the hydrogen atoms have partial positive charges. As a result, water is a polar molecule with an electrical dipole moment.
- Water can form an unusually large number of intermolecular hydrogen bonds (four) for a molecule of its size. These factors lead to strong attractive forces between molecules of water, giving rise to water's high surface tension and capillary forces. The capillary action refers to the tendency of water to move up a narrow tube against the force of gravity. This property is relied upon by all vascular plants, such as trees.
- The boiling point of water (like all other liquids) is dependent on the barometric pressure. For example, on the top of Mount Everest water boils at 68 °C, compared to 100 °C at sea level at a similar latitude (since latitude modifies atmospheric pressure slightly). Conversely, water deep in the ocean near geothermal vents can reach temperatures of hundreds of degrees and remain liquid.
- Water has a high specific heat capacity, 4181.3 J kg^{-1} K^{-1}, as well as a high heat of vaporization (40.65 kJ mol^{-1}), both result from the extensive hydrogen bonding between its molecules. These two unusual properties allow water to moderate Earth's climate by buffering large fluctuations in temperature.
- Solid ice has a density of 917 kg m^{-3}. The maximum density of liquid water occurs at 3.98 °C where it is 1000 kg m^{-3}.
- Elements that are more electropositive than hydrogen such as lithium, sodium, calcium, potassium and caesium displace hydrogen from water, forming hydroxides. Since hydrogen is a flammable gas, when given off it is dangerous and the reaction of water with the more electropositive of these elements can be violently explosive so they are often stored in oil.

Most known pure substances display simple behaviour when they are cooled, they shrink. Liquids contract as they are cooled because the molecules move slower and they are less able to overcome the attractive intermolecular forces drawing them closer to each other. Once the freezing temperature is reached, the substances solidify, causing them to contract even more because crystalline solids are usually tightly packed.

Water however water has the anomalous property of becoming **less dense when it is cooled to its solid form, ice**.

When liquid water is cooled, it initially contracts as expected, until a temperature of 3.98 °C is reached (~4 °C). After that, it expands slightly until it reaches the freezing point, and then when it freezes, it expands by approximately 9%.

Just above the freezing point, the water molecules begin to locally arrange into ice-like structures with an extended hydrogen

bonded network. This creates some "openness" in the liquid water, accounting for the decrease in its density. This is in opposition to the usual tendency for cooling to increase the density. At 3.98 °C these opposing tendencies cancel out, producing the density maximum.

Since water expands to occupy a 9% greater volume in the form of ice and is less dense, it floats on liquid water, as in icebergs. Fortunately this happens, since in colder climates where water is susceptible to freezing, if it all turned solid during the winter, it would kill all the life within it.

The extended structure of the water molecule in liquid and solid form seen in the models below provides the explanation for the variation of density with temperature.

Topic hierarchy

7.2A: Structure and Hydrogen Bonding

7.2B: The Self Ionization of Water

7.2C: Water as a Brønstead Acid or Base

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7.2A: Structure and Hydrogen Bonding

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7.2B: The Self Ionization of Water

Solvated H^+ ions

The hydron (a completely free or "naked" hydrogen atomic nucleus) is far too reactive to exist in isolation and readily hydrates in aqueous solution. The simplest hydrated form of the hydrogen cation, the hydronium (hydroxonium) ion H_3O^+ (aq), is a key object of Arrhenius' definition of acid. Other "simple" hydrated forms include the Zundel cation $H_5O_2^+$ which is formed from a hydron and two water molecules, and the Eigen cation $H_9O_4^+$, formed from a hydronium ion and three water molecules. The hydron itself is crucial in the more general Brønsted-Lowry acid-base theory, which extends the concept of acid-base chemistry beyond aqueous solutions. Both of these complexes represent ideal structures in a more general hydrogen bonded network defect. A freezing-point depression study determined that the mean hydration ion in cold water is on average approximately $H_3O^+(H_2O)_6$: where each hydronium ion is solvated by 6 water molecules. Some hydration structures are quite large: the $H_3O^+.20H_2O$ magic ion number structure (called magic because of its increased stability with respect to hydration structures involving a comparable number of water molecules).

Structure from Lancaster site

In 1806 Theodor Grotthuss proposed a theory of water conductivity. He envisioned the electrolytic reaction as a sort of "bucket line" where each oxygen atom simultaneously passes and receives a single hydrogen atom. It was an astonishing theory to propose at the time, since the water molecule was thought to be OH not H_2O and the existence of ions was not fully understood. The theory became known as the Grotthuss mechanism. The transport mechanism is now thought to involve the inter-conversion between the Eigen and Zundel solvation structures, Eigen to Zundel to Eigen (E-Z-E).

Water

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7.2C: Water as a Brønstead Acid or Base

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SECTION OVERVIEW

7.3: Definitions and Units in Aqueous Solution

Topic hierarchy

7.3A: Molarity and Molality

7.3B: Standard State

7.3C: Activity

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7.3A: Molarity and Molality

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7.3B: Standard State

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7.3C: Activity

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7.4: Some Bronstead Acids and Bases

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7.4A: Carboxylic Acids - Examples of Mono-, Di-, and Polybasic Acids

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7.4B: Inorganic Acids

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7.4C: Inorganic Bases - Hydroxides

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7.4D: Inorganic Bases - Nitrogen Bases

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7.5: The Energetics of Acid Dissociation in Aqueous Solution

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7.5A: Hydrogen Halides

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7.5B: H_2S, H_2Se, and H_2Te

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7.6: Trends within a Series of Oxoacids $E\ O\ n\ (\ O\ \ H\ )\ m$

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SECTION OVERVIEW

7.7: Aquated Cations - Formation and Acidic Properties

Topic hierarchy

7.7A: Water as a Lewis Base

7.7B: Aquated Cations as Bronstead Acids

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7.7A: Water as a Lewis Base

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7.8: Amphoteric Oxides and Hydroxides

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7.8A: Amphoteric Behavior

Oxides and Hydroxides

An early classification of substances arose from the differences observed in their solubility in acidic and basic solutions. This led to the classification of oxides and hydroxides as being either *acidic* or *basic*. Acidic oxides or hydroxides either reacted with water to produce an acidic solution or were soluble in aqueous base. Basic oxides and hydroxides either reacted with water to produce a basic solution or readily dissolved in aqueous acids. The diagram below shows there is strong correlation between the acidic or basic character of oxides (E_xO_y) and the position of the element, E, in the periodic table.

Oxides of metallic elements are generally basic oxides, and oxides of nonmetallic elements acidic oxides. Take for example, the reactions with water of calcium oxide, a metallic oxide, and carbon dioxide, a nonmetallic oxide:

$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2$
$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$ Calcium oxide reacts with water to produce a basic solution of calcium hydroxide, whereas carbon dioxide reacts with water to produce a solution of carbonic acid.

There is a gradual transition from basic oxides to acidic oxides from the lower left to the upper right in the periodic table.

Basicity of the oxides increase with increasing atomic number down a group:
$BeO < MgO < CaO < SrO < BaO$ Note as well that acidity increases with increasing oxidation state of the element:
$MnO < Mn_2O_3 < MnO_2 < Mn_2O_7$
in keeping with the increase in covalency. Oxides of intermediate character, called *amphoteric oxides*, are located along the diagonal line between the two extremes. Amphoteric species are molecules or ions that can react as an acid as well as a base. The word has Greek origins, *amphoteroi* (ἀμφότεροι) meaning "both". Many metals (such as copper, zinc, tin, lead, aluminium, and beryllium) form amphoteric oxides or hydroxides. Amphoterism depends on the oxidation state of the oxide.

For example, zinc oxide (ZnO) reacts with both acids and with bases: In acid: $ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O$
In base: $ZnO + 2OH^- + H_2O \rightarrow [Zn(OH)_4]^{2-}$

This reactivity can be used to separate different cations, such as zinc(II), which dissolves in base, from manganese(II), which does not dissolve in base.

Aluminium hydroxide is another amphoteric species:

As a base (neutralizing an acid): $Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$
As an acid (neutralizing a base): $Al(OH)_3 + NaOH \rightarrow Na[Al(OH)_4]$

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7.8B: Periodic Trends in Amphoteric Properties

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7.9: Solubilities of Ionic Salts

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7.9A: Solubility and Saturated Solutions

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7.9B: Sparingly Soluble Salts and Solubility Products

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7.9C: The Energetics of the Dissolution of an Ionic Salt - $\Delta_{sol} G^\circ$

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7.9D: The Energetics of the Dissolution of an Ionic Salt - Hydration of Ions

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7.9E: Soubilities - Some Concluding Remarks

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7.10: Common-Ion Effect

Learning Objectives

- Recognize common ions from various salts, acids, and bases.
- Calculate concentrations involving common ions.
- Calculate ion concentrations involving chemical equilibrium.

The common ion effect is used to describe the effect on an equilibrium when one or more species in the reaction is shared with another reaction. This results in a shifting of the equilibrium properties.

Introduction

The solubility products K_{sp}'s are equilibrium constants in heterogeneous equilibria (i.e., between two different phases). If several salts are present in a system, they all ionize in the solution. If the salts contain a common cation or anion, these salts contribute to the concentration of the common ion. Contributions from all salts must be included in the calculation of concentration of the common ion. For example, a solution containing sodium chloride and potassium chloride will have the following relationship:

$$[\mathrm{Na^+}] + [\mathrm{K^+}] = [\mathrm{Cl^-}]$$

Consideration of *charge balance* or *mass balance* or both leads to the same conclusion.

Common Ions

When NaCl and KCl are dissolved in the same solution, the $\mathrm{Cl^-}$ ions are *common* to both salts. In a system containing NaCl and KCl, the $\mathrm{Cl^-}$ ions are common ions.

$$\mathrm{NaCl} \rightleftharpoons \mathrm{Na^+} + \mathrm{Cl^-}$$
$$\mathrm{KCl} \rightleftharpoons \mathrm{K^+} + \mathrm{Cl^-}$$
$$\mathrm{CaCl_2} \rightleftharpoons \mathrm{Ca^{2+}} + 2\,\mathrm{Cl^-}$$
$$\mathrm{AlCl_3} \rightleftharpoons \mathrm{Al^{3+}} + 3\,\mathrm{Cl^-}$$
$$\mathrm{AgCl} \rightleftharpoons \mathrm{Ag^+} + \mathrm{Cl^-}$$

For example, when AgCl is dissolved into a solution already containing NaCl (actually $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ions), the $\mathrm{Cl^-}$ ions come from the ionization of both AgCl and NaCl. Thus, $[\mathrm{Cl^-}]$ differs from $[\mathrm{Ag^+}]$. The following examples show how the concentration of the common ion is calculated.

Example 7.10.1

What are $[\mathrm{Na^+}]$, $[\mathrm{Cl^-}]$, $[\mathrm{Ca^{2+}}]$, and $[\mathrm{H^+}]$ in a solution containing 0.10 M each of NaCl, $\mathrm{CaCl_2}$, and HCl?

Solution

Due to the conservation of ions, we have

Extra close brace or missing open brace

but

$$\begin{aligned}[\mathrm{Cl^-}] &= 0.10\,(\text{due to } \mathrm{NaCl}) \\ &\quad + 0.20\,(\text{due to } \mathrm{CaCl_2}) \\ &\quad + 0.10\,(\text{due to } \mathrm{HCl}) \\ &= 0.40\,\mathrm{M}\end{aligned}$$

Exercise 7.10.1

John poured 10.0 mL of 0.10 M NaCl, 10.0 mL of 0.10 M KOH, and 5.0 mL of 0.20 M HCl solutions together and then he made the total volume to be 100.0 mL. What is $[\mathrm{Cl}^-]$ in the final solution?

Answer

$$[\mathrm{Cl}^-] = \frac{0.1\ \mathrm{M} \times 10\ \mathrm{mL} + 0.2\ \mathrm{M} \times 5.0\ \mathrm{mL}}{100.0\ \mathrm{mL}} = 0.020\ \mathrm{M}$$

Le Chatelier's Principle states that if an equilibrium becomes unbalanced, the reaction will shift to restore the balance. If a common ion is added to a weak acid or weak base equilibrium, then the equilibrium will shift towards the reactants, in this case the weak acid or base.

Example 7.10.2

Consider the lead(II) ion concentration in this *saturated* solution of $\mathrm{PbCl_2}$. The balanced reaction is

$$\mathrm{PbCl_2\,(s)} \rightleftharpoons \mathrm{Pb^{2+}\,(aq)} + 2\,\mathrm{Cl^-\,(aq)} \tag{7.10.1}$$

Defining s as the concentration of dissolved lead(II) chloride, then:

$$[\mathrm{Pb}^{2+}] = s$$

$$[\mathrm{Cl}^-] = 2s$$

These values can be substituted into the solubility product expression, which can be solved for s:

$$\begin{aligned} K_{sp} &= [\mathrm{Pb}^{2+}][\mathrm{Cl}^-]^2 \\ &= s \times (2s)^2 \\ 1.7 \times 10^{-5} &= 4s^3 \\ s^3 &= \frac{1.7 \times 10^{-5}}{4} \\ &= 4.25 \times 10^{-6} \\ s &= \sqrt[3]{4.25 \times 10^{-6}} \\ &= 1.62 \times 10^{-2}\ mol\ dm^{-3} \end{aligned}$$

The concentration of lead(II) ions in the solution is 1.62 x 10^{-2} M. Consider what happens if sodium chloride is added to this saturated solution. Sodium chloride shares an ion with lead(II) chloride. The chloride ion is **common** to both of them; this is the origin of the term "common ion effect".

Look at the original equilibrium expression in Equation 7.10.1. What happens to that equilibrium if extra chloride ions are added? According to *Le* Chatelier, the position of equilibrium will shift to counter the change, in this case, by removing the chloride ions by making extra solid lead(II) chloride.

Of course, the concentration of lead(II) ions in the solution is so small that only a tiny proportion of the extra chloride ions can be converted into solid lead(II) chloride. The lead(II) chloride becomes even *less soluble*, and the concentration of lead(II) ions in the solution *decreases*. This type of response occurs with any sparingly soluble substance: it is less soluble in a solution which contains any ion which it has in common. This is the common ion effect.

A Simple Example

If an attempt is made to dissolve some lead(II) chloride in some 0.100 M sodium chloride solution instead of in water, what is the equilibrium concentration of the lead(II) ions this time? As before, define s to be the concentration of the lead(II) ions.

$$[\mathrm{Pb}^{2+}] = s$$

The calculations are different from before. This time the concentration of the chloride ions is governed by the concentration of the sodium chloride solution. The number of ions coming from the lead(II) chloride is going to be tiny compared with the 0.100 M coming from the sodium chloride solution.

In calculations like this, it can be assumed that the concentration of the common ion is entirely due to the other solution. This simplifies the calculation.

So we assume:

$$[\mathrm{Cl}^-] = 0.100\ M$$

The rest of the mathematics looks like this:

$$\begin{aligned} K_{sp} &= [\mathrm{Pb}^{2+}][\mathrm{Cl}^-]^2 \\ &= s \times (0.100)^2 \\ 1.7 \times 10^{-5} &= s \times 0.00100 \end{aligned}$$

therefore:

$$\begin{aligned} s &= \frac{1.7 \times 10^{-5}}{0.0100} \\ &= 1.7 \times 10^{-3}\ \mathrm{M} \end{aligned}$$

Finally, compare that value with the simple saturated solution:

Original solution:

$$[\mathrm{Pb}^{2+}] = 0.0162\ M$$

Solution in 0.100 M NaCl solution:

$$[\mathrm{Pb}^{2+}] = 0.0017\ M$$

The concentration of the lead(II) ions has decreased by a factor of about 10. If more concentrated solutions of sodium chloride are used, the solubility decreases further.

> Adding a common ion to a system at equilibrium affects the equilibrium composition, but **not** the ionization constant.

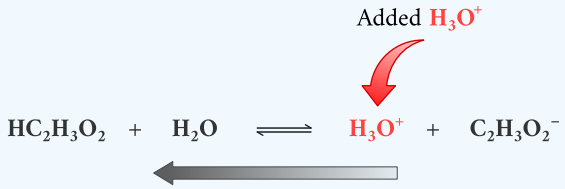
Common Ion Effect with Weak Acids and Bases

Adding a common ion prevents the weak acid or weak base from ionizing as much as it would without the added common ion. The common ion effect suppresses the ionization of a weak acid by adding more of an ion that is a product of this equilibrium.

Example 7.10.3A

The common ion effect of $\mathrm{H_3O^+}$ on the ionization of acetic acid

When a strong acid supplies the common ion H_3O^+
the equilibrium shifts to form more $HC_2H_3O_2$.



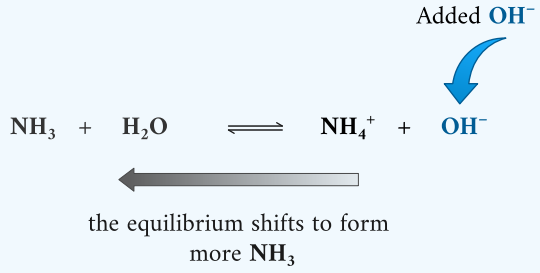
The common ion effect can be conceptualized as an applied Le Chatelier effect. Adding products will shift the equilibrium to more favor the reactants. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

The common ion effect suppresses the ionization of a weak base by adding more of an ion that is a product of this equilibrium.

Example 7.10.3B

Consider the common ion effect of OH^- on the ionization of ammonia

When a strong base supplies the common ion OH^-
the equilibrium shifts to form more NH_3.



The common ion effect can be conceptualized as an applied Le Chatelier effect. Adding products will shift the equilibrium to more favor the reactants. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Adding the common ion of hydroxide shifts the reaction towards the left to decrease the stress (in accordance with Le Chatelier's Principle), forming more reactants. This decreases the reaction quotient, because the reaction is being pushed towards the left to reach equilibrium. The equilibrium constant, $K_b = 1.8 \times 10^{-5}$, does not change. The reaction is put out of balance, or equilibrium.

$$Q_a = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

At first, when more hydroxide is added, the quotient is greater than the equilibrium constant. The reaction then shifts right, causing the denominator to increase, decreasing the reaction quotient and pulling towards equilibrium and causing Q to decrease towards K.

Common Ion Effect on Solubility

Adding a common ion decreases solubility, as the reaction shifts toward the left to relieve the stress of the excess product. Adding a common ion to a dissociation reaction causes the equilibrium to shift left, toward the reactants, causing precipitation.

Example 7.10.4

Consider the reaction:

$$\mathrm{PbCl_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2\,Cl^-\,(aq)}$$

What happens to the solubility of $\mathrm{PbCl_2\,(s)}$ when 0.1 M NaCl is added?

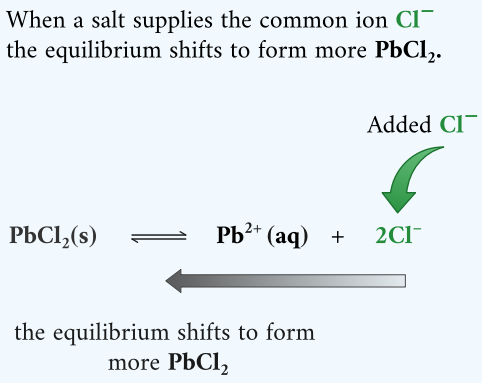
Solution

$$K_{sp} = 1.7 \times 10^{-5}$$

$$Q_{sp} = 1.8 \times 10^{-5}$$

Identify the common ion: $\mathrm{Cl^-}$

Notice: $Q_{sp} > K_{sp}$ The addition of NaCl has caused the reaction to shift out of equilibrium because there are more dissociated ions. Typically, solving for the molarities requires the assumption that the solubility of $\mathrm{PbCl_2\,(s)}$ is equivalent to the concentration of $\mathrm{Pb^{2+}}$ produced because they are in a 1:1 ratio.



The common ion effect can be conceptualized as an applied Le Chatelier effect. Adding products will shift the equilibrium to more favor the reactants. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Because K_{sp} for the reaction is 1.7×10^{-5}, the overall reaction would be

$$(s)(2s)^2 = 1.7 \times 10^{-5}.$$

Solving the equation for s gives $s = 1.62 \times 10^{-2}$ M. The coefficient on $\mathrm{Cl^-}$ is 2, so it is assumed that twice as much $\mathrm{Cl^-}$ is produced as $\mathrm{Pb^{2+}}$, hence the '2s.' The solubility equilibrium constant can be used to solve for the molarities of the ions at equilibrium.

The molarity of $\mathrm{Cl^-}$ added would be 0.1 M because $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ are in a 1:1 ratio in the ionic salt, NaCl. Therefore, the overall molarity of $\mathrm{Cl^-}$ would be $2s + 0.1$, with $2s$ referring to the contribution of the chloride ion from the dissociation of lead chloride.

$$\begin{aligned} Q_{sp} &= [\mathrm{Pb^{2+}}][\mathrm{Cl^-}]^2 \\ &= 1.8 \times 10^{-5} \\ &= (s)(2s + 0.1)^2 \\ s &= [Pb^{2+}] \\ &= 1.8 \times 10^{-3} M \\ 2s &= [\mathrm{Cl^-}] \\ &\approx 0.1 M \end{aligned}$$

Notice that the molarity of $\mathrm{Pb^{2+}}$ is lower when NaCl is added. The equilibrium constant remains the same because of the increased concentration of the chloride ion. To simplify the reaction, it can be assumed that $[\mathrm{Cl^-}]$ is approximately 0.1 M since

the formation of the chloride ion from the dissociation of lead chloride is so small. The reaction quotient for $\mathrm{PbCl_2\,(s)}$ is greater than the equilibrium constant because of the added $\mathrm{Cl^-}$. This therefore shift the reaction left towards equilibrium, causing precipitation and lowering the current solubility of the reaction. Overall, the solubility of the reaction decreases with the added sodium chloride.

References

1. Harwood, William S., F. G. Herring, Jeffry D. Madura, and Ralph H. Petrucci. General Chemistry Principles and Modern Applications. 9th ed. New Jersey: Prentice Hall, 2007.

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SECTION OVERVIEW

7.11: Coordination Complexes - An Introduction

Topic hierarchy

7.11A: Definitions and Terminology

7.11B: Investigating Coordination Complex Formation

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7.12: Stability Constants of Coordination Complexes

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7.12A: Determination of Stability Constants

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7.13A: Ionic Size and Charge

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7.13B: Hard and Soft Metal Centers and Ligands

Hard and Soft Acids and Bases, Pearson's HSAB

This theory proposes that ***soft acids react faster and form stronger bonds with soft bases, whereas hard acids react faster and form stronger bonds with hard bases***, all other factors being equal. The classification in the original work was largely based on equilibrium constants for the reaction of two Lewis bases competing for a Lewis acid.

Hard acids and hard bases tend to have the following characteristics:

- small atomic/ionic radius
- high oxidation state
- low polarizability
- high electronegativity (bases)

Examples of **hard acids** are: H^+, light alkali ions (Li through K are considered to have small ionic radii), Ti^{4+}, Cr^{3+}, Cr^{6+}, BF_3. Examples of **hard bases** are: OH^-, F^-, Cl^-, NH_3, CH_3COO^-, CO_3^{2-}. The affinity of hard acids and hard bases for each other is mainly **ionic** in nature.

Soft acids and soft bases tend to have the following characteristics:

- large atomic/ionic radius
- low or zero oxidation state bonding
- high polarizability
- low electronegativity

Examples of **soft acids** are: CH_3Hg^+, Pt^{2+}, Pd^{2+}, Ag^+, Au^+, Hg^{2+}, Hg_2^{2+}, Cd^{2+}, BH_3. Examples of **soft bases** are: H^-, R_3P, SCN^-, I^-. The affinity of soft acids and bases for each other is mainly **covalent** in nature.

HSAB acids and bases This provides a qualitative approach to looking at the reactions of metal ions with various ligands since, from the diagram above, it is expected that whereas Al(III) and Ti(III) would prefer to react with O-species over S-species, the reverse would be predicted for Hg(II).

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CHAPTER OVERVIEW

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8.1B: Oxidation States

8.1C: Stock Nomenclature

8.2: Standard Reduction Potentials, E°, and the Relationship Between E°, ΔG°, and K

8.2A: Half-Cells and Galvanic Cells

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8.1: Introduction

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8.1A: Oxidation and Reduction

The simplest possible chemical reaction involves the transfer of one or more electrons between two atoms. In the simple reaction:

$$2\,\mathrm{Na} + \mathrm{Cl_2} \longrightarrow 2\,\mathrm{NaCl} \tag{8.1A.1}$$

we assume that sodium transfers an electron to chlorine creating the sodium ion and the chloride ion. We can write the two steps of this reaction as:

$$\mathrm{Na} \longrightarrow \mathrm{Na_1^+} + \mathrm{e\text{-}1} \tag{8.1A.2}$$

and

$$\mathrm{Cl_2} + 2\,\mathrm{e\text{-}1} > 2\,\mathrm{Cl\text{-}1} \tag{8.1A.3}$$

The first of these steps involves the loss of an electron and is called an oxidation reaction, while the second step involves the gain of an electron and is called a reduction reaction. The simple nemonic "Leo goes Ger" or Loss of electrons - oxidation; Gain of electrons - reduction has been used by several generations of students to remember these definitions. (OK! This is Simba, my apologies to Lion King aficionados.) Oxidation and reduction reactions (usually called redox reactions) are important in biochemistry and important families of enzymes are called reductases or oxidases based on their reduction or oxidation catalysis. We recognize ethanol as common drinking alcohol, but most people don't realize that ethanol is generated by fermentation reactions that naturally take place in the intestines. The body always has a small amount of ethanol being transported across the intestine walls. As a result, the body has an enzyme to metabolize ethanol called ethanol oxidase. (You might want to think about this. The body didn't invent ethanol to compensate for the consumption of fermented beverages like beer and wine since there are relatively recent on an evolutionary time scale. Ethanol oxidase is present in the body because it had to be there to compensate for the background ethanol. I would suspect that all mammals have this enzyme, not just people. Other things that are ingested by people for their psychotropic effects do not necessarily have enzymes for their detoxification, thus they stay in the tissues longer and have a greater potential for doing damage. If you follow my dictum of not consuming anything for which you don't have an enzyme, you'll be relatively safe.) Redox chemistry also forms the basis of corrosion chemistry and battery chemistry (electrochemistry). Simple electrochemical reactions If we take a piece of zinc metal and put it into a beaker of HCl, we will quickly notice the formation of bubbles on the surface of the zinc. Were we to leave the zinc in the acid for several minutes, we'd easily observe that the zinc is being dissolved while a gas is being liberated. This process is illustrated below: The reaction taking place here is obviously:

$$Zn + 2H + 1 - - - - - - > Zn + 2 + H2 \tag{8.1A.4}$$

In this reaction, the hydrogen ions are being reduced while the zinc is being oxidized. A similar reaction may be observed if we place a zinc bar into a solution containing copper sulfate. Here the reaction is:

$$Zn + Cu + 2 - - - - - > Cu + Zn + 2 \tag{8.1A.5}$$

Again the zinc is being oxidized while the copper is being reduced. Unlike the case of zinc in acid, the reaction will only continue until the copper has formed a film on the surface of the zinc, at which point the reaction stops since zinc ions are no longer able to escape to the solution.

Rules for assigning oxidation numbers:

1. The oxidation number of a free element = 0.
2. The oxidation number of a monatomic ion = charge on the ion.
3. The oxidation number of hydrogen = + 1 and rarely - 1.
4. The oxidation number of oxygen = - 2 and in peroxides - 1.
5. The sum of the oxidation numbers in a polyatomic ion = charge on the ion. Elements in group 1, 2, and aluminum are always as indicated on the periodic table.

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8.1B: Oxidation States

Rules for assigning oxidation numbers: 1. The oxidation number of a free element = 0. 2. The oxidation number of a monatomic ion = charge on the ion. 3. The oxidation number of hydrogen = + 1 and rarely - 1. 4. The oxidation number of oxygen = - 2 and in peroxides - 1. 5. The sum of the oxidation numbers in a polyatomic ion = charge on the ion. Elements in group 1, 2, and aluminum are always as indicated on the periodic table. K2CO3 The sum of all the oxidation numbers in this formula equal 0. Multiply the subscript by the oxidation number for each element. To calculate O.N. of C K = (2) (+ 1) = + 2 O = (3) (- 2) = - 6 therefore, C = (1) (+ 4) = + 4 HSO4 - To calculate O.N. of S The sum of all the oxidation numbers in this formula equal -1. Multiply the subscript by the oxidation number for each element. H = (1) (+ 1) = + 1 O = (4) (- 2) = - 8 therefore, S = (1) (+ 6) = + 6 Calculate O.N. in following compounds: 1. Sb in Sb2O5 2. N in Al(NO3)3 3. P in Mg3(PO4)2 4. S in (NH4)2SO4 5. Cr in CrO4 -2 6. Hg in Hg(ClO4)2 7. B in NaBO3 8. Si in MgSiF6 9. I in IO3 - 10. N in (NH4)2S 11. Mn in MnO4 - 12. Br in BrO3 - 13. Cl in ClO - 14. Cr in Cr2O7 -2 15. Se in H2SeO3 Reducing Agents and Oxidizing Agents Reducing agent - the reactant that gives up electrons. The reducing agent contains the element that is oxidized (looses electrons). If a substance gives up electrons easily, it is said to be a strong reducing agent. Oxidizing agent - the reactant that gains electrons. The oxidizing agent contains the element that is reduced (gains electrons). If a substance gains electrons easily, it is said to be a strong oxidizing agent. Example: Fe2O3 (cr) + 3CO(g) 2Fe(l) + 3CO2 (g) Notice that the oxidation number of C goes from +2 on the left to +4 on the right. The reducing agent is CO, because it contains C, which loses e - . Notice that the oxidation number of Fe goes from +3 on the left to 0 on the right. The oxidizing agent is Fe2O3, because it contains the Fe, which gains e - . Practice Problems: In any Redox equation, at least one particle will gain electrons and at least one particle will lose electrons. This is indicated by a change in the particle's oxidation number from one side of the equation to the other. For each reaction below, draw arrows and show electron numbers as in the example here. The top arrow indicates the element that gains electrons, reduction, and the bottom arrow indicates the element that looses electrons, oxidation. An arrow shows what one atom of each of these elements gaines or looses. 1. Mg + O2 MgO 2. Cl2 + I - Cl - + I2 3. MnO4 - + C2O4 -2 Mn+2 + CO2 4. Cr + NO2 - CrO2 - + N2O2 -2 5. BrO3 - + MnO2 Br - + MnO4 - 6. Fe+2 + MnO4 - Mn+2 + Fe+3 7. Cr + Sn+4 Cr+3 + Sn+2 8. NO3 - + S NO2 + H2SO4 9. IO4 - + II2 10. NO2 + ClO - NO3 - + Cl - Balancing Redox Equations by the Half-reaction Method 1. Decide what is reduced (oxidizing agent) and what is oxidized (reducing agent). Do this by drawing arrows as in the practice problems. 2. Write the reduction half-reaction. The top arrow in step #1 indicates the reduction half-reaction. Show the electrons gained on the reactant side. Balance with respect to atoms / ions. To balance oxygen, add H2O to the side with the least amount of oxygen. THEN: add H + to the other side to balance hydrogen. 3. Write the oxidation half-reaction. The bottom arrow in step #1 indicates the oxidation half-reaction. Show the electrons lost on the product side. Balance with respect to atoms / ions. To balance oxygen, add H2O to the side with the least amount of oxygen. THEN: add H + to the other side to balance hydrogen. 4. The number of electrons gained must equal the number of electrons lost. Find the least common multiple of the electrons gained and lost. In each half-reaction, multiply the electron coefficient by a number to reach the common multiple. Multiply all of the coefficients in the half-reaction by this same number. 5. Add the two half-reactions. Write one equation with all the reactants from the half-reactions on the left and all the products on the right. The order in which you write the particles in the combined equation does not matter. 6. Simplify the equation. Cancel things that are found on both sides of the equation as you did in net ionic equations. Rewrite the final balanced equation. Check to see that electrons, elements, and total charge are balanced. There should be no electrons in the equation at this time. The number of each element should be the same on both sides. It doesn't matter what the charge is as long as it is the same on both sides. Practice Problems: 1. Identify the oxidizing agent and reducing agent in each equation: H2SO4 + 8HI H2S + 4I2 + 4H2O CaC2 + 2H2O C2H2 + Ca(OH)2 Au2S3 + 3H2 2Au + 3H2S Zn + 2HCl H2 + ZnCl2 2. To make working with redox equations easier, we will omit all physical state symbols. However, remember that they should be there. An unbalanced redox equation looks like this: MnO4 - + H2SO3 + H + Mn+2 + HSO4 - + H2O Study how this equation is balanced using the half-reaction method. It is important that you understand what happens in each step. Be prepared to ask questions about this process in class tomorrow.

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SECTION OVERVIEW

8.2: Standard Reduction Potentials, E°, and the Relationship Between E°, ΔG°, and K

8.2A: Half-Cells and Galvanic Cells

8.2B: Defining and Using Standard Reduction Potentials - E°

8.2C: Dependence of Reduction Potentials on Cell Conditions

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8.2A: Half-Cells and Galvanic Cells

4.2: Electrochemical potentials

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SECTION OVERVIEW

8.3: The Effect of Complex Formation or Precipitation on Reduction Potentials

Topic hierarchy

8.3A: Half-Cells Involving Silver Halides

8.3B: Modifying the Relative Stabilities of Different Oxidation States of a Metal

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8.3A: Half-Cells Involving Silver Halides

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8.3B: Modifying the Relative Stabilities of Different Oxidation States of a Metal

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8.4A: Disproportionation

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8.4B: Stabilizing Species Against Disproportionation

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8.5: Potential Diagrams

4.5: Pourbaix diagrams

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SECTION OVERVIEW

8.6: Frost-Ebsworth Diagrams

Topic hierarchy

8.6A: Frost-Ebsworth Diagrams and their Relationship to Potential Diagrams

8.6B: Interpretation of Frost-Ebsworth Diagrams

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8.6A: Frost-Ebsworth Diagrams and their Relationship to Potential Diagrams

4.3: Latimer and Frost diagrams

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8.6B: Interpretation of Frost-Ebsworth Diagrams

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8.7B: Values of Δ f G ∘ for Aqueous Ions

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8.8: Applications of Redox Reactions to the Extraction of Elements from their Ores

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8.8A: Ellingham Diagrams

It is possible to use plots of the free energy of formation of metal oxides vs. temperature to predict the temperatures at which a metal is stable and the temperatures at which it will spontaneously oxidize. For temperatures at which the free energy of formation of the oxide is positive, the reverse reaction is favored and the oxide will spontaneously decompose to the metal. From evaluation of the thermodynamic data presented in this figure, it can be seen that at 1100oC, Al will oxidize in an environment that has an oxygen partial pressure of 10-32 atm or greater, while chromium will oxidize in an oxygen partial pressure of 10-19 atm or higher. In general, a vacuum environment will be oxidizing to these elements unless a reducing species such as hydrogen is present. If inadequate oxygen is present, a nonprotective oxide film may be formed which could promote alloy depletion and loss of strength.

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CHAPTER OVERVIEW

9: Non-aqueous Media

An inorganic nonaqueous solvent is a solvent other than water, that is not an organic compound. Common examples are liquid ammonia, liquid sulfur dioxide, sulfuryl chloride and sulfuryl chloride fluoride, phosphoryl chloride, dinitrogen tetroxide, antimony trichloride, bromine pentafluoride, hydrogen fluoride, pure sulfuric acid and other inorganic acids. These solvents are used in chemical research and industry for reactions that cannot occur in aqueous solutions or require a special environment.

9.1: Introduction to Non-aqueous Media
9.2: Relative Permittivity
9.3: Energetics of Ionic Salt Transfer from Water to an Organic Solvent
9.4: Acid-Base Behaviour in Non-Aqueous Solvents
9.4A: Strengths of Acids and Bases
9.4B: Levelling and Differentiating Effects
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9.8C: Physical Properties of Fluorosulfonic Acid
9.9: Superacids
9.10: Bromine Trifluoride
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9.11: Dinitrogen Tetraoxide
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9.11B: Reactions in N_2O_4
9.12: Ionic Liquids
9.12A: Molten Salt Solvent Systems
9.12B: Ionic Liquids at Ambient Temperatures

9.13: Supercritical Fluids
9.13A: Properties of Supercritical Fluids and Their Uses as Solvents
9.13B: Supercritical Fluids as Media for Inorganic Chemistry

Alkali Metal–Liquid Ammonia Solutions. *Most metals are insoluble in virtually all solvents, but the alkali metals (and the heavier alkaline earth metals) dissolve readily in liquid ammonia to form solvated metal cations and solvated electrons, which give the solution a deep blue color. Image copyrighted by* the Klein research group.

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9.1: Introduction to Non-aqueous Media

The Brønsted theory encompasses any type of solvent that can donate and accept H^+ ions, not just aqueous solutions. The strength of an acid or a base varies depending on the solvent. Non-aqueous acid-base chemistry follows similar rules to those developed for acids and bases in water. For example in liquid ammonia, the solvent autodissociates in the reaction:

$$2NH_{3(l)} \rightleftharpoons NH_4^+ + NH_2^-$$

This equilibrium is analogous to the autodissociation of water, but has a smaller equilibrium constant (K ≈ 10^{-30}). It follows by analogy to water that NH_4^+ is the strongest acid and NH_2^- is the strongest base that can exist in liquid ammonia. Because ammonia is a basic solvent, it enhances the acidity and suppresses the basicity of substances dissolved in it. For example, the ammonium ion (NH_4^+) is a weak acid in water (K_a = 6 x 10^{-10}), but it is a strong acid in ammonia. Similarly, acetic acid is weak in water but strong in ammonia. Solvent leveling in fact makes CH_3COOH and NH_4Cl both strong acids in ammonia, where they have equivalent acid strength.

Strong acids that are leveled in water have different acid strengths in acidic solvents such as HF or anhydrous acetic acid. For example, acid dissociation of HX in acetic acid (CH_3COOH) involves protonating the solvent to make its conjugate acid ($CH_3COOH_2^+$) and the X^- anion. Because $CH_3COOH_2^+$ is a stronger acid that H_3O^+, the anion X^- (which is a spectator in water) can become a weak base in CH_3COOH:

$$HX + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + X^-$$

It follows that acidic solvents magnify the Brønsted basicities of substances that cannot accept protons in water. Conversely, basic solvents magnify the acidity of substances that cannot donate a proton to OH^-.

The acidity and basicity of non-aqueous solvents is difficult to quantify precisely, but one good relative measure is the Hammett acidity function, H_o, which is defined analogously to pH according to the Henderson-Hasselbach equation:

$$H_o = pK_a + \log\left(\frac{[\text{base}]}{[\text{conjugate acid}]}\right)$$

For non-aqueous solvents, or for acidic or basic compounds in dissolved in solvents that do not themselves dissociate, H_o is a rough measure of the pH of the solvent or compound in question. Anhydrous HF and H_2SO_4 have H_o values of approximately -10 and -12 respectively.

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9.2: Relative Permittivity

The dielectric constant (symbol: ε) of a solvent is a measure of its polarity. The higher the dielectric constant of a solvent, the more polar it is.

eg:

The dielectric constant of water is higher than that of methanol; water is more polar than methanol. One practical consequence is a covalent solute dissociates into ions to a greater extent in water than in methanol.

equilibrium constant for dissociation of MX = Kdis

One must not confuse the dielectric constant of a solvent with its dipole moment. The dipole moment of a solvent, or of any covalent compound, is a microscopic property, meaning it is a property of the molecule of the compound. In contrast, the dielectric constant of a solvent is a a macroscopic property, meaning it is a property of a pure sample of the solvent. Given below is the scattergram of the dielectric constants of sixteen solvents against their dipole moments, showing that there is no clear correlation between the dielectric constant of a solvent and its dipolar moment.

graph1

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9.3: Energetics of Ionic Salt Transfer from Water to an Organic Solvent

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SECTION OVERVIEW

9.4: Acid-Base Behaviour in Non-Aqueous Solvents

pH values are at present undefined in aprotic solvents, as the definition of pH assumes presence of hydronium ions. In other solvents, the concentration of the respective solvonium/solvate ions should be used, such as pCl in POCl3.

Topic hierarchy

9.4A: Strengths of Acids and Bases

9.4B: Levelling and Differentiating Effects

9.4C: 'Acids' in Acidic Solvents

9.4D: Acids and Bases - A Solvent-Oriented Definition

9.4E: Protic and Aprotic Solvents

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9.4A: Strengths of Acids and Bases

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9.4B: Levelling and Differentiating Effects

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9.4C: 'Acids' in Acidic Solvents

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9.4D: Acids and Bases - A Solvent-Oriented Definition

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9.4E: Protic and Aprotic Solvents

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9.5: Liquid Sulfur Dioxide

Sulfur dioxide is a versatile inert solvent widely used for dissolving highly oxidizing salts.

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SECTION OVERVIEW

9.6: Liquid Ammonia

9.6A: Physical Properties

9.6B: Self-Ionization of Ammonia

9.6C: Reactions in Liquid NH_3

9.6D: Solutions of s-block Metals in Liquid NH_3

9.6E: Redox Reactions in Liquid NH_3

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9.6A: Physical Properties

Despite low boiling point (-33.4 ºC), easy to handle.

Solubilities, relatively high dielectric constant (ammonia, eo= 26.7 @ -60ºC; water, eo = 82 @ 18 ºC).

Hence, ionic compounds can be soluble but the lower eo compared to water means that salt with highly charged, non-polarisable anions such as carbonates, sulphates, and phosphates are insoluble.

NH3 is more polarizable than H2O, so salts with more polarizable anions are more soluble, hence the solubility trends.

$$F^- < Cl^- < Br^- < I^- \tag{9.6A.1}$$

$$PO_{43}{}^- < SO_{42}{}^- < OAc^- < NO_3 \tag{9.6A.2}$$

specific solvation

NH3 is a better a-donor than H2O and ammine complexes are formed, especially with the later transition (Ni2+, Cu2+) and B metals (Ag+, Zn2+). Hence higher solubilities for compounds of these metals than those of the A-metals.

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9.6B: Self-Ionization of Ammonia

Self-ionization of ammonia is much "weaker" than water.

$$2\,NH_3 \rightleftharpoons NH_4^+ + NH_2^- \tag{9.6B.1}$$

with $K \approx 10^{-30}$ @ 223K. Since ammonia is better proton acceptor than water, the ionization of acids is relatively enhanced in liquid ammonia. For example, acetic acid is a strong acid in liquid ammonia. Liquid ammonia will therefore tolerate very strong bases such as $C_5H_5^-$ that would otherwise be hydrolyzed in water.

Ammonia is kinetically stabilized to reduction (but easily oxidized) by many reagents, e.g., the reaction

Extra close brace or missing open brace

and is very favorable but slow in the absence of a catalyst such as Fe3+.

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9.6C: Reactions in Liquid NH3

Much of the chemistry in liquid ammonia can be classified by analogy with related reactions in aqueous solutions. Comparison of the physical properties of NH_3 with those of water shows NH_3 has the lower melting point, boiling point, density, viscosity, dielectric constant and electrical conductivity; this is due at least in part to the weaker hydrogen bonding in NH_3 and because such bonding cannot form cross-linked networks, since each NH_3 molecule has only one lone pair of electrons compared with two for each H2O molecule.

Solvolysis: synthesis of amides

$$\mathrm{OPCl_3 + 6\,NH_3 \longrightarrow OP(NH_2)_3 + 3\,NH_4Cl} \tag{9.6C.1}$$

$$\mathrm{SiCl_4 + 8\,NH_3 \longrightarrow Si(NH_2)_4 + 4\,NH_4Cl} \tag{9.6C.2}$$

Metatheses reactions: solubility reversals

$$\mathrm{RCl + AgNO_3 \xrightarrow{H_2O} AgCl\,(s) + RNO_3} \tag{9.6C.3}$$

$$\mathrm{AgCl + KNO_3 \xrightarrow{NH_3} KCl\,(s) + AgNO_3} \tag{9.6C.4}$$

$$\mathrm{Ba(NO_3)_2 + 2\,AgCl \xrightarrow{NH_3} BaCl_2\,(ppt) + 2\,AgNO_3} \tag{9.6C.5}$$

Sodamide as a base

$$\mathrm{Na + NH_3 \longrightarrow NaNH_2 + H_2\,(g)} \tag{9.6C.6}$$

$$\mathrm{NaNH_2 + C_5H_6 \longrightarrow NaC_5H_5 + NH_3} \tag{9.6C.7}$$

NaC_p (useful reagent)

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9.6D: Solutions of s-block Metals in Liquid NH_3

Solvated electron as a reducing agent (Birch reduction), many examples of compounds in very unusual low oxidation states.

$$[Ni(CN)_4]_2^- + Na \xrightarrow{NH_3} [Ni(CN)_4]_4^- \tag{9.6D.1}$$

$$Fe(CO)_5 + Na \xrightarrow{NH_3} [Fe(CO)_4]_2^- \tag{9.6D.2}$$

$$Mo(CO)_6 + Na \xrightarrow{NH_3} [Mo(CO)_4]_4^- \tag{9.6D.3}$$

$$[Pt(NH_3)_4]_2^+ + Na \xrightarrow{NH_3} [Pt(NH_3)_4] \tag{9.6D.4}$$

Reduction of salts of Group IV and V elements give polyhedral anions, many examples. Ge_{94}^-, Sn_{52}^-, Sn_{93}^-, Pb_{52}^-, Bi_{42}^-, P_{72}^-, and As_{64}^-

Liquid Ammonia Solutions

A remarkable feature of the alkali metals is their ability to dissolve reversibly in liquid ammonia. Just as in their reactions with water, reacting alkali metals with liquid ammonia eventually produces hydrogen gas and the metal salt of the conjugate base of the solvent—in this case, the amide ion (NH_2^-) rather than hydroxide:

$$M(s) + NH_3(l) \rightarrow \tfrac{1}{2} H_2(g) + M^+(am) + NH_2^-(am) \tag{9.6D.5}$$

where the (am) designation refers to an ammonia solution, analogous to (aq) used to indicate aqueous solutions. Without a catalyst, the reaction in Equation 9.6D.5 tends to be rather slow. In many cases, the alkali metal amide salt (MNH_2) is not very soluble in liquid ammonia and precipitates, but when dissolved, very concentrated solutions of the alkali metal are produced. One mole of Cs metal, for example, will dissolve in as little as 53 mL (40 g) of liquid ammonia. The pure metal is easily recovered when the ammonia evaporates.

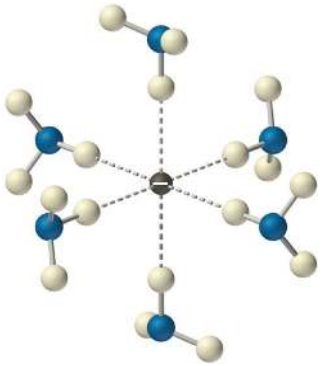


Figure 9.6*D*.1: Solvated electrons. The presence of solvated electrons (e^-, NH_3) in solutions of alkali metals in liquid ammonia is indicated by the intense color of the solution and its electrical conductivity. (CC BY-SA-NC 3.0; anonymous)

Solutions of alkali metals in liquid ammonia are intensely colored and good conductors of electricity due to the presence of solvated electrons (e^-, NH_3), which are not attached to single atoms. A solvated electron is loosely associated with a cavity in the ammonia solvent that is stabilized by hydrogen bonds. Alkali metal–liquid ammonia solutions of about 3 M or less are deep blue (Figure 9.6*D*.2) and conduct electricity about 10 times better than an aqueous $NaCl$ solution because of the high mobility of the solvated electrons. As the concentration of the metal increases above 3 M, the color changes to metallic bronze or gold, and the conductivity increases to a value comparable with that of the pure liquid metals.

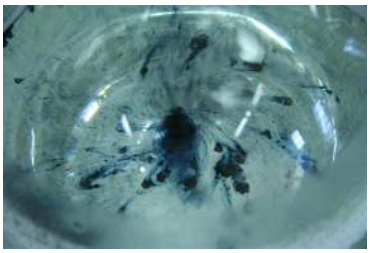
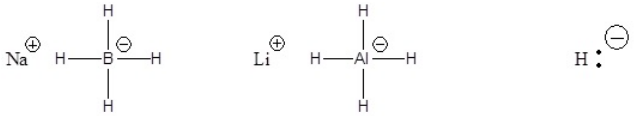


Figure 9.6D.2: Alkali Metal–Liquid Ammonia Solutions. Most metals are insoluble in virtually all solvents, but the alkali metals (and the heavier alkaline earth metals) dissolve readily in liquid ammonia to form solvated metal cations and solvated electrons, which give the solution a deep blue color. Image copyrighted by the Klein research group (Christian Joest, 2013).

The most common sources of the hydride nucleophile are lithium aluminum hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$). Note! The hydride anion is not present during this reaction; rather, these reagents serve as a source of hydride due to the presence of a polar metal-hydrogen bond. Because aluminum is less electronegative than boron, the Al-H bond in $LiAlH_4$ is more polar, thereby, making $LiAlH_4$ a stronger reducing agent.



Sodium Borohydride **Lithium Aluminum Hydride** **Hydride Nucleophile**

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9.6E: Redox Reactions in Liquid NH_3

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SECTION OVERVIEW

9.7: Liquid Hydrogen Fluoride

9.7A: Physical Properties

9.7B: Acid-Base Behavior in Liquid HF

9.7C: Electrolysis in Liquid HF

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9.7A: Physical Properties

Hydrofluoric acid is difficult to work with because is corrodes glass and silica giving gaseous SiF_4 or the $[SiF_6]_2^-$ so it must be stored in PTFE or dry Cu or Monel metalI.

$$4\,HF + SiO_2 \longrightarrow SiF_4 + 2\,H_2O \tag{9.7A.1}$$

Liquid range: 190 to 292.5 K
Relative permittivity 84 at 273 K; 175 at 200 K

Liquid HF undergoes self-ionization: Kself =2 x10-12 at 273 K

$$3\,HF \rightleftharpoons [H_2F]^+ + [HF_2]^- \tag{9.7A.2}$$

dihydridofluorine(1+) ion
difluorohydrogenate(1-) ion

Large electronegativity difference between H (xP = 2.2) and F (xP = 4.0) results in the presence of extensive intermolecular hydrogen bonding in the liquid.

- Hydrogen bonded molecules (~7 molecules on average) in liquid phase
- Cyclic (HF)x species are present in the gas phase

Warning

$HF\,(l)$ causes burns that are slow to heal or even get progressively worse. Exercise *extreme* caution if using this solvent.

Very few compounds exist which are strong enough F- acceptors to be considered acids. An example is SbF_5 which leads to pure HF having superacid properties. Pure HF has a dielectric constant of 84 and is a good solvent like water which is surprisingly gentle. It can be used for example to remove Fe from metalloproteins without damaging the apoprotein primary structure.

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9.7B: Acid-Base Behavior in Liquid HF

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9.7C: Electrolysis in Liquid HF

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9.8: Sulfuric Acid and Fluorosulfonic Acid

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9.8A: Physical Properties of Sulfuric Acid

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9.8B: Acid-Base Behaviour in Liquid H_2SO_4

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9.8C: Physical Properties of Fluorosulfonic Acid

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9.9: Superacids

The term *superacid* was originally coined by James Bryant Conant in 1927 to describe acids that were stronger than conventional mineral acids.[1] George A. Olah prepared the so-called magic acid, so-named for its ability to attack hydrocarbons, by mixing antimony pentafluoride (SbF_5) and fluorosulfonic acid (FSO_3H). The name was coined after a candle was placed in a sample of magic acid. The candle dissolved, showing the ability of the acid to protonate hydrocarbons, which under aqueous acidic conditions cannot be protonated.

At 140 °C , FSO_3H–SbF_5 converts methane into the tertiary-butyl carbocation, a reaction that begins with the protonation of methane:[2]

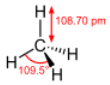
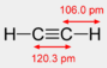
- $CH_4 + H^+ \rightarrow CH_5^+$
- $CH_5^+ \rightarrow CH_3^+ + H_2$
- $CH_3^+ + 3CH_4 \rightarrow (CH_3)_3C^+ + 3H_2$

Fluoroantimonic acid, $HSbF_6$, can produce solutions with H_0 down to –28.[3] Fluoroantimonic acid is made by combining HF and SbF_5. In this system, HF releases its proton (H^+) concomitant with the binding of F^- by antimony pentafluoride, which (as described below) is a Lewis acid. The resulting anion (SbF−6) is both a weak nucleophile and an extraordinarily weak base.

Superacids are useful in reactions such as the isomerization of alkanes. Industrially, anhydrous acid-exchanged zeolites, which are superacid catalysts, are used on a massive scale to isomerize hydrocarbons in the processing of crude oil to gasoline. Superbases such as lithium diethylamide ($LiNEt_2$), alkyllithium compounds (RLi), and Grignard reagents (RMgX) useful in a broad range of organic reactions. $LiNEt_2$ deprotonates C-H bonds to generate reactive carbanions. RLi and RMgX are powerful nucleophiles.

The use of superbases in nonaqueous media allows us to rank the acidities (and measure the pKa's) of different classes of molecules. This ranking is particularly important in understanding the reactions of organic molecules. Note that the order of acidities for hydrocarbons is alkynes >> alkenes, aromatics >> alkanes. This ordering has to do with the hybridization of the carbon atom that forms the carbanion. The negatively charged lone pair of the carbanion is stabilized in orbitals that have high s character (e.g., sp vs. sp^2 or sp^3). This is because s orbitals have finite probability density at the nucleus and "feel" the positive nuclear charge (thereby stabilizing the extra negative charge on carbon) more than p orbitals. Resonance effects also stabilize carbanions. Thus, cyclopentadiene is more acidic than even an alkyne because the negative charge is delocalized over the entire (aromatic) $C_5H_5^-$ ring when the C_5H_6 is deprotonated.

Table 3.1.1: Carbon acid acidities in pKa in DMSO. Reference acids in bold.

name	formula	structural formula	pKa
Methane	CH_4		~ 56
Propene	C_3H_6		~ 44
Benzene	C_6H_6		~ 43
Acetylene	C_2H_2		25
Cyclopentadiene	C_5H_6		18

https://en.Wikipedia.org/wiki/Superacid

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SECTION OVERVIEW

9.10: Bromine Trifluoride

Bromine trifluoride is an interhalogen compound with the formula BrF_3. It is a straw-colored liquid with a pungent odor. It is soluble in sulfuric acid but explodes on contact with water and organic compounds. It is a powerful fluorinating agent and an ionizing inorganic solvent. It is used to produce uranium hexafluoride (UF_6) in the processing and reprocessing of nuclear fuel.

Topic hierarchy

9.10A: Physical Properties

9.10B: Fluoride Salts and Molecular Fluorides in BrF_3

9.10C: Reactions in BrF_3

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9.10A: Physical Properties

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9.10B: Fluoride Salts and Molecular Fluorides in BrF_3

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9.10C: Reactions in BrF_3

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SECTION OVERVIEW

9.11: Dinitrogen Tetraoxide

Topic hierarchy

9.11A: Physical Properties of N_2O_4

9.11B: Reactions in N_2O_4

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9.11A: Physical Properties of N_2O_4

N_2O_4 is a red-brown liquid with a sharp, unpleasant chemical odor. Low-boiling (boiling point 21.15°C) and held as a liquid by compression. Density 1.448 g / cm3. Consists of an equilibrium mixture of brown NO2 (nitrogen dioxide) and colorless N2O4 (dinitrogen tetroxide). It is a good oxidizing and nitrating agent.

$$\mathrm{Li} + \mathrm{N_2O_4} \longrightarrow \mathrm{LiNO_3} + \mathrm{NO} \tag{9.11A.1}$$

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9.11B: Reactions in N_2O_4

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9.12: Ionic Liquids

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9.12A: Molten Salt Solvent Systems

When a solid salt melts, it forms a solution of the cations and anions. For example, KOH melts at temperatures above 400 °C and dissociates into K^+ and OH^- ions which can act as a solvent for chemical reactions. Because of the autodissociation of the OH^- solvent, water is always present in a molten KOH flux, according to the acid-base equilibrium:

$$2OH^- \rightleftharpoons H_2O + O^{2-} \tag{9.12A.1}$$

It follows that in this very basic solvent, water (the conjugate acid of the solvent) is the strongest acid that can exist. The conjugate base of the solvent, O^{2-}, is the strongest base. This autodissociation equilibrium allows for the acidity of a flux to be easily tuned through the addition or boiling off of water. A "wet" flux is more acidic, and can dissolve metal oxides that contain the basic O^{2-} anion. Conversely a "dry" flux is more basic and will cause oxides to precipitate. Molten hydroxide fluxes can thus be used in the synthesis of oxide crystals, such as the perovskite superconductor ($K_{1-X}Ba_XBiO_3$). Eutectic mixtures of NaOH and KOH are relatively low melting (≈ 200 °C) and can be used as solvents for crystallizing a variety of basic oxides

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9.12B: Ionic Liquids at Ambient Temperatures

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SECTION OVERVIEW

9.13: Supercritical Fluids

Topic hierarchy

9.13A: Properties of Supercritical Fluids and Their Uses as Solvents

9.13B: Supercritical Fluids as Media for Inorganic Chemistry

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9.13A: Properties of Supercritical Fluids and Their Uses as Solvents

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9.13B: Supercritical Fluids as Media for Inorganic Chemistry

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CHAPTER OVERVIEW

10: Hydrogen

In 1671, Robert Boyle discovered and described the reaction between iron filings and dilute acids, which resulted in the production of hydrogen gas. In 1766-81, Henry Cavendish was the first to recognize that hydrogen gas was a discrete substance, and that it produced water when burned. He named it "flammable air". In 1783, Antoine Lavoisier gave the element the name hydrogen (from the Greek υδρο- *hydro* meaning "water" and -γενης *genes* meaning "creator") when he and Pierre-Simon Laplace reproduced Cavendish's finding that water was produced when hydrogen was burned. Hydrogen was liquefied for the first time by James Dewar in 1898 by using *regenerative cooling* and his invention, the **vacuum flask**. He produced solid hydrogen the next year. **Deuterium** was discovered in December 1931 by Harold Urey, and **tritium** was prepared in 1934 by Ernest Rutherford, Mark Oliphant, and Paul Harteck. Heavy water, which consists of deuterium in the place of regular hydrogen, was discovered by Urey's group in 1932.

10.1: Hydrogen - The Simplest Atom
10.2: The \(H^+\) and \(H^-\) Ions
10.2A: The Hydrogen Ion (Proton)
10.2B: The Hydride Ion
10.3: Isotopes of Hydrogen
10.3A: Protium and Deuterium
10.3B: Kinetic Isotope Effects
10.3C: Deuterated Compounds
10.3D: Tritium
10.4: Dihydrogen
10.4A: Occurence
10.4B: Physical Properties
10.4C: Synthesis and Uses
10.4D: Reactivity
10.5: Polar and Non-Polar E-H Bonds
10.6: Hydrogen Bonding
10.6A: The Hydrogen Bond
10.6B: Trends in Boiling Points, Melting Points, and Enthalpies of Vaporization for p-block Binary Hydrides
10.6C: Infrared Spectroscopy
10.6D: Solid State Structures
10.6E: Hydrogen Bonding in Biological Systems
10.7: Binary Hydrides - Classification and General Properties
10.7A: Classification
10.7B: Metallic Hydrides
10.7C: Saline Hydrides
10.7D: Molecular Hydrides and Complexes Derived from them
10.7E: Covalent Hydrides with Extended Structures

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10.1: Hydrogen - The Simplest Atom

- Hydrogen (not carbon) forms more compounds than any other element! The isotopes are:
- - ^{1}H
  - ^{2}D (0.0156%)
  - ^{3}T (Formation: $^{14}N(p,n)^{14}O$ and then (using the neutron) $^{14}N(n,^{3}H)^{12}C$
    Abundance: 10^{-15} - 10^{-16} %, Decay: $^{3}H(b-)^{3}He$ $t_{½}$ = 12.35 y.
- The different name arise because isotope effects, which affect kinetics and equilibria, are especially marked for hydrogen.
- Deuterium is obtained by fractional distillation of water (or hydrogen sulphide?) or electrolysis of water. D_2O is used as a moderator in nuclear reacters and as a source of D for chemical studies of all sorts.
- Made in the lab from the action of acid on Zn or Fe and industrially by the catalysed reaction of steam with hydrocarbons, coal and other organic materials to give "synthesis gas, "syngas":

  $$CH_4 + H_2O \text{ alt } CO + H_2$$

  H_2 can also be made by the "water-gas reaction" and the catalysed "water-gas shift reaction":

  $$H_2O + CO \text{ alt } CO + H_2$$

  $$CO + H_2O \text{ alt } CO_2 + H_2$$

  The hydrogen can be isolated by absorption of the carbon dioxide, and removal of residual CO and CO_2. (The "syngas" is an important industrial raw material itself.)
- It, and "syngas" are used in the production of organics via alcohols:

  $$2CO + 4H_2 \text{ alt } CH_3CH_2OH + H_2O$$

  and the production of ammonia via the Haber process:

  $$N_2 + 3H_2 \text{ alt } 2NH_3$$
- Hydrogen has a bond energy of 434.1 kJ mol^{-1}. It will burn in air but reacts explosively with oxygen and some halogens via chain reactions:

  $$Br_2 + light \text{ alt } 2Br \text{ chain initiation}$$

  $$Br + H_2 \text{ alt } HBr + H \text{ chain propagation}$$

  $$H + Br_2 \text{ alt } HBr + Br$$

  $$H + HBr \text{ alt } H_2 + Br$$

  $$2Br \text{ alt } Br_2 \text{ chain termination}$$

  Notice there is no direct H-H bond fission in this processs.

The Bonding of Hydrogen

As mentioned before, hydrogen is found bonded in two covalent situations:

a. The complexed proton, e.g. H_3O^+ or NH_4^+, and "conventional" covalent situations, e.g. CH_4. The distinction between these two is rather artificial, except that the cations would have a rather more polarized and labile X-H bond, and are prone to transferring the proton to another molecule, i.e. behaviour as an acid.
b. Hydrides such as KH, which contain the H- ion.

It has some special ways of bonding as well:

1. The formation of metallic hydrides, that is, hydrides which have metallic properties as apposed to ionic H^- containing materials, for example $PdH_{0.4\text{-}0.7}$.

   Note that the density of Pd is = 11.99 g cm^{-3} or 11.99/106.42 = 0.113 mol cm^{-3}

   so in $PdH_{0.7}$ the density of hydrogen is 0.113 x 0.7 = 0.0789 mol cm^{-3} or 0.0789 x 1.008 = 0.0790 g cm^{-3}

i.e. more than liquid hydrogen where the density (at -252.78 ^{o}C) is 0.07099 g cm^{-3}!

The form of the hydrogen in metals is ambiguous: it tends to migrate towards the negative end of a potential gradient in wires, so it seems proton-like. On the other hand, salt like properties and M-H bond distances in some metal hydrides are more suggestive of H^- compounds. (Perhaps only a small part of the hydrogen is cationic in nature.)

2. The formation of covalent hydrogen bridges for example in B_2H_6 and $(CO)_5CrHCr(CO)_5$. These are prototypes for 2e$^-$ - 3-centre bonding.
3. A newish class of hydrogen bonds called "agostic" have been identified in certain transition metal compounds which seem to be a sort of frozen intermediate in the catalytic activation of C—H bonds. They come as "open" and "closed": alt
4. So called "hydrogen bonding" described in the following section.

The Hydrogen Bond

- When hydrogen is bonded to an electronegative element, X, usually F, O, N or Cl, and there is another molecule around with a Lewis base donor atom,Y , a very strong largely electrostatic bond can form: $X^{d-}—H^{d+}\cdots\cdots Y$ The X—H bond is slightly longer than it would be without the proximity of the Y, and the H$\cdots\cdots$Y "bond" is much longer than a H—Y bond would be. Usually, hydrogen bonding is identified if this distance appreciably less than the sum of the van der Waals' radii for H and Y (e.g. <(1.30 + 1.40) = 2.70 Å for H$\cdots\cdots$O. In many cases the position of the hydrogen must be inferred: in this case O—H should be about 0.37 + 0.70 = 1.07 Å so an O to O distance less than about 2.70 + 1.07 = 3.75 Å would imply a hydrogen bond is present.)
- The text refers to the case of crystalline $NaHCO_3$ where there are 4 O to O distances: 3.12, 3.15 and 3.19 Å which are well over the van der Waals' contact distance, and 2.55 Å which is somewhat less, and tells us where the H is to be found.
- The hydrogen bond can also be identified by a shift in the infra-red stretching frequency to lower wavelengths. It is also broadened and made more intense. For example, free O—H comes at 3500 cm^{-1} but can be lowered several hundred wave-numbers by H-bonding.
- The table below gives some approximate hyhdrogen bond enthalpies:

Bond	Energy kJ mol^{-1}
F—H$\cdots\cdots$F	30
N—H$\cdots\cdots$N	25
O—H$\cdots\cdots$O	25
N—H$\cdots\cdots$F	21
O—H$\cdots\cdots$N	20
C—H$\cdots\cdots$O	11
N—H$\cdots\cdots$O	10

- Hydrogen bonding affects boiling points (and heats of vaporization) producing some anomalies. See text Figure 9-1.
- There are specially stong hydrogen bonds that are 4e$^-$ - 3-centre bonds. Examples include [FHF]- with a centered proton and F to F distance of 2.26 Å.

Ice and Water

- There are 9 forms of ice which exist at high presssure, except the normal ice I.
- The normal hexagonal ice structure is depicted in Fig 9-2.
- In liquid water, an ice-like structure persists, but there are additional "interstitial" water molecules, and the whole system is "fluxional". The density of liquid water is greater than that of ice. The density is maximum at 4 ^{o}C.

Hydrates and Water Clathrates

Most hydrates are salts containing water in addition to the cations and anions. The water is sometimes in the first coodination sphere of the cations and is sometimes rather more loosely held:

$CuSO_4.5H_2O$ alt $CuSO_4.3H_2O$ alt $CuSO_4.H_2O$ alt $CuSO_4$ anhydrous

The water molecules are successively more difficult to remove, as the sulphate takes their place in the Cu^{2+} coordination sphere.

Sometimes the water is so tightly bound, a decomposition occurs on heating:

$ScCl_3.6H_2O$ alt $ScOCl + 2HCl + 5H_2O$

"Gas hydrates" are an example of a class of "clathrate" compounds:

a. There is a cubic symmetry form that features a 46-water molecule unit cell including six medium sized and two small cages. With the medium-sized cages trapping a "guest" molecule each the formula would be $X.(7.67)H_2O$. All eight cages filled would give $X.(5.76)H_2O$. Clathrates of the first type are known for Ar, Kr Xe, Cl_2, SO_2 and CH_3Cl (among others).
b. Another geometry, also cubic has 136 H_2O's in the unit cell and features 8 larger cages and 16 smaller ones. Molcules such as $CHCl_3$ and CH_3CH_2Cl can be trapped.
c. One other class made with the salts of R_4N^+ or R_3S^+ have the anions acting as part of the "host" structure. Examples are: $[(C_4H_9)_4N][C_6H_5CO_2].(39.5)H_2O$ or $[(C_4H_9)_3S]F.(20)H_2O$.

Hydrides

Many hydrogen compounds are collectively called hydrides, including many cases where the hydrogen is actually *less* electronegative than the atom to which it is bound, and which are not individually named hydrides, in addition to those where it is more electronegative, upto the saline hydrides containing H^-. In addition, there is the class of metallic hydrides, See Figure 9-4:

Covalent

1. Neutral - Group IVB (14) CH_4 (methane), SiH_4 (silane) etc
2. Somewhat basic - Group VB (15) NH_3, PH_3 (phosphine) etc
3. Weakly acidic - Group VIB (16) H_2O, H_2S (hydrogen sulphide) etc
4. Strongly acidic - Group VIIB (17) HCl, HI (hydrogen halides) etc
5. The boron hydrides (B_nH_m)
6. Hydride anions eg $LiAlH_4$ (alanate), $LiBH_4$ (borohydride or boranate)

   Preparation:

   ($8LiH + Al_2Cl_6$ alt $2LiAlH_4 + 6LiCl$)

   ($2NaH + B_2H_6$ alt $2NaBh_4$)

   Typical Reactions:

   $2LiAlH_4 + 2SiCl_4$ alt $2SiH_4 + 2LiCl + Al_2Cl_6$

   $I_2 + LiBH_4$ alt $B_2H_6 + 2NaI + H_2$

Saline

Some are made by direct reaction: M + H2 alt MH (Li - Cs)

or MH_2 (Mg - Ba)

The hydrides of Li and Be have covalent character, especially BeH_2 which is really a polymer. Most saline hydrides react violently with water to give H_2

They are also powerful hydride transfer reagents, sometimes useful for making other hydrides:

$B(OR)_3 + NaH$ alt $Na[BH(OR)_3]$

$4NaH + TiCl4$ alt $Ti^o + 4NaCl + 2H_2$

$NaH + ROH$ alt $NaOR + H_2$

Transition metal

These include the stoichiometric hydrides, for example UH_3 and $HCo(CO)_4$ and hydride anions, for example $[ReH_9]^{2-}$.

There are also the non-stoichiometric (interstitial) ones including $PdH_{0.7}$ and $ZrH_{1.9}$.

Dihydrogen as a Ligand

Dihydrogen complexes, where the hydrogen molecule is bonded sideways on to the metal, but the H-H bond is largely intact have been discovered only recently. The metal accepts electrons from the H-H s-orbital, and donates electrons back to the H-H s*-orbital. Both types of bonding should lead to weakening and ultimate cleavage of the H-H bond to give normal hydrides, and only very a few special cases short of this. An example is:



$W(CO)_3P(Pr^i_3)_2 + H_2$  $W(CO)_3P(Pr^i_3)_2(H_2)$

H-H by neutron diffraction = 0.75 Å, by X-ray diffraction = 0.84 Å and in H_2 = 0.74 Å

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SECTION OVERVIEW

10.2: The H + and H − Ions

Topic hierarchy

10.2A: The Hydrogen Ion (Proton)

10.2B: The Hydride Ion

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10.2A: The Hydrogen Ion (Proton)

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SECTION OVERVIEW

10.3: Isotopes of Hydrogen

Hydrogen has three naturally occurring isotopes, denoted ^{1}H, ^{2}H and ^{3}H. Other, highly unstable nuclei (^{4}H to ^{7}H) have been synthesized in the laboratory but are not observed in nature.

- ^{1}H is the most common hydrogen isotope with an abundance of more than 99.98%. Because the nucleus of this isotope consists of only a single proton, it is given the descriptive, but rarely used formal name of protium.
- ^{2}H, the other stable hydrogen isotope, is known as deuterium and contains one proton and one neutron in its nucleus. Essentially all deuterium in the universe is thought to have been produced at the time of the Big Bang, and has endured since that time. Deuterium is not radioactive, and does not represent a significant toxicity hazard. Water enriched in molecules that include deuterium instead of normal hydrogen is called heavy water. Deuterium and its compounds are used as a non-radioactive label in chemical experiments and in solvents for ^{1}H-NMR spectroscopy. Heavy water is used as a neutron moderator and coolant for nuclear reactors. Deuterium is also a potential fuel for commercial nuclear fusion.
- ^{3}H is known as tritium and contains one proton and two neutrons in its nucleus. It is radioactive, decaying into helium-3 through beta decay with a half-life of 12.32 years. It is sufficiently radioactive that it can be used in luminous paint, making it useful in such things as watches where the glass moderates the amount of radiation getting out. Small amounts of tritium occur naturally because of the interaction of cosmic rays with atmospheric gases; tritium has also been released during nuclear weapons tests. It is used in nuclear fusion reactions, as a tracer in isotope geochemistry, and specialized in self-powered lighting devices. Tritium has been used in chemical and biological labeling experiments as a radiolabel.

Hydrogen is the only element that has different names for its isotopes in common use today. During the early study of radioactivity, various heavy radioactive isotopes were given their own names, but these names are no longer used, except for deuterium and tritium.

nuclide symbol	Z(p)	N(n)	isotopic mass (u)	half-life	decay mode	Daughter Isotope	Isotopic composition
^{1}H	1	0	1.00782503207(10)	**Stable**	-	-	0.999885(70)
^{2}H - D	1	1	2.0141017778 (4)	**Stable**	-	-	0.000115(70)
^{3}H - T	1	2	3.0160492777 (25)	12.32(2) y	β	^{3}He	<1>17 atoms

Topic hierarchy

10.3A: Protium and Deuterium

10.3B: Kinetic Isotope Effects

10.3C: Deuterated Compounds

10.3D: Tritium

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10.3A: Protium and Deuterium

Properties of hydrogen

The difference of mass between isotopes of most elements is only a small fraction of the total mass and so this has very little effect on their properties, this is not the case for hydrogen. Consider chlorine with Z=17, there are 2 stable isotopes ^{35}Cl (75.77%) and ^{37}Cl (24.23%). The increase is therefore 2 in 35 or less than 6%. Deuterium and tritium are about double and triple the mass of protium and show significant physical and chemical differences particularly with regard to those properties related to mass, e.g. rate of diffusion, density, etc.

Some physical properties of the hydrogen isotopes.

isotope	MP /K	BP /K	ΔH_{diss} /kJmol^{-1}	Interatomic Distance /pm
H_2	13.99	20.27	435.99	74.14
D_2	18.73	23.67	443.4	74.14
T_2	20.62	25.04	446.9	74.14

Differences between H_2O and D_2O

Property	H_2O	D_2O
Melting point /K	273.15	276.97
Boiling point /K	373.15	374.5
Temperature of maximum density /K	277	284.2
Maximum density /g cm^3	0.99995	1.1053
Relative permittivity (at 298 K)	78.39	78.06
Kw (at 298 K)	1 *10^{14}	2 * 10^{15}
Symmetric stretch, ν_1 /cm^{-1} (gaseous molecule)	3657	2671

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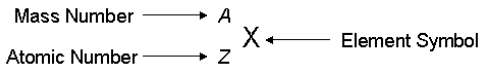
10.3B: Kinetic Isotope Effects

The **kinetic isotope effect** (KIE) is a phenomenon associated with isotopically substituted molecules exhibiting different reaction rates. Isotope effects such as KIEs are invaluable tools in both physical and biological sciences and are used to aid in the understanding of reaction kinetics, mechanisms, and solvent effects.

Introduction

Research was first introduced on this topic over 50 years ago and has grown into an enormous field. The scientists behind much of the understanding and development of kinetic isotope effects were Jacob Bigeleisen and Maria Goeppert Mayer who published the first paper on isotope effects [J. Chem. Phys., 15, 261 (1947)]. Kinetic isotope effects specifically explore the change in rate of a reaction due to isotopic substitution.

An element is identified by its symbol, mass number, and atomic number. The atomic number is the number of protons in the nucleus while the mass number is the total number of protons and neutrons in the nucleus. Isotopes are two atoms of the same element that have the same number of protons but different numbers of neutrons. Isotopes are specified by the mass number.



As an example consider the two isotopes of chlorine, you can see that their mass numbers vary, with ^{35}Cl being the most abundant isotope, while their atomic numbers remain the same at 17.

$$^{35}Cl \text{ and } ^{37}Cl \tag{10.3B.1}$$

The most common isotope used in light atom isotope effects is hydrogen (^{1}H) commonly replaced by its isotope deuterium (^{2}H). Note: Hydrogen also has a third isotope, tritium (^{2}H). Isotopes commonly used in heavy atom isotope effects include carbon (^{12}C, ^{13}C, nitrogen (^{14}N, ^{15}N), oxygen, sulfur, and bromine. Not all elements exhibit reasonably stable isotopes (i.e. Fluorine, ^{19}F), but those that due serve as powerful tools in isotope effects.

Potential Energy Surfaces

Understanding potential energy surfaces is important in order to be able to understand why and how isotope effects occur as they do. The harmonic oscillator approximation is used to explain the vibrations of a diatomic molecule. The energies resulting from the quantum mechanic solution for the harmonic oscillator help to define the internuclear potential energy of a diatomic molecule and are

$$E_n = \left(n + \frac{1}{2}\right) h\nu \tag{10.3B.2}$$

where

- n is a positive integer (n=1,2,3...),
- h is Planck's constant and
- ν is the frequency of vibration.

The Morse potential is an analytic expression that is used as an approximation to the intermolecular potential energy curves:

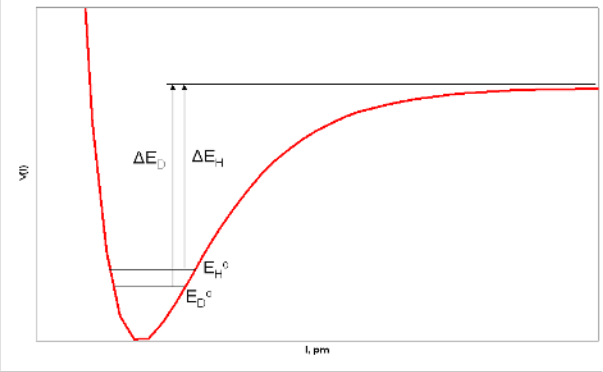
$$V(l) = D_e\left(1 - e^{-\beta(l-l_o)}\right)^2 \tag{10.3B.3}$$

where

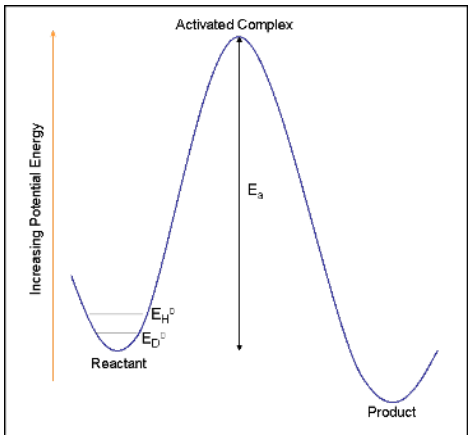
- $V(l)$ is the potential energy,
- D_e is the dissociation energy of the molecule,
- β is the measure of the curvature of the potential at its minimum,
- l is displacement, and
- l_o is the equilibrium bond length.

The D_e, β, and l_o variables can be looked up in a textbook or CRC handbook.

Below is an example of a Morse potential curve with the zero point vibrational energies of two isotopic molecules (for example R-H and R-D where R is a group/atom that is much heavier than H or D). The y-axis is potential energy and the x axis is internuclear distance. In this figure E_D^o and E_H^o correspond to the zero point energies of deuterium and hydrogen. The zero point energy is the lowest possible energy of a system and equates to the ground state energy. Zero point energy is dependent upon the reduced mass of the molecule as will be shown in the next section. The heavier the molecule or atom, the lower the frequency of vibration and the smaller the zero point energy. Lighter molecules or atoms have a greater frequency of vibration and a higher zero point energy. We see this is the figure below where deuterium is heavier than hydrogen and therefore has the lower zero point energy.



This results in different bond dissociation energies for R-D and R-H. The bond dissociation energy for R-D (E_D) is greater than the bond dissociation energy of R-H (E_H). This difference in energy due to isotopic replacement results in differing rates of reaction, the effect that is measured in kinetic isotope effects. The reaction rate for the conversion of R-D is slower than the reaction rate for the conversion of R-H.



It is important to note that isotope replacement does not change the electronic structure of the molecule or the potential energy surfaces of the reactions the molecule may undergo. Only the rate of the reaction is affected.

Activation Energies

The energy of the vibrational levels of a vibration (i.e., a bond) in a molecule is given by

$$E_n = \left(n + \frac{1}{2}\right) h\nu \tag{10.3B.4}$$

where we assume that the molecule is in its ground state and we can compare zero-point vibrational energies,

$$E_o = \left(\frac{1}{2}\right) hv \tag{10.3B.5}$$

Using the harmonic oscillator approximation the fundamental vibrational frequency is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{10.3B.6}$$

where

- k is the force constant of the bond and
- μ is the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{10.3B.7}$$

The Arrhenius equation is used to determine reaction rates and activation energies and since we are interested in the change in rate of reactions with different isotopes, this equation is very important,

$$k = Ae^{-\frac{E_a}{kT}} \tag{10.3B.8}$$

where

- k is the reaction rate,
- E_a is the activation energy, and
- A is the Arrhenius constant.

The Arrhenius equation can be used to compare the rates of a reaction with R-H and R-D,

$$k_H = A_H e^{-\frac{E_a^H}{kT}} \tag{10.3B.9}$$

$$k_D = A_D e^{-\frac{E_a^D}{kT}} \tag{10.3B.10}$$

where k_H and k_D are the rates of reaction associated with R-H and the isotope substituted R-D. We will then assume the Arrhenius constants are equal ($A_H = A_D$). The ratio of the rates of reaction gives an approximation for the isotope effect resulting in:

$$\frac{k_H}{k_D} = e^{-\frac{E_a^H - E_a^D}{kT}} \tag{10.3B.11}$$

By using the relationship that for both R-H and R-D

$$E_o = \left(\frac{1}{2}\right) h\nu \tag{10.3B.12}$$

a substitution can be made resulting in

$$\frac{k_H}{k_D} = e^{\frac{h(\nu_H - \nu_D)}{2kT}} \tag{10.3B.13}$$

The vibrational frequency (Equation 5) can then be substituted for R-H and R-D and the value of the expected isotope effect can be calculated.

$$\frac{k_H}{k_D} = e^{\frac{h\left(\frac{k_{RH}}{\mu_{RH}} - \frac{k_{RD}}{\mu_{RD}}\right)}{4\pi kT}} \tag{10.3B.14}$$

The same general procedure can be followed for any isotope substitution.

In summary, the greater the mass the more energy is needed to break bonds. A heavier isotope forms a stronger bond. The resulting molecule has less of a tendency to dissociate. The increase in energy needed to break the bond results in a slower reaction rate and the observed isotope effect.

Kinetic Isotope Effects

Kinetic Isotope Effects (KIEs) are used to determine reaction mechanisms by determining rate limiting steps and transition states and are commonly measured using NMR to detect isotope location or GC/MS to detect mass changes. In a KIE experiment an atom is replaced by its isotope and the change in rate of the reaction is observed. A very common isotope substitution is when hydrogen

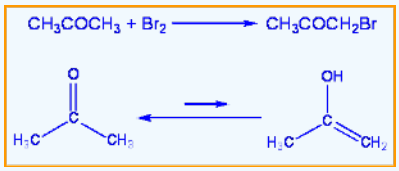
is replaced by deuterium. This is known as a deuterium effect and is expressed by the ratio k_H/k_D (as explained above). Normal KIEs for the deuterium effect are around 1 to 7 or 8. Large effects are seen because the percentage mass change between hydrogen and deuterium is great. Heavy atom isotope effects involve the substitution of carbon, oxygen, nitrogen, sulfur, and bromine, with effects that are much smaller and are usually between 1.02 and 1.10. The difference in KIE magnitude is directly related to the percentage change in mass. Large effects are seen when hydrogen is replaced with deuterium because the percentage mass change is very large (mass is being doubled) while smaller percent mass changes are present when an atom like sulfur is replaced with its isotope (increased by two mass units).

Primary KIEs

Primary kinetic isotope effects are rate changes due to isotopic substitution at a site of bond breaking in the rate determining step of a reaction.

Example

Consider the bromination of acetone: kinetic studies have been performed that show the rate of this reaction is independent of the concentration of bromine. To determine the rate determining step and mechanism of this reaction the substitution of a deuterium for a hydrogen can be made.



When hydrogen was replaced with deuterium in this reaction a $\frac{k_H}{k_D}$ of 7 was found. Therefore the rate determining step is the tautomerization of acetone and involves the breaking of a C-H bond. Since the breaking of a C-H bond is involved, a substantial isotope effect is expected.

Heavy Atom Isotope Effects

A rule of thumb for heavy atom isotope effects is that the maximum isotopic rate ratio is proportional to the square root of the inverse ratio of isotopic masses.



- Expected:

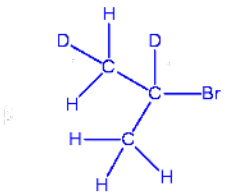
$$\frac{k_{32}}{k_{34}} = \sqrt{\frac{34}{32}} = 1.031 \tag{10.3B.15}$$

- Experimental:

$$\frac{k_{32}}{k_{34}} = 1.072 \tag{10.3B.16}$$

Secondary KIEs

Secondary kinetic isotope effects are rate changes due to isotopic substitutions at a site other than the bond breaking site in the rate determining step of the reaction. These come in three forms: α, β, and γ effects.



β secondary isotope effects occur when the isotope is substituted at a position next to the bond being broken.

$$(CH_3)_2CHBr + H_2O \xrightarrow{k_H} (CH_3)_2CHOH \quad (10.3B.17)$$

$$(CD_3)_2CHBr + H_2O \xrightarrow{k_D} (CD_3)_2CHOH \quad (10.3B.18)$$

This is thought to be due to hyperconjugation in the transition state. Hyperconjugation involves a transfer of electron density from a sigma bond to an empty p orbital (for more on hyperconjugation see outside links).

Solvent Effects in Reactions

Reactions may be affected by the type of solvent used (for example H_2O to D_2O or ROH to ROD). There are three main ways solvents effect reactions:

1. The solvent can act as a reactant resulting in a primary isotope effect.
2. Rapid hydrogen exchange can occur between substrate molecules labeled with deuterium and hydrogen atoms in the solvent. Deuterium may change positions in the molecule resulting in a new molecule that is then reacted in the rate determining step of the reaction.
3. The nature of solvent and solute interactions may also change with differing solvents. This could change the energy of the transition state and result in a secondary isotope effects.

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Problems

1. Describe the difference between primary and secondary kinetic isotope effects.
2. Estimate the k_{N-H}/k_{N-D} for a deuterium substitution on nitrogen given that v_H=9.3x1013 Hz and the activation energy is equal to 5.31 kJ/mol.
3. Using the 'rule of thumb' for heavy isotope effects, calculate the expected effect for a bromine isotope substitution, ^{79}Br and ^{81}Br.
4. Explain some of the main ways kinetic isotope effects are used.
5. As discussed, the rate-limiting step in the bromination of acetone is the breaking of a carbon-hydrogen bond. Estimate kC-H/KC-D for this reaction at 285 K. (Given: vtilde$_{C-H}$=3000 cm^{-1} and vtilde$_{C-D}$=2100 cm^{-1})

Solutions

1. Primary isotope effects involve isotopic substitution at the bond being broken in a reaction, while secondary isotope effects involve isotopic Substitution on bonds adjacent to the bond being broken.
2. 8.5
3. 1.0126
4. To determine reaction mechanisms, to determine rate limiting steps in reactions, to determine transition states in reactions.
5. 9.685

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10.3C: Deuterated Compounds

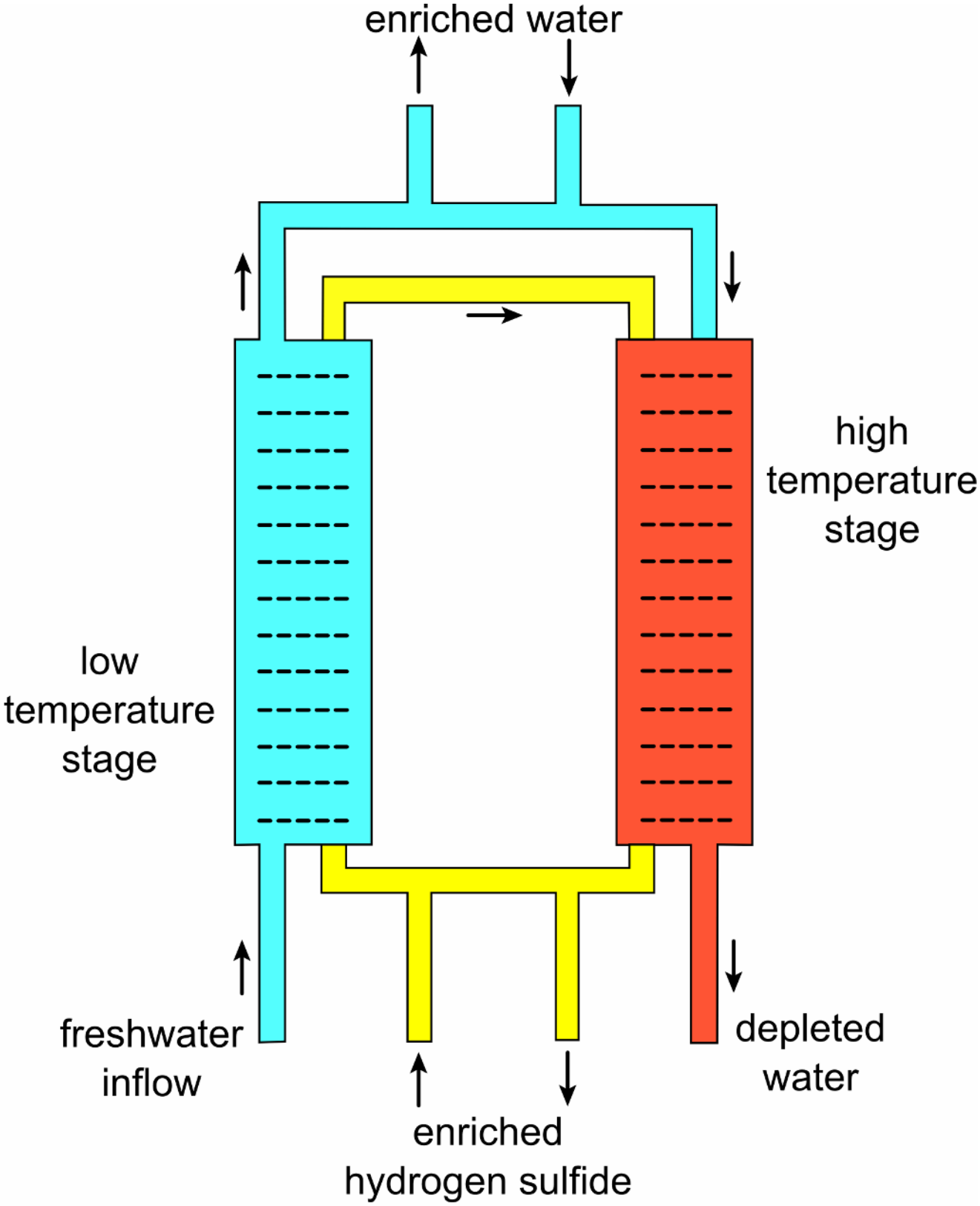
Heavy Water

Given that the boiling point of D_2O is 101.4 °C (compared to 100.0 °C for H_2O), evaporation or fractional distillation can be used to increase the concentration of deuterium in a sample of water by the selective removal of the more volatile light water, H_2O. Thus bodies of water that have no outlet, such as the Great Salt Lake in Utah, USA and the Dead Sea in the Jordan Rift Valley, which maintain their level solely by evaporation, have significantly higher concentrations of deuterated water than do lakes or seawater with at least one outlet.

Heavy water is 10.6% denser than ordinary water, a difference not immediately obvious since they are otherwise physically and chemically similar. The difference can be observed by freezing a sample and dropping it into normal water, where it sinks. With respect to taste and smell, rats given a choice between distilled normal water and heavy water avoided the heavy water, based on smell, and it may be that they detected a different taste as well.

The difference in weight increases the strength of water's hydrogen-oxygen bonds, and this in turn is sufficient to cause differences that are important to some biochemical reactions. The human body naturally contains deuterium equivalent to about five grams of heavy water, which is harmless. When a large fraction of water (> 50%) in higher organisms is replaced by heavy water, the result is cell dysfunction and death.

In normal water, about 1 molecule in 3,200 is HDO (one hydrogen in 6,400 is in the form of D), and heavy water molecules (D_2O) only occur in a proportion of about 1 molecule in 41 million (i.e. one in $6{,}400^2$). Thus semiheavy water molecules are far more common than "pure" (homoisotopic) heavy water molecules. Deuterium oxide was initially obtained by the electrolysis of ordinary water over a considerable period of time. This method of production requires a large cascade of stills or electrolysis chambers and consumes large amounts of power, so that chemical methods are generally now preferred. The most important chemical method is the Girdler sulfide process.



In this process, demineralised and deaerated water is trickled through a series of perforated (seive) plates in a tower, while hydrogen sulfide gas (BP -60 °C) flows upward through the perforations. Deuterium migration preferentially takes place from the gas to the liquid water. This "enriched" water from the cold tower (maintained at 32 °C) is fed to the hot tower (at 130 °C) where

deuterium transfer takes place from the water to the hydrogen sulfide gas. An appropriate "cascade" setup accomplishes enrichment via the reversible reaction:

$$H_2O + HDS \rightleftharpoons HDO + H_2S \tag{10.3C.1}$$

The equilibrium constant, K for, this reaction in terms of the concentrations, can be written as:

K = ([HDO][H_2S]) / ([H_2O][HDS]) or alternatively:

K = ([HDO]/[H_2O]) / ([HDS]/[H_2S])

If H and D were the same chemically, the equilibrium constant for the reaction would be equal to unity. However, what is found is that K is not equal to unity, and furthermore it is temperature dependent:

at 25 °C, K = 2.37
at 128 °C, K = 1.84

From the above information, at 32 °C, the equilibrium favours the concentration of deuterium in water. However, at around 130 °C, the equilibrium is now relatively more favorable to the concentration of deuterium in the hydrogen sulfide. In other words, the concentration of HDO in H_2O is greater than the concentration of HDS in H_2S but the relative concentration of HDS in H_2S increases with increasing temperature, making it possible to separate D from H.

In the first stage, the gas is enriched from 0.015% deuterium to 0.07%. The second column enriches this to 0.35%, and the third column achieves an enrichment between 10% and 30% deuterium oxide, D_2O. Further enrichment to "reactor-grade" heavy water (> 99% D_2O) still requires distillation or electrolysis. The production of a single litre of heavy water requires ~340,000 litre of feed water.

In 1934, Norway built the first commercial heavy water plant with a capacity of 12 tonnes per year. From 1940 and throughout World War II, the plant was under German control and the Allies decided to destroy the plant and its heavy water to inhibit German development of nuclear weapons. In late 1942, a planned raid by British airborne troops failed, both gliders crashing. The raiders were killed in the crash or subsequently executed by the Germans. On the night of 27 February 1943 Operation Gunnerside succeeded. Norwegian commandos and local resistance managed to demolish small, but key parts of the electrolytic cells, dumping the accumulated heavy water down the factory drains. Had the German nuclear program followed similar lines of research as the United States Manhattan Project, the heavy water would not have been crucial to obtaining plutonium from a nuclear reactor, but the Germans did not discover the graphite reactor design used by the allies for this purpose.

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10.3D: Tritium

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SECTION OVERVIEW

10.4: Dihydrogen

Hydrogen is a colorless, odorless and tasteless gas that is the most abundant element in the known universe. It is also the lightest (in terms of atomic mass) and the simplest, having only one proton and one electron (and no neutrons in its most common isotope). It is all around us. It is a component of water (H_2O), fats, petroleum, table sugar ($C_6H_{12}O_6$), ammonia (NH_3), and hydrogen peroxide (H_2O_2)—things essential to life, as we know it.

Topic hierarchy

10.4A: Occurence

10.4B: Physical Properties

10.4C: Synthesis and Uses

10.4D: Reactivity

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10.4A: Occurence

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10.4B: Physical Properties

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10.4C: Synthesis and Uses

In the laboratory, H_2 can be prepared by the action of a dilute non-oxidizing acid on a reactive metal such as zinc, with a Kipp's apparatus.

$$Zn + 2\,H\,(aq)^{+} \rightleftharpoons Zn\,(aq)^{2+} + H_2$$

Aluminium can produce H_2 upon treatment with bases:

$$2\,Al + 6\,H_2O + 2\,OH^{-} \rightleftharpoons 2\,Al(OH)_4{}^{-} + 3\,H_2$$

The electrolysis of water is another simple method of producing hydrogen. A low voltage current is passed through the water, and gaseous dioxygen forms at the anode while gaseous hydrogen forms at the cathode. Typically the cathode is made from platinum or other inert metal when producing hydrogen for storage. If, however, the gas is to be burnt on site, oxygen is desirable to assist the combustion, and so both electrodes would be made from inert metals. (Iron, for instance, would oxidize, and thus decrease the amount of oxygen given off.) The theoretical maximum efficiency (electricity used versus energetic value of hydrogen produced) is in the range 80-94%.

$$2\,H_2O\,(l) \rightleftharpoons 2\,H_2\,(g) + O_2\,(g)$$

In 2007, it was discovered that an alloy of aluminum and gallium in pellet form added to water could be used to generate hydrogen. The process creates alumina, but the expensive gallium, which prevents the formation of an oxide skin on the pellets, can be re-used. This has important potential implications for a hydrogen economy, as hydrogen could be produced on-site without the need of being transported.

Industrial preparation of hydrogen

Steam reforming is a method for producing hydrogen, carbon monoxide or other useful products from hydrocarbon fuels such as natural gas. This is achieved in a processing device called a reformer which reacts steam at high temperature with the fossil fuel.

At high temperatures (700 - 1100 °C) and in the presence of a metal-based catalyst (nickel), steam reacts with methane to yield carbon monoxide and hydrogen.

$$CH_4 + H_2O \longrightarrow CO + 3\,H_2$$

In order to produce more hydrogen from this mixture, more steam is added and the water gas shift reaction is carried out:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

The mixture of CO and H_2 is called "synthesis gas or syngas". Syngas is used as an intermediate in producing synthetic petroleum for use as a fuel or lubricant via the Fischer-Tropsch process and previously the Mobil methanol to gasoline process.

Enzymatic route from xylose

In 2013 a low-temperature, 50 °C, atmospheric-pressure, enzyme-driven process to convert xylose into hydrogen with nearly 100% of the theoretical yield was announced. The process employed 13 enzymes, including a novel **polyphosphate xylulokinase** (XK).

It was noted that: "Approximately 50 million metric tons of dihydrogen are produced annually from nonrenewable natural gas, petroleum, and coal. H_2 production from water remains costly. Technologies for generating H_2 from less costly biomass, such as microbial fermentation, enzymatic decomposition, gasification, steam reforming, and aqueous phase reforming, all suffer from low product yields."

Applications of Hydrogen

Large quantities of H_2 are used by the petroleum and chemical industries. The largest application of H_2 is for the processing ("upgrading") of fossil fuels, and in the production of ammonia. The key consumers of H_2 in the petrochemical plant include hydrodealkylation, hydrodesulfurization, and hydrocracking. H_2 has several other important uses. H_2 is used as a hydrogenating agent, particularly in increasing the level of saturation of unsaturated fats and oils (found in items such as margarine), and in the production of methanol. It is similarly the source of hydrogen in the manufacture of hydrochloric acid. H_2 is used as a reducing

agent of metallic ores.

Nitrogen is a strong limiting nutrient in plant growth. Carbon and oxygen are also critical, but are more easily obtained by plants from soil and air. Even though air is 78% nitrogen, atmospheric nitrogen is nutritionally unavailable because nitrogen molecules are held together by strong triple bonds. Nitrogen must be 'fixed', i.e. converted into some bioavailable form, through natural or man-made processes. It was not until the early 20th century that Fritz Haber developed the first practical process to convert atmospheric nitrogen to ammonia, which is nutritionally available.

Fertilizer generated from ammonia produced by the Haber process is estimated to be responsible for sustaining one-third of the Earth's population. It is estimated that half of the protein within human beings is made of nitrogen that was originally fixed by this process; the remainder was produced by nitrogen fixing bacteria and archaea.

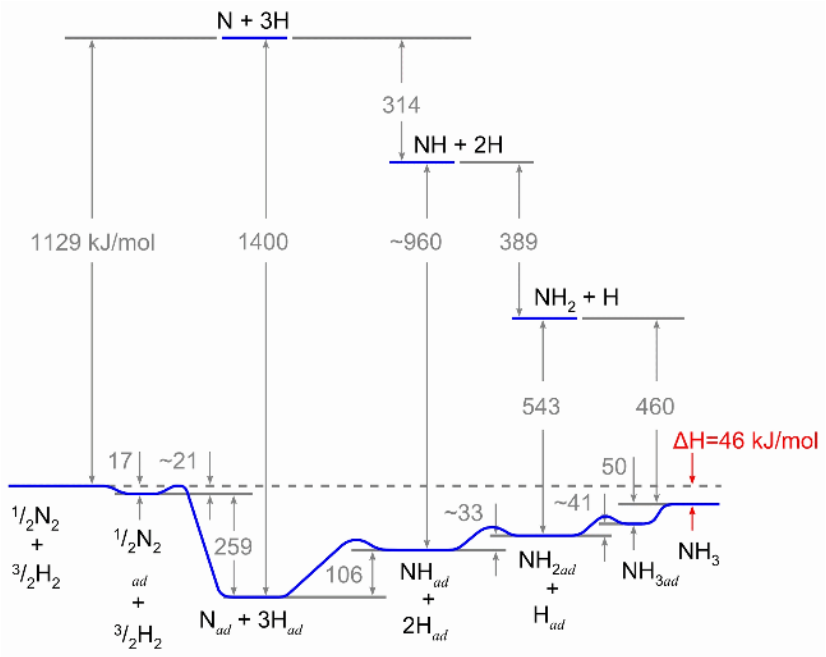
Dozens of chemical plants worldwide produce ammonia, consuming more than 1% of all man-made power. Ammonia production is thus a significant component of the world energy budget. Modern ammonia-producing plants depend on industrial hydrogen production to react with atmospheric nitrogen using a magnetite catalyst or over a promoted Fe catalyst under high pressure (100 standard atmospheres (10,000 kPa)) and temperature (450 °C) to form anhydrous liquid ammonia. This step is known as the ammonia synthesis loop (also referred to as the **Haber-Bosch process**):

$$3\,H_2 + N_2 \rightleftharpoons 2\,NH_3 \;\Delta H = -92.4\,kJ\,mol^{-1}$$

Nitrogen (N_2) is very unreactive because the molecules are held together by strong triple bonds. The Haber process relies on catalysts that accelerate the cleavage of this triple bond.

At room temperature, the equilibrium is strongly in favor of ammonia, but the reaction doesn't proceed at a detectable rate. Thus two opposing considerations are relevant to this synthesis. One possible solution is to raise the temperature, but because the reaction is exothermic, the equilibrium quickly becomes quite unfavourable at atmospheric pressure. Low temperatures are not an option since the catalyst requires a temperature of at least 400 °C to be efficient. By increasing the pressure to around 200 atm the equilibrium concentrations are altered to give a profitable yield.

The reaction scheme, involving the heterogeneous catalyst, is believed to involve the following steps:



1. N_2 (g) → N_2 (adsorbed)

2. N_2 (adsorbed) → 2 N (adsorbed)
3. H_2(g) → H_2 (adsorbed)
4. H_2 (adsorbed) → 2 H (adsorbed)
5. N (adsorbed) + 3 H (adsorbed) → NH_3 (adsorbed)
6. NH_3 (adsorbed) → NH_3 (g)

Reaction 5 actually consists of three steps, forming NH, NH_2, and then NH_3. Experimental evidence suggests that reaction 2 is the slow, rate-determining step. This is not unexpected given that the bond broken, the nitrogen triple bond, is the strongest of the bonds that must be broken.

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10.4D: Reactivity

The position of H in the Periodic Table

In some respects, H does not seem to have a perfect position in the Periodic Table and so many designers have it in more than one position, e.g. in Group 1 or Group 17 and even in Group 14.

Ionization energy of hydrogen

Hydrogen has a single outer electron, like the alkali metals, but they all form positive ions quite readily whereas hydrogen has little tendency to do so. Hydrogen often tends to share its electron with nonmetals rather than losing it to them.

The first ionization energies for H, Li, Na and K are 1312, 520.2, 495.8 and 418.8 $kJmol^{-1}$. The high IE for H (even bigger than for Xe) can be attributed to the very small size of the atom and the strong attractive force between the proton and electron.

$H(g) \rightarrow H^+(g) + e \; \Delta H^{\ominus} = 1312 \; kJmol^{-1}$

$Xe(g) \rightarrow Xe^+(g) + e \; \Delta H^{\ominus} = 1170 \; kJmol^{-1}$

The free proton can only be obtained under extreme conditions such as by an electric arc or in a discharge tube and even then only exists for about half a second. H^+ can be found in solvated form where the solvation energy provides the energy needed to overcome the very high ionization energy. Examples are in ammonia, alcohol or water with species like NH_4^+, ROH_2^+ and $H_3O_4^+$ being formed.

The hydrated proton ($H_3O_4^+$) will be covered in Lecture 6 on acid-base chemistry.

Electron affinity of hydrogen

Hydrogen, like the halogens, exists as diatomic molecules and H atoms have electron configurations with one electron short of a filled outer shell hence the idea of placing H in Group 17. However unlike the halogens with large EA values, the EA for hydrogen is quite small. The formation of H^- is much less favourable than the formation of a chloride ion, as seen from the thermodynamic profiles below and it is rare whereas halide ions are common and stable. In addition H has a lower electronegativity value than any of the halogens.

Much more energy is required as well to break the H-H bond compared to the Cl-Cl bond where the steps for comparison are: $\frac{1}{2}H_2$ (g) $\rightarrow$ H· (g) $\Delta H = 218 \; kJmol^{-1}$
H· (g) + e $\rightarrow$ H^- (g) $\Delta H = -72.8 \; kJmol^{-1}$
so overall for hydrogen
$\frac{1}{2}H_2$ (g) + e $\rightarrow$ H^- (g) $\Delta H = +145.2 \; kJmol^{-1}$
and
$\frac{1}{2}Cl_2$ (g) $\rightarrow$ Cl· (g) $\Delta H = 121 \; kJmol^{-1}$
Cl· (g) + e $\rightarrow$ Cl^- (g) $\Delta H = -348.6 \; kJmol^{-1}$
overall for chlorine
$\frac{1}{2}Cl_2$ (g) + e $\rightarrow$ Cl^- (g) $\Delta H = -227.6 \; kJmol^{-1}$ As a result, only the most active elements, whose Ionization Energies are low, can form ionic hydrides, e.g. NaH.

The covalent radius for H is 37 pm and the estimated radius for H^- is ~140 pm indicating a substantial increase. This comes about as a result of the interelectronic repulsion when a second electron is added to the 1s atomic orbital. All the alkali metal hydrides crystallize with the NaCl-type structure and are all considered ionic. They are sometimes called "saline" hydrides.

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10.5: Polar and Non-Polar E-H Bonds

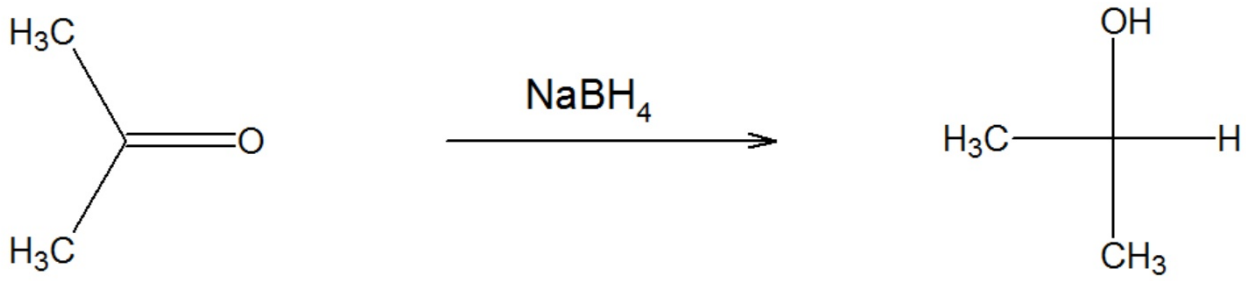
Hydride reducing agents

LiH and Al_2Cl_6 gives lithium aluminium hydride (lithal $LiAlH_4$), NaH reacts with $B(OCH_3)_3$ to give sodium borohydride ($NaBH_4$). These find wide scope and utility in organic chemistry as reducing agents.

$LiAlH_4$ is commonly used for the reduction of esters and carboxylic acids to primary alcohols; previously this was a difficult conversion that used sodium metal in boiling ethanol (the Bouveault-Blanc reduction). The solid is dangerously reactive toward water, releasing gaseous hydrogen (H_2). Some related derivatives have been discussed for hydrogen storage.

$NaBH_4$ is used in large amounts for the production of sodium dithionite from sulfur dioxide: Sodium dithionite is used as a bleaching agent for wood pulp and in the dyeing industry. $NaBH_4$ consists of the tetrahedral BH_4^- anion in the crystalline form and is found to exist as three polymorphs: α, β and γ. The stable phase at room temperature and pressure is α-$NaBH_4$, which is cubic and adopts an NaCl-type structure. Millions of kilograms are produced annually, far exceeding the production levels of any other hydride reducing agent.

$NaBH_4$ will reduce many organic carbonyls, depending on the precise conditions. Most typically, it is used in the laboratory for converting ketones and aldehydes to alcohols. For example, reduction of acetone (propanone) to give propan-2-ol.



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SECTION OVERVIEW

10.6: Hydrogen Bonding

Topic hierarchy

10.6A: The Hydrogen Bond

10.6B: Trends in Boiling Points, Melting Points, and Enthalpies of Vaporization for p-block Binary Hydrides

10.6C: Infrared Spectroscopy

10.6D: Solid State Structures

10.6E: Hydrogen Bonding in Biological Systems

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10.6A: The Hydrogen Bond

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10.6B: Trends in Boiling Points, Melting Points, and Enthalpies of Vaporization for p-block Binary Hydrides

Hydrogen bonds

A hydrogen bond is the name given to the electrostatic attraction between polar molecules that occurs when a hydrogen (H) atom bound to a highly electronegative atom such as nitrogen (N), oxygen (O) or fluorine (F) experiences attraction to some other nearby highly electronegative atom. The name is something of a misnomer, as it represents a particularly strong dipole-dipole attraction, rather than a typical covalent bond.

The 2011 IUPAC definition specifies that "*The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X-H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.*"

These hydrogen-bond attractions can occur between molecules (intermolecular) or within different parts of a single molecule (intramolecular). The hydrogen bond (5 to 30 kJ/mole) is stronger than a van der Waals interaction, but weaker than covalent or ionic bonds. This type of bond can occur in inorganic molecules such as water and in organic molecules like DNA and proteins.

Intermolecular hydrogen bonding is responsible for the high boiling point of water (100 °C) compared to the other group 16 hydrides that have no hydrogen bonds. Intramolecular hydrogen bonding is partly responsible for the secondary and tertiary structures of proteins and nucleic acids. It plays an important role in the structure of polymers, both synthetic and natural.

BP's of MG hydrides with Noble gases for comparison /K

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10.6C: Infrared Spectroscopy

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10.6D: Solid State Structures

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10.6E: Hydrogen Bonding in Biological Systems

Hydrogen bonding in biological systems.

Base pairs, which form between specific nucleobases (also termed nitrogenous bases), are the building blocks of the DNA double helix and contribute to the folded structure of both DNA and RNA. Dictated by specific hydrogen bonding patterns, Watson-Crick base pairs (guanine-cytosine and adenine-thymine) allow the DNA helix to maintain a regular helical structure that is subtly dependent on its nucleotide sequence. The complementary nature of this based-paired structure provides a backup copy of all genetic information encoded within double-stranded DNA. The regular structure and data redundancy provided by the DNA double helix make DNA well suited to the storage of genetic information, while base-pairing between DNA and incoming nucleotides provides the mechanism through which DNA polymerase replicates DNA, and RNA polymerase transcribes DNA into RNA. Many DNA-binding proteins can recognize specific base pairing patterns that identify particular regulatory regions of genes.

Hydrogen bonding in base pairs

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SECTION OVERVIEW

10.7: Binary Hydrides - Classification and General Properties

Binary hydrides are a class of compounds that consist of an element bonded to hydrogen, in which hydrogen acts as the more electronegative species. Free hydride anions exist only under extreme conditions. Instead, most hydride compounds have hydrogen centers with a hydridic character.

Topic hierarchy

10.7A: Classification

10.7B: Metallic Hydrides

10.7C: Saline Hydrides

10.7D: Molecular Hydrides and Complexes Derived from them

10.7E: Covalent Hydrides with Extended Structures

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10.7A: Classification

Compounds of Hydrogen

The chemistry of hydrogen depends mainly on four processes:

1. donation of the valency electron to form the hydrogen ion, H^+
2. accepting an electron to form the hydride ion H^-
3. sharing the electron with a partner atom to form a pair bond (covalent bond) H-H
4. sharing the electron with an ensemble of atoms to form a metallic bond $H\cdot$

While H_2 is not very reactive under standard conditions, it does form compounds with most elements. Hydrogen can form compounds with elements that are more electronegative, such as halogens (e.g., F, Cl, Br, I), or oxygen; in these compounds hydrogen takes on a partial positive charge. When bonded to fluorine, oxygen, or nitrogen, hydrogen can participate in a form of medium-strength noncovalent bonding called hydrogen bonding, which is critical to the stability of many biological molecules. Hydrogen also forms compounds with less electronegative elements, such as the metals and metalloids, in which it takes on a partial negative charge. These compounds are often known as hydrides.

The term "hydride" suggests that the H atom has acquired a negative or anionic character, denoted H-, and is used when hydrogen forms a compound with a more electropositive element. The existence of the hydride anion, suggested by Gilbert N. Lewis in 1916 for group I and II saline hydrides, was demonstrated by Moers in 1920 by the electrolysis of molten lithium hydride (LiH), producing a stoichiometry quantity of hydrogen at the anode.

Although hydrides can be formed with almost all main-group elements, the number and combination of possible compounds varies widely; for example, there are over 100 binary borane hydrides known, but only one binary aluminium hydride. A simple binary indium hydride has not yet been identified, although larger complexes exist.

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10.7B: Metallic Hydrides

Metallic hydrides (also known as interstitial hydrides) involve hydrogen bonds with transition metals. One interesting and unique characteristic of these hydrides are that they can be nonstoichiometric, meaning basically that the fraction of H atoms to the metals are not fixed. Nonstoichiometric compounds have a variable composition. The idea and basis for this is that with metal and hydrogen bonding there is a crystal lattice that H atoms can and may fill in between the lattice while some might, and is not a definite ordered filling. Thus it is not a fixed ratio of H atoms to the metals. Even so, metallic hydrides consist of more basic stoichiometric compounds as well.

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10.7C: Saline Hydrides

Saline hydrides (also known as ionic hydrides or *pseudohalides*) are compounds form between hydrogen and the most active metals, especially with the alkali and alkaline-earth metals of group one and two elements. In this group, the hydrogen acts as the hydride ion (H^-). They bond with more electropositive metal atoms. Ionic hydrides are usually binary compounds (i.e., only two elements in the compound) and are also insoluble in solutions.

$$2A_{(s)} + H_{2(g)} \rightarrow 2AH_{(s)} \tag{3}$$

with A as any group 1 metal.

$$A_{(s)} + H_{2(g)} \rightarrow AH_{2(s)} \tag{4}$$

with A as any group 2 metal.

Ionic hydrides combine vigorously with water to produce hydrogen gas.

Example 10.7C.1: Alkali Metal Hydrides

As ionic hydrides, alkali metal hydrides contain the hydride ion H^- as well. They are all very reactive and readily react with various compounds. For example, when an alkali metal reacts with hydrogen gas under heat, an ionic hydride is produced. Alkali metal hydrides also react with water to produce hydrogen gas and a hydroxide salt:

$$MH_{(s)} + H_2O_{(l)} \rightarrow MOH_{(aq)} + H_{2(g)} \tag{10.7C.1}$$

The instability of the hydride ion compared to the halide ions can be seen by comparison of the ΔH_f for alkali metal hydrides and chlorides.

Cation	ΔH_f MH / kJmol^{-1}	ΔH_f MCl / kJmol^{-1}
Li	-90.5	-409
Na	-56.3	-411
K	-57.7	-436
Rb	-52.3	-430
Cs	-54.2	-433

Saline hydrides are formed by the Group 1 and 2 metals when heated with dihydrogen (H_2). They are white, high melting point solids that react immediately with protic solvents, for example:

$$NaH + H_2O \rightarrow NaOH + H_2 \tag{10.7C.2}$$

(Their moisture sensitivity means that reaction conditions must be water-free.)

Evidence for the ionic nature of these hydrides is:

1. molten salts show ionic conductivity.
2. X-ray crystal data gives reasonable radius ratios expected for ionic compounds.
3. Observed and calculated Lattice Energies (from Born-Haber cycles etc.) are in good agreement (i.e. show little covalency).

NaH is capable of deprotonating a range of even weak Brønsted acids to give the corresponding sodium derivatives.

$$NaH + Ph_2PH \rightarrow Na[PPh_2] + H - 2 \tag{10.7C.3}$$

Sodium hydride is sold by many chemical suppliers as a mixture of 60% sodium hydride (w/w) in mineral oil. Such a dispersion is safer to handle and weigh than pure NaH. The compound can be used in this form but the pure grey solid can be prepared by

rinsing the oil with pentane or tetrahydrofuran, THF, care being taken because the washings will contain traces of NaH that can ignite in air. Reactions involving NaH require an inert atmosphere, such as nitrogen or argon gas. Typically NaH is used as a suspension in THF, a solvent that resists deprotonation but solvates many organosodium compounds.

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10.7D: Molecular Hydrides and Complexes Derived from them

Molecular hydrides - covalent hydrides and organic compounds

Hydrogen forms a vast number of compounds with carbon, (the hydrocarbons), and an even larger array with heteroatoms that, because of their general association with living things, are called organic compounds. The study of their properties is covered in organic chemistry and their study in the context of living organisms is covered in biochemistry. By some definitions, "organic" compounds are only required to contain carbon. However, most of them also contain hydrogen, and because it is the carbon-hydrogen bond which gives this class of compounds most of its particular chemical characteristics, carbon-hydrogen bonds are required in some definitions of the word "organic" in chemistry. Millions of hydrocarbons are known, and they are usually formed by complicated synthetic pathways, which seldom involve direct reaction with elementary hydrogen.

Most molecular hydrides are volatile and many have simple structures that can be predicted by the VSEPR model. There are a large number of B hydrides known (boranes) and although the simplest BH_3 has been found in the gas phase it readily dimerises to give B_2H_6.

In inorganic chemistry, hydrides can serve as bridging ligands that link two metal centers in a coordination complex. This function is particularly common in group 13 elements, especially in boranes (boron hydrides) and aluminium complexes, as well as in clustered carboranes, (composed of boron, carbon and hydrogen atoms). The bonding of the bridging hydrogens in many of the boranes is explained in terms of 3 centre - 2 electron bonds.

Diborane is a colourless and highly unstable gas at room temperature with a repulsively sweet odour. Diborane mixes well with air, easily forming explosive mixtures. Diborane will ignite spontaneously in moist air at room temperature.

MP = -164.85 °C, BP= -92.5 °C
B-H (terminal) 119 pm, (bridge) 131 pm

Metallic (interstitial) hydrides

Many transition metal elements form metallic (interstitial) hydrides, in which H_2 molecules (and H atoms) can occupy the holes in the metal's crystal structure. They are traditionally termed 'compounds', even though they do not strictly conform to the definition of a compound; more closely resembling common alloys such as steel. These systems are usually non-stoichiometric, with variable amounts of hydrogen atoms in the lattice.

Palladium is unique in its ability to reversibly absorb large amounts of H_2 or D_2 (up to 900 times its own volume of hydrogen, but no other gases, at room temperature) to form palladium hydride. Structural studies show that the absorbed H fits into octahedral holes in the cubic close packed Pd lattice with a non-stoichiometric formula approximating to $PdH_{0.6}$ for the β-form. This material has been considered as a means to carry hydrogen for vehicular fuel cells. Interstitial hydrides show some promise as a way for safe hydrogen storage. During the last 25 years many interstitial hydrides have been developed that readily absorb and discharge hydrogen at room temperature and atmospheric pressure. At this stage their application is still limited, as they are capable of storing only about 2 weight percent of hydrogen, insufficient for automotive applications.

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10.7E: Covalent Hydrides with Extended Structures

Covalent hydrides refer to hydrogen centers that react as hydrides, or those that are nucleophilic. In these substances, the hydride bond, formally, is a covalent bond much like the bond that is made by a proton in a weak acid. This category includes hydrides that exist as discrete molecules, polymers, oligomers, or hydrogen that has been chem-adsorbed to a surface. A particularly important type of covalent hydride is the complex metal hydride, a powerful (reducing) soluble hydride that is commonly used in organic syntheses (for example, sodium borohydride or $NaBH_4$). Transition metal hydrides also include compounds that can be classified as covalent hydrides. Some are even classified as interstitial hydrides and other bridging hydrides. Classical transition metal hydrides feature a single bond between the hydrogen center and the transition metal.

Contributors and Attributions

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CHAPTER OVERVIEW

11: Group 1 - Alkali Metals

The alkali metals make up Group 1 of the periodic table. This family consists of the elements lithium, sodium, potassium, rubidium, cesium, and francium (Li, Na, K, Rb, Cs, and Fr, respectively). Group one elements share common characteristics. They are all soft, silver metals. Due to their low ionization energy, these metals have low melting points and are highly reactive. The reactivity of this family increases as you move down the table. Alkali metals are noted for how vigorously they react with water.

Topic hierarchy

- 11.1: Introduction
- 11.2: Occurence, Extraction, and Uses
  - 11.2A: Occurence
  - 11.2B: Extraction
  - 11.2C: Major Uses of the Alkali Metals and their Compounds
- 11.3: Physical Properties
  - 11.3A: General Properties
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  - 11.3C: Radioactive Isotopes
  - 11.3D: NMR Active Nuclei
- 11.4: The Metals
  - 11.4A: Appearance
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- 11.5: Halides
- 11.6: Oxides and Hydroxides
  - 11.6A: Oxides, Peroxides, Superoxides, Suboxides, and Ozonides
  - 11.6B: Hydroxides
- 11.7: Salts of Oxoacids - Carbonates and Hydrogencarbonates
- 11.8: Aqueous Solution Chemistry and Macrocyclic Complexes
  - 11.8A: Hydrated Ions
  - 11.8B: Complex Ions
- 11.9: Non-Aqueous Coordination Chemistry

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11.1: Introduction

Chemistry 242 - Inorganic Chemistry II
Chapter 10 - Lithium, Sodium, Potassium, Rubidium and Caesium

Introduction

- The common metals of this group are sodium (2.6% in the lithosphere, NaCl) and potassium (2.4%, $KClMgCl_2.6H_2O$, carnallite).
- Salt mines are considered to be good places to leave radioactive waste because they are not subject to groundwater flow - that is why the salt got left there in the first place!
- NaOH, Na_2CO_3, Na_2SO_4, $Na_3P_3O_9$ and Na_4SiO_4 are among the top 50 industrial chemicals.
- Potassium salts, notable K_2SO_4 or KNO_3, are an important component of fertilizer.
- Lithium alkyls are important reagents in synthesis.
- Na^+ and K^+ are very important physiological ions, and Li^+ salts are used to treat certain mental disorders.
- Except Li, *the chemistry is predominantly that of the M^+ ions*. There may be a hint of covalentcy in certain chelate complexes.
- Li^+ would have a ratio of charge/radius similar to Mg^{2+} hence certain similarities.
- Other "look alikes" are $NH4^+$ which is similar to K^+ and Tl^+ which is a bit like Rb^+ or Ag^+.

Preparation and Properties

- Lithium and sodium are made by electrolysis of the molten salts or low melting eutectics.
- potassium, rubidium and cesium are made by the reaction of sodium vapour with the molten chlorides:

  > $MCl(l) + Na(g) \rightleftharpoons NaCl(l) + M(g)$

  Their vapours are more volatile so that the equilibrium (which is on the side of the halides of the metals desired!)) is disturbed.
- The metals are all silvery in colour except Cs which is yellow. They can all be cut with a knife, lithium being the hardest.
- A sodium - potassium (77.2%) alloy melts at -10 and is a useful, if dangerous, reducing agent.
- The metals are normally protected from air under oil. Lithium, sodium and potassium can be handled quickly in air, and rubidium and cesium are handled under argon.
- All react with water to produce hydrogen: lithium slowly, sodium vigorously, potassium violently enough to ignite the hydrogen, and the rest explosively.
- The products of combustion in a free supply of air are:

  > $Li \rightleftharpoons Li_2O$ (oxide) $\rightleftharpoons 2OH^-$ in water.
  >
  > $Na \rightleftharpoons Na_2O_2$ (peroxide) $\rightleftharpoons 2OH^- + 2H_2O_2$ in water
  >
  > M(K, Rb and Cs) $\rightleftharpoons MO_2$ (suboxide) $\rightleftharpoons O2 + 2OH^- + H_2O_2$ with water

  The difference is attributed to lattice energy effects, that is it is the size of the metal ion that makes one of the potential oxides more stable.
- All metals will reat with alcohols to give the alkoxide.
- All dissolve in mercury to give amalgams. The most useful is th liquid amalgam formed when less than about 6% Na is dissolved in mercury. It is a relatively gentle reducing agent compared to pure sodium.

The Metals in Liquid Ammonia

They all dissolve in ammonia to give solutions which are a beautiful royal blue when relatively dilute and take on a metallic bronze appearance when concentrated. The most important equilibria in the more dilute solutions are:

> $Na(s) \rightleftharpoons Na(NH_3) \rightleftharpoons Na^+(NH_3) + e^-)NH_3)$
>
> $2e^-(NH_3) \rightleftharpoons e_2^-(NH_3)$

The electrons, which are responsible for the blue colour, are trapped in 3.0-3.4 Å cavities in the solvent. The solutions have a lower density than the pure solvent as a result.

At high concentrations, metal atoms cluster, and the solutions become quite metallic in properties, thus the appearance and high electrical conductivity.

Solutions of sodium in liquid ammonia are slowly decomposed by light an drapidly by the catalytic effect of transition metal ions such as Fe(III) to give sodamide and hydrogen:

> $Na(NH_3) + NH_3 \rightleftharpoons NaNH_2(s) + ½H_2(g)$

For potassium, rubidium an dcesium, whose amides are soluble in liquid ammonia the reaction is reversible under hydrogen pressure:

> $e^-(NH_3) + NH_3 \rightleftharpoons NH_2^- + ½H_2(NH_3)\ K = 5x10^4$

The alkali metals are also slightly soluble in other amines, THF and glymes but to a much lesser extent.

Compounds

Oxides - see above.

Hydroxides - The most important are NaOH and KOH which are very deliquescent waxy looking solids, usually sold a pellets or flakes. They are very corrosive alkaline compounds which should be handled with care.

Ionic Salts - Salts of virtually all acids are known. They are colourless unless teh anions are coloured, or there are lattice defects. Lithium is different:

a. Li_3N is formed slowly from Li and N_2 at room temperature and is ruby red.
b. LiOH is a "covalentish" OH bridged polymer which is not very alkaline compared to the rest.
c. LiF is rather *insoluble*.
d. LiCl and LiBr are quite *soluble* in a number of polar organic solvents such as alcohols, acetone, ethyl acetate and pyridine (LiCl).
e. Lithium salts are often hydrated, e/g/ $LiClO_4.3H_2O$.

Insoluble salts of the others:

Finding insoluble salts for identification and gravimetric analysis was difficult - there are so few! Examples are: $NaZn(UO_2)(CH_3CO_2)_9.6H_2O$ and $K^+_3[Co(NO_2)_6]^{3-}$ (or Rb^+ or Cs^+).

Hydrates and Complexes in Solutions

Hydrates

See table 10-1. Li^+, Na^+ and K^+ probably have 4 molecules of water in their first (or primary) hydration sphere, while Rb^+ and Cs^+ probably have 6. The larger the central ions, the smaller the area of ordering of the water around it, so the effective size of the ions decreases going down the group. This is important in understanding the mobility of the ions, for example down an ion exchange column.

The Crown Ethers and Cryptands

The alkali metals are complexed quite strongly by THF and glymes, but the effect becomes really marked for the so-called "crown ethers". Two examples are shown below:

Each of these crown ethers has an affinity fro a particular metal ion, for example, for 18-crown-6, the binding constants are in the order:

$Li^+ < (Na^+,Cs^+) < Rb^+ < K^+$ That is, this crown ether likes K^+ best.

Li^+ is most strongly bound in dicylohexyl-14-crown-4
Na^+ "fits" well in benzo-15-crown-5
Rb^+ "fits" best in dicyclohexyl-21-crown-7
Cs^+ "fits" best in dicyclohexyl-24-crown-8

The stability orders differ depending on the method of comparison (calculation, gas-phase, solution etc): experimetally in solution, it appears that *any* crown with $–CH_2CH_2–$ bridges prefers K^+ because of the 5-membered chelate ring size rather than

the size of the hole on the crown - the macrocycle just puckers up to fit,but solvent effects may also be very important.

The complexes are used to get normally insoluble ionic compounds into organic solutions and can also help produce metal electrides like in ammonia.

Cryptands and Cryptates

Cryptands are polycyclic cages, usually including nitrogen as well as oxygen to get the necessary junctions. Metal ions are encapsulated even more securely inside them leadin gto cryptates. alt

Some remarkable compounds have been made:

> $2Na(NEt_3) + 2,2,2\text{-crypt}$ alt $[Na(2,2,2\text{-crypt})]^+Na^-(s)$

Bear in mind that:

> $2Na$ alt $Na^+ + Na^-\ DH = 438\ kJ\ mol^{-1}$

This compound is stable up to -10 ^oC and has a structure similar to $[Na(2,2,2\text{-crypt})]^+I^-$ which has normal stability. There is also a $[Na(2,2,2\text{-crypt})]^+e^-$ known.

Encapsulated Metals in Biology

The transport of alkali metal ions, notably through cell walls, is biologically important and involves certain natural macrocyclic compounds such as valinomycin (Fig 10-VII) and nonactin (Fig 10-3).

Organometallic Compounds

Lithium Compounds

The lithium compounds are very important synthetic reagents. They can be made in hydrocarbon solvents (which is how they are sold) by reactions such as:

> $C_2H_5Cl + Li$ alt $C_2H_5Li + LiCl(S)$
>
> $C_4H_9Li + CH_3I$ alt $C_4H_9I + CH_3Li$

The pure compounds are air-sensitive low melting solids or liquids and are associated into small aggregates with multicentre bonding e.g. $Li_4(CH_3)_4$ (Figure 10-4) or $Li_6(C_2H_5)_6$.

Organosodium and Potassium Compounds

The organometallic compounds of sodium and potassium are predominantly ionic. The most important are NaC_5H_5 (made from Na in l-NH_3 and C_5H_5 monomer: it is usually a Diels-Alder dimer) and NaC^{o}CR.

Other Alkali Metal Compounds

Look at this section independently.

Summary

a. Lithium:

1. Reacts relatively slowly with water or oxygen, but readily forms the nitride.
2. Has a marked tendency towards covalency, notably in its organometallic compounds.
3. Is often hydrated in its "ionic" compounds.
4. The hydroxide is not a strong base.
5. Some salts are not very soluble in water, but do dissolve in donor organic solvents.

b. Sodium, Potassium, Rubidium and Caesium:

1. Are all very reactive with water and oxygen. Nitrides are not stable at room temperature.
2. Compounds are always predominantly ionic.
3. Hydroxides are strong bases.
4. Salts are almost all water soluble.

c. All elements in the group:

1. Form blue reducing solutions in ammonia.

2. Form stable complexes with crown ethers or cryptands which are significantly soluble in organic solvents.

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11.2C: Major Uses of the Alkali Metals and their Compounds

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11.3A: General Properties

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11.3B: Atomic Spectra and Flame Tests

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11.3C: Radioactive Isotopes

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11.3D: NMR Active Nuclei

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11.6B: Hydroxides

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11.7: Salts of Oxoacids - Carbonates and Hydrogencarbonates

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11.8A: Hydrated Ions

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11.8B: Complex Ions

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11.9: Non-Aqueous Coordination Chemistry

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CHAPTER OVERVIEW

12: Goup 2- Alkaline Earth Metals

Alkaline earth metals make up the second group of the periodic table. This family includes the elements beryllium, magnesium, calcium, strontium, barium, and radium (Be, Mg, Ca, Sr, Ba, and Ra, respectively). Group 2 elements share common characteristics. Each metal is naturally occurring and quite reactive. These metals are silver and soft, much like the alkali metals of Group 1. These metals also react with water, though not as vigorously. Beryllium, interestingly, does not react with water. E

Topic hierarchy

- 12.1: Introduction
- 12.2: Occurence, Extraction, and Uses
  - 12.2A: Occurrence
  - 12.2B: Extraction
  - 12.2C: Major Uses of Group 2 Metals and their Compounds
- 12.3: Physical Properties
  - 12.3A: General Properties
  - 12.3B: Flame Tests
  - 12.3C: Radioactive Isotopes
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  - 12.4A: Appearance
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- 12.5: Halides
  - 12.5A: Beryllium Halides
  - 12.5B: Halides of Mg, Ca, Sr, and Ba
- 12.6: Oxides and Hydroxides
  - 12.6A: Oxides and Peroxides
  - 12.6B: Hydroxides
- 12.7: Salts of Oxoacids
- 12.8: Complex Ions in Aqueous Solution
  - 12.8A: Aqua Species of Beryllium
  - 12.8B: Aqua Species of Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}
  - 12.8C: Complexes with Ligands other than Water
- 12.9: Complexes with Amido or Alkoxy Ligands
- 12.10: Diagonal Relationships between Li and Mg, and between Be and Al
  - 12.10A: Lithium and Magnesium
  - 12.10B: Beryllium and Aluminium

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12.1: Introduction

- Beryllium is found in the mineral beryl, $Be_3Al_2(SiO_3)_6$. Beryl with around 2.9% Cr^{3+} substituting for Al^{3+} is emerald.
- Beryllium compounds are dangerously toxic and can pass through the skin - care!
- The other elements are faily common in a variety of minerals e.g. limestone, $CaCO_3$, dolomite, $CaCO_3.MgCO_3$ and carnallite, $KCl.MgCl(6H_2O)$. Less common are strontianite, $SrCO_3$, and barytes, $BaCO_3$.
- Radium, the bottom member of the group is radioactive with a half-life (^{226}Ra)of about 1600 years as a a-emitter. It was first isolated from uranium ore, pitchblende, by M. and P. Curie, by laborious frational cyrstallizations.
- Atomic radii are smaller than those group 1, while there are two valence electrons. Therefore, the elements are harder, with higher melting and vaporizing points. The enthalpies are correspondingly higher.
- The ionic radii of the M^{2+} ions are much smaller than group 1 M^+ ions so that hydration and lattice energies compensate for the higher ionization enthalpies needed to reach the M^{2+} state.
- The beryllium ion is too small to form many ionic compounds, and magnesium ion is also quite small so they are treated separately.
- Calcium, Strontium and Barium are a "well-behaved" group of three elements with a nice gradual change in properties.

Beryllium

Beryllium is obtained by the reduction of $BeCl_2$ by Ca or Mg or the Mg reduction of BeF_2. It is a very light metal, unreactive with air or water at ordinary temperatures. It dissolves in strong non-complexing acids (except HNO_3 which passivates it) to give the $[Be(H_2O)_4]^{2+}$ ion. Be also dissolves in strong aqueous bases like NaOH to evolve hydrogn and yield the beryllate, $Be(OH)_4^{2-}$ ion. Its amphoteric behaviour is similar to aluminum. Beryllium salts, which usually come hydrated, are acidic in solution due to hydrolysis:

> $$[Be(H_2O)]^{2+} + H_2O \text{ alt } [Be(H_2O)_3(OH)]^+ + H_3O^+$$

Beryllium compounds are fairly covalent and the chemistry is dominated by the Be attempting to obtain an octet. There are two important strategies identified:

1. The simple Beryllium compounds can react with Lewis bases forming, for example, $BeCl_2(OEt_2)_2$, and complex anions are also formed e.g. BeF_4^{2-}, and $[Be(H_2O)_4]^{2+}$.
2. Polymerization occurs through bridging groups to give chain polymers, e.g. $(BeF_2)_n$, $(BeCl_2)_n$ and $(Be(CH_3)_2)_n$. In the halides, the bridges are not electron deficient, but in the alkyls, three-centre, two-electron bonds must be invoked. alt For bulkier groups, for example certain alkoxides, the chain lengths can be reduced, or polymerization can even be inhibited, e.g. $(Be(OBu^t)_2)_3$ and $Be(OC_6H_4(But)_2)_2$ (below): alt In the gas phase the polymers break down so that the chloride is linear $BeCl_2$. By rapidly cooling the vapour, short aggregates with two or three Be's can be isolated. Short chain anions such as $M_2[Be_4Cl_{10}]$ ($M^+ = K^+$, Rb^+, Tl^+ or NH_4^+)have similar structures.

The compounds BeO and BeS have the wurtzite and blende structures respectively (both are known for ZnS - see Chapter 4) but the bonding would have to be considered quite covalent. $Be(OH)_2$ in insoluble in water.

"Basic beryllium acetate", $Be_4O(CH_3CO_2)_6$, which is soluble in nonpolar solvents e.g. benzene, has a tetrahedral arrangement of Be atoms around the oxygen atom, and an acetate bridging each of the six edges of the tetrahedron (Figure 11-2).

Magnesium

Magnesium, a rather important metal, is mostly made from dolomite and/or seawater. Magnesium can be concentrated using both sources as follows: Dolomite is heated to give an intimate mixture, MgO.CaO, and then the magnesium is ion exchanged out using seawater:

> $$MgO.CaO + 2H_2O \text{ alt } Mg(OH)_2.Ca(OH)_2$$
>
> $$Mg(OH)_2.Ca(OH)_2 + Mg^{2+} \text{ alt } 2Mg(OH)_2 + Ca^{2+}$$

This works because $Mg(OH)_2$ is much less soluble than $Ca(OH)_2$.

There are three common ways to get the magnesium metal itself:

1. The "calcined" dolomite is be heated with ferrosilicon, and the magnesium distills out:

   > *MgO.CaO + FeSi*  *Mg + ill-defined silicates of Ca and Fe*

2. A low-melting mixture of $MgCl_2$, $CaCl_2$ and NaCl is electrolysed. Magnesium is preferentially reduced at the cathode.
3. Magnesium oxide is reduced with coke at 2000 ^oC which gives an equilibrium mixture of Mg and CO. Rapid cooling separates the metal from the gaseous CO.

Magnesium is a silvery-white metal protected by an oxide coating. It is attacked by acids (which dissolve the oxide film first) with the evolution of H_2 (even with HNO_3, which usually reacts to give NO or NO_2). It will react with water if its surface is amalgamated. It is used in ultra-light alloys and it is the metal at the centre of chlorophyll.

Magnesium behaves somewhere between Be and the rest of the group 2 elements. Its hydroxide is not very water soluble, while the rest are, and it has some pretty covalent organo-compounds, the grignard reagents are the most important.

Calcium, Strontium and Barium

These metals are made by reduction of their halides by sodium in relatively small quantities. They are all softish and silvery when freashly cut, but they react readily with oxygen and water. Calcium is most used to make the hydride, CaH_2, a useful reducing and drying agent.

Binary Compounds

Oxides

- They are all white high-melting compounds with the NaCl structure.
- The most important is probably CaO, made from $CaCO_3$ and is a major ingredient in cement.
- All except MgO, which can be fairly inert, produce a soluble, stongly basic hydroxide with water, and the carbonate with CO_2. MgO quite is insoluble in water and is only very mildly basic. It is used as a stomach antacid ("milk of magnesia").

Halides

- Anhydrous calcium chloride is an important drying agent, often mixed with a little cobalt chloride which is blue when anhydrous and pink when hydrated and acts as an indicator of the condition of the dessicant. Magnesium Chloride is also hygroscopic. The affinity for water decreases down th egroup so that Sr and Ba halides are normally anyhdrous.

Other Compounds

- Calcium carbide, CaC_2, made from CaO and carbon at high temperature can be a source of acetylene.
- The hydrides are all ionic although MgH_2 has come covalent character.

Oxo Salts, Ions and Complexes

- All form oxo salts (CO_3^{2-}, SO_4^{2-} etc). $MgSO_4.7H_2O$ is "Epsom salts", a mild laxative, $MgCO_3$ is used as an antacid. $CaSO_4.½H_2O$ is known as "plaster of Paris" which sets with water to give $CaSO_4.2H_2O$, "gypsum". $BaSO_4$ is used as an imaging material to obtain medical X-rays of the intestinal tract.
- They become less soluble down the group.
- In aqueous solution the ions are probably at least 6-coordinate.
- There are some chelate complexes with oxygen ligands, the best known being $[Ca(EDTA)]^{2-}$ and also Capolyphospates which can be used to sequester Ca an dalso in its analysis.
- The strong complexation of Mg by porphyrins is quite unusual since the ligating atoms are all nitrogen.

Summary

a. Beryllium:

   1. Forms covalent compounds almost exclusively, even with the most electronegative elements.
   2. Does not form Be^{2+} compounds, but readily achieves a maximum coordination number of 4 by forming complex ions e.g. BeF_4^{2-} and $[Be(H_2O)_4]^{2+}$ with essentially covalent bonding within the complex.
   3. Forms covalent organometallic compounds.

4. Oxide and specially the hydroxide are amphoteric. (The hydroxide is water soluble.)
5. The hydride, halides and alkoxides are oligomeric or polymeric with covalent bridges, and are easily cleaved by Lewis bases.

b. Magnesium:

1. Forms ionic compounds with partial covalent character.
2. Forms many compounds containing the uncomplexed Mg^{2+} ion and tend to be 6-coordinated by the counter ions.
3. Forms important organometallic compounds which are mainly covalent.
4. Oxide and especially the hydroxide are weakly basic. (The hydroxide is not water soluble.)
5. The halides are essentially ionic.
6. The hydride is partly covalent.

c. Calcium, Strontium and Barium:

1. Form only ionic substances.
2. Form basic oxides and strongly basic hydroxides, more and more soluble down the group.
3. Form readily hydrated halide salts, especially towards the top of the group.
4. Hydrides are ionic.

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12.5A: Beryllium Halides

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12.5B: Halides of Mg, Ca, Sr, and Ba

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12.6A: Oxides and Peroxides

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12.8A: Aqua Species of Beryllium

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12.8B: Aqua Species of $M\ g\ 2+$, $C\ a\ 2+$, $S\ r\ 2+$, and $B\ a\ 2+$

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12.8C: Complexes with Ligands other than Water

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12.9: Complexes with Amido or Alkoxy Ligands

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SECTION OVERVIEW

12.10: Diagonal Relationships between Li and Mg, and between Be and Al

A Diagonal Relationship is said to exist between certain pairs of diagonally adjacent elements in the second and third periods of the periodic table. These pairs (Li & Mg, Be & Al, B & Si etc.) exhibit similar properties; for example, Boron and Silicon are both semiconductors, form halides that are hydrolyzed in water and have acidic oxides. Such a relationship occurs because crossing and descending the periodic table have opposing effects. On crossing a period of the periodic table, the size of the atoms decreases, and on descending a group the size of the atoms increases. Similarly, on moving along the period the elements become progressively more covalent, less reducing and more electronegative, whereas on descending the group the elements become more ionic, more basic and less electronegative. Thus, on both descending a group and crossing by one element the changes cancel each other out, and elements with similar properties which have similar chemistry are often found - the atomic size, electronegativity, properties of compounds (and so forth) of the diagonal members are similar.

Topic hierarchy

12.10A: Lithium and Magnesium

12.10B: Beryllium and Aluminium

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12.10A: Lithium and Magnesium

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CHAPTER OVERVIEW

13: The Group 13 Elements

Group 13 is sometimes referred to as the boron group, named for the first element in the family. These elements are--not surprisingly--located in column 13 of the periodic table. This group includes boron, aluminum, gallium, indium, thallium, and ununtrium (B, Al, Ga, In, Tl, and Uut, respectively). These elements all have three valence electrons. Boron is the only metalloid in this family. The rest of the elements are considered to be poor metals.

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13.2: Occurence, Extraction, and Uses

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13.10: Metal Borides

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13.1: Introduction to Group 13 Elements

Bird

Introduction

- Sources:
  - Ulexite: $NaCa[B_5O_6(OH)_6].5H_2O$
  - Borax: $Na_2[B^4O^5(OH)^4].8H^2O$
  - Colmanite: $Ca_2[B_3O_4(OH)_3].2H_2O$
  - Kenite: $Na_2[B_4O_5(OH)_4].2H_2O$

  See the figure for the borate anions in te above.
- There are *no* ionic B^{3+} compounds, c.f. Mg^{2+} and Li^+.
- The compounds which are coordinatively unsaturated (e.g.BCl_3) are very strong Lewis bases.
- Tetrahedral adducts and anions are common, for example:

  > $F_3B{:}O(C_2H_5)_2\ BF_4^-\ B(C_6H_5)_4^-$
- The boron hydrides (boranes) are a class unto themselves together with the carboranes and all the anions. They frequently feature closed and open polyhedra based on fragments of an icosahedron, but not always.
- Boron resembles silicon more than aluminum in some ways:
  - B_2O_3 and $B(OH)_3$ are acidic rather like SiO_2 and $Si(OH)_4$ whereas the Al compounds are weakly amphoteric.
  - The borates have some features in common with the silicates.
  - The halide compounds of B and Si are readily hydrolysed (except BF_3) whereas the halide compounds of Al are only partly hydrolysed.
  - The B and silicon hydrides are volatile molecular compounds, which inflame in air, while AlH_3 is an involatile solid.

Manufacture and Properties of Boron

Boron is quite difficult to isolate, because it is refractory and reactive at high temperature and so it is difficult to contain:

1. $B_2O_3 + 3Mg$  $2B + MgO$ (98% - Wash with NaOH, HCl and HF)
2. $2BCl_3 + 3Zn$  $3ZnCl_2 + 2B$ (900 ^oC)
3. $2BX_3 + 3H_2$  $6HX + 2B$ (Tantalum catalyst)

Boron is rather inert in most forms which contain icosahedral cages. It is attacked by hot oxidizing acids.

Amorphous boron is more reactive, if white hot, and is attacked by NH_3 to form boron nitride which is isomorphous with graphite.

Oxygen Compounds of Boron

See Figure 12-1.

The "anhydrous" borates involve the ions: BO_3^{3-}, $B_3O_6^{3-}$, $(BO_2)_n^{n-}$, and larger aggregates.

The hydrated ones feature: BO_3 units which are planar and BO_4 unitsd which are tetrahedral and formally have a -ve charge on the boron. The charge on the ion is equal to th number of these latter units. The structures without BO_4 units hydrate readily.

Boric Acid

See Figure 12-2 for a summary.

- Note that $B_2O_3 + SiO_2$ is "pyrex".
- Note that $B(OH)_3$, normally a weak acid, can be considerably strengthened to the point where it can be titrated with NaOH by "chelation" by an organic compound with neighbouring OH groups e.g. glycerol: 
- In general, equilibria involve the processes:

  > $B\text{-}O\text{-}H + H\text{-}O\text{-}B$  $B\text{-}O\text{-}B + H_2O$
  >
  > $B\text{-}O\text{-}H + O\text{-}H^-$  $B\text{-}O^- + H_2O$

Halides of Boron

Trihalides

BF_3 is the most important and is used on an industrial scale. It is a gas boiling at -101 ^oC.

It is a very strong Lewis acid:

$$BF_3 + :F^- \rightleftharpoons BF_4^-$$

$$BF_3 + :L \rightleftharpoons F_3B:L$$

Unlike the others, BF_3 is only partly hydrolysed:

$$4BF_3 + 6H_2O \rightleftharpoons 3H_3O^+ + 3BF_4^- + B(OH)_3$$
$$BF_4^- + H_2O \rightleftharpoons BF_3(OH) + HF$$
$$(BCl_3 + 3H_2O \rightleftharpoons B(OH)_3 + 3HCl)$$

In synthetic organic chemistry it is used as follows:

The conversion of ethers or alcohols with acids to esters e.g:

$$H^+ + RCOOH \rightleftharpoons [RCOOH_2]^+$$
$$[RCOOH_2]^+ + BF_3 \rightleftharpoons [RCO\}^+ + F_3B:OH_2$$
$$[RCO]^+ + R'OH \rightleftharpoons RCOOR' + H^+$$

Friedel-Crafts alkylations and acylations:

$$RX + BF_3 \rightleftharpoons R^+ + BF_3X^-$$
$$R^+ + PhH \rightleftharpoons PhR + H^+$$
$$H^+ + BF_3X^- \rightleftharpoons BF_3 + HX$$

Fluoroboric acid: "HBF_4" is sold as a 40% solution in water. It is a strong acid and source of BF_4^- ions useful for crystallizations where a coordinating anion is to be avoided.

Reactions of the Trihalides of Boron.

1. Adduct formation - the main thing to remember that the order of acid strength is counter to naive expectations because of p-bonding effects whnich are strongest for B-F bonds and lead to BF_3 being least willing to go from sp^2 to sp^3. hybridized.
2. Halide exchange reactions:

   $$BCl_3 + BBr_3 \rightleftharpoons BCl_2Br + BBr_2Cl$$

   The exchange, presumably through a bridged intermediate, is very facile, so pure mixed compounds cannot be obtained.
3. Elimination of halide - covers the various solvolyses in addition to hydrolysis:

   $$BCl_3 + 3C_2H_5OH \rightleftharpoons B(OC_2H_5)_3 + 3HCl$$
   $$BCl_3 + 3NH(C_2H_5)_2 \rightleftharpoons B(N(C_2H_5)_2)_3 + 3HCl$$

   This will happen with any solvent with an exchangeable H.

Subhalides of Boron

They have a B:X ratio less than 1:3

- There are halides BF and BCl.
- There are halides B_2X_4 known for F, Cl, Br and I. Rotation about the B-B bond is easy. Any multiiple bonding tendency involves the boron to halogen bonds as in BX_3. (This is in contrast with the aminoboranes - see below.)
- B_nX_n compounds have polyhedral cages of boron each carrying one X group. The largest range of compounds is known for Cl where n = 4, 8, 9, 10 and 11. B_4Cl_4 is tetrahedral, B_8Cl_8 is a triangular dodecahedron, and B_9Cl_9 is a rectangularly tricapped

trigonal prism. Look them up!

The Hydrides of Boron - the Boranes

Table 12-1 lists the hydrides up to $B_{10}H_{14}$

Figure 12-4 shows some of their structures as perspective drawings. Note that the lines are intended to clarify the shape of the molecule and do not necessarily represent $2e^-$ - 2-centre bonds.

Note also the nomenclature - the prefix gives the number of boron atoms and the number in parentheses the number of hydrogen atoms, e.g. pentaborane(9) is B_5H_9.

Synthesis

Diborane (b.p. -92.6 ^oC can be made by several methods:

$$3NaBH_4 + 4BF_3 \text{ alt } 2B_2H_6 + 3NaBF_4$$
$$2NaBH_4 + I_2 \text{ alt } B_2H_6 + 2NaI + H_2$$
$$BF_3 + 6NaH \text{ alt } B_2H_6 + 6NaF$$

The last is the main industrial method. The higher boranes are made by thermolysis of diborane under various conditions.

Structures

The connectivities in the boranes cannot be explained using 2e- - 2-centre bonding only, that is the molecules are electron deficient. Valence bond theory has been "extended" by designating three types of $2e^-$ - 3-centre bonding in addition to a normal $2e^-$ - 2-centre B-H and B-B bonds:



An example of the use of this scheme for $B_{10}H_{14}$ is shown below:



Each hydrogen must have one bond *ending* at it and each boron must have a total of 4 bonds *ending* at it. If an atom is *in the middle* of a three-centre bond, the curved line passing through it counts as only one bond.

Thus, for example, B_6 has one normal bond to a terminal hydrogen and one normal bond to B_2, plus it is *at the end* of two three-centre bonds through the bridging hydrogens for a total of four bonds i.e eight electrons.

B_2 has one normal bond from B_6, one normal bond from its terminal hydrogen, is *at the end* of a "closed" three-centre bond from B_1 and B_2, and it is *in the centre* of an "open" three-centre bond from B_5 to B_7. This is also equivalent to four bonds.

In some cases, more than one "resonance" (canonical) structure can be formulated to account for the observed molecular shape.

Reactions of the boranes

Diborane

1. With oxygen (explosive):

$$B_2H_6 + 3O_2 \text{ alt } B_2O_3 + 3H_2O$$

2. With water:

$$B_2H_6 + 3H_2O \text{ alt } B(OH)_3 + 6H_2$$

or alcohols:

$$B_2H_6 + 3HOR \text{ alt } B(OR)_3 + 6H_2$$

3. Substitution reactions:

$$B_2H_6 + HCl \text{ alt } B_2H_5Cl + H_2$$

$$B_2H_6 + 6Cl_2 \rightarrow 2BCl_3 + 6HCl$$

4. Cleavage with Lewis bases:

Symmetrical:

$$B_2H_6 + N(CH_3)_3 \rightarrow 2H_3BN(CH_3)_3$$

Unsymmetrical:

$$B_2H_6 + 2NH_3 \rightarrow [H_2B(NH_3)_2]^+[BH_4]^-$$

5. Reduction:

$$2B_2H_6 + 2Na \rightarrow NaBH_4 + NaB_3H_8$$

$$B_2H_6 + NaBH_4 \rightarrow NaB_3H_8 + H_2$$

$$5B_2H_6 + 2NaBH_4 \rightarrow Na_2B_{12}H_{12}$$

Pentaborane(9)

This molecule illustrates two general trends: Attack by bases can remove the somewhat acidic bridging hydrogen:

$$B_5H_9 + NaH \rightarrow NaB_5H_8 + H_2$$

The pyramidal B_5H_9 loses one of its four bridging hydrogens and the resulting ion is "fluxional", that is, the location of the missing bridge is not stationary, and all the atoms in the base of the pyramid (four borons, four terminal hydrogens and three bridging hydrogens) appear equivalent on the time scale of nmr experiments which might otherwise have distinguished them.

Attack by electrophiles can lead to substitution at the apex of the pyramid:

$$B_5H_9 + I_2 \rightarrow B_5H_8I(apical) + HI$$

Decaborane(14)

Once again the bridging hydrogens can be removed by base:

$B_{10}H_{14} + OH^- \rightarrow B_{10}H_{13}^- + H_2O$

or converted to terminal hydrogens by reducing agents:

$$B_{10}H_{14} + 2Na \rightarrow Na_2B_{10}H_{14}$$

In this reaction, the product has two bridging hydrogens between B_1 and B_5 and B_7 and B_8.

Other nucleophiles will add at B_6 and B_9 with loss of two bridging hydrogens. Again, the two that are left bridge between B_1 and B_5 and B_7 and B_8:

$$B_{10}H_{14} + 2CH_3CN \rightarrow 6,9\text{-}(CH_3CN)_2B_{10}H_{12} + H_2$$

Electrophiles substitute terminal hydrogens at the bottom of the "basket" in the 1 and 3 or 2 and 4 positions, e.g.:

$$B_{10}H_{14} + I_2 \rightarrow 2,4\text{-}I_2B_{10}H_{12} + 2HI$$

There are two reactions that lead to a closed cage:

$$B_{10}H_{14} + 2Et_3NBH_3 \rightarrow [Et_3NH]^+_2[B_{12}H_{12}]^{2-}$$

and

$$(SEt_2)_2B_{10}H_{14} + HCCH \rightarrow B_{10}C_2H_{12} + H_2 + 2SEt_2$$

Polyhedral Borane Anions and Carboranes

Realize that two carbon atoms can replace two B^-'s in a *closo*-borane anion $B_nH_n^{2-}$. Derived molecule or molecule ions are the nido structures, which are missing one vertex relative to the closo structure and the more open arachno structures which are missing two vertices. Figure 12-12 shows structures from B_4 to B_{12}. see also Figure 12-8.

Skip the chemistry of these species.

The Tetrahydroborate Ion (BH_4^-)

This is an important reducing agent, source of H^-, and reagent to make other less ionic borohydrides.

$NaBH_4$ is stable in dry air and alkaline aqueous solution. (It will react with water initially but the reaction stops as the concentration of the hydrolysis product, sodium borate, builds up.)

$LiBH_4$ is similar to $NaBH_4$ but more sensitive to water.

$Al(BH_4)_3$ is liquid which explodes with air or water. It probably has pairs of hydrogen bridges like diborane.

$Zr(BH_4)_4$ is a molecular solid with three bridging hydrogens connecting each boron to the zirconium.

Boron-Nitrogen Compounds

The following are really equivalent representations, but the text uses the right-hand one to indicate a weaker bond:



Amine Boranes

This is the class of amine - BH_3 Lewis adducts. They contain the unit shown above. The safest synthesis is:

> $H_3NRCl + LiBH_4$  $H_2RN{:}BH_3 + LiCl + H_2$

Aminoboranes

These have the structure:



The molecules are flat, and rotation about the B—N bond is restricted, therefore the left-hand structure must be is a significant contributor. It is perhaps not correct to represent them as *canonical* structures since the geometries would be so different. The cleanest synthetic route is, for example:

> $(CH_3)_2NH + BCl_3$  $(CH_3)_2HN{:}BCl_3$
> $(CH_3)_2HN{:}BCl_3$  $(CH_3)_2N{:}BCl_2 + HCl$ (on heating)
> $(CH_3)_2N{:}BCl_3 + 2RMgBr$  $(CH_3)_2N{:}BR_2 + 2MgClBr$

Borazine

This six membered ring can be synthesised by several routes:

Unlike benzene, borazine undergoes addition reactions:



Notice where the H^{d+} and the Cl^{d-} end up: This illustrates how unrealistic the formal charges on the boron and nitrogen atoms really are!

Like benzene, borazine can form p-complexes with transition metals:

Aluminium, Gallium, Indium and Thallium

Aluminium is the most common metallic element in the crust of the earth, but the common minerals, for example, felspars and micas are rather difficult to process. Aluminum is obtained from bauxite, ($Al_2O_3.nH_2O$) and cryolite, Na_3AlF_6 by electrolysis. Gallium and Indium occur in traces in bauxite and all three are found in certain sulphite ores of other metals. While aluminium is obviously the most important, gallium is used in gallium arsenide semiconductors. The elements are all much more metallic than boron, but there are a number of borderline covalent compounds. All are trivalent, but for thallium the univalent state (Tl^+)

becomes the dominant state as covalent bond strenghts diminish down the group. Some thallium III compounds are thermodynamically unstable:

$$TlX_3 \longrightarrow TlX + X_2$$

The MX_3 compounds (halides and organometallic) are Lewis bases like boron. The strengths vary in the sequence:

$$B > Al > Ga > (In \quad Tl)$$

The trihalides are not monomers like BX_3 but are more or less associated e.g. Al_2Cl_6 and $(AlF_3)_n$.

All give aqua ions $[M(H_2O)_6]^{3+}$ in their salts obtained from aqueous solution.

Occurence, Extraction and Properities of the Elements

To obtain aluminum, bauxite is dissolved in sodium hydroxide to give sodium aluminate, $NaAl(OH)_4$. The insolubles which include hydrated iron oxide are filtered off, and the pH adjusted (with CO_2)to reprecipitate the aluminum as $Al(OH)_3.3H_2O$ which is then dehydrated to Al_2O_3 and dissolved in molten cryolite, Na_3AlF_6 for electrolysis. The other (less reactive) metals can be obtained by electrolysis of aqueous solutions.

- The metals are all soft and quite reactive.
- Aluminum is "passivated" by a film of oxide which prevents it reacting with oxygen, water and even dilute nitric acid. (If the surface is amalgamated, reaction with water can occur.)
- The metals dissolve in non-oxidizing dilute acids. Aluminum and gallium are amphoteric and will dissolve in sodium hydroxide.
- They react with the halogens and sulphur.
- Thallium reacts slowly because the Tl^+ salts which are formed are often insoluble and coat and passivate the metal surface.

The Oxides

- The most important are g-alumina, used as a stationay phase in liquid-solid chromatography and a-alumina, used as a catalyst in petroleum cracking.
- The gemstone, ruby is Al_2O_3 contaminated with traces of Cr^{3+} in place of the Al^{3+} and sapphire has Fe^{2+}, Fe^{3+} and Ti^{4+} replacing some of the Al^{3+}.

The Halides

- All the M(III) trihalides are known except the triiodide of thallium. The compound, TlI_3 is actually $Tl^+[I_3]^-$.
- The coodination numbers are 4 to 6 depending on the relative metal and halogen sizes.
- The 4-coordinate compounds are molecular compounds and have lower melting-points.
- They are strong Lewis bases and some can be used as Friedel-Crafts reaction catalysts:

  > $RCOCl + "AlCl_3"$ alt $RCO^+ + AlCl_4^-$

  The carbocation goes on to attacks the other organic reagent electrophilicly.

The Aqua Ions, Oxo salts and Aqueous Chemistry

The aqua ions all undergo hydrolysis:

$$[M(H_2O)_6]^{3+} \longrightarrow [M(H_2O)_5(OH)]^{2+} + H^+(aq)$$

Element	K_a
Al	1.12×10^{-5}
Ga	2.5×10^{-3}
In	2×10^{-4}
Tl	$\sim 7 \times 10^{-2}$

Salts of weak acids cannot exist in solution because the anions would be protonated and the hydroxides would precipitate.

The "hydroxides" of aluminum and gallium are amphoteric:

> $M(OH)_3(s) \rightleftharpoons M^{3+} + 3OH^-$
> $M(OH)_3(s) \rightleftharpoons MO_2^- + H^+ + H_2O$

Depending on the conditions, bridging hydroxide is also common:

> $2[M(H_2O)_5(OH)]^{2+} \rightleftharpoons [(H_2O)_5MOM(H2O)_5]^{4+} + H_2O$ (etc)

Hydroxides

The real hydroxides, by extension of the above, are complicated structures involving bridging OH^-, terminal H_2O and perhaps $[M(OH)_4]^-$ for some metals.

Alums

These are the compounds for which aluminum was originally named. They are double salts of formula $MM'(SO_4)_2.12H_2O$ where M^+ is usually an alkali metal ion (not Li^+) and M'^{3+} is Al^{3+} or another trivalent ion. For example, plain "alum" or "potash alum" is the potassium/aluminum salt and "chrome alum" is the potassium/chromium(III) salt. These compounds are characterized by easily grown octahedral crystals. Each metal ion is 6-coordinated by water.

Coordination Compounds

Examples are: $[Al(H_2O)_6]^{3+}$, $[AlF_6]^{3-}$, $Cl_3Al(N(CH_3)_3)_2$, $[Al(ox)_3]^{3-}$ and Al(8-hydroxyquinolinate)$_3$

Hydrides

The metal hydrides are not very stable except "AlH_3" which is an air-sensitive polymeric material. The tetrahydroaluminate ion AlH_4^- is an important reducing agent and hydride source which usually comes as lithium aluminum hydride. The analogous gallium compound exists. The compounds are very sensitive to hydrolysis which is very exothermic and can be explosive.

The is a series of MH_3 Lewis adducts with donor molecules which are generally more stable to, for example, hydrolysis than the parent hydrides.

Lower Valent Compounds

This section is mainly about Tl^+ which resembles K^+ and Ag^+ in its chemistry. This section was not covered in depth in lectures. Skip it.

Summary of the Periodic Trends for the Elements of Group 13

1. Boron
    a. Forms no simple B^{3+} cation.
    b. Forms covalent compounds almost exclusively, and polyatomic ions are internally covalently bonded.
    c. Has a maximum covalence of 4 corresponding to an octet.
    d. The trivalent compounds are usually strong Lewis acids.
    e. Its oxide and "hydroxide" are acidic.
    f. Forms many polyatomic borates.
    g. The trihalides are easily hydrolysed.
    h. Forms many hydrides and hydride anions which are polyhedral clusters: the boranes, carboranes and the borane anions. The simplest BH_4^- is a very important synthetic reagent
2. Aluminum
    a. Readily forms the Al^{3+} ion which is usually coordinated.
    b. Much more metallic than boron and forms many ionic compounds.
    c. Forms molecular compounds and ionic lattices with cordination numbers from 4 up to 6 and higher.
    d. Forms oxides which are chemically and thermally fairly inert.

e. Forms a mainly basic but quite amphoteric hydroxide.
f. Forms partially hydrolysable halides.
g. Forms a polymeric hydride and the AlH_4^- ion. The latter is important.

3. Gallium, Indium, and Thallium.
   a. Readily form M^{3+} aquo species and have a rich coordination chemistry.
   b. Form increasingly stable M^+ compounds especially thallium. Covalent bonds successively weaken down the group enhancing this trend.
   c. Halides are increasingly aggregated with the increasing size of the metals.
   d. Hydrides and hydride ions are not very important or stable.

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SECTION OVERVIEW

13.2: Occurence, Extraction, and Uses

Topic hierarchy

13.2A: Occurrence

13.2B: Extraction

13.2C: Major Uses of the Group 13 Elements and their Compounds

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13.3: Physical Properties

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13.3A: Electronic Configurations and Oxidation States

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13.3B: NMR Active Nuclei

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SECTION OVERVIEW

13.4: The Elements

A non-metal can be classified as an element that mostly lacks metallic attributes. Physically, non-metals tend to be highly volatile (easily vaporised), have low elasticity, and are good insulators of heat and electricity; chemically, they tend to have high ionization energy and electronegativity values, and gain or share electrons when they react with other elements or compounds. Seventeen elements are generally classified as nonmetals; most are gases (hydrogen, helium, nitrogen, oxygen, fluorine, neon, chlorine, argon, krypton, xenon and radon); one is a liquid (bromine); and a few are solids (carbon, phosphorus, sulfur, selenium, and iodine).

On moving across the periodic table, nonmetals are seen to adopt structures with progressively fewer nearest neighbours. Polyatomic nonmetals have structures with either three nearest neighbours, as is the case (for example) of carbon (in its standard state of graphite), or two nearest neighbours (for example) in the case of sulfur. Diatomic non-metals, such as hydrogen, have one nearest neighbour, and the monatomic noble gases, such as helium, have none. This gradual fall in the number of nearest neighbours is associated with a reduction in metallic character and an increase in nonmetallic character.

Allotropes are different structural forms of the same element in which changes in the connectivity of the covalent bonding between atoms results in substances with quite different chemical and/or physical properties. The change between allotropic forms is triggered by factors such as pressure, light, and temperature. Therefore the stability of a particular allotrope depends on particular conditions.

If covalent connectivity is the same but packing is different then you have **polymorphs** (eg. Monoclinic and Rhombic sulfur (S8) are polymorphs not different allotropes. S8 and S12 are different allotropes of S.

Many nonmetals have allotropes (that are less stable than their standard form) with either nonmetallic or metallic properties. Graphite, the standard state of carbon, has a lustrous appearance and is a fairly good electrical conductor. The diamond allotrope of carbon is nonmetallic, being translucent and having relatively poor electrical conductivity.

Catenation is the ability to form element-element bonded molecular networks.

Topic hierarchy

13.4A: Appearance

13.4B: Structures of the Elements

13.4C: Reactivity

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13.4A: Appearance

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13.4B: Structures of the Elements

Allotropes of boron

Boron can be prepared in several crystalline and amorphous forms. The best known crystalline forms are α-rhombohedral, β-rhombohedral, and β-tetragonal. Under special circumstances, boron can form α-tetragonal, and γ-orthorhombic allotropes. Two amorphous forms, one a finely divided powder and the other a glassy solid, are also known and a further 14 allotropes have been reported.

B12 icosahedral unit	
α-rhombohedral	
β-rhombohedral	

γ-orthorhombic
high pressure form

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13.4C: Reactivity

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13.5: Simple Hydrides

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13.5A: Neutral Hydrides

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13.5B: The [M H 4] − Ions

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13.6: Halides and Complex Halides

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13.6A: Boron Halides - BX_3 and B_2X_4

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13.6C: Lower Oxidation State Al, Ga, In, and Tl Halides

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SECTION OVERVIEW

13.7: Oxides, Oxoacids, Oxoanions, and Hydroxides

Topic hierarchy

13.7A: Boron Oxides, Oxoacids, and Oxoanions

13.7B: Aluminium Oxides, Oxoacids, Oxoanions, and Hydroxides

13.7C: Oxides of Ga, In, and Tl

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13.7A: Boron Oxides, Oxoacids, and Oxoanions

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13.7B: Aluminium Oxides, Oxoacids, Oxoanions, and Hydroxides

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13.7C: Oxides of Ga, In, and Tl

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13.8: Compounds Containing Nitrogen

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13.8A: Nitrides

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13.8B: Ternary Boron Nitrides

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13.8C: Molecular Species Containing B-N or B-P Bonds

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13.8D: Molecular Species Containing Group 13 Metal-Nitrogen Bonds

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SECTION OVERVIEW

13.9: Aluminium to Thallium - Salts of Oxoacids, Aqueous Solution Chemistry, and Complexes

Topic hierarchy

13.9A: Aluminium Sulfate and Alums

13.9B: Aqua Ions

13.9C: Redox Reactions in Aqueous Solution

13.9D: Coordination Complexes of the M^{3+} Ions

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13.9A: Aluminium Sulfate and Alums

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13.9B: Aqua Ions

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13.9C: Redox Reactions in Aqueous Solution

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13.9D: Coordination Complexes of the M^{3+} Ions

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13.10: Metal Borides

In metal borides, the bonding of boron varies depending on the atomic ratio B/M. Diborides have B/M = 2, as in the well-known superconductor MgB_2; they crystallize in a hexagonal AlB_2-type layered structure. Hexaborides have B/M = 6 and form a three-dimensional boron framework based on a boron octahedron (Fig. 1a). Tetraborides, i.e. B/M = 4, are mixtures of diboride and hexaboride structures. Cuboctahedron (Fig. 1b) is the structural unit of dodecaborides, which have a cubic lattice and B/M = 12. When the composition ratio exceeds 12, boron forms B_{12} icosahedra (Fig. 1c) which are linked into a three-dimensional boron framework, and the metal atoms reside in the voids of this framework.[1][2][3]

This complex bonding behavior originates from the fact that boron has only three valence electrons; this hinders tetrahedral bonding as in diamond or hexagonal bonding as in graphite. Instead, boron atoms form polyhedra. For example, three boron atoms make up a triangle where they share two electrons to complete the so-called three-center bonding. Boron polyhedra, such as B_6 octahedron, B_{12} cuboctahedron and B_{12} icosahedron, lack two valence electrons per polyhedron to complete the polyhedron-based framework structure. Metal atoms need to donate two electrons per boron polyhedron to form boron-rich metal borides. Thus, boron compounds are often regarded as electron-deficient solids.[4]

Icosahedral B_{12} compounds include[2] α-rhombohedral boron ($B_{13}C_2$), β-rhombohedral boron (MeB_x, 23≤x), α-tetragonal boron ($B_{48}B_2C_2$), β-tetragonal boron (β-AlB_{12}),[5] AlB_{10} or AlC_4B_{24}, YB_{25}, YB_{50}, YB_{66}, NaB_{15} or $MgAlB_{14}$, γ-AlB_{12},[5] BeB_3 [6] and SiB_6.[7]



Fig. 2. Relationship between the ionic radius of trivalent rare-earth ion and chemical composition of icosahedron-based rare-earth borides.

YB_{25} and YB_{50} decompose without melting that hinders their growth as single crystals by the floating zone method. However, addition of a small amount of Si solves this problem and results in single crystals [8] with the stoichiometry of $YB_{41}Si_{1.2}$.[9] This stabilization technique allowed the synthesis of some other boron-rich rare-earth (RE) borides.

Albert and Hillebrecht reviewed binary and selected ternary boron compounds containing main-group elements, namely, borides of the alkali and alkaline-earth metals, aluminum borides and compounds of boron and the nonmetals C, Si, Ge, N, P, As, O, S and Se. [10] They, however, excluded the described here icosahedron-based rare-earth borides. Note that rare-earth elements have *d*- and *f*-electrons that complicates chemical and physical properties of their borides. Werheit *et al.* reviewed Raman spectra of numerous icosahedron-based boron compounds.[11]

Figure 2 shows a relationship between the ionic radius of trivalent rare-earth ions and the composition of some rare-earth borides. Note that scandium has many unique boron compounds, as shown in figure 2, because of the much smaller ionic radius compared with other rare-earth elements.[3][12]

In understanding the crystal structures of rare-earth borides, it is important to keep in mind the concept of partial site occupancy, that is, some atoms in the described below unit cells can take several possible positions with a given statistical probability. Thus, with the given statistical probability, some of the partial-occupancy sites in such a unit cell are empty, and the remained sites are occupied.[13]

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13.11: Electron-Deficient Borane and Carbaborane Clusters - An Introduction

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CHAPTER OVERVIEW

14: The Group 14 Elements

Group 14 of the periodic table is often referred to as the carbon group. It is located in column 14 of the periodic table and houses the elements carbon, silicon, germanium, tin, lead, and ununquadium (C, Si, Ge, Sn, Pb, and Uuq, respectively). Each element in this group contains four valence electrons. A unique feature of this group is that the elements can form different anions and cations. Carbon forms a 4- anion whereas silicon and germanium form 4+ cations. Tin and lead can even form 2+ cat

Topic hierarchy

- 14.1: Introduction
- 14.2: Occurence, Extraction, and Uses
  - 14.2A: Occurrence
  - 14.2B: Extraction and Manufacture
  - 14.2C: Uses
- 14.3: Physical Properties
  - 14.3A: Ionization Energies and Cation Formation
  - 14.3B: Some Energetic and Bonding Considerations
  - 14.3C: NMR Active Nuclei
  - 14.3D: Mossbauer Spectroscopy
- 14.4: Allotropes of Carbon
  - 14.4A: Graphite and Diamond - Structure and Properties
  - 14.4B: Graphite - Intercalation Compounds
  - 14.4C: Fullerenes - Synthesis and Structure
  - 14.4D: Fullerenes - Reactivity
  - 14.4E: Carbon Nanotubes
- 14.5: Structural and Chemical Properties of Silicon, Germanium, Tin, and Lead
  - 14.5A: Structures
  - 14.5B: Chemical Properties
- 14.6: Hydrides
  - 14.6A: Binary Hydrides
  - 14.6B: Halohydrides of Silicon and Germanium
- 14.7: Carbides, Silicides, Germides, Stannides, and Plumbides
  - 14.7A: Carbides
  - 14.7B: Silicides
  - 14.7C: Zintl Ions Containing Si, Ge, Sn, and Pb
- 14.8: Halides and Complex Halides
  - 14.8A: Carbon Halides
  - 14.8B: Silicon Halides
  - 14.8C: Halides of Germanium, Tin, and Lead
- 14.9: Oxides, Oxoacids, and Hydroxides
  - 14.9A: Oxides and Oxoacids of Carbon
  - 14.9B: Silica, Silicates, and Aluminosilicates

14.9C: Oxides, Hydroxides, and Oxoacids of Germanium, Tin, and Lead
14.10: Siloxanes and Polysiloxanes (Silicones)
14.11: Sulfides
14.12: Cyanogen, Silicon Nitride, and Tin Nitride
14.12A: Cyanogen and its Derivatives
14.12B: Silicon Nitride
14.12C: Tin(IV) Nitride
14.13: Aqueous Solution Chemistry and Salts of Oxoacids of Germanium, Tin, and Lead

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14.1: Introduction

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14.2: Occurence, Extraction, and Uses

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14.2A: Occurrence

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14.3: Physical Properties

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14.3A: Ionization Energies and Cation Formation

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14.3B: Some Energetic and Bonding Considerations

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14.3C: NMR Active Nuclei

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14.3D: Mossbauer Spectroscopy

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SECTION OVERVIEW

14.4: Allotropes of Carbon

Carbon is capable of forming many allotropes in addition to the well known diamond and graphite forms. The physical properties of carbon vary widely with the allotropic form. For example, diamond is highly transparent, but graphite is opaque and black. Diamond is the hardest naturally-occurring material known, while graphite is soft enough to form a streak on paper (hence its name, from the Greek word "γράφω" which means "to write"). Diamond has a very low electrical conductivity, while graphite is a very good conductor. Under normal conditions, diamond, carbon nanotubes, and graphene have the highest thermal conductivities of all known materials.

All carbon allotropes are solids under normal conditions, with graphite being the most thermodynamically stable form. They are chemically resistant and require high temperature to react even with oxygen. The system of carbon allotropes spans a range of extremes:

Synthetic nanocrystalline diamond is the hardest material known.	Graphite is one of the softest materials known.
Diamond is the ultimate abrasive.	Graphite is a very good lubricant, displaying superlubricity.
Diamond is an excellent electrical insulator, and has the highest breakdown electric field of any known material.	Graphite is a conductor of electricity.
Diamond is the best known naturally occurring thermal conductor	Some forms of graphite are used for thermal insulation (i.e. firebreaks and heat shields), but some other forms are good thermal conductors.
Diamond is highly transparent.	Graphite is opaque.
Diamond crystallizes in the cubic system.	Graphite crystallizes in the hexagonal system.
Amorphous carbon is completely isotropic.	Carbon nanotubes are among the most anisotropic materials ever produced.

Topic hierarchy

14.4A: Graphite and Diamond - Structure and Properties

14.4B: Graphite - Intercalation Compounds

14.4C: Fullerenes - Synthesis and Structure

14.4D: Fullerenes - Reactivity

14.4E: Carbon Nanotubes

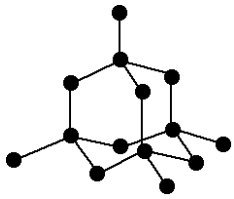
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14.4A: Graphite and Diamond - Structure and Properties

Covalent Network Solids are giant covalent substances like diamond, graphite and silicon dioxide (silicon(IV) oxide). This page relates the structures of covalent network solids to the physical properties of the substances.

Diamond

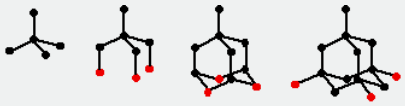
Carbon has an electronic arrangement of 2,4. In diamond, each carbon shares electrons with four other carbon atoms - forming four single bonds.



In the diagram some carbon atoms only seem to be forming two bonds (or even one bond), but that's not really the case. We are only showing a small bit of the whole structure. This is a giant covalent structure - it continues on and on in three dimensions. It is not a molecule, because the number of atoms joined up in a real diamond is completely variable - depending on the size of the crystal.

How to draw the structure of diamond

Don't try to be too clever by trying to draw too much of the structure! Learn to draw the diagram given above. Do it in the following stages:



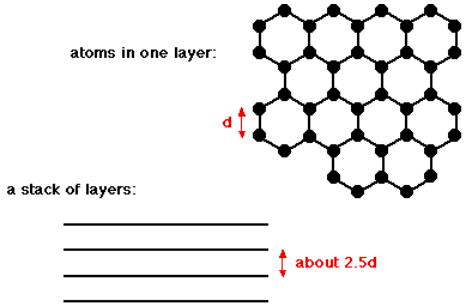
Practice until you can do a reasonable free-hand sketch in about 30 seconds.

Physical Properties of Diamond

- has a very high melting point (almost 4000°C). Very strong carbon-carbon covalent bonds have to be broken throughout the structure before melting occurs.
- is very hard. This is again due to the need to break very strong covalent bonds operating in 3-dimensions.
- doesn't conduct electricity. All the electrons are held tightly between the atoms, and aren't free to move.
- is insoluble in water and organic solvents. There are no possible attractions which could occur between solvent molecules and carbon atoms which could outweigh the attractions between the covalently bound carbon atoms.

Graphite

Graphite has a layer structure which is quite difficult to draw convincingly in three dimensions. The diagram below shows the arrangement of the atoms in each layer, and the way the layers are spaced.



Notice that you cannot really draw the side view of the layers to the same scale as the atoms in the layer without one or other part of the diagram being either very spread out or very squashed. In that case, it is important to give some idea of the distances involved. The distance between the layers is about 2.5 times the distance between the atoms within each layer. The layers, of course, extend over huge numbers of atoms - not just the few shown above.

> *You might argue that carbon has to form 4 bonds because of its 4 unpaired electrons, whereas in this diagram it only seems to be forming 3 bonds to the neighboring carbons. This diagram is something of a simplification, and shows the arrangement of atoms rather than the bonding.*

The Bonding in Graphite

Each carbon atom uses three of its electrons to form simple bonds to its three close neighbors. That leaves a fourth electron in the bonding level. These "spare" electrons in each carbon atom become delocalized over the whole of the sheet of atoms in one layer. They are no longer associated directly with any particular atom or pair of atoms, but are free to wander throughout the whole sheet. The important thing is that the delocalized electrons are free to move anywhere within the sheet - each electron is no longer fixed to a particular carbon atom. There is, however, no direct contact between the delocalized electrons in one sheet and those in the neighboring sheets. The atoms within a sheet are held together by strong covalent bonds - stronger, in fact, than in diamond because of the additional bonding caused by the delocalized electrons.

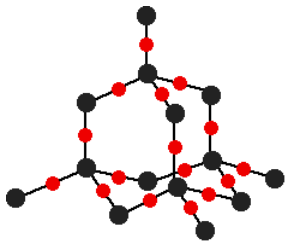
So what holds the sheets together? In graphite you have the ultimate example of van der Waals dispersion forces. As the delocalized electrons move around in the sheet, very large temporary dipoles can be set up which will induce opposite dipoles in the sheets above and below - and so on throughout the whole graphite crystal.

Graphite has a high melting point, similar to that of diamond. In order to melt graphite, it isn't enough to loosen one sheet from another. You have to break the covalent bonding throughout the whole structure. It has a soft, slippery feel, and is used in pencils and as a dry lubricant for things like locks. You can think of graphite rather like a pack of cards - each card is strong, but the cards will slide over each other, or even fall off the pack altogether. When you use a pencil, sheets are rubbed off and stick to the paper. Graphite has a lower density than diamond. This is because of the relatively large amount of space that is "wasted" between the sheets.

Graphite is insoluble in water and organic solvents - for the same reason that diamond is insoluble. Attractions between solvent molecules and carbon atoms will never be strong enough to overcome the strong covalent bonds in graphite. conducts electricity. The delocalized electrons are free to move throughout the sheets. If a piece of graphite is connected into a circuit, electrons can fall off one end of the sheet and be replaced with new ones at the other end.

Silicon dioxide: SiO_2

Silicon dioxide is also known as silica or silicon(IV) oxide has three different crystal forms. The easiest one to remember and draw is based on the diamond structure. Crystalline silicon has the same structure as diamond. To turn it into silicon dioxide, all you need to do is to modify the silicon structure by including some oxygen atoms.



Notice that each silicon atom is bridged to its neighbors by an oxygen atom. Don't forget that this is just a tiny part of a giant structure extending on all 3 dimensions.

Silicon Dioxide has a high melting point - varying depending on what the particular structure is (remember that the structure given is only one of three possible structures), but around 1700°C. Very strong silicon-oxygen covalent bonds have to be broken

throughout the structure before melting occurs. Moreover, it hard due to the need to break the very strong covalent bonds.Silicon Dioxide does not conduct electricity since there aren't any delocalized electrons with all the electrons are held tightly between the atoms, and are not free to move.Silicon Dioxide is insoluble in water and organic solvents. There are no possible attractions which could occur between solvent molecules and the silicon or oxygen atoms which could overcome the covalent bonds in the giant structure.

Introduction

- There are more compounds of carbon than of any other element except hydrogen. Most of carbon chemistry is handled in different courses (organic and biochemistry).
- There are no compounds containing anything like C^{4+} but some carbides contain a species approximating C^{4-}.
- There are transient ionic species: carbonium ions such as F_3C^+, and carbanions such as $(NC)_3C^-$. Notice the attached groups which would help to stabilize these species.
- Transient divalent carbon occurs in carbenes, R_2C:
- The strong C—C single bond and the ability to form double, C=C, and triple, CºC, bonds contributes to the huge versatility of carbon.

The Chemistry and Physical Properties of Diamond Graphite and the Fullerenes

Carbides

These come in three general types:

Ionic carbides are formed by elements of groups 1, 2 and aluminum. The actual for of the carbon varies, for example, aluminum carbide, based on its hydrolysis product seems to contain "C^{4-}" units:

$$\mathrm{Al_4C_3 + 6\,H_2O \longrightarrow 2\,Al(OH)_3 + 3\,CH_4} \qquad (14.4A.1)$$

but calcium carbide seems to contain $[C^{o}C]^{2-}$ units:

$$\mathrm{CaC + 2\,H_2O \longrightarrow Ca(OH)_2 + HC^{o}H} \qquad (14.4A.2)$$

Interstitial carbides are compounds of the transition metals with metallic properties and the C in tetrahedral holes in the metal atom lattice. The best known example is the extremely hard tungsten carbide, WC, used in cutting tools.

Covalent carbides include B_4C_3 and SiC (carborundum - an abrasive with a diamond-like structure)

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14.4B: Graphite - Intercalation Compounds

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14.4C: Fullerenes - Synthesis and Structure

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14.4D: Fullerenes - Reactivity

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14.4E: Carbon Nanotubes

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14.5: Structural and Chemical Properties of Silicon, Germanium, Tin, and Lead

Chemistry 242 - Inorganic Chemistry II
Chapter 15 - Silicon, Germanium, Tin and Lead

Introduction

- Silicon is th most abundant element after oxygen in the earth's crust occuring mostly as the silicates and quartz (SiO2).
- The other elements are acutally quite rare (~10^{-3}%) but tin an dlead are found in concetrated pockets of their ores (cassiterite, SnO_2 and galena, PbS_2) from which they are easily obtained, so they have been known and used since antiquity.
- The existence of germanium ('ekasilicon") was predicted by Mendleev when he constructed the first reasobably complete periodic table. It was isolated in 1886 from coal and zinc ores.
- The main uses of tin an dlead are as the metals and as synthetic reagents as their organo compounds. Silicon and germanium are the basis of the semicondutor industry.

Multiple Bonding

Because of the great versatility of carbon, it is interesting to compare the other members of group 14.

- Carbon dioxide is molecular gas whereas silicon dioxide is a network solid (in all its forms several forms).
- Dehydration of alcohols, ROH yields both alkenes and ROR depending on the conditions, but dehydrating R_3SiOH yields only $R_3SiOSiR_3$.
- Replacement of the hydrogen with tertiary butyl groups allows the isolation of similar compounds of silicon, germanium and tin.
- Silicon can use empty d-orbitals for pp - dp bonding. Examples are planar $(H_3Si)_3N$ *vs* pyramidal $(H_3C)_3N$ and linear H_3SiNCO vs H_3CNCO which is bent at the nitrogen. In both cases the nitrogen lone pair is delocalized by p-bonding with the silicon(s).

  In CR_3OCR_3 the Si-O-Si angle is around 109 ^{o} whereas in $R_3SiOSiR_3$ the angles range from 140 to 180 ^{o} indicative of Si=O dp - pp bonding.

  $(CH_3)_3COH$ is a very weak acid but $(CH_3)_3SiOH$ is stronger because the ion $(CH_3)_3SiO^-$ is stabilized by dp - pp bonding.

Stereochemistry

See Table 15-1 for summary information about the tetravalent state:

- All show tetrahedral coordination.
- Five coordinate complexes e.g. MX_5^- or M_nX_{5-n}- can be trigonal bipyramids or rarely square pyramidal if a constraining chelating ligand is used, e.g.$[XSi(O_2C_2H_4)_2]^-$.
- 6-coordinatate complexes are normally octahedral.

See table 15-2 for summary information about divalent states.

- Very often, but not always, the lone pair is stereochemically active and influences the molcular shape. F_2Pb is bent and so is $SiCl_3^-$.

Isolation and Properties of the Elements

- Silicon and germanium can be made by reduction of their dioxides by carbon or calcium carbide in an electric furnace, and then purified further by zone-refining.
- Tin and Lead are obtained by carbon reduction of their oxides or sulphides. I ffuther purification is necessary they can be dissolved in acid and redeposited electrolytically.
- Silicon and germanium are relatively inert but the following reactions occur:

  > *$Si + 2X_2$ alt SiX_4 (X_2 is a halogen)*
  >
  > *Si + excess OH^- alt silicates*
  >
  > *Si + excess HX alt no reaction except HF will give SiF_6^{2-}*

  Germanium is somewhat more reactive and will dissolve in sulphuric or nitric acids.

Tin and lead dissolve in several acids, hot alkalis and also react with halogens.

Hydrides

Compounds MH_4 all exist as spontaneously flammable gases and are not very important.

Chlorides

Compounds MCl_4 are all colourless liquids except $PbCl_4$ which is yellow. They are hydrolysed easily to give hydrous oxides. In hydrochloric acid the lower members, tin and lead, give MCl_6^{2-} ions in aqueous solution. The compounds are intermediates in the synthesis of organo compounds for example the infamous tetraethyl lead.

Oxygen Compounds

- Silica comes on three forms: quartz and crystobalite which are both crystalline, and silica glass. The glass has a very low coefficient of expansion and high melting point so it is relatively resistant to heat and sudden temperature changes. It is also transparent to a large part of the ultraviolet spectrum and therefore used in cells for spectrophotometry in that region.
- There are several important oxides of lead: PbO exists in a red from, litharge, and a yellow form, massicot. It is the most used Pb source of lead for synthesis. Pb_2O_3 which behaves like a mixture of PbO and PbO_2 although it is a well defined structure is called "red lead". It is used as an anti-rust coating for steel. Lead dioxide, PbO_2 is maroon in colour and has a structure similar to rutile (TiO_2). It is one of the electrode materials in lead/acid batteries.
- The oxides vary from acidic for SiO_2 to basic for tin and lead.

Complex Compounds

Anionic Complexes

Silicon forms a very stable fluoroanion:

$$SiO_2(s) + 6HF(aq) \text{ alt } 2H^+(aq) + SiF_6^{2-}(aq) + 2H_2O$$

The same anion is formed by the incomplete hydrolysis of SiF_4:

$$SF_4 + 2H_2O \text{ alt } SiO2 + SiF_6^{2-} + 2H^+ + 2HF$$

The other MF_6^{2-} ions are hydrolysed by bases or even water in the case of the lead complex ion. All the elements give analogous chloroanions, except silicon. The other fairly important anionic complex is obtained with oxalate, $[M(ox)_3]^{2-}$.

Cationic Complexes and Neutral Adducts

Can be formed with chelating uninegative oxygen donor ligands, e.g. $[Pb(acac)_3]^+$.

The MX_4 compounds are Lewis acids and can form adducts which are sometimes neutral MX_4L or MX_4L_2 molecular compounds but can also be ionic $[MX_2L_2]X_2$.

Alkoxides, Carboxylates and Oxo Salts

Typical preparative routes are, for alkoxides:

$$MCl_4 + 4ROH + 4(Et)_3N \text{ alt } M(OR)_4 + 4(Et)_3NHCl$$

Note the use of the triethylamine to "remove" the HCl which would be formed in its absence.

Carboxylates can be made by direct reaction:

$$Pb_3O_4 + 8CH_3COOH \text{ alt } Pb(CH_3COO)_4 + 2Pb(CH_3COO)_2 + 8H_2O$$

Lead tetraacetate is used as an oxidizing agent in certain organic reactions.

Tin and Lead (IV) salts are hydrated e.g $Pb(SO_4)_2.2H_2O$ and subject to extensive hydrolysis in aqueous solution.

The Divalent State

- This oxidation state becomes more and more stab;le down the group.
- Silicon dihalides are only transient species. GeF_2 and $GeCl_2$ can be isolated.

- Tin II fluoride and chloride are well known and useful. (SnF_2 is the active ingredient in many fluoridated toothpastes.) In solution, tin II is easily oxidized by air. The sulphates and nitrates are heavily hydrolysed: $Sn_3(OH)_4(NO_3)_2$ and $Sn_3(OH)_2SO_4$.
- Lead II is the best defined divalent state. Most lead II salts are not very water soluble. The exception are the nitrate and the acetate. The solid halides are always anyhdrous.

Silenes and Other Organic Compounds

It is possible to make some compounds containing a Si=Si or Ge=Ge double bonds.

The earliest attempts tried the reaction:

> $2R_2SiCl_2 + Na/K \text{ in THF} \xrightarrow{\text{alt}} R_2Si{=}SiR_2 + 4K/NaCl$

Without the bulky R groups cyclic polymers are generated typically with 6 silicons in a ring. By using sufficiently bulky organic groups, it was possible to prepare transient dimers, $R_2Si{=}SiR_2$, or monomers R_2Si. The first silene stable enough to isolate was prepared by the photochemical decomposition of $(mes)_2Si(SiMe_3)_2$:

> $2(mes)_2Si(SiMe_3)_2 \xrightarrow{\text{alt}} (mes)_2Si{=}Si(mes)_2 + Me_3Si\text{-}SiMe_3$



Unlike the carbon analogs, the molecule is not perfectly flat. The Si=Si double bond is 9% shorter than a normal Si-Si single bond, c.f. 13% in an olefin.

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14.5A: Structures

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14.5B: Chemical Properties

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14.6: Hydrides

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14.6A: Binary Hydrides

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14.6B: Halohydrides of Silicon and Germanium

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14.7: Carbides, Silicides, Germides, Stannides, and Plumbides

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14.7A: Carbides

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14.7C: Zintl Ions Containing Si, Ge, Sn, and Pb

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CHAPTER OVERVIEW

14.8: Halides and Complex Halides

14.8A: Carbon Halides

14.8B: Silicon Halides

14.8C: Halides of Germanium, Tin, and Lead

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14.8A: Carbon Halides

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14.9: Oxides, Oxoacids, and Hydroxides

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14.9A: Oxides and Oxoacids of Carbon

Carbon Monoxide

- A colorless and very dangerously toxic gas - it has no smell - boiling point -190 ^{o}C.
- It is thermodynamically unstable with respect to carbon and carbon dioxide, but the equilibrium is only established at high temperature:

$$2\,CO\,(g) \longrightarrow C\,(s) + CO_2\,(g) \tag{14.9A.1}$$

- An important primary industrial chemical, involved in several reaction sequences:

$$CH_4 + 2\,H_2O \longrightarrow CO_2 + 4\,H_2 \tag{14.9A.2}$$

$$C + H_2O \longrightarrow CO + H_2\ (+\,H_2O)''\text{water gas}'' \tag{14.9A.3}$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (\text{"water gas shift" reaction})$$

  Mixtures of carbon monoxide and hydrogen are called "synthesis gas" or "syngas".

- Formally CO is the anhydride of formic acid, HCCH, but CO does not react at room temperature with water.
- Carbon monoxide is unique in that it is a weak Lewis base (s-donor through carbon) but a very strong p-acceptor. Asa ligand it stabilizes transition metals in low zero or negative oxidation states.

Carbon Dioxide and Carbonic Acid

- Carbon dioxide makes up about 0.03% (300 ppm) of the earth's atmosphere. It is mainly produced from volcanic activity, fermentation of organic matter and fires of al types.
- Solid carbon dioxide sublimes at -78 ^{o}C at atmospheric pressure, making it a useful refrigerant ("dry ice").
- Carbonic acid H_2CO_3 is produced only very slowly when CO_2 is dissolved in water. The equilibrium constants usually quoted are:

$$\frac{[H^+]\{HCO_3{}^-\}}{[H_2CO_3]} = 4.16 \times 10^{-7} \tag{14.9A.4}$$

$$\frac{[H+][CO_3{}^{2-}]}{[HCO_3{}^-]} = 4.84 \times 10^{-11} \tag{14.9A.5}$$

but the first is incorrect because the real $[H_2CO_3]$ is much lower than what is calculated based on dissolved CO_2. The real constant is probably closer to 2x10^{-4} more in keeping with a compound with a C=O bond - see Chapter 7 section 12.

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14.9B: Silica, Silicates, and Aluminosilicates

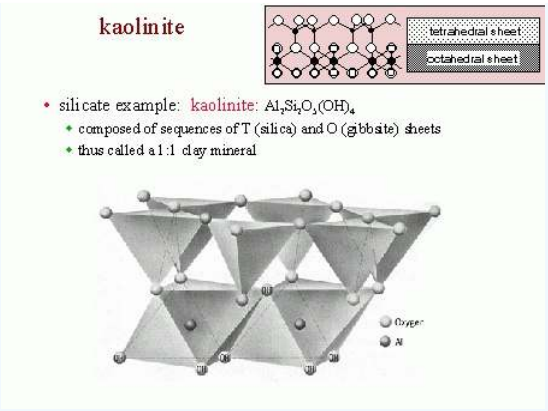


Figure 2: The structure of an individual cage of Faujasite. of Wikipedia.

While you are admiring this beautiful picture of faujasite, remember that the oxygen atoms have two unshared electron pairs in addition to the (Al,Si)-O-Si(or Al) bonds. Thus the oxygen atoms are sites to interact with positive site of molecules that passes by these structures. At present over 150 synthetic zeolites & zeotypes and 40 natural zeolites are known. Synthesis of zeolite is a very active field of study.

Aluminosilicates have three major minerals: **Andalusite, sillimanite**, and **kyanite**. Zeochem has been developing and manufacturing molecular sieve adsorbents since 1977. Simply put, their adsorbents are used to "screen" out impurities from a variety of applications by attracting and trapping the targeted contaminants. For example, in natural gas processing, molecular sieves are used to remove specific molecules from the gas stream to allow for more efficient downstream processing. Faujasite is a typical zeolite.

Applications of Zeolites?

As you have read above that there are many different kinds of zeolites, each with a definite structure and associate with it are unique properties. In terms of applications, we are assuming zeolites as porous aluminosilicates with large tunnels and cages for a fluid (gas and liquid) to pass through. The applications are based on the interactions between the fluid phase and the atoms or ions of the zeolites. In general terms, zeolites have many applications:

1. As selective and strong adsorbers: remove toxic material, selective concentrate a particular chemical, as Molecular Sieve. This link will be a very good to discuss zeolites. Currently, the site is under construction, but it has a very good framework. Even many deorderants are zeolite type.
2. As selective ion exchangers: for example used in water softener.
3. Superb solid acid catalysts, when the cations are protons H^+. As catalysts, their environmental advantages include decreased corrosion, improved handling, decreased environmentally toxic waste and minimal undesirable byproducts.
4. As builder: a material that enhance or protecting the cleaning power of a detergent. Sodium aluminosilicate is an ion exchange builder often used in laundry detergent as a builder. A builder inactive the hardness of water by either keeping calcium ions in solution, by precipitation, or by ion exchange.

123 ppm CaCO3 = 123 g per 106 g of water.

$$123\ \text{g}\ CaCO_3 \times \frac{1\ \text{mol}\ CaCO_3}{100\ \text{g}\ CaCO_3} \times \frac{2\ \text{mol}\ H^+}{1\ \text{mol}\ CaCO_3} \times \frac{1\ \text{mol}\ z\text{-}A}{12\ \text{mol}\ H^+} \times \frac{1926\ \text{g}\ z\text{-}A}{1\ \text{mol}\ z\text{-}A} \times \frac{100}{80}$$

= 494 g *zeolite A*

That 80 % of protons of the *zeolite A* is used means that we require a little more *zeolite A* than stoichiometric quantities.

DISCUSSION

Zeolites are aluminosilicates with open frames strcutures discussed above. Replacement of each Si atom by an Al atom in silicates results in having an extra negative charge on the frame. These charges must be balanced by trapping positive ions: H^+, Na K^+, Ca^{2+}, Cu^{2+} or Mg^{2+}. Water molecules are also trapped in the frame work of zeolites.

In this example, we assume that when we soak the zeolite in water containing Ca^{2+}, and Mg^{2+} ions, these ions are more attrative to the zeolite than the small, singly charged protons. We further assumed that 80 percent of the protons in zeolite are replaced by other ions.

✔ 58.5 g/mol.

```
              1 mol  0.8*12 mol NaCl 100 58.5 g NaCl
10 kg z-A -------- --------------- --- -----------
          2.190 kg   1 mol z-A      20  1 mol NaCl

   = 12822 g NaCl = 12.8 kg NaCl
```

DISCUSSION

How much salt is required if 60% of the sodium ions are effectively used to replace all the divalent ions?

Contributors and Attributions

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

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14.10: Siloxanes and Polysiloxanes (Silicones)

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14.11: Sulfides

Compounds with C-S bonds

Carbon disulphide is perhaps the most important as a solvent and a synthetic reagent. It gives rise to other carbon sulphur compounds such as:

$$\mathrm{RO^-} - + \mathrm{CS_2} \longrightarrow \mathrm{ROCS_2^-} \ (\text{xanthates}) \tag{14.11.1}$$

$$\mathrm{HS^-} + \mathrm{CS_2} \longrightarrow \mathrm{CS_3^{2-}} \ (\text{thiocarbonate}) \tag{14.11.2}$$

$$\mathrm{R_2HN} + \mathrm{CS_2} \longrightarrow \mathrm{R_2NCS_2^-} \ (\text{dithiocarbamates}) \tag{14.11.3}$$

These ions are important ligands for transition metals, and the dithiocarbamtes are sued as agricultural fungicides.

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14.12: Cyanogen, Silicon Nitride, and Tin Nitride

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14.12A: Cyanogen and its Derivatives

Compounds with C-N Bonds: Cyanides and Related Compounds

Cyanogen (NºC–CºN) is a poisonous and flammable gas (bp -21 ºC. Although its heat of formation is strongly endothermic 297 kJ mol^{-1} is is fairly stable. Impure cyanogen polymerizes to form "paracyanogen". Cyanogen is prepared by nitrogen dioxide catalyzed oxidation of hydrogen cyanide by oxygen:

$$2\,HCN + NO_2 \longrightarrow (CN)_2 + NO + H_2O \tag{14.12A.1}$$

$$NO + ½O_2 \longrightarrow NO_2 \tag{14.12A.2}$$

It is also formed by oxidation od CN^- with Cu^{2+}:

$$Cu^{2+} + 2\,CN^- \longrightarrow CuCN + ½(CN)_2 \tag{14.12A.3}$$

Notice the similarity between the above reaction and the one below:

$$Cu^{2+} + 2\,I^- \longrightarrow CuI + ½(I)_2 \tag{14.12A.4}$$

The term "pseudo halogen/halide" is often applied to molecules and derived ions such as $(CN)_2$ and CN^-. Notice also the existence of HCN which has its parallel in the hydrohalic acids and the reaction of cyanogen with base:

$$(CN)_2 + 2\,OH^- \longrightarrow CN^- + OCN^- + H_2O \tag{14.12A.5}$$

Compare:

$$(Cl)_2 + 2\,OH^- \longrightarrow Cl^- + OCl^- + H_2O \tag{14.12A.6}$$

The reaction of cyanogen with oxygen produces one of the hottest flames known at about 5000 ºC.

Hydrogen cyanide boils at 25.6 ºC. It is very poisonous and has an odor of almonds which not everyone can smell. It is a very good solvent due to its high dielectric constant, e = 107. It is made on an industrial scale (~300 000 tons in 1980) as follows:

$$CH_4 + 3\,O_2 + 2\,NH_3 \longrightarrow 2\,HCN + 6\,H_2O \tag{14.12A.7}$$

with Pt/Rh or Pt/Ir catalyst and 800 oC.

or

$$CH_4 + NH_3 \longrightarrow HCN + 3\,H_2 \tag{14.12A.8}$$

with Pt catalyst and 1200 oC

Cyanides are made industrially via the calcium cyanamide salt by the processes:

$$CaC_2 + N_2 \xrightarrow{1100\ degrees} CaNCN + C \tag{14.12A.9}$$

$$CaNCN + C + Na_2CO_3 \longrightarrow CaCO_3 + 2\,NaCN \tag{14.12A.10}$$

or

$$NaNH_2 + C \longrightarrow NaCN\ (500 - 600\,oC) \tag{14.12A.11}$$

(NCN^{2-} which yields cyanamide itself, H_2NCN, by hydrolysis of the salt, is isoelectronic with CO_2.)

Cyanide is important, among other things, as a very good p-acceptor ligand like CO.

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14.12B: Silicon Nitride

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14.12C: Tin(IV) Nitride

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14.13: Aqueous Solution Chemistry and Salts of Oxoacids of Germanium, Tin, and Lead

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CHAPTER OVERVIEW

15: The Group 15 Elements

The nitrogen family includes the following compounds: nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), and bismuth (Bi). All Group 15 elements have the electron configuration ns^2np^3 in their outer shell, where n is the principal quantum number.

Topic hierarchy

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15.2: Occurence, Extraction, and Uses

- 15.2A: Occurrence
- 15.2B: Extraction
- 15.2C: Uses

15.3: Physical Properties

- 15.3A: Bonding Considerations
- 15.3B: NMR Active Nuclei
- 15.3C: Radioactive Isotopes

15.4: The Elements

- 15.4A: Nitrogen
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- 15.4C: Arsenic, Antimony, and Bismuth

15.5: Hydrides

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- 15.5B: Hydrides, \(E_2H_4\) (E = N, P, As)
- 15.5C: Chloramine and Hydroxylamine
- 15.5D: Hydrogen Azide and Azide Salts

15.6: Nitrides, Phosphides, Arsenides, Antimonides, and Bismuthides

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- 15.6B: Phosphides
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15.7: Halides, Oxohalides, and Complex Halides

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- 15.7B: Oxofluorides and Oxochlorides of Nitrogen
- 15.7C: Phosphorus Halides
- 15.7D: Phosphoryl Trichloride, \(POCl_3\)
- 15.7E: Arsenic and Antimony Halides
- 15.7F: Bismuth Halides

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- 15.8D: Dinitrogen Tetraoxide, \(N_2O_4\), and Nitrogen Dioxide, \(NO_2\)
- 15.8E: Dinitrogen Pentaoxide, \(N_2O_5\)

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15.11E: Chiral Phosphate Anions
15.12: Oxoacids of Arsenic, Antimony, and Bismuth
15.13: Phosphazenes
15.14: Sulfides and Selenides
15.14A: Sulfides and Selenides of Phosphorous
15.14B: Arsenic, Antimony, and Bismuth Sulfides
15.15: Aqueous Solution Chemistry and Complexes

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15.1: Introduction

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15.2A: Occurrence

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15.2C: Uses

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15.3: Physical Properties

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15.3A: Bonding Considerations

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15.3B: NMR Active Nuclei

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15.3C: Radioactive Isotopes

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15.4: The Elements

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15.4A: Nitrogen

- Nitrogen forms a range of different types of compounds:
  - In combination with the most electropositive element ionic nitrides (N^{3-}) are formed.
  - Also forms anionic species NR_2^- and NR^{2-}.
  - Forms cationic compounds NR_4^+ for the maximum covalency of four bonds.
  - Forms compounds with single, double and triple covalent bonds to itself, carbon and oxygen.
  - There are some paramagnetic compounds of nitrogen, i.e. with an odd number of electrons, notably certain oxides.
- In its three-covalent compounds, the following generallities apply:
  - Nitrogen is almost always a Lewis donor (except in very special cases, e.g. NF_3).
  - Although based on a tetrahedral shape with the lone-pair occupying one site, optical isomers of potentially chiral compounds :NRR'R" cannot be isolated because the molecules invert so easily through a planar transition state (like an umbrella turning inside-out).
  - There are a few cases where the lone-pair is delocalized into empty orbitals on the attached groups in which nitrogen atom is planar. An example is $N(SiMe_3)_3$.
- Probably due to repulsion between the lone pairs, nitrogen-nitrogen single bonds are rather weak, e.g. 160 kJ mol^{-1} in H_2N-NH_2 as compared to a carbon-carbon bond dissociation energy of around 350 kJ mol^{-1} in CH_3-CH_3.
- The ability to form multiple bonds via pp - pp overlap is one of the things that distinguishes nitrogen from the other members of group 15. Because of the lone pairs, molecules will normally not be linear. alt

Occurence and Properties of the Element

- Dinitrogen constitutes 78% of the atmosphere. The ratio of the abundances of the two stable isotopes is $^{14}N/^{15}N = 272.0$ so ^{15}N at natural abundance is somewhat useful for nmr studies, and when it is enriched it, can be used in tracer studies.
- Nitrogen is obtained by low temperature distillation (fractionation) of air. It will normally still be contaminated with about 30 ppm of oxygen and some argon. It can be prepared pure by thermally decomposing sodium azide, NaN_3.
- The NºN bond is very stron with a dissociation energy of 944.7 kJ mol^{-1}. For this reason, many hitrogen compounds are "endothermic" that is they have positive heats of formation.
- Compared to other molecules with triple bonds, nitrogen is very unreactive. It will react with lithium at room temperature, and there are bacteria which are able to activate it by a mechanism that remains unclear.
- At high temperatures it is more reactive:

$N_2 + 3H_2$ alt $2NH_3$

$N_2 + O_2$ alt $2NO$

$N_2 + 3Mg$ alt Mg_3N_2

$N_2 + CaC_2$ alt CaN

$CN + C$

Nitrides

- The ionic ones only occur with the most electropositive elements. Hydrolysis yields ammonia.
- Transition metals tend to form non-stoichiometric compounds.
- The important covalent nitrides are covered in the section concerning the other element

Hydrides

Ammonia

- This topic has been covered to some extent elsewhere.
- The following sequence of conversions is industrially important: alt
- Ammonia is very soluble in water due to extensive hydrogen bonding. Th eresulting solutions are conventionally called ammonium hydroxide, but:

$NH_3 + H_2O$ $NH_4^+ + OH^-$ $Kb = 1.77x10^{-5}$

i.e. there is not much ammonium ion in solutions of ammonia!

- Ammonium salts are mostly soluble, and the ammonium ion, r = 1.48 Å, resembles potassium ion, r = 1.33, Å or rubidium ion, r = 1.48 Å.
- Ammonium salts sublime via this type of reaction:
  $NH_4Cl(s)$ $NH_3(g) + HCl(g)$
  $NH_4NO_3(s)$ $NH_3(g) + HNO_3(g)$

  But with oxidizing anions, decomposition can occur:

  $NH_4NO_3(l)$ $N_2O(g) + 2H_2O$
  $(NH_4)_2Cr_2O_7(s)$ $N_2(g) + 4H_2O(g) + NH_3$

Hydrazine

- Hydrazine bp 114 ºC is explosive when pure but organo-substitued hydrazines are more stable.
- Preparation:

  $NH_3 + NaOCl$ $NaOH + NH_2Cl$ $NH_3 + NH_2Cl + NaOH$ $N_2H_4 + NaCl + H_2O$ but the following reaction is catalysed by traces of transition metal ions, notable Cu^{2+}:

  $NH_2Cl + NH_2Cl$ $2NH_4Cl + +N_2$ Therefore, the reaction is perfomed in the presence of gelatin which complexes the metal ions and suppresses their catalytic effect.

- Hydrazine is a "bifunctional" base:
  $N_2H_4 + H_2O$ $N_2H_5^+ + OH^-$ $K_b1 = 8.5x10^{-7}$
  $N_2H_5^+ + H_2O$ $N_2H_6^{2+} + OH^-$ $Kb2 = 8.9x10^{-15}$

  These equilibria leasd to two sets of hydrazinium salts.

- Hydrazine and the substituted hydrazines are used as reducing agents. In combination with N_2O_4 as oxidant, alkylhydrizines are used in teh vernier rocket engines on things like the space shuttle.

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15.4B: Phosphorus

- Phosphorus is found extensively non-crystalline phosphate rocks such as apatite, $Ca_3(PO_4)_2.CaX_2$ where $X^- = F^-$ and/or Cl^- and/or OH^-.

  Arsenic, antimony and bismuth come mainly from sulphide ores such as mispickel, FeAsS, and stibnite, Sb_2S_3.

- Apart from the hydrides such as phosphine, PH_3, the elements are very different to nitrogen.

  The differences arise from lower pp - pp bonding effectiveness replaced by use of the d-orbitals for dp - pp bonding, and gradual increasing stability of the lower oxidation states on descending the group:

  - compare O=N-OR with $P(-O-R)_3$.
  - Compare the oxides of nitrogen with multiple bonding in all of them with P_4O_6 and P_4O_{10} containing only single bonds.
  - Compare nitric acid, $HONO_2$, with pp - pp bonding with phosphoric acid, $(HO)_3PO$, where phosphorus uses a d-orbital to form a p-bond to the oxygen (perhaps).

- Unlike nitrogen, the rest of the elements of group 15 can exceed 4-covalency, e.g. PF_5, PF_6^- by using empty d-orbitals.
- As ligands with electron rich transition metals, all the group 15 elements, except nitrogen, can use their empty d-orbitals to act as p-acceptors (i.e. they are "soft").

The Elements

- Phosphorus, the most reactive can be obtained by carbon reduction of calcium phosphate:

  > $Ca_3(PO_4)_2 + 6SiO_2 + 10C$ alt $P_4 + 6CaSiO_3 + 10CO$

  The yellow phosphorus, P_4 must be collected under water since it inflames in air.

- The other elements can be obtained by carbon reduction of their oxides.
- Reactivity:
  - All the elements will react directly with oxygen especially if heated.
  - The products of reaction with oxidizing acids, e.g. nitric acid illustrate the increasing metallic character down the group. The products are: H_3PO_4, H_3AsO_4, Sb_4O_6 and $Bi(NO_3)_3$. Note that the products are in the V oxidation state for phosphorus and arsenic, and the III-state for antimony and bismuth. Bismuth produces a nitrate salt.
  - Compounds can be formed by direct reaction with other non-metals. One important compound is gallium arsenide, a semiconductor which is particularly heat resistant.

Hydrides

- The hydrides are all gases and increasingly unstable down the group. The classical (Sherlock Holmes style) test for arsenic is to generate AsH_3 by reduction and observe the metallic arsenic mirror produced by decomposition of the gas on the glass of the test tube above the reaction mixture.
- The (Lewis) basic properties decrease down the group. There are some phosphonium, PH_4^+ compounds, but water tends to be a stronger base than PH_3 so they tend to decompose in water.

Halides and Oxo Halides

- Refer to Figure 17-1 for some reactions of PCl_3 which are typical of the group.
- Note that the solid state structures sometimes differ from the gas phase ones, for example, PCl_5 is probably like PF_5, a trigonal bipyramidal molecule in the gas phase, but in the solid state it is ionic: $[PCl_4]^+[PCl_6]^-$. PBr_5, in the solid state, is $[PBr_4]^+Br^-$.
- The Oxo trihalides, notably PCl_3O, undergo reaction similar to the trihalides.
- SbOCl and BiOCl are obtained when hydrocloric acid solutions containing Sb^{3+} or Bi^{3+} are diluted.
- The pentaflourides are all good flouride ion acceptors to give non-coordinating anions such as AsF_6^- and the corresponding "super acids".

Oxides

- The oxides of the elements in the V state are most stable (relative to III) for phosphorus in addition to being the most acidic.
- "Phosphorus pentoxide" which is actually P_4O_{10} is one of the most powerful dessicating agents known. It reacts with water to produce phosphoric acid, and can remove water from nitric acid, to give dinitrogen pentoxide and from sulphuric acid, itself a powerful dessicant to give sulphur trioxide.

  Its structure is a tetrahedron of phosphorus atoms connected by oxygens on th esix edges of the tetrahedron and each carrying a terminal oxygen atom.
- The phosphorus III oxide, P_4O_6 is formed when phosphorus burns in a limited supply of oxygen. One of its forms is similar to P_4O_{10} except that the terminal oxygen atoms are absent. It hydrolyses to phosphorous acid, H_3PO_3. Arsenic and Antimony produce similar compounds.
- The oxide and hydroxide of bismuth III, Bi_2O_3 and $Bi(OH)_3$, obtained by adding base to solutions of Bi^{3+} salts, are not acidic at all.

Sulphides

- Some are somewhat related to the oxides but the numbers of terminal sulphurs varies more, others are chain or ribbon structures. Skip the details.

The Oxo Acids and their Esters

- The oxo acids have already been covered to some extent in chapter 5.
- Phosphorous acid is obtained by controlled hydrolysis of PCl_3 or P_4O_6. Its formula is best written $HP(O)(OH)_2$ to illustrate its structure with only two acidic hydrogens (on oxygen).
- Similarly, hypophosphorous acid is best written $H_2P(O)(OH)$. It is a monobasic acid.
- Phosphite esters, $P(OR)_3$, are related to PX_3 compounds. These compounds are easily oxidised to phosphate esters: $OP(OR)_3$.
- The phosphite esters undergo the Michaelis-Arbusov reaction with alkyl halides:

  $$P(OR)_3 + R'X \xrightarrow{\text{alt}} [(RO)_3PR']^+X^- \xrightarrow{\text{alt}} (RO)_2(R')PO + RX$$

  The dialkyl phosphonates produced are structurally similar to phosphorous acid where R replaces H.
- (Ortho)phosphoric acid, H_3PO_4, when pure is a solid melting at 42.5 ^oC. It i ssold as "syrupy phosphoric acid", an 85% solution in water. It is made by hydrolysing P_4O_{10} or treating phosphate rocks with sulphuric acid. Its dehydration to pyrophosphoric acid $(HO)_2(O)POP(O)(OH)_2$ is slow.
- Phosphate esters are important in biochemical processes for energy storage and transfer. The mechanism of their hydrolysis has been extensively studied in this context.

Complexes of the Group 15 Elements

- Antimony forms some complexes, particularly with chelating oxy-ligands. One of the oldest know in the complex with tartrate, $K_2[Sb_2(d\text{-}C_4H_2O_6)_2].3H_2O$ known as "tartar emetic".
- Bismuth should behave much more like a true metal, but the simple aquo ion, $[Bi(H_2O)_6]_{3+}$ does not seem to exist. There is a range of extensively hydrolysed clusters ions containing several bismuth III ions bridged by oxygen, and carrying OH groups. Skip the details!

Phosphorus-Nitrogen Compounds

- Six and eight membered ring systems and linear polymers containing ...-N=P-N=P-... chains can be generated by the reaction:

  $$nPCl_5 + nNH_4Cl \xrightarrow{\text{alt}} (NPCl_2)n + 4nHCl \ (Solvents: C_2H_2Cl_4 \text{ or } C_6H_5Cl)$$

  Then the chlorine atoms can be replace by alkoxy, alkyl, or aryl groups by reaction with NaOR or LiR reagents. The resulting compounds can be made into useful fibres or elastomers.

Compounds with Element-Element Double Bonds

- Just as in group 14, therehave been attempts to stabilize compounds with multiple bonds betweemn the group 15 elements and just as in group 14, bulky groups get the job done. Molecules with double bonds between two phosphorus atoms, a phosphorus

and an arsenic or two arsenic atoms have been sythesized using groups such as 2,4,6-$(Me_3C)_3C_6H_2$ and $(Me_3Si)_3C$ have been used. The typical synthetic routes (where E = P or As) are:

> $2RPCl_2 + 2Mg \rightarrow RP{=}PR + 2MgCl_2$

or

> $RECl_2 + H_2E'R' \rightarrow RE{=}E'R' + 2HCl$ *(In the presence of base)*

Allotropes of phosphorus

Elemental phosphorus exists in a number of different allotropes.

White phosphorus

The most important form of elemental phosphorus from the perspective of applications and the chemical literature is white phosphorus. It consists of tetrahedral P4 molecules, in which each atom is bound to the other three atoms by a single bond. This P4 tetrahedron is also present in liquid and gaseous phosphorus up to the temperature of 800 °C when it starts decomposing to P2 molecules. Solid white phosphorus exists in two forms. At low-temperatures, the β form is stable. At high-temperatures the α form is predominant. These forms differ in terms of the relative orientations of the constituent P4 tetrahedra.

The history of the match is linked to the discovery of the allotropes of phosphorus.

white	
red	
violet - Hittorf	

black

Phosphorene is an allotrope of phosphorus normally used to designate a single layer of black phosphorus that may be somewhat flattened. Conceptually the structure is similar to the carbon-based graphene, hence the name phosphorene. However phosphorene is a semiconductor, unlike graphene which is a semimetal. Recently a sample that was about 20 layers thick was shown to demonstrate high-speed data communication on nanoscale optical circuits.

White phosphorus is the most reactive, the least stable, the most volatile, the least dense, and the most toxic of the allotropes. White phosphorus gradually changes to red phosphorus. This transformation is accelerated by light and heat, and samples of white phosphorus almost always contain some red phosphorus and accordingly appear yellow. For this reason, white phosphorus that is aged or otherwise impure is sometimes called yellow phosphorus. White phosphorus glows in the dark (when exposed to oxygen) with a very faint tinge of green and blue, is highly flammable and pyrophoric (self-igniting) upon contact with air and is toxic (causing severe liver damage on ingestion). Owing to its pyrophoricity, white phosphorus has been used as an additive in napalm. The odour of combustion of this form has a characteristic garlic smell, and samples are commonly coated with white "phosphorus pentoxide", which consists of P_4O_{10} tetrahedra with oxygen inserted between the phosphorus atoms and at their vertices. White phosphorus is insoluble in water but soluble in carbon disulfide.

Red phosphorus

In 1847 Anton von Schrotter found that sunlight changed white/yellow into red phosphorus, even when moisture and atmospheric oxygen were rigorously excluded. The red product was separated from the residual yellow phosphorus by treatment with carbon disulfide. Red phosphorus was also prepared from the yellow variety by heating it to about 250 °C. in an inert gas. Heating to higher temperatures reconverted the red modification to the yellow one.
Red phosphorus exists as an amorphous network and does not ignite in air at temperatures below 240 °C.

Violet phosphorus

In 1865, Johann Hittorf heated red phosphorus in a sealed tube at 530 °C. The upper part of the tube was kept at 444 °C. Brilliant opaque monoclinic, or rhombohedral, crystals sublimed.
This form is sometimes known as "Hittorf's phosphorus" (or violet or α-metallic phosphorus).

Black phosphorus

Black phosphorus is the thermodynamically stable form of phosphorus at room temperature and pressure. It is obtained by heating white phosphorus under high pressures (12,000 atmospheres). In appearance, properties and structure it is similar to graphite, being black and flaky, a conductor of electricity, and having puckered sheets of linked atoms.
Black phosphorus has an orthorhombic structure and is the least reactive allotrope: a result of its lattice of interlinked six-membered rings. Each atom is bonded to three other atoms.

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15.4C: Arsenic, Antimony, and Bismuth

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15.5: Hydrides

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15.5A: Trihydrides, EH_3 (E = N, P, As, Sb, and Bi)

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15.5B: Hydrides, E_2H_4 (E = N, P, As)

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15.5C: Chloramine and Hydroxylamine

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15.5D: Hydrogen Azide and Azide Salts

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15.6: Nitrides, Phosphides, Arsenides, Antimonides, and Bismuthides

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15.6A: Nitrides

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15.6B: Phosphides

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15.6C: Arsenides, Antimonides, and Bismuthides

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15.7: Halides, Oxohalides, and Complex Halides

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15.7A: Nitrogen Halides

Nitrogen Halides

- Most compounds NX_3 are known, together with the mixed ones for F and X. Some, for example $NI_3.nNH_3$ are explosive.
- N_2F_2 and N_2F_4 are known.
- The halogen azides XN_3 are also known.
- NF_3 is exceptional in that it has no basic properties. Salts of NF_4^+ such as $[NF_4]^+[BF_4]^-$ can be prepared and are powerful oxidizing agents.

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15.7B: Oxofluorides and Oxochlorides of Nitrogen

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15.7C: Phosphorus Halides

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15.7D: Phosphoryl Trichloride, $POCl_3$

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15.7E: Arsenic and Antimony Halides

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15.7F: Bismuth Halides

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SECTION OVERVIEW

15.8: Oxides of Nitrogen

Topic hierarchy

15.8A: Dinitrogen Monoxide, N_2O

15.8B: Nitrogen Monoxide, NO

15.8C: Dinitrogen Trioxide, N_2O_3

15.8D: Dinitrogen Tetraoxide, N_2O_4, and Nitrogen Dioxide, NO_2

15.8E: Dinitrogen Pentaoxide, N_2O_5

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15.8A: Dinitrogen Monoxide, $N\ 2\ O$

Dinitrogen monoxide (Nitrous Oxide)

- Nitrous oxide, N=N=O, also known as "laughing gas" is used as an anesthetic. It is prepared by the decomposition of molten ammonium nitrate. See above.

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15.8B: Nitrogen Monoxide, NO

Nitrogen Monoxide (Nitric Oxide)

- Nitric oxide is a colourless paramagnetic gas.
- It is made, for example, by the reduction of concentrated nitric acid by copper, or reduction of nitrates and nitrites:
  $HNO_3 + 3Cu$  $3Cu(NO_3)_2 + 4H_2O + 2NO$
- Its reaction include:
  - Oxidation to NO_2 by oxygen or to nitric acid by permanganate (used for its analysis).
  - Reduction to N_2O (e.g. by sulphur dioxide) or NH_2OH (e.g. by Cr_{2+}).
  - It disproportionates at high temperature to N_2O and NO_2.
- It is implicated in blood pressure control.
- An odd-electron molecule, the bond order (which is most clearly rationalized using molecular orbital theory) is 2.5, with the odd electron in a p-antibonding orbital. This electron is easily lost to give the N^oO^+ ion which is isolectronic with C^oO or C^oN^-. The bond in NO^+ is 0.09 Å shorter than in NO, and the stretching vibration frequency increases from 1840 cm^{-1} to 2150-2400 cm^{-1} depending on how the NO^+ is behaving as a s-donor or p-acceptor ligand.

  Note that dimerization to O=N-N=O would not increase the (total) number of bonds, and turns out to be energetically unrewarding.
- Nitrosonium salts include $[NO]^+_2SO_4^{2-}$ implicated in the "lead chamber process" for the manufacture of sulphuric acid.

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15.8C: Dinitrogen Trioxide, $N\ 2\ O\ 3$

- This blue liquid, ON-NO_2, is made from equimolar quantities of NO and NO_2. The N-N bond is 1.89 Å long, i.e. very weak.

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15.8D: Dinitrogen Tetraoxide, N_2O_4, and Nitrogen Dioxide, NO_2

Nitrogen Dioxide and Dinitrogen Tetroxide

- These two oxides are almost always present in an equilibrium mixture:

	alt	alt
Solid at -11.2 ^oC (mp) straw coloured	0.01%	99.99%
Vapour a 21.5 ^oC (bp) Brown	0.1%	99.9%
Gas at 140 ^oC Dark brown	100%	0%

The N-N bond in N_2O_4 is longish at 1.75 Å: the adjacent formal positive charges may be partly responsible. Since the unpaired electon in NO_2 can be considered (using molecular orbital theory) to reside in an antibonding p-orbital centred largely on the nitrogen, the formation of N_2O_4 is more favorable than in the other paramagnetic oxides, NO and ClO_2. There are two other isomers of N_2O_4 which are possible: $ONONO_2$ and ONOONO but thse appear to be less stable.

- The most important reactions are:
  - With water: $2NO_2$ (or N_2O_4) alt $HNO_3 + HNO_2$ (then $3HNO_2$ alt $HNO_3 + NO + H_2O$)
  - Using it, it is possible to prepare anyhdrous nitrates which are not accessible by other routes. As an example, copper will dissolve in liquid N_2O_4 to give $Cu(NO_3)_2.N_2O_4$ (The other product is NO)

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15.8E: Dinitrogen Pentaoxide, $N\ 2\ O\ 5$

- An unstable colorless solid made by dehydration of nitric acid by phosphorus pentoxide (P_4O_{10}). In the solid state, its structure is that of the nitronium nitrate, $NO_2^+NO_3^-$.

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SECTION OVERVIEW

15.9: Oxoacids of Nitrogen

Topic hierarchy

15.9A: Isomers of \(H_2N_2O_2\)

15.9B: Nitrous Acid, \(HNO_2\)

15.9C: Nitric Acid, \(HNO_3\), and its Derivatives

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15.9A: Isomers of $H_2N_2O_2$

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15.9B: Nitrous Acid, HNO_2

Nitrous Acid

- Nitrous acid can be prepared by:
  $Ba(NO_2)_2(aq) + H_2SO_4(aq)$ alt $BaSO_4(s) + HNO_2(aq)$
- It readily diproportionates to nitric acid and nitic oxide.

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15.9C: Nitric Acid, HNO_3, and its Derivatives

The Nitronium Ion

- This ion is present in nitric acid which autoionizes thus:
  $2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$

  It is also formed in mixtures of nitric and sulphuric acid:

  $HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + HSO_4^- + H_2O$
- It is the electrophile in organic nitration reactions.
- It can be isolated as its perchlorate $[NO_2]^+[ClO_4]^-$ and as its pyrosulphate:
  $HNO_3 + SO_3 \rightleftharpoons [NO_2]^+[HS_2O_7]^-$
- It is linear and isoelectronic with CO_2

Summary of Reaction and Interconversions Among the Oxides, Oxo Acids and Oxo Anions of Nitrogen

These species and many of their interconversions are of considerable industrial and environmental importance:

Reactions that do not involve disproportionation	Reactions involving disproportionation
(a) $2NO_2 + O_3 \rightleftharpoons N_2O_5 + O_2$	
(b) $2NO_2 + H_2O_2 \rightleftharpoons 2HNO_3$	
(c) $2NO_2 \rightleftharpoons N_2O_4$	
(d) $N_2O_4 + \text{xs Cu} \rightleftharpoons Cu(NO_3)_2$	
(e) $2HNO_2 + 2HI \rightleftharpoons I_2 + 2NO + 2H_2O$	
(f) $Fe^{2+} + HNO_2 + H^+ \rightleftharpoons Fe^{3+} + NO + H_2O$	(a') $2NO_2 + H_2O \rightleftharpoons HNO_3 + HNO_2$
(g) $2NO + O_2 \rightleftharpoons 2NO_2$	(b') $N_2O_4 \rightleftharpoons NO^+ + NO_3^-$
(h) $2Cu + NO_2 \rightleftharpoons Cu_2O + NO$	(c') $N_2O_4 + 3H_2SO_4 \rightleftharpoons NO^+ + NO_2^+ + 3HSO_4^- + H_3O^+$
(i) $C + NO_2 \rightleftharpoons CO_2 + \frac{1}{2}N_2$	(d') $3HNO_3 \rightleftharpoons HNO_2 + 2NO + H_2O$
(j) $NO_2 + 2H_2 \rightleftharpoons \frac{1}{2}N_2 + 2H_2O$	(e') $3NO \rightleftharpoons N_2O + NO_2$
(k) $2NO_2 + 7H_2 \rightleftharpoons 2NH_3 + 4H_2O$	
(l) $N_2 + 3H_2 \rightleftharpoons 2NH_3$	
(m) $4NH_3 + 3O_2 \rightleftharpoons 2N_2 + 6H_2O$	
(n) $4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$	
(o) $N_2 + O_2 \rightleftharpoons 2NO$	

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15.10: Oxides of Phosphorous, Arsenic, Antimony, and Bismuth

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15.10A: Oxides of Phosphorous

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15.10B: Oxides of Arsenic, Antimony, and Bismuth

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SECTION OVERVIEW

15.11: Oxoacids of Phosphorous

Topic hierarchy

15.11A: Phosphinic Acid, H_3PO_2

15.11B: Phosphonic Acid, H_3PO_3

15.11C: Hypodiphosphoric Acid, $H_4P_2O_6$

15.11D: Phosphoric Acid, H_3PO_4, and its Derivatives

15.11E: Chiral Phosphate Anions

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15.11A: Phosphinic Acid, \(H_3PO_2\)

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15.11B: Phosphonic Acid, $H\ 3\ \ P\ \ O\ 3$

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15.11C: Hypodiphosphoric Acid, $H\ 4\ P\ 2\ O\ 6$

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15.11D: Phosphoric Acid, $H\ 3\ P\ O\ 4$, and its Derivatives

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15.11E: Chiral Phosphate Anions

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15.12: Oxoacids of Arsenic, Antimony, and Bismuth

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15.13: Phosphazenes

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15.14: Sulfides and Selenides

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15.14A: Sulfides and Selenides of Phosphorous

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15.14B: Arsenic, Antimony, and Bismuth Sulfides

Learning Objectives

In this lecture you will learn the following

- Organoaresnic and organoantimony compounds.
- Preparation and reactivity of pentavlent As and Sb compounds.

Organoelement compounds of group 15

Organic chemistry of non-metal phosphorus, metalloids such as arsine and antimony along with metallic element bismuth is termed as organoelement chemistry. The importance given to organoarsenic compounds earlier due to their medicinal values was waded out after antibiotics were discovered and also their carcinogenic and toxic properties were revealed. Also, the synthetically important organometallic compounds of group 13 and 14 masked the growth of group 15 elements. However, the organoelement compounds of phosphorus, arsenic and antimony find usefulness as ligands in transition metal chemistry due to their σ-donor and π-acceptor abilities which can be readily tuned by simply changing the substituents. These donor properties are very useful in tuning them as ligands to make suitable metal complexes for metal mediated homogeneous catalysis. Although organoelement compounds can be formed in both +3 (trivalent and tricoordinated) and +5(pentavalent and tetra or pentacoordinated) oxidation states, trivalent compounds are important in coordination chemistry.

For organoelement compounds of group 15, the energy of E—C bond decreases in the order, E = P > As > Sb > Bi, and in the same sequence E—C bond polarity increases.

Organometallic compounds of As(V) and Sb(V)

Due to the strong oxidizing nature of pentahalides, the direct alkylation or arylation to generate ER_5 is not feasible, but can be prepared in two steps.
A few representative methods of preparation are given below:



Structures and properties

Pentaalkyl or pentaaryl derivatives are moderately thermally stable. On heating above 100°C, they form trivalent compounds as shown below:



Reaction with water,



Pentavalent compounds readily form “tetrahedral onium” cations and “octahedral and hexacoordinatged ate” anions.



In solid state, Ph_5As adopts trigonal bipyramidal geometry, whereas Ph_5Sb prefers square based pyramidal geometry although the energy difference between the two is marginal.

The salts of the type $[R_4E]^+$ adopt tetrahedral geometry, whereas hexacoordinated anions $[R_6E]^-$assume octahedral geometry.

Mixed organo-halo compounds of the type R_nEX_{5-n} adopt often dimeric structures due to the presence of lone pairs of electrons on X which can readily coordinate to the second molecule. The following structural types can be anticipated.



The thermal stability of R_nEX_{5-n} decreases with decreasing 'n'. Thermal reactions are essentially the reverse reactions of addition reactions used in the preparation of R_5E.



Objectives In this lecture you will learn the following

- Preparation of trivalent compounds.
- Mono and bis derivatives.
- Reaction of organo arsenic and antimony compounds.
- Structural features of organolead compounds.

Organometallic compound of As(III) and Sb(III).

Direct synthesis

Mono- derivatives



Bis derivatives:



Reactions of trialkyl derivatives, R_3E



The transition metal chemistry of R_3E, phosphines, arsines or stibines has been extensively studied because of their distinct donor and acceptor properties. Among them, the phosphines or tertiary phosphines (R_3P) are the most valuable ligands in metal mediated homogeneous catalysis. Interestingly, the steric and electronic properties can be readily tuned by changing the substituents on phosphorus atoms. Chapter 16 is fully dedicated to the chemistry of phosphines.

Properties

Trialkyl derivatives are highly air-sensitive liquids with low boiling points and some of them are even pyrophyric. Triphenyl derivatives are solids at room temperature and are moderately stable and oxidizing agents such as $KMnO_4$, H_2O_2 or TMNO are needed for oxidation to form $Ph_3E{=}O$.
Cyclic and acyclic derivatives containing E—E bonds

E—E single bonds:

The E—E bond energies suggest that they do not have greater stability and the stability decreases down the group.
The simplest molecules include $Ph_2P—PPh_2$, $Me_2As—AsMe_2$ prepared by coupling reactions:



The weakness of E—E bonds accounts for many interesting reactions and a few of such reactions are listed below:



Cyclic and polycyclic derivatives can be prepared by employing any of the following methods:



Problems:

1. Confirm that the octahedral structure of $[Ph_6Bi]^-$ is consistent with VSEPR theory.

   Solution:
   Octahedral similar to PF_6^-
   5 (Bi valence electrons) + 6 (each Ph) + 1 (-ve charge) = 12 electrons

   i.e. six pairs, octahedral geometry

2. Comment on the stability of $BiMe_3$ and $Al_2(^iBu)_6$ with respect to their thermal decomposition and give chemical equations for their decomposition.

   Solution:
   Similar to other heavy p-block elements, Bi—C bonds are weak and readily undergo homolytic cleavage. The resulting methyl radicals will react with other radicals or form ethane

   The $Al_2(^iBu)_6$ dimer readily dissociates. At elevated temperature dissociation is followed by β-hydrogen elimination. This type of elimination is common for organometallic compounds that have alkyl groups with β-hydrogens, can form stable M—H bonds, and can provide a coordination site on the central metal.

   The decomposition reaction is:

3. Using a suitable Grignard reagent, how would you prepare (i) MeC(Et)(OH)Ph; (ii) $AsPh_3$.

   Solution:

   i. Add a Grignard reagent to a C=O bond, then acidify.

      Several possibilities, e.g.
      Me-C(O)-Et + PhMgBr → Me-C(OMgBr)(Et)(Ph) → MeC(Et)(OH)Ph or Me-C(O)-Ph + EtMgBr → etc
   ii. $AsCl_3 + 3PhMgBr \rightarrow AsPh_3 + 3MgBrCl$.

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15.15: Aqueous Solution Chemistry and Complexes

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CHAPTER OVERVIEW

16: The Group 16 Elements

The oxygen family, also called the chalcogens, consists of the elements found in Group 16 of the periodic table and is considered among the main group elements. It consists of the elements oxygen, sulfur, selenium, tellurium and polonium. These can be found in nature in both free and combined states.

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16.3A: NMR Active Nuclei and Isotopes as Tracers

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16.4: The Elements

Introduction

- Oxygen is another very ubiquitous (found everywhere) element. Compounds are known with every element except helium, neon and krypton.
- Oxygen forms ionic oxides containing O^{2-} with metals.
- Oxygen is frequently bi-covalent, X-O-Y or X=O.
- O^- will form one covalent bond, eg OH^- and O^+ can form three, eg H_3O^+. Vary rarely, tetracovalent O^{2+} is found. An example is $Be_4O(ac)_6$ where the O^{2+} is at the centre of a tetrahedron of Be atoms.

Ionic Oxides

- The formation of an ionic oxide requires a high lattice energy, and low ionization potential of the cation to overcome the highly endothermic O=O bond dissociation energy, 496 kJ mol^{-1}, and electron attachment enthalpy for 2 electrons, 752 kJ mol^{-1} in total.

Covalent Oxides

- The compounds with non-metals are covalent and can be molecular, e.g. CO_2 or network structures, e.g. SiO_2.
- The same two examples demonstrate the ability of oxygen to be involved in pp - pp bonding or pp - dp bonding. (The Si-O-Si bonds in SiO_2 are nearly linear.)

Acid-Base Properties of Oxides

- The oxygen anions, oxide, O^{2-}, superoxide, O_2^-, and peroxide, O_2^{2-} are hydrolysed istantly by water:

$$O^{2-} + H_2O \rightleftharpoons 2OH^-$$
$$O_2^- + H_2O \rightleftharpoons O_2 + HO_2^- + OH^-$$
$$O_2^{2-} + H_2O \rightleftharpoons HO_2^- + OH^-$$

- **Acidic Oxides**: The non-metal oxides in this category are sometimes called "acid anyhdrides":

$$N_2O_5 + H_2O \rightleftharpoons 2HNO_3$$
$$SO_3 + H_2O \rightleftharpoons H_2SO_4$$
$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

- Sometime neutral water is not enough and a base is needed:

$$Sb_2O_5 + 2OH^- + 5H_2O \rightleftharpoons 2Sb(OH)_6^-$$

- Sometimes an acidic oxide is needed:

$$Na_2O + SiO_2 \rightleftharpoons Na_2SiO_3$$

Some oxides are **amphoteric** and others are more inclined to undergo redox reactions than acid base reactions if they are not inert, e.g. MnO_2.

Occurence, Isolation and Allotropy

- There are three natural isotopes of oxygen of relative abundance: ^{16}O = 99.759%, ^{17}O = 0.0374% and ^{18}O = 0.2039%

  The heavier ones can be enriched by fractionation of liquid oxygen and they are used in tracer studies.

- There are two molecular forms (allotropes), dioxygen, O_2 the common form, and trioxygen, ozone, O_3.
- Dioxygen is a paramagnetic molcule with 2 unpaired electrons. Molecular orbital theory provides a ready explanation for this: valence bond theory does not.
- Ozone is a paramagnetic bent molecule formed when dioxygen is passed through an electric discharge or irradiated with ultra-violet light. Its sharp odour can be smelled aroung electric motors and some older photcopiers. The liquid is dark blue. Liquid dioxygen is pale blue.

Chemical Properties of Oxygen and Ozone

- Ozone is the more oxidizing of the two.
- Ozone can be measured by the reaction:

$$O_3 + KI + H_2O \rightleftharpoons I_2 + 2KOH + O_2$$

  The iodine is titrated with thiosulphate.

- Ozone is used in place of chlorine for water treatment.
- Oxygen is a common contaminent in organic and aqueous solvents, and it can be very difficult to remove.

Hydrogen Peroxide

- Hydrogen peroxide, H_2O_2, is a colorless liquid boiling at 152.1 ^oC.
- It is ~40% more dense than water, and like water it is extensively hydrogen bonded. When pure it can decompose explosively. The most stable rotational conformation has a tortion angle of 96.5^o - see Figure18-1.
- It is unstable with respect to water and dioxygen by -97 kJ mol^{-1}.
- It is somewhat more acidic than water:

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \quad k = 1.5x10^{-12}$$

- There are two principle methods of synthesis:

  a. 

  b.
$$2HSO_4^- \rightleftharpoons HO(O)_2S\text{-}O\text{-}O\text{-}S(O)_2OH + 2e^- \text{ (by electrolysis)}$$
$$HO(O)_2S\text{-}O\text{-}O\text{-}S(O)_2OH + H_2O \rightleftharpoons H\text{-}O\text{-}O\text{-}S(O)_2OH + H_2SO_4 \text{ (fast)}$$
$$H\text{-}O\text{-}O\text{-}S(O)_2OH + H_2O \rightleftharpoons H_2SO_4 + H_2O_2 \text{ (slow)}$$

  The H_2O_2 can be obtained 90-98% pure by distillation.

- Hydrogen peroxide is a good oxidizing agent, fast in base and slower in acid and often acts via a free radical mechanism.

The Peroxides and Superoxides

- Ionic **peroxides** are formed by the alkali and alkaline earth elements (not Be). They are also oxidizing agents.
- Paramagnetic ionic **superoxides** are formed by potassium, rubidium and cesium. They are very powerful oxidizing agents.
- Other covalent peroxides include the peroxo acids, e.g. peroxosulphuric and peroxodisulphuric acid, the intermediates in the production of H_2O_2 shown above, and the dangerously explosive organic peroxides ROOR which form by free radical oxidation of ethers. (They are the reason why ethers shold never be distilled to dryness unless the peroxides have been destroyed immediately beforehand by washing with with $FeSO_4$ or passing the ether over activated alumina. A solution of Fe^{2+} and SCN^- is used to test for their presence - look for the formation of the blood red $[Fe^{III}(SCN)]^{2+}$ ion.)

The Dioxygenyl Radical (O_2^+)

See notes on Chapter 21.

Dioxygen as a Ligand

Read this section - oxygen binding to transition metals is of interest because of its binding by haemoglobin and myoglobin. Note the structural types.

Oxygen Compounds as Ligands

More transition metal chemistry. Skip it for now.

Oxygen Florides

See notes on Chapter 20.

Chemistry 242 - Inorganic Chemistry II
Chapter 19 - Sulphur, Selenium, Tellurium and Polonium

Introduction

These elements differ considerably from oxygen:

- a. Their electronegativity is lower.
  b. Their covalent bonding is generally weaker.
  c. Hydrogen bonding, where it is a possibility is very weak.
- The do not form compounds where pp - pp bonding is needed, but rather use dp - pp bonding especially with oxygen.
- A covalence exceeding 4 is possible by the use of empty d-orbitals. The 6-coordinate geometry is increasingly favoured down the group.
- There are sulphur compounds with very long chains (second only to carbon)
- Tellurium an dpolonium are fairly metallic in their properties.

Occurence an dReactions of the Elements

- Sulphur occurs "native" (i.e. as sulpur) in deposits from which it is extracted with high pressure hot water (Frasch process). It is also obtained from hydrogen sulphide in natural gas and petroleum - if it were left, it cause a pollution problem when the fuels are burned.

  $$2H_2S + SO_2 \xrightarrow{alt} 3S + H_2O$$

- Selenium and tellurium come from silver and copper smelting flue gases. (These metals come from sulphide ores. Selenium and tellurium tend to be found with sulphur.)
- Sulphur forms a number of allotropes:
  - Behaviour on melting:

Solid	~112 ^oC (just melted)	160 ^oC	444.6 ^oC (just boiling)	Vapour phase
S_8 Yellow	$S_{13.8}$	S_n (n is maximum) Dark brown	S_n, (incl S_3, S_4 Dark red)	S_8 going to S_2 at higher temperatures

  A rubbery material called "plastic sulphur" can be obtaind by quickly cooling molten sulphur.

  - There are several crystalline modifications of S_8 stable at different temperatures.
  - It is possible to isolate other rings sizes from 6 to 20. Engel's sulpur contains S_6 rings.
- Sulphur is used extensively to harden synthetic and natural rubbers - "vulcanization". Bridging S_2 units are of the things that hold proteins in their correct shapes.

Hydrides

- The main one is hydrogen sulphide, H_2S, which smells of rotten eggs and is very much more poisonous than hydrogen cyanide.
- The compounds are all gases whose stability decreases down the group.
- The acidity of the hydrides increases down the group.
- The series of sulphanes, H_2S_n where n is 2 to 6 have been characterized. There are higher ones, but their separation is impossible since the chains tend to break. They are synthesized by the reaction:

  $$S_nCl_2 + 2H_2S \xrightarrow{alt} H_2S_{n+2} + 2HCl$$

Halides and Oxohalides of Sulphur

Sulphur Flourides

- Synthesis:

  $$S_8 + xs\ F_2 \xrightarrow{alt} SF_6\ (+ SF_4 + S_2F_{10})$$
  $$SCl_2(l) + 4NaF(s) + SF_4(g) + Na_2S + 2NaF$$

- Sulphur tetrafluoride (bp = -30 °C) is quite reactive, for example it is easily hydrolysed:

  $$SF_4 + 2H_2O \rightarrow SO_2 + 4HF$$

  It is used as a selective fluorinating agent:

  $>C=O$ is converted to $>CF_2$

  $-C(O)OH$ is converted to $-CF_3$

- Sulphur hexafluoride (sublimes at -64 °C) is very inert kinetically (since the hydrolysis is thermodynamically very favorable). Presumably it cannot further expand its coordination sphere to a reaction intermediate.

  It is used as a gaseous electrical insulator, much better than air, because of its high dielectric constant and lack of reactivity.

Sulphur Chlorides

- **Disulphur Dichloride and Sulphur Dichloride**

  $$\frac{1}{4}S_8(s) + Cl_2(g) \rightarrow S_2Cl_2$$

  (SCl_2 is unstable, decomposing slowly to S_2Cl_2 and chlorine.)

  Sulphur dichloride or disulphur dichloride will dissolve more sulphur to form sulphanes upto around $S_{100}Cl_2$.

- **Thionyl Chloride**

  $$SO_2 + PCl_5 \rightarrow SOCl_2 + POCl_3$$

  Thionyl chloride is a liquid (bp = 80 °C) which is rapidly hydrolysed:

  $$SOCl_2 + H_2O \rightarrow SO_2(g) + 2HCl(g)$$

  Because the hydrolysis products are both gases, one of its great uses in inorganic chemistry is in the dehydration of hydrated metal chlorides to produce the anhydrous substance.

- **Sulphuryl Chloride**

  $$SO_2 + Cl_2 \rightarrow SO_2Cl_2 \; FeCl_3 \; catalyst$$

  It is used as a chlorinating agent in organic synthesis.

Oxides and Oxo Acids

Take note of Table 19-1 in the text - it contains an important summary of the sulphur oxoacids. Know the names and structures.

Sulphur Dioxide

- is a gas boiling at -10 °C which is a useful solvent when liquified and can act as a ligand towards transition metals.
- Although it is formally the anhydride of sulphurous acid, H_2SO_3 it does not react with water to any significant extent. However, the soluble salts of bisulphite, HSO_3^{2-}, and sulphite, SO_3^{2-} are well characterized.

Sulphur Trioxide

- This oxide is the anyhdride of sulphuric acid, and does indeed react with water to produce it.
- It is produced by the oxidation of sulphur dioxide with oxygen catalysed by a heterogeneous catalyst such as V_2O_5 (the "contact process") or a homogeneous catalyst such as nitric oxide (the "lead chamber process").

Thiosulphate Ion

- This ion is formed by the reaction of sulphur with sulphite:

  $$SO_3^{2-}(aq) + S(s) \rightarrow S_2O_3^{2-}(aq)$$

- It is used in iodometric titrations forming the tetrathionate ion:

  $$S_2O_3^{2-} + I_2 \rightarrow 2I^{2-} + S_4O_6^{2-}$$

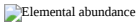
- It is used as "fixer" in photography, specifically, it dissolves silver chloride by complexing the silver ion as $[Ag(S_2O_3)_2]^{3-}$:

  $$AgCl(s) + 2Na_2S_2O_3(aq) \rightarrow Na_3[Ag(S_2O_3)_2] + NaCl$$

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16.4A: Dioxygen

Oxygen is a member of the chalcogen group (Group 16) of the periodic table and is a highly reactive nonmetallic element and oxidizing agent that readily forms compounds (notably oxides) with most elements. By mass, oxygen is the third-most abundant element in the universe, after hydrogen and helium. At standard temperature and pressure, STP, two atoms of the element bind to form dioxygen, O_2, a diatomic gas that is colourless, odourless, and tasteless.



Discovery

Oxygen was discovered independently by Carl Wilhelm Scheele, in Uppsala, Sweden in 1773 or earlier, and Joseph Priestley in Wiltshire, UK in 1774, but Priestley is generally given the credit since his work was published first. The name oxygen was coined in 1777 by Antoine Lavoisier, whose experiments with oxygen helped to discredit the then-popular phlogiston theory of combustion and corrosion. Its name derives from the Greek roots οξυζ oxys, "acid", literally "sharp", referring to the sour taste of acids and -γενης *genes* meaning "creator", because at the time of naming, it was mistakenly thought that all acids required oxygen in their composition.

Allotropes of oxygen

There are 2 main allotropes of oxygen although a third has recently been shown to form under high pressures.

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Some allotropes of oxygen

O_2 - dioxygen	O_3 - ozone	O_8 - red oxygen

Dioxygen - O_2

The common allotrope of elemental oxygen is often just called oxygen, O_2, but to help distinguish it from the element may be called dioxygen or molecular oxygen. Elemental oxygen is most commonly encountered in this form, as about 21% (by volume) of the Earth's atmosphere is O_2, the remainder largely being dinitrogen, N_2. At STP, dioxygen is a colourless, odourless gas, in which the two oxygen atoms are chemically bonded to each other giving rise to two unpaired electrons occupying two degenerate molecular orbitals. The electron configuration of O_2 molecules in this form, a diradical, indicates that they should be paramagnetic. This is a classic example of where a simple Lewis structure fails to account for the properties and where an MO approach correctly provides the explanation.

Lewis structure for dioxygen MO diagram for dioxygen The electron configuration (ignoring 1s orbitals) is:
$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^2$ and from this the Bond Order is found to be ½(2 -2 + 2 + 4 -2) = 2 that is, a double bond as shown in the Lewis structure as well. The difference though is that the Lewis structure does not predict the molecule to be paramagnetic. The bond length is 121 pm and the bond energy is 498 $kJmol^{-1}$.

A video clip showing liquid dioxygen being poured between the faces of a magnet and attracted into the magnet field has been prepared as a Harvard Natural Sciences Lecture Demonstration.

With 2 electrons to be placed in 2 degenerate orbitals, a number of variations are possible and the arrangement above where the 2 electrons are parallel is considered to be the most stable. Note that the spin multiplicity is given by the formula, 2S+1 and so for S=1 from s=½ + ½ then 2S+1 = 3 i.e. a spin triplet.

MO diagram for 2e 2o
a) e^-s parallel (triplet $^3\Sigma_g$), b) 2 e^-s in 1 orbital (singlet $^1\Delta_g$), c) e^-s opposed (singlet $^1\Sigma_g$) Singlet oxygen is the name commonly used for the electronically excited state shown in b) and it is less stable than the normal triplet state a) by 94.7 $kJmol^{-1}$. In isolation, singlet oxygen can persist for over an hour at room temperature. The other singlet state at 157.8 $kJmol^{-1}$ shown in c) is very short lived and relaxes quickly to b). Because of differences in their electron shells, singlet and triplet oxygen differ in their chemical properties. Singlet oxygen is highly reactive.

Reactions of triplet dioxygen are restricted by conservation of spin state rules and at ambient temperatures this prevents direct reaction with all but the most reactive substrates, e.g. white phosphorus. At higher temperatures, or in the presence of suitable catalysts, reactions proceed more readily. For instance, most flammable substances are characterised by an autoignition temperature above which they will undergo combustion in air without an external flame or spark.

The energy difference between the ground state and singlet oxygen is 94.7 $kJmol^{-1}$ which would correspond to a transition in the near-infrared at ~1263 nm. In the isolated molecule, this transition is strictly forbidden by spin, symmetry and parity selection rules, making it one of nature's most forbidden transitions. In other words, direct excitation of ground state oxygen by light to form singlet oxygen is very improbable. As a consequence, singlet oxygen in the gas phase is extremely long lived (72 minutes). Interaction with solvents however, can reduce the lifetime to microseconds or even nanoseconds.

Various methods for the production of singlet oxygen exist. A photochemical method involves the irradiation of normal oxygen gas in the presence of an organic dye as a sensitizer, such as methylene blue. Singlet oxygen can be produced chemically as well. One of the chemical methods is by the reaction of hydrogen peroxide with sodium hypochlorite. This is convenient in small laboratories and for demonstrative purposes:
$H_2O_2 + NaOCl \rightarrow O_2(^1\Delta_g) + NaCl + H_2O$ In photosynthesis, singlet oxygen can be produced from the light-harvesting chlorophyll molecules. One of the roles of carotenoids in photosynthetic systems is to prevent damage caused by any singlet oxygen that is produced by either removing excess light energy from chlorophyll molecules, or quenching the singlet oxygen molecules directly.

Biological considerations

Molecular dioxygen is a potentially strong oxidizing agent, based on its position in the electrochemical series. The standard redox potential is:

$O_2 + 4H^+ + 4e^- \rightleftarrows 2\ H_2O\ E^{\ominus} = +1.229$ V

which is comparable to potassium dichromate (1.33 V). Nevertheless, reactions of dioxygen with most substrates tend to proceed very slowly at room temperature, in the gas phase or in solution. This relative inertness (unexpected considering it is a diradical) is critical for sustaining life in a dioxygen atmosphere. Perhaps one of the reasons for this stablilty is that the reaction above shows that a 4 electron change is required and this is highly improbable so that it is more likely that a sequence of steps involving 1 electron changes actually takes place.

$O_2 + e^- \rightarrow O_2^{-*}$ (superoxide)
$O_2^{-*} + e^- + 2H^+ \rightarrow H_2O_2$ (peroxide)
$H_2O_2 + e^- + H^+ \rightarrow OH^*$ (hydroxy radical)
$OH^* + e^- + H^+ \rightarrow H_2O$ (water)

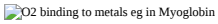
The first step, that generates superoxide, has an adverse potential of -0.32 V ($\Delta G^{\ominus}$= +30.9 $kJmol^{-1}$) which imparts some kinetic stability to the molecule. Note that both dioxygen and superoxide ion are free radicals that exhibit paramagnetism. Species like superoxide, peroxide and the hydroxy radical are far too reactive to be allowed to accumulate in living systems and the primary defence of the cell appears to be to destroy them as soon as they are formed. This is done by a variety of enzymes including superoxide dismutase (SOD) and catalases. Parts of the immune system of higher organisms, however, create peroxide, superoxide, and singlet oxygen to destroy invading microbes. Reactive oxygen species also play an important role in the hypersensitive response of plants against pathogen attack.

Another issue with dioxygen is its low solubility in water at room temperature and atmospheric pressure. Dioxygen is more soluble in water than is dinitrogen. Water in equilibrium with air contains approximately 1 molecule of dissolved O_2 for every 2 molecules of N_2, despite the atmospheric ratio of approximately 1:4. The solubility of oxygen in water is temperature-dependent, and about twice as much (14.6 mgL^{-1}) dissolves at 0 °C than at 20 °C (7.6 mgL^{-1}). At 25 °C and 1 standard atmosphere (101.3 kPa) of air, freshwater contains about 6.04 milliliters (mL) of dioxygen per liter, whereas seawater contains about 4.95 mgL^{-1}. At 5 °C the solubility increases to 9.0 mgL^{-1} (50% more than at 25 °C) for water and 7.2 mgL^{-1} (45% more) for sea water.

The oxygen in water is unavailable to mammals so that divers (and diving mammals such as whales and seals) are entirely dependent on the oxygen

carried in the air in their lungs or their gas supply. For divers this is complicated since at higher partial pressures oxygen can cause acute toxicity leading to convulsions. Scuba (self-contained underwater breathing apparatus) divers using compressed air are restricted to diving above 30 m. If the diver descends to depths near 100 m they can become unconsciousness from nitrogen narcosis and death usually results. A dive to 30 m for 20 minutes puts the scuba diver at risk of nitrogen narcosis and decompression illness. By contrast, the elephant seal can dive to 1 km for 1 hour without risk of either condition.

Respiratory pigments are capable of fixing dioxygen from the atmosphere, transporting it to the reacting site and then releasing it. In addition they are able to counteract small fluctuations in supply or demand by storing dioxygen.



O_2 can bind to a single metal center either "end-on" (η1-) or "side-on" (η2-). In Haemoglobin and Myoglobin it is "end-on".

fully oxygenated Haemoglobin
(with 4 Fe porphins and O_2's highlighted)

Iron based proteins like haemoglobin and myglobin as well as copper based proteins like haemocyanin perform this role in mammalian systems and lobsters, etc.

Molecular dioxygen, O_2, is essential for cellular respiration in all aerobic organisms. Oxygen is used in mitochondria to help generate adenosine triphosphate (ATP) during oxidative phosphorylation. The reaction for aerobic respiration is essentially the reverse of photosynthesis and is simplified as:
$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O\ \Delta H = -2880\ kJmol^{-1}$ In vertebrates, O_2 diffuses through membranes in the lungs and into red blood cells. Haemoglobin binds O_2, changing its colour from bluish red to bright red (CO_2 is released from another part of haemoglobin through the Bohr effect). Other animals use haemocyanin (molluscs and some arthropods) or haemerythrin (spiders and lobsters). A liter of blood can dissolve 200 cm^3 of O_2.

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16.4B: Ozone

Ozone is colourless or slightly bluish gas (blue when liquified), slightly soluble in water and much more soluble in inert non-polar solvents such as carbon tetrachloride or fluorocarbons, where it forms a blue solution. At 161 K (-112 °C), it condenses to form a dark blue liquid. It is dangerous to allow this liquid to warm to its boiling point, because both concentrated gaseous ozone and liquid ozone can detonate.

Most people can detect about 0.01 μmol/mol of ozone in air where it has a very specific sharp odour somewhat resembling chlorine bleach. Exposure of 0.1 to 1 μmol/mol produces headaches, burning eyes and irritation to the respiratory passages. Even low concentrations of ozone in air are very destructive to organic materials such as latex, plastics and animal lung tissue.

Seaside air was once considered to be healthy because of its "ozone" content. It is now recognised that the smell in reality is released from bacteria following the breakdown of species from rotting seaweed! (dimethyl sulfoxide, DMS). Birds appear to be attracted to the smell since for them it indicates a plankton bloom, and therefore the presence of fish feeding on the marine plants.

Ozone may be formed from O_2 by electrical discharges and by action of high energy electromagnetic radiation. Unsuppressed arcing breaks down the chemical bonds of the atmospheric oxygen surrounding the contacts [$O_2 \rightarrow 2O$]. Free radicals of oxygen in and around the arc recombine to create ozone [O_3]. Certain electrical equipment generate significant levels of ozone. This is especially true of devices using high voltages, such as ionic air purifiers, laser printers, photocopiers, tasers and arc welders. Electric motors using brushes can generate ozone from repeated sparking inside the unit. Large motors that use brushes, such as those used by elevators or hydraulic pumps, will generate more ozone than smaller motors. Ozone is similarly formed in the Catatumbo lightning storms phenomenon on the Catatumbo River in Venezuela, which helps to replenish ozone in the upper troposphere. It is the world's largest single natural generator of ozone. The lightning originates from a mass of storm clouds at a height of more than 5 km, and occurs during 140 to 160 nights a year, 10 hours per day and up to 280 times per hour.

From the imgkid gallery (accessed 31 Jan 2015).

Ozone-Oxygen cycle

Ninety percent of the ozone in the atmosphere sits in the stratosphere, the layer of atmosphere between about 10 and 50 kilometers altitude. The ozone layer is mainly found in the lower portion of the stratosphere, from approximately 20 to 30 kilometres (12 to 19 mi) above Earth, though the thickness varies seasonally and geographically. Here the concentration of O_3 varies from two to eight ppm which is much larger than the average ozone concentration in the Earth's atmosphere which is only about 0.3 parts per million.

The natural level of ozone in the stratosphere can be considered to be a result of a balance between sunlight that creates ozone and chemical reactions that destroy it.

Creation: photolysis of an oxygen molecule by high energy UV light splits it into two oxygen atoms. The wavelength in the UV needed to achieve this can be estimated from the O=O Bond Energy of 498 $kJmol^{-1}$.
By dividing this by $6.022 * 10^{23}$ bonds/mol the Energy per bond is found to be $8.27 * 10^{-19}$ J/bond.
The wavelength required for photolysis can be evaluated from $E = hc / \lambda$
$\lambda = hc / E = (6.626 * 10^{-34}$ Js x $3 * 10^{8}$ m/s) / ($8.27 * 10^{-19}$ J) so λ= 240 nm, i.e. visible light cannot break the O=O bond, but UV-C light with energy > 240 nm can break the O=O bond. {UV ranges are: UV-A (400-315 nm), UV-B (315-280 nm), and UV-C (280-200 nm).}

$O_2 + h\nu \rightarrow 2O$

Each oxygen atom then rapidly combines with an oxygen molecule to form an ozone molecule:

$O + O_2 \rightarrow O_3$ **The ozone-oxygen cycle**: the ozone molecules formed by the reaction above absorb radiation again having an appropriate wavelength in the UV. The triatomic ozone molecule becomes diatomic molecular oxygen plus a free oxygen atom: $O_3 + h\nu$ (240-310 nm) $\rightarrow O_2 + O$

The atomic oxygen produced quickly reacts with another oxygen molecule to reform ozone:

$O + O_2 \rightarrow O_3$ + K.E.

where "K.E." denotes the excess energy of the reaction which is manifested as extra kinetic energy. These two reactions form the ozone-oxygen cycle, in which the chemical energy released when O and O2 combine is converted into kinetic energy of molecular motion. The overall effect is to convert penetrating UV-B light into heat, without any net loss of ozone. This cycle keeps the ozone layer in a stable balance while absorbing 97-99% of the Sun's medium-frequency ultraviolet light (from about 200 nm to 315 nm wavelength) and preventing it from reaching the Earth's surface, to the benefit of both plants and animals. This reaction is one of two major sources of heat in the stratosphere (the other being the kinetic energy released when O_2 is photolyzed into O atoms).

Removal: reaction of an oxygen atom with an ozone molecule leads to production of two oxygen molecules:

$O_3 + O^{\cdot} \rightarrow 2\ O_2$

and if two oxygen atoms meet, they can react to form one oxygen molecule:

$2\ O^{\cdot} \rightarrow O_2$

The overall amount of ozone in the stratosphere is determined by a balance between production by solar radiation and removal. The removal rate is slow, since the concentration of O atoms is very low. Certain free radicals, the most important being hydroxyl (OH), nitric oxide (NO) and atoms of chlorine (Cl) and bromine (Br), catalyze the recombination reaction, leading to an ozone layer that is thinner than it would be if the catalysts were not present.

Most of the OH and NO are naturally present in the stratosphere, but human activity, especially emissions of chlorofluorocarbons (CFCs) and halons, has greatly increased the Cl and Br concentrations, leading to ozone depletion. Each Cl or Br atom can catalyze tens of thousands of decomposition reactions before it is removed from the stratosphere.

Follow the Ozone Hole Watch at NASA and see the ozone depletion Wikipedia page.

Ozone depletion

Ozone depletion describes two distinct but related phenomena observed since the late 1970s: a steady decline of about 4% per decade in the total volume of ozone in the ozone layer, and a much larger springtime decrease in stratospheric ozone over Earth's polar regions. Note that the Antarctic would be in darkness (no sunshine) for the winter months, sunshine returning in springtime (September). The latter phenomenon is referred to as the ozone hole.

The most important process in depletion is catalytic destruction of ozone by atomic halogens. The main source of these halogen atoms in the stratosphere is photodissociation of man-made halocarbon refrigerants, solvents, propellants, and foam-blowing agents (CFCs, HCFCs, freons, halons), substances that are referred to as ozone-depleting substances (ODS).

In the simplest example of such a cycle, a chlorine atom reacts with an ozone molecule, taking an oxygen atom with it (forming ClO) and leaving a normal oxygen molecule. The chlorine monoxide (ClO) produced can react with a second molecule of ozone to yield another chlorine atom and two molecules of oxygen. These gas-phase reactions can be written such that in the first step a chlorine atom changes an ozone molecule to ordinary oxygen:

$Cl^{\cdot} + O_3 \rightarrow ClO + O_2$

The ClO generated can then destroy a second ozone molecule and recreate the original chlorine atom, which can repeat the first reaction and continue a cycle to destroy ozone.

$ClO + O_3 \rightarrow Cl^{\cdot} + 2\ O_2$ In theory, a single chlorine atom could keep on destroying ozone (acting as a catalyst) for up to two years (the time scale for transport back down to the troposphere) were it not for reactions that remove Cl by forming reservoir species such as hydrogen chloride (HCl). In practise, the average chlorine atom reacts with 100,000 ozone molecules before it is removed from the catalytic cycle.

On a per atom basis, bromine is even more efficient than chlorine at destroying ozone, but at present there is much less bromine in the atmosphere. Both chlorine and bromine significantly contribute to the overall depletion of ozone.

The Montreal Protocol on Substances that Deplete the Ozone Layer (a protocol to the Vienna Convention for the Protection of the Ozone Layer) is an international treaty designed to protect the ozone layer by phasing out the production of numerous substances

that are responsible for ozone depletion. It was agreed on in 1987, and entered into force on January 1, 1989, with numerous revisions since then.

The bans on the production of CFCs, halons, and other ozone-depleting chemicals such as carbon tetrachloride and trichloroethane have led to the expectation of a recovery of the ozone layer to 1980 values somewhere between 2050 and 2070. This was the estimate given in a summary document of the Scientific Assessment of the Ozone Depletion 2014 published by the UN Environment Programme (UNEP) and the UN World Meterological Organization (WMO).

Among the key findings of the report were that the authors noted that what happens after 2050 will then largely depend on concentrations of CO_2, methane and nitrous oxide - the three main long-lived greenhouse gases in the atmosphere.

NASA view of the largest ozone hole observed above the Antarctic on 24 Sep 2006. Ozone is much less stable than the diatomic allotrope O_2, breaking down in the lower atmosphere to normal dioxygen. The O - O distances in O_3 are 127.2 pm and the O - O - O angle is 116.78°. The bonding can be expressed as a resonance hybrid with a single bond on one side and double bond on the other producing an overall average bond order of 1.5 for each side.
Ozone is a powerful oxidant (far more so than dioxygen) and has many industrial and consumer applications related to oxidation. This same high oxidizing potential, however, causes ozone to damage mucous and respiratory tissues in animals, and also tissues in plants, above concentrations of about 100 ppb. This makes ozone a potent respiratory hazard and pollutant near ground level.

Ozone oxidizes nitric oxide to nitrogen dioxide: $NO + O_3 \rightarrow NO_2 + O_2$

This reaction is accompanied by chemiluminescence. The NO_2 can be further oxidized:

$NO_2 + O_3 \rightarrow NO_3 + O_2$

The NO_3 formed can react with NO_2 to form N_2O_5.

Ozone does not react with ammonium salts, but it oxidizes ammonia to ammonium nitrate:

$2\ NH_3 + 4\ O_3 \rightarrow NH_4NO_3 + 4\ O_2 + H_2O$ Ozone reacts with carbon to form carbon dioxide, even at room temperature: $C + 2\ O_3 \rightarrow CO_2 + 2\ O_2$

Red oxygen - O_8

On increasing the pressure of dioxygen at room temperature, the "solid oxygen β-phase" undergoes phase transitions to the δ-phase at 9 GPa and the ε-phase at 10 GPa. Its volume decreases significantly, and it changes colour from blue to deep red. The structure of this red ε-phase, determined in 2006, is based on an O_8 cluster (see structure above). It was confirmed that this structure is formed up to 96 GPa. The box-like cluster is an unusual conformation first recognised for oxygen, and as yet has not been experimentally or theoretically reported for any other diatomic molecule.

Liquid oxygen is already used as an oxidant in rockets, and it has been speculated that red oxygen could make an even better oxidant, because of its higher energy density.

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16.4C: Sulfur - Allotropes

Allotropes of sulfur

No other element forms more solid allotropes than sulfur. At present, about 30 well characterized sulfur allotropes are known of which the most common form found in nature is the greenish-yellow orthorhombic α-sulfur, containing puckered rings of S_8.

α-sulfur

When pure it has a greenish-yellow colour (traces of cyclo-S7 in commercially available samples make it appear yellower). It is practically insoluble in water and is a good electrical insulator with poor thermal conductivity. It is quite soluble in carbon disulfide: 35.5 g/100 g solvent at 25 °C. It has a rhombohedral crystal structure. This is the predominant form found in "flowers of sulfur", "roll sulfur" and "milk of sulfur". It contains S8 puckered rings, alternatively called a crown shape. The S-S bond lengths are all 206 pm and the S-S-S angles are 108° with a dihedral angle of 98°. At 95.3 °C, α-sulfur converts to β-sulfur.

β-sulfur

This is a yellow solid with a monoclinic crystal form and is less dense than α-sulfur. Like the α- form it contains puckered S8 rings and only differs from it in the way the rings are packed in the crystal. It is unusual because it is only stable above 95.3 °C, below this it converts to α-sulfur. It can be prepared by crystallising at 100 °C and cooling rapidly to slow down formation of α-sulfur. It has a melting point of about 120 °C and decomposes at around this temperature.

γ-sulfur

This form, first prepared by F.W Muthmann in 1890, is sometimes called "nacreous sulfur" or "mother of pearl sulfur" because of its appearance. It crystallises in pale yellow monoclinic needles. It contains puckered S8 rings like α-sulfur and β-sulfur and only differs from them in the way that these rings are packed. It is the densest form of the three. It can be prepared by slowly cooling molten sulfur that has been heated above 150 °C or by chilling solutions of sulfur in carbon disulfide, ethyl alcohol or hydrocarbons. It is found in nature as the mineral rosickyite.

Some allotropes of Sulfur

S_6 - cyclohexasulfur	
α-S_8	

https://chem.libretexts.org/@go/page/34267

S_{12} - cyclododecasulfur

S_6 - cyclo-hexasulfur

This was first prepared by M.R. Engel in 1891 who reacted HCl with thiosulfate, $HS_2O_3^-$. Cyclo-S_6 is orange-red and forms rhombohedral crystals. It is called ρ-sulfur, ε-sulfur, Engel's sulfur and Aten's sulfur. Another method of preparation involves reacting a polysulfane with sulfur monochloride: $H_2S_4 + S_2Cl_2 \rightarrow$ cyclo-S_6 + 2 HCl (dilute solution in diethyl ether)

The sulfur ring in cyclo-S_6 has a "chair" conformation, reminiscent of the chair form of cyclohexane. All of the sulfur atoms are equivalent.

Cyclo-dodecasulfur

Thermodynamically, S12 is the second most stable sulfur ring after S8. Therefore, S12 is formed in many chemical reactions in which elemental sulfur is a product. In addition, S12 is a component of liquid sulfur at all temperatures. The same holds for S18 and S20 which are often formed together with S12. Its structure can be visualised as having sulfur atoms in three parallel planes, 3 in the top, 6 in the middle and three in the bottom.

Liquid sulfur after equilibration contains sulfur homocycles of all sizes and some of these can be isolated by quenching, extraction, fractional precipitation and crystallization depending on their differing solubilities.

Cyclo-S_{12} can be prepared by heating elemental sulfur to about 200 °C for 5-10 min and then allowing the mixture to cool to 140-160 °C within about 15 min. Once the melt has become less viscous, it is poured in as thin a stream as possible into liquid nitrogen in order to quench the equilibrium. Recrystallization of the yellow powder from CS_2 allows the isolation of an adduct which slowly loses the solvent to give the cyclo-dodecasulfur.

Note that both B and S form stable E_{12} species but the structures (and coordination numbers) are quite different.

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16.4D: Sulfur - Reactivity

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16.4E: Selenium and Tellurium

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16.5: Hydrides

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16.5A: Water, $H\ 2\ O$

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16.5B: Hydrogen Peroxide, $H\ 2\ O\ 2$

Hydrogen peroxide (H_2O_2) is the simplest peroxide (a compound with an oxygen-oxygen single bond) and in its pure form is a colourless liquid that is slightly more viscous than water. It is a strong oxidizer and is used as a bleaching agent and disinfectant. For safety reasons it is normally used as an aqueous solution, also colourless. For consumers, it is usually available from pharmacies at 3 and 6 wt% concentrations. The concentrations are sometimes described in terms of the volume of oxygen gas generated; one milliliter of a 20-volume solution generates twenty milliliters of oxygen gas when completely decomposed. For laboratory use, 100 volume, 30 wt% solutions are the most common. Concentrated H_2O_2, or 'high-test peroxide' is a reactive oxygen species and has been used as a propellant in rocketry. Diluted H_2O_2 (between 1.9% and 12%) mixed with ammonium hydroxide has been used to bleach human hair. The chemical's bleaching property lends its name to the phrase "Hollywood peroxide blonde". Hydrogen peroxide can be used for tooth whitening and when mixed with baking soda and salt forms a recipe for home-made toothpaste.

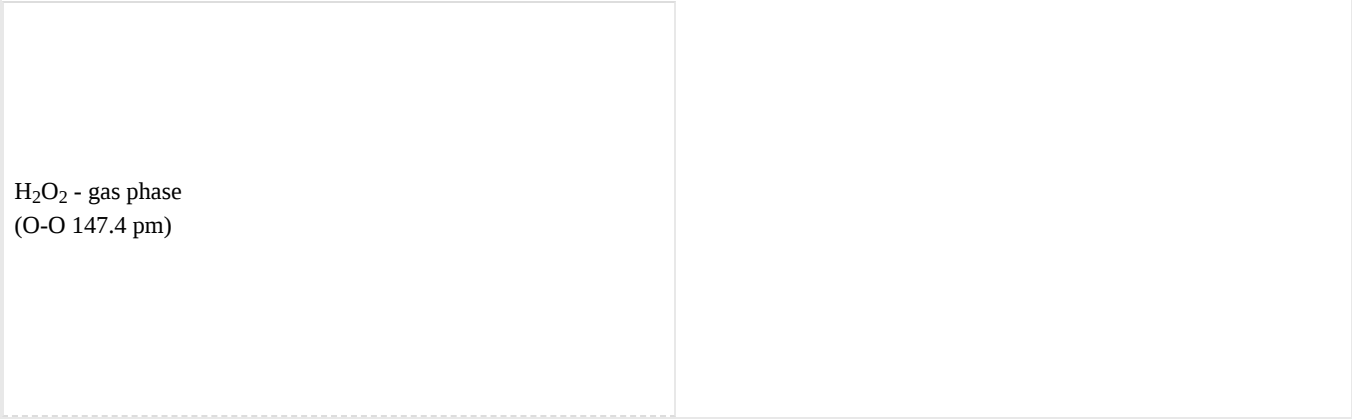
Discovery

Hydrogen peroxide was first described in 1818 by Louis Jacques Thénard, who produced it by treating barium peroxide with nitric acid. An improved version of this process used hydrochloric acid, followed by addition of sulfuric acid to precipitate the barium sulfate byproduct. Thénard's process was used from the end of the 19th century until the middle of the 20th century.

Pure hydrogen peroxide was long believed to be unstable as early attempts to separate it from the water, which is present during synthesis, all failed. This instability was due to traces of impurities (transition metals salts) which catalyze the decomposition of the hydrogen peroxide. Pure hydrogen peroxide was first obtained in 1894 - almost 80 years after its discovery - by Richard Wolffenstein, who produced it via vacuum distillation.

Determination of the molecular structure of hydrogen peroxide proved to be very difficult. In 1892 the Italian physical chemist Giacomo Carrara (1864-1925) determined its molecular weight by freezing point depression, which confirmed that its molecular formula was H_2O_2. At least half a dozen hypothetical molecular structures seemed to be consistent with the available evidence. In 1934, the English mathematical physicist William Penney and the Scottish physicist Gordon Sutherland proposed a molecular structure for hydrogen peroxide which was very similar to the presently accepted one and which subsequent evidence cumulatively proved to be correct.

The structure of hydrogen peroxide



H_2O_2 - gas phase
(O-O 147.4 pm)

H_2O_2 - solid phase
(O-O 145.8 pm)

Although the O-O bond is a single bond, the molecule has a relatively high barrier to rotation of 29.45 $kJmol^{-1}$ (2460 cm^{-1}); for comparison, the rotational barrier for ethane is just 12.5 $kJmol^{-1}$. The increased barrier is thought to be due to the repulsion between the lone pairs of the adjacent oxygen atoms.

The molecular structures of gaseous and crystalline H_2O_2 are significantly different. This difference is attributed to the effects of hydrogen bonding, which is absent in the gaseous state.

Preparation via the anthraquinone process

The anthraquinone process is a process for the production of hydrogen peroxide, which was developed by BASF. The industrial production of hydrogen peroxide is based on the reduction of oxygen with hydrogen, by the direct synthesis from the elements. Instead of hydrogen itself, however, a 2-alkyl-anthrahydroquinone (generated from the corresponding 2-alkyl-anthraquinone by catalytic hydrogenation with palladium) is used. Oxygen and the organic phase react to give hydrogen peroxide and the anthraquinone can be recycled.

The hydrogen peroxide is then extracted with water in a second step and separated by fractional distillation. The anthraquinone thus acts as a catalyst with the overall reaction given by the equation:
$H_2 + O_2 \rightarrow H_2O_2$ If **ozone** is used instead of oxygen, dihydrogen trioxide, H_2O_3 can be produced by this method.

Decomposition

Hydrogen peroxide is thermodynamically unstable and decomposes to form water and oxygen with a $\Delta H^{\ominus}$ of -98.2 $kJmol^{-1}$ and a $\Delta S^{\ominus}$ of 70.5 $Jmol^{-1}K^{-1}$.

$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$ The rate of decomposition increases with rising temperature, concentration and pH, with cool, dilute, acidic solutions showing the best stability. Decomposition is catalysed by various compounds, including most transition metals and their compounds (e.g. manganese dioxide, silver, and platinum). Certain metal ions, such as Fe^{2+} or Ti^{3+}, can cause the decomposition to take a different path, with free radicals such as ($HO^{\cdot}$) and ($HOO^{\cdot}$) being formed.

The decomposition of hydrogen peroxide liberates oxygen and heat; this can be dangerous as spilling high concentrations of hydrogen peroxide on an inflammable substance can cause an immediate fire.

Metal oxides, peroxides and superoxides

When the group 1 metals are heated in an excess of air or in O_2, the principal products obtained depend on the metal: lithium **oxide**, Li_2O, sodium **peroxide**, Na_2O_2, and the **superoxides** KO_2, RbO_2 and CsO_2.

$4Li + O_2 \rightarrow 2Li_2O$ oxide formation
$2Na + O_2 \rightarrow Na_2O_2$ peroxide formation
$K + O_2 \rightarrow KO_2$ superoxide formation

The superoxides and peroxides contain the paramagnetic $[O_2]^-$ ($\mu \sim 1.73$ BM) and diamagnetic $[O_2]^{2-}$ ions respectively. See the MO diagram for O_2 above for comparison.

All of the monoxides are known, M_2O, and the heavier peroxides and superoxides will decompose to form the oxides. They are all ionic and strong bases with the basicity increasing down the group.

$O^{2-} + H_2O(aq) \rightarrow 2\ OH^-(aq)$ Sodium peroxoborate is a solid peroxygen compound with exceptional storage stability and no shock sensitivity. It is cheap and readily available, being produced mainly as a solid ingredient of domestic washing formulations, in which it acts as sources of H_2O_2 in solution for stain bleaching. World annual production in 1995 was approximately 750,000 tonnes, and its use in washing powders dates back to 1907 with Henkel's original "Persil" product in Germany.

Sodium peroxoborate has the empirical formula "$NaBO_3.xH_2O$". Two forms that are commercially available correspond stoichiometrically to x = 1 or 4, and are known as the "monohydrate" and "tetrahydrate', respectively. Structurally, however, sodium peroxoborate was shown in 1961 to be the disodium salt of a 1,4.-diboratetroxane dianion. Hence, the "monohydrate" really corresponds to the anhydrous salt, and the "tetrahydrate" to a hexahydrated form of it. The monohydrate form dissolves better than the tetrahydrate and has higher heat stability; it is prepared by heating the tetrahydrate. The compound exists as a dimer as shown below.

The reagent offers low toxicity and a long shelf life. Sodium peroxoborate is a useful reagent in synthetic chemistry as a substitute for the unstable, highly concentrated hydrogen peroxide solutions that can pose a significant explosion hazard and are not commercially available.

Persil and the structure of $Na_2B_2(O_2)_2(OH)_4.6H_2O$

Return to the course outline or move on to Lecture 5: Structure of the elements (Groups 1 and 2 metals, Boron, Carbon and Phosphorus, Sulfur).

References

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16.5C: Hydrides, H_2E (E = S, Se, Te)

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16.5D: Polysulfanes

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16.6: Metal Sulfides, Polysulfides, Polyselenides, and Polytellurides

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16.6A: Sulfides

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16.6B: Polysulfides

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16.6C: Polyselenides, and Polytellurides

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16.7: Halides, Oxohalides, and Complex Halides

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16.7A: Oxygen Fluorides

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16.7D: Halides of Selenium and Tellurium

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16.8A: Oxides of Sulfur

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SECTION OVERVIEW

16.9: Oxoacids and their Salts

Oxides of fluorine, chlorine, bromine and iodine [1]

In compounds such as the oxides and oxyacids the halogens (except F) occur in high oxidation states. Some properties of oxides are shown below:

Property	OF_2	O_2F_2	Cl_2O	ClO_2	I_2O_5
Physical appearance and general characteristics	Colourless (very pale yellow) gas; explosive and toxic	Yellow solid below 119 K; decomposes above 223 K	Brownish yellow gas; explosive at high concentrations	Yellowish gas or liquid; explosive above 15% volume in air	white crystalline hygroscopic solid
Melting point /K	49	119	153	213	573 decomp
Boiling point /K	128	210	275	284	-
ΔfH°(298 K) / kJ mol^{-1}	24.7	18	80.3	102.6	-158.1
Dipole moment /D	0.3	1.44	0.78	1.78	-
O-X bond distance /pm	141	157.5	170.0	147.3	180 (term) 195 (bridging)

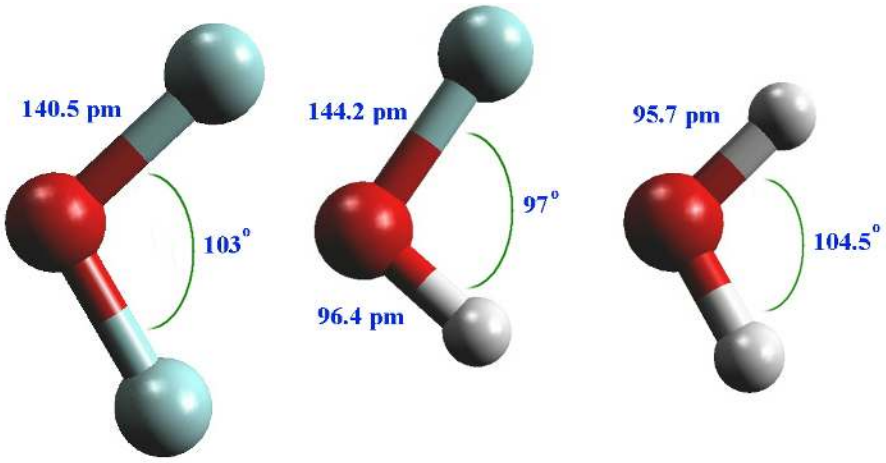
Oxygen difluoride was first prepared in 1929; it was obtained by the electrolysis of slightly moist molten potassium fluoride and hydrofluoric acid.[2][3] More recently it has been prepared by the reaction of difluorine with 2% aqueous NaOH solution:

$$2F_2 + 2NaOH \rightarrow OF_2 + 2NaF + H_2O \tag{1}$$

Although OF_2 is the most stable of the oxygen fluorides, conditions must be controlled so as to minimize losses due to decomposition via the secondary reaction.

$$OF_2 + 2OH^- \rightarrow O_2 + 2F^- + H_2O \tag{2}$$

This reaction occurs slowly with water at room temperature, more rapidly with base and explosively with steam. The shape of the OF_2 molecule has been compared with HOF and H_2O and the three give bent structures where the bond angles range from 97 to 104.5 °.



The basic shape of O_2F_2 resembles that of H_2O_2 except that the internal dihedral angle is smaller (87° cf. to 111°). The very long O-F bonds (157.5 pm) probably explains why the molecule is able to easily dissociate.

There are at least 10 oxides of chlorine known, of which only 2 will be discussed.

Cl_2O is best prepared by treating fresh yellow mercuric oxide with Cl_2 gas:

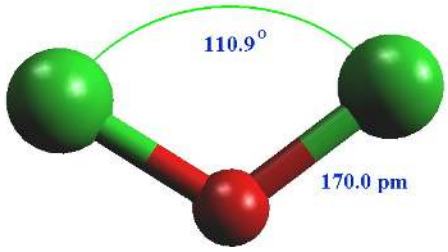
\[2 Cl_2 + 2 HgO \rightarrow Cl_2O + HgCl_2 \cdot HgO \tag{3}

It can also be prepared by reaction of Cl_2 gas with moist sodium carbonate, Na_2CO_3.

\[2Cl_2 + 2Na_2CO_3 + H-2O \rightarrow Cl_2O + 2NaCl + 2NaHCO_3 \tag{4}

Dichlorine monoxide is very water soluble (a saturated solution at -9.4 °C contains 143.6 g Cl_2O per 100 g H_2O) and it hydrolyses to hypochlorous acid.

$$Cl_2O + H_2O \rightarrow 2HOCl \tag{5}$$



Cl_2O

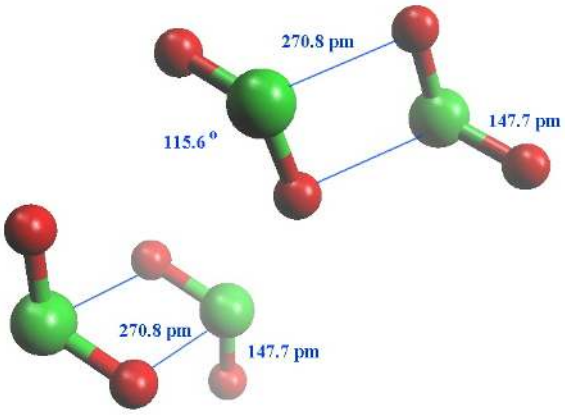
Much of the Cl_2O is used to prepare hypochlorites, especially $Ca(OCl)_2$ that is used for water treatment of swimming pools.

Chlorine dioxide (ClO_2) was mentioned in the first lecture as being an important industrial chemical for bleaching flour and wood pulp and for water treatment. Over 95% of the chlorine dioxide produced in the world today is made from sodium chlorate:

$$2NaClO_3 + 2NaCl + 2H_2SO_4 \rightarrow 2ClO_2 + Cl_2 + 2Na_2SO_4 + 2H_2O \tag{6}$$

ClO_2 was first discovered by Humphry Davy (1778-1829) in 1811 and was the first of the chlorine oxides to have been isolated. The yellow paramagnetic gas explosively decomposes into chlorine and oxygen and the decomposition is initiated by light. Thus, it is never handled in concentrated form, but is almost always used as a dissolved gas in water in a concentration range of 0.5 to 10 grams per liter. Its solubility increases at lower temperatures: it is thus common to use chilled water (5 °C) when storing at concentrations above 3 grams per liter. In many countries, such as the USA, chlorine dioxide gas may not be transported at any concentration and is almost always produced at the application site using a chlorine dioxide generator. Chlorine dioxide is less corrosive than chlorine and superior for the control of legionella bacteria. It is more effective as a disinfectant than chlorine in most circumstances against water borne pathogenic microbes such as viruses, bacteria and protozoa.

The oxidation number of the Cl is considered to be +3 and Pauling originally proposed that resonance structures be used to account for this. An alternative explanation by Brockway extended this to resonance between 3 electron 2 centre bonds. For many years it was claimed that a dimer was not formed and considering that ClO_2 is a radical this might have been one mechanism to provide some stability by using up the odd electron in a 2 electron 2 centre bond. In 1992, Rehr and Jansen conducted magnetic susceptibility and single crystal studies at various temperatures and it was found that below about 170 K the sample became diamagnetic and did indeed form a dimer. They noted that to avoid explosions all equipment had to be scrupulously cleaned with aqua regia prior to use and temperatures kept low.

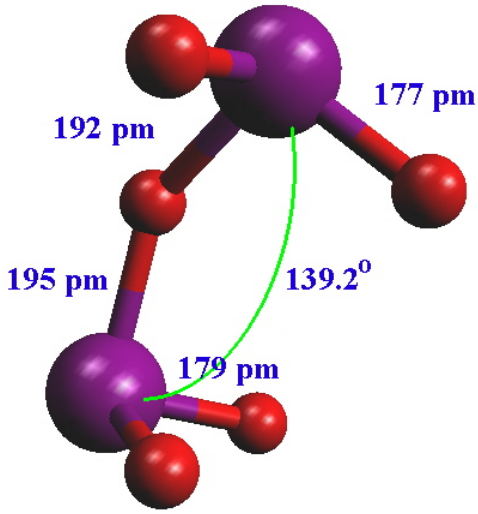


ClO_2

The oxides of bromine are less numerous than for chlorine and they are generally unstable at room temperature decomposing to the elements. For example, BrO_2 is a pale yellow crystalline solid formed quantitatively by low-temperature ozonolysis of dibromine.

$$Br_2 + 4O_3 \rightarrow 2BrO_2 + 4O_2$$

The oxides of iodine are the most stable of the halogens and the first of these to be prepared was I_2O_5 which was independently discovered by Joseph Louis Gay-Lussac (1778-1850) and H. Davy in 1813 although the structure was not determined until 1970. The white hygroscopic crystals are very soluble in water and commercial I_2O_5 has been found to consist of HI_3O_8 or $I_2O_5.HIO_3$. Likewise crystals of commercial iodic(V) acid, HIO_3, were investigated using single-crystal and powder X-ray diffraction and the crystals turned out again to be HI_3O_8 or $HIO_3{\cdot}I_2O_5$.



partially staggered conformation of I_2O_5

I_2O_5 is one of only a few chemicals that is capable of oxidizing carbon monoxide rapidly and completely at room temperature:

$$I_2O_5 + 5\ CO \rightarrow I_2 + 5\ CO_2$$

This reaction has been used as the basis of an analytical method for sampling CO in the atmosphere. I_2O_5 can be used for the oxidation of a number of other small molecules including: NO, C_2H_4, SO_3, H_2S.

Oxoacids and their salts

Numerous oxoacids of the halogens exist and chlorine is able to form a complete series of such acids ranging from HOCl to $HClO_4$ where the formal oxidation state is +1,+3,+5 and +7. [1]

Oxoacids of chlorine	Oxoacids of bromine	Oxoacids of iodine
Hypochlorous acid HOCl, pKa=7.53	Hypobromous acid HOBr, pKa=8.69	Hypoiodous acid HOI, pKa=10.64
Chlorous acid HOClO ($HClO_2$), pKa=2.0		
Chloric acid $HOClO_2$ ($HClO_3$), pka=-1.0	Bromic acid $HOBrO_2$ ($HBrO_3$)	Iodic acid $HOIO_2$ (HIO_3)
Perchloric acid $HOClO_3$ ($HClO_4$), pka=~-8	Perbromic acid $HOBrO_3$ ($HBrO_4$)	Periodic acid $HOIO_3$ (HIO_4)
		Orthoperiodic acid $(HO)_5IO$ (H_5IO_6)

HOF has been isolated by reaction of difluorine gas with ice at 230 K but it does not ionise in water or give stable salts and on warming to room temperature it decomposes to HF.
$2\ HOF \rightarrow 2\ HF + O_2$

The hypohalous acids (X=Cl, Br, I) are conveniently prepared by the reaction of the dihalogen with mercury oxide:
$2\ X_2 + 3\ HgO + H_2O \rightarrow 2\ HOX + Hg_3O_2X_2$

The hypohalous salts formed from the heavier halogens are all weak acids with the hypochlorites being important industrial reagents.
Bleaching powder is a mixture of $CaCl_2$, $Ca(OH)_2$ and $Ca(OCl)_2$ and is manufactured by the reaction of dichlorine on $Ca(OH)_2$. The sodium salt is a well known disinfectant and bleaching agent

Each of these hypohalites are unstable and disproportionate at room temperature to the halates and halide ion:
$3[OX]^- \rightarrow [XO_3]^- + 2X^-$
The equilibrium constants for these reactions vary with X such that for Cl, $K=10^{27}$ for Br, $K=10^{15}$ and for I, $K=10^{20}$. The reaction speed increases down the group so that for OI^- the decomposition is very fast.

Chlorous acid, chloric acid and bromic acid cannot be isolated as pure compounds but exist in aqueous solution and are prepared from the barium salts.
$Ba(ClO_2)_2 + H_2SO_4(aq) \rightarrow 2\ HClO_2(aq) + BaSO_4(s)$
and $Ba(XO_3)_2 + H_2SO_4 \rightarrow 2\ HXO_3 + BaSO_4$ (X= Cl, Br)

Iodic acid (HIO_3) is a stable white solid at room temperature and is prepared from I_2 and nitric acid or from I_2O_5 in water.
$I_2O_5 + H_2O \rightarrow 2HIO_3$

The structure below shows trigonal pyramidal HIO_3 units and these are connected by extensive H-bonding. In aqueous solution it is a reasonably strong acid with pKa ~ 0.77.

Potassium chlorate is a white crystalline substance that is used:

- as a pesticide. In Finland it was sold under the trade name Fegabit.
- as an oxidizing agent,
- to prepare oxygen,
- as a disinfectant,
- in safety matches, and
- in explosives and fireworks.

Potassium chlorate will readily decompose if heated in contact with a catalyst, typically manganese (IV) dioxide (MnO_2). Thus, it may be simply placed in a test tube and heated over a burner and this can provide a convenient source of dioxygen for school laboratories. The reaction is as follows:
$2\ KClO_3(s) + heat \rightarrow 3\ O_2(g) + 2\ KCl(s)$

The materials used need to be of high purity since even small amounts of impurities can lead to explosions and it is considered good practice to test a new batch of potassium chlorate with a small reaction first (less than 1 g!) Even commercial oxygen generators have been known to explode and cause problems such as at least one plane crash and a fire on the space station MIR. [10]

Both potassium bromate and iodate are used in volumetric analysis and in particular the iodate is a primary standard being available in high purity and with excellent stablity. In the standardisation of thiosulfate for example potassium iodate is used a source of diiodine.

$[IO_3]^- + 5\ I^- + 6\ H^+ \rightarrow 2\ I_2 + 3\ H_2O$

Iodate is used in Andrew's titrations for determination of hydrazine and in the determination of I^- in SnI_4 in the CHEM3101 laboratory programme.

HIO_3	H_5IO_6 orthoperiodic acid

Several different I(VII) oxyacids are known including periodic acid (HIO_4) and orthoperiodic acid (H_5IO_6). In the latter case there is extensive H-bonding present in the solid state resulting in a 3D network. Wherease perchloric acid exists as discrete monomeric units HIO_4 is again extensively H-bonded through *cis*- edge-sharing octahedra.

The reactions involving the various oxyacids in aqueous solution is complicated, as seen by the following equilibria:

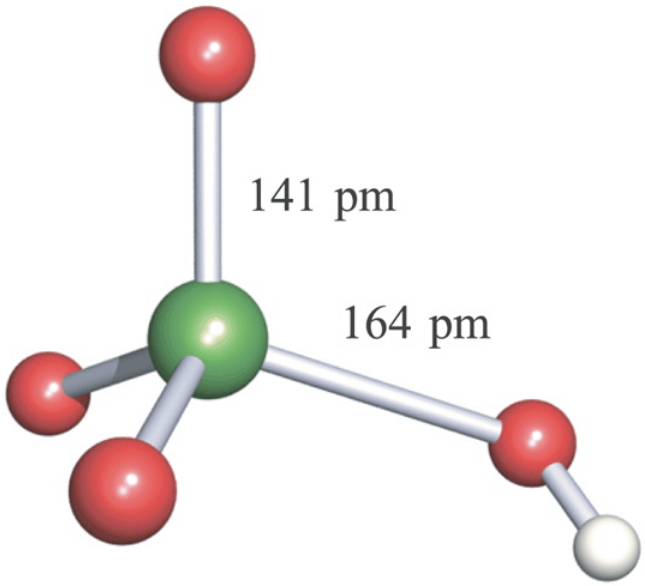
$[H_3IO_6]^{2-} + H^+ \rightarrow [IO_4]^- + 2H_2O$

$2[H_3IO_6]^{2-} \rightarrow 2[HIO_5]^{2-} + 2H_2O$

$2[HIO_5]^{2-} \rightarrow [H_2I_2O_{10}]^{4-} \rightarrow [I_2O_9]^{4-} + H_2O$

Perchlorates

Count Friederich von Stadion is credited with the preparation of the first perchlorate compound in 1816 which he obtained by mixing potassium chlorate with concentrated sulfuric acid and allowing it to stand for 24 hours with frequent agitation. The water-insoluble residue was potassium perchlorate. Perchloric acid is the only oxoacid of chlorine that can be isolated and in the vapour phase the Cl-O bonds are not equivalent unless deprotonated when they become the same length.



$HClO_4$ Pure perchloric acid is a colourless mobile, shock-sensitive liquid and at least 6 different hydrates are known and the monohydrate forms an H-bonded crystalline lattice $[H_3O]^+\ [ClO_4]^-$

The perchlorate anion is not a good ligand and it is sometimes used for the isolation of metal complexes. Perchlorate salts are often soluble in acetone which can provide a very useful solvent system for reactions. Unfortunately though the solids are often unstable and can lead to violent explosions. I know someone who lost the tip of their finger when attempting to grind up 1 or 2 mg of complex for an IR spectrum!

Perchlorates in groundwater

Texas chemists have shown evidence for a natural atmospheric origin of perchlorate. For many, perchlorate is almost synonymous with the rocket fuel that has found its way into U.S. groundwater and surface water and subsequently into foods such as lettuce and milk. Perchlorate taints drinking water in 35 US states at levels of at least 4 ppb. When groundwaters of a 60,000-sq-mile region in Texas and New Mexico were sampled, > 80% of the wells returned positive and unexpectedly high levels of perchlorate and it was found even in samples that were unlikely ever to have been exposed to synthetic contamination. The perchlorate levels in many of the Texas samples were more than 20 ppb, and some were as high as 60 ppb. However, there were regions such as the southern high plains (Texas Panhandle) where there was no clear historical or current evidence of the extensive presence of rocket fuel or Chilean fertilizer sources. The occurrence of easily measurable concentrations of perchlorate in such places was difficult to understand. In the southern high plains groundwater, perchlorate was better correlated with iodate, known to be of atmospheric origin, compared to any other species. They showed that perchlorate was readily formed by a variety of simulated atmospheric processes. For example, it could be formed from chloride aerosol by electrical discharge and by exposing aqueous chloride to high concentrations of ozone. They further reported that perchlorate was present in many rain and snow samples, strongly suggesting that some perchlorate was formed in the atmosphere and a natural perchlorate background of atmospheric origin existed.[4][5][6]

Although the scientists were fairly certain that the perchlorate in the Texas wells was of natural origin, they still needed more evidence to prove it. Researchers at Louisiana State University (LSU) and Oak Ridge National Laboratory (ORNL) developed a new stable-isotope ratio technique that could provide the missing piece of information.

To distinguish between natural and synthetic perchlorate it is important to recognise that perchlorate is a non-volatile oxyanion and that once formed it does not exchange oxygen atoms with those in the ambient environment. This means its oxygen ratio signature is fixed. So by looking at both the $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios it is possible to tell whether it is from a natural source or not.

In this approach, all three stable oxygen isotopes are measured after a thermal decomposition method generates O_2 from perchlorate crystals. Measuring just $^{18}O/^{16}O$ won't give you the answer, because $^{18}O/^{16}O$ ratios for anthropogenic and atmospheric perchlorate overlap. But if you measure $^{17}O/^{16}O$ at the same time and compare the two ratios, it is possible to determine its origin. Most oxygen-containing compounds on earth have a correlation between $^{18}O/^{16}O$ and $^{17}O/^{16}O$. Any deviation from this relationship is referred to as the ^{17}O anomaly, or $\Delta^{17}O$. The results of studies on Chilean perchlorates from the Atacama desert caliche deposits found that $\Delta^{17}O$ was between 4 and 10 whereas for man-made perchlorates the value was generally less than -0.2. [7]

In the human body, perchlorate inhibits the uptake of iodide by the thyroid and thus may lower the amount of thyroid hormone in the body. Insufficient levels of this hormone can cause permanent neurological damage in children.

The changes in perchlorate concentrations in surface water adjacent to a site of fireworks displays from 2004 to 2006 was monitored. Preceding the fireworks displays, perchlorate concentrations in surface water ranged from 0.005 to 0.081 µg/L, with a mean value of 0.043 µg/L. Within 14 h after the fireworks, perchlorate concentrations spiked to values ranging from 24 to 1028 times the mean baseline value. A maximum perchlorate concentration of 44.2 µg/L was determined following the July 4th event in 2006. After the fireworks displays, perchlorate concentrations decreased toward the background level within 20 to 80 days, with the rate of attenuation correlating to surface water temperature.[8]

The Pentagon, NASA, the US Department of Energy, and defense contractors - who could face expensive cleanups of perchlorate contamination - vigorously objected when the EPA proposed a 1-ppb limit for drinking water. The US military suggested a limit of 200 ppb.

Aqueous Solution Chemistry

The diagrams below show the variation of redox potentials with acid and base, It should be noted that the couples $½X_2/X^-$ are independent of pH and together with the estimated value for F_2 indicate a steady decrease in oxidising strength moving down the group.

F_2 (+2.866 V) > Cl_2 (+1.358 V) > Br_2 (+1.066 V) > I_2 (+0.536 V)

The reason the potential for difluorine must be estimated is that it is too strong an oxidant and will oxidise water to O_2 so the potential can not be easily measured!

Given that the value listed for dichlorine is also greater than what is needed to oxidise water (+1.229 V) this should happen as well however this is not the case since there is a slow kinetic step in the oxidation of water. Note as well that this is the same reason why aqueous solutions of potassium permanganate can be prepared, although they are not stable over time.

We already mentioned the variation of acid strength of the HX acids and in a similar way the magnitudes of the E° for the half-reactions

$\frac{1}{2}X_2 + e^- \rightarrow X^-$

are best described in terms of bond-energies, electron affinities and hydration energies.

$\frac{1}{2}X_2 \rightarrow X(g) \rightarrow X^-(g) \rightarrow X^-(aq)$

Overall this causes Cl_2 to be a more powerful oxidant than Br_2 or I_2, partly because of a more negative enthalpy of formation of the anion but by taking into consideration the strong interaction with the small Cl^- ion with water.

The majority of the couples are pH dependent so that an increase in pH causes a dramatic lowering of the E° value. This is expected since if we consider an example where BrO_3^- is converted to $\frac{1}{2}Br_2$ by the reaction:

$BrO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}Br_2 + 3\ H_2O$ (E° = +1.495 V)

the equilibrium constant includes a term with $[H^+]^6$ so that if the pH is changed from pH=1 to pH=14 then H^+ effectively changes by 10^{-14} and the estimated difference can be seen in E° as:

$\Delta G° = - RT\ln(K)$

$\Delta G° = - nE°F$

from which just looking at the effect of pH is $\sim(RT/nF)\ln([H^+]^6)$

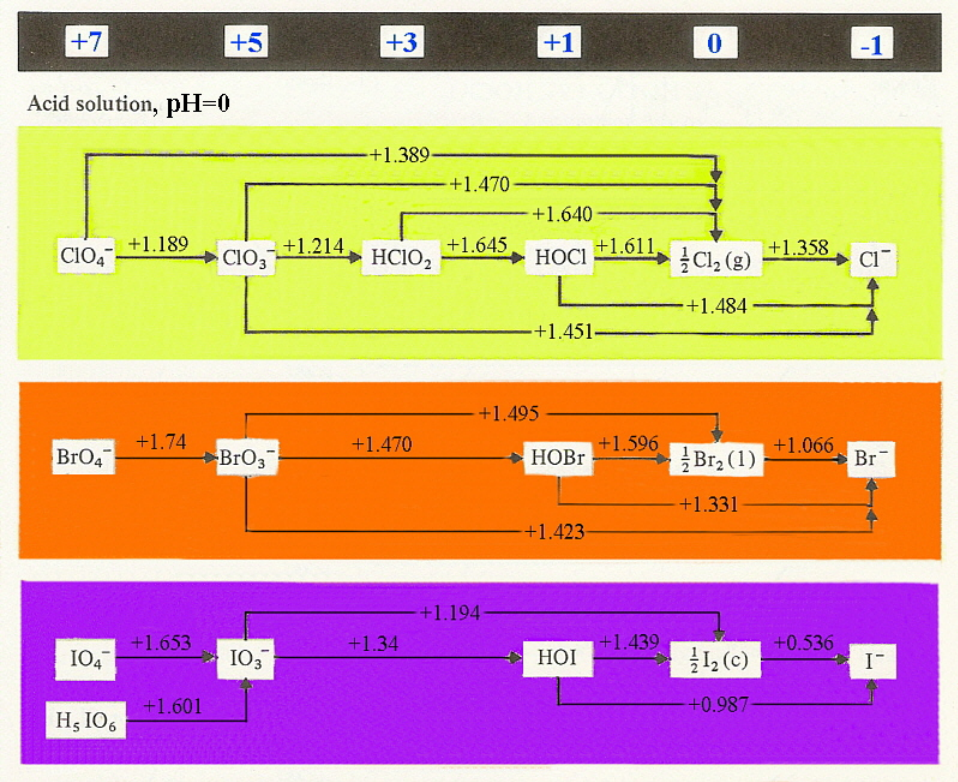
or roughly (0.0592/5) * 14 * 6

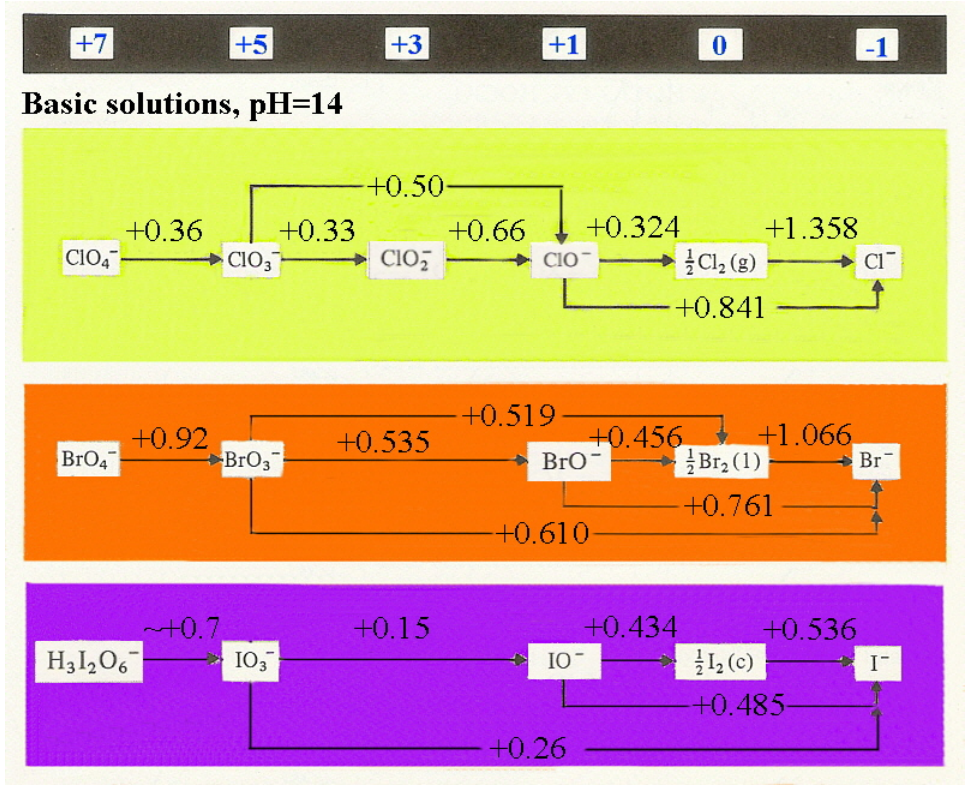
that is an effect of ~+0.99 V

Experimentally the measured E° for

$BrO_3^- + 3H_2O + 5e^- \rightarrow \frac{1}{2}Br_2 + 6\ OH^-$ (E° = +0.519 V)

so estimated value is +1.495 - 0.99 = +0.51 V and found is +0.519 V showing excellent agreement.





Redox processes in acid solutions

Redox processes in basic solutions

These diagrams indicate that in acid, periodate and perbromate are more powerful oxidising agents than perchlorate when being reduced to halate ions (I +1.653, Br +1.74, Cl +1.189 V) and that iodate and iodine are much weaker oxidants compared to the other halates (I +1.34, Br +1.470, Cl +1.214 V) or halogens (I +0.535, Br +1.066, Cl +1.358 V).

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return to course outline

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Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

Topic hierarchy

16.9A: Dithionous Acid, \(H_2S_2O_4\)

16.9B: Sulfurous and Disulfurous Acids, \(H_2SO_3\) and \(H_2S_2O_5\)

16.9C: Dithionic Acid, \(H_2S_2O_6\)

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16.9A: Dithionous Acid, $H_2S_2O_4$

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16.9D: Sulfuric Acid, $H\ 2\ S\ O\ 4$

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16.9F: Polyoxoacids with S-O-S Units

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16.9H: Thiosulfuric Acid, $H_2S_2O_3$, and Polythionates

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16.9I: Oxoacids of Selenium and Tellurium

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16.10: Compounds of Sulfur and Selenium with Nitrogen

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16.11: Aqueous Solution Chemistry of Sulfur, Selenium, and Tellurium

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CHAPTER OVERVIEW

17: The Group 17 Elements

The halogens are located on the left of the noble gases on the periodic table. These five toxic, non-metallic elements make up Group 17 of the periodic table and consist of: fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). Although astatine is radioactive and only has short-lived isotopes, it behaves similar to iodine and is often included in the halogen group. Because the halogen elements have seven valence electrons, they only require one additional electron to form a full octet. This characteristic makes them more reactive than other non-metal groups.

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17.1: Introduction

Chemistry 242 - Inorganic Chemistry II
Chapter 20 - The Halogens: Fluorine, Chlorine Bromine, Iodine and Astatine

Introduction

- All elements except helium, neon and krypton fro some sort of halogen compound.
- The structures vary from ionic to covalent.
- Halides are often the source materials for thsynthesis of other substances.
- The halides are often the "generic" compounds used to illustrate the range of oxidation states for the other elements.
- The class of fluorocarbons is an important group of organic chemicals which often have unique properties.

Occurence and Isolation, and Properties of the Elements

Fluorine

- Occurs in fluorspar, CaF_2, cryolite, Na_3AlF_6 and fluorapatie, $3Ca_3(PO_4)_2.Ca(F,Cl)_2$. It is actually more abundant than chlorine.
- It is made by electrolysis, for example, of a misture of 2 to 3 parts of HF with KF which melts at 70 - 100 ^oC. It is a pale yellow gas, bp -118 ^oC.
- It is the most reactive of all the elements and attacks all the others except He, Ne and Ar so it has to be handled in special apparatus: stainless steel and copper because they become coated with a protective fluoride layer and are the materials of choice. (If all traces of HF are removed, fluorine can be handled in glass apparatus also, but this is nearly impossible.)
- Fluorine will also attack many compounds yielding flourides.
- The reason for its great reactivity seems to be connected with the weak F-F bond probably due to strong repulsion between the non-bonding (lone-pair) electrons. (In this respect it is similar to hydrazine and hydrogen peroxide.)

Chlorine

- Occurs mainly as rock salt, NaCl, potassium chloride and magnesium chloride.
- Chlorine is manufactured by the electrolysis of brine. At one time this was done using a mercury cathode, which also produced sodium amalgam, thence sodium hydroxide by hydrolysis. The sodium hydroxide was often recombined with the chlorine to form sodium hypochlorite (bleach) for use in the paper industry. The mercury is now recognized as a major polluent. Now "memberane" cells are used to prevent the electrolytes around the two electodes from mixing.
- Chlorine is a green gas bp -34.6 ^oC.

Bromine

- It occurs with chlorine and can be obtained by displacement from bromides with chlorine.
- Bromine is a brown liquid, mp -7.2, bp 58.8 ^oC.

Iodine

- Iodine is found in brines, and as IO_3^- with deposits of $NaNO_3$.
- It is black solid with a metallic sheen. It sublime at room temperature and its vapour is purple. It also forms purple solution in non-polar solvents.
- The brown solution obtained by dissolving iodine in potassium iodide contains the linear I_3^- ion.

  The intense blue complex with starch used in iodometric titrations contains the I_5^- ion.

Halides

They can be made by:

1. Direct reaction. In the case of fluorine, particularly, high oxidation states can be reached.
2. Reaction with an oxide.
3. Halogen exchange reactions.
4. By dehydration of hydrated halides.

Molecular Halides

As a class of compounds, the halides illustrate the distinction between ionic solids, network solids and molecular compounds (which can be solids liquids or gases). This section deals with all three, its heading notwithstanding!

- Broadly, the more covalent the halide, the more likely it is to be truly molecular. Examples would be BCl_3 or IF_3.
- As the compounds become less covalent, halogen bridges are found, leading first to dimers such as Al_2Cl_6.
- As the covalency continues to decrease, the amount of bridging increases and network solids can be found. An example is $(AlF3)_n$ in which all the aluminum is 6-coordinated and all the fluorines are bridging (2-coordinate). The bonding remains quite covalent.
- At the ionic limit one finds salts such as sodium chloride, where the forces between sodium and chloride ions are almost entirely electrostatic. Both ions are 6-coordinate in NaCl.
- The position along the above progression is influenced by factors such as the electronegativity of the components, their size, and the possibility of multiple bonding which might stabilize a monomeric molecular compound such as BF_3 (pp - pp) or SF_6 (dp - pp).

The particularly high electronegativity of fluorine leads to some special properties in its compounds:

- CF_3COOH is a strong acid unlike CH_3COOH.
- NF_3 and $N(CF_3)_3$ are not at all basic, unlike ammonia.
- $-CF_3$ groups are quite inert to nucleophilic attack, unlike $-CH_3$.
- $-CF_3$ mimics a big halogen with an electronegativity around that of -Cl.

Halogen Oxides

Fluorine forms two oxygen compounds:

a. Oxygen Fluoride, OF_2 a yellow gas produced by:

> $F_2 + NaOH(aq) \rightarrow OF_2$

b. Dioxygen difluoride, O_2F_2 a yellow-orange solid produced by:

> $F_2(g) + O_2(g) \rightarrow O_2F_2$ *(Electric discharge through the reactants)*

Chlorine does not react directly with oxygen, but forms a dangerously exposive paramagnetic oxide ClO_2 in the following reaction:

> $NaClO_3 + SO_2 + H_2SO_4 \rightarrow 2ClO_2 + 2NaHSO_4$

It is used as a chlorinating agent in organic synthesis well diluted with air!

Iodine forms one important oxide, I_2O_5, by dehydration of HIO_3:

> $HIO_3 \rightarrow I_2O_5 + H_2O$ *(240 °C)*

Its use is as a reagent for quantitative analysis for carbon monoxide:

> $5CO + I_2O_5 \rightarrow I_2 + 5CO_2$

then the iodine is titrated as triiodide with thiosulphate:

> $I_2 + I^- \rightarrow I_3^-$
> $S_2O_3^{2-} + I_3^- \rightarrow 3I^- + S_4O_6^{2-}$ *(starch as indicator)*

Oxo Acids

- The reaction of the halogens with water produces hypohalous acids, HOX, and halide ion in solution:

  > $X_2 + H_2O \rightarrow HOX + H^+ + X^-$

  The pure compounds are unknown except HOF which is none too stable itself.

The solutions can be used to obtain the salts e.g. sodium hypochloride, bleach. The XO^- ions disproprortionate further in basic solution, (IO^- very rapidly even in neutral solution):

$$3XO^- \rightleftharpoons 2X^- + XO_3^-$$

- For chlorine the following reactions are important:
  - Production of chlorite, ClO_2^-, and chlorate, ClO_3^-:

$$ClO_2 + 2OH^- \rightleftharpoons ClO_2^- + ClO_3^- + H_2O$$

  - Perchlorate is produced by electrolytic oxidation of chlorate:

$$ClO_3^- + H_2O \rightleftharpoons ClO_4^- + 2H^+ + 2e^-$$

- Periodate species are unlike the others due to the large size and low electronegativity of iodine. The following equilibria are important:

$$H_5IO_5 \rightleftharpoons H^+ + H_4IO_6^- \; K = 10^{-3}$$
$$H_4IO_6^- \rightleftharpoons IO_4^- + 2H_2O \; k = 29$$
$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^= \; k = 1x10^{-7}$$

Periodate is used as an oxidizing agent in organic synthesis.

Interhalogens

- The species are molecules or molecule ions, for example, BrCl, IF_5, Br_3^+, I_3^-.
- The neutral species will be XX'_n where n is odd and 7 or less and X' will be the lighter halogen. The range of isolable compounds is governed by steric effects.
- Most are made by direct reactions.

Organic Compounds of Fluorine

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SECTION OVERVIEW

17.2: Occurrence, Extraction, and Uses

Topic hierarchy

17.2A: Occurrence

17.2B: Extraction

17.2C: Uses

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17.2A: Occurrence

9 F 18.9984032	The Group 17 elements include: fluorine, chlorine, bromine, iodine and astatine and according to Housecroft and Sharpe [1] their chemistry is "probably better understood than that of any other group of elements, except the alkali metals". They share common properties such as forming singly bonded atoms as in the diatomic molecules (F_2, Cl_2, Br_2, I_2, and At_2), and forming singly charged anions (F^-, Cl^-, Br^-, I^-, and At^-). For this four lecture course, we will omit the chemistry of astatine since it is radioactive and the most stable isotopes of astatine have half-lives of less than a minute. As a consequence of this, only trace quantities (less than 50 ng) of astatine compounds have been investigated, severely limiting characterisation of properties. Discussions of the chemistry of the elements in Group 17 therefore focus on four elements: F, Cl, Br, and I. In 1825, the Swedish chemist Jöns Jakob Berzelius applied the term **halogens** (from the Greek *hals*, "salt," and *gennan*, "to form or generate") for an element that produces a salt when it forms a compound with a metal. None of the halogens are found naturally in their elemental form. They are invariably found as salts of the **halide** ions (F^-, Cl^-, Br^-, and I^-). [Note that Br was not discovered until 1826, after the term halogen was proposed, so it was added to the list of halogens later]. The mineral fluorspar (also called fluorite) consisting mainly of calcium fluoride, was first described as far back as 1530 by Georgius Agricola. This is a major source of **fluorine** in the form of fluoride ions as was cryolite (Na_3AlF_6) until the major deposits in Greenland ran out in 1987.
17 Cl 35.453	In nature, **chlorine** is found primarily as the chloride ion, a component of the salt that is deposited in the earth or dissolved in the oceans - about 1.9% of the mass of seawater is chloride ions. Even higher concentrations of chloride are found in the Great Salt Lake in Utah, which is 9% Cl^- ion by weight, the Dead Sea and in underground brine deposits. Most chloride salts are soluble in water, thus, chloride-containing minerals are usually only found in abundance in dry climates or deep underground. Common chloride minerals include halite (sodium chloride), sylvite (potassium chloride), and carnallite (potassium magnesium chloride hexahydrate). Over 2000 naturally-occurring organochlorine compounds are known.
53 I 126.90447	The largest **bromine** reserve in the United States is located in Columbia and Union County, Arkansas, U.S. China's bromine reserves are located in the Shandong Province and Israel's bromine reserves are contained in the waters of the Dead Sea.
85 At (210)	**Iodine** naturally occurs in the environment chiefly as a dissolved iodide in seawater, although it is also found in some minerals and soils. This element also exists in small amounts in the mineral caliche, found in Chile, between the Andes and the sea. A type of seaweed, kelp, tends to be high in iodine as well.

X	Isotopes	Earth's crust (ppm)	Sea water (ppm)	Universe (ppm)
F	100% - 19	950	0.0001	0.4
Cl	(75.77%, 35) (24.23%, 37)	130	18000	1
Br	(50.69%, 79) (49.31%, 81)	3	67.3	0.007
I	100%, 127	1.4	0.05	0.001

Extraction

Difluorine F_2

HF is the starting material for the preparation of most fluorine containing compounds and this is isolated as a byproduct from the production of phosphoric acid. Treatment of minerals such as fluorspar/ fluorite CaF_2, (often associated with phosphate-containing minerals) with sulfuric acid gives hydrogen fluoride by the following reaction:

$$CaF_2 + H_2SO_4 \rightarrow 2\ HF + CaSO_4$$

Difluorine is prepared by the electrolysis of HF. Since F_2 is strongly oxidising, this is the only viable method that can be performed on an industrial scale and given the extreme reactivity of the F_2, it requires strictly controlled conditions. It is believed that many

were blinded or killed during the many years in trying to perfect the process and experiment with the toxic gas.

"Henry Moissan (1852-1907) eventually succeeded in preparing fluorine in 1886 by the electrolysis of a solution of potassium hydrogen difluoride (KHF_2) in liquid hydrogen fluoride (HF). The mixture was needed because hydrogen fluoride is a non-conductor. The device was built with platinum/iridium electrodes in a platinum holder and the apparatus was cooled to -50 °C. The result was to completely isolate the hydrogen produced from the negative electrode from the fluorine produced at the positive one. This is essentially still the way fluorine is produced today. For this achievement, he was awarded the Nobel Prize in 1906."[5].

It is recorded that he died shortly after his return from collecting his Nobel Prize and that death was a result of acute appendicitis. It is not known whether his studies on fluorine contributed to his early death.

"The modern electrolysis cell contains a steel or copper cathode, ungraphitized carbon anode, and a Monel metal (Cu/Ni) diaphragm that is perforated below the surface of the electrolyte, but not above it, thus preventing the H_2 and F_2 products from recombining. As electrolysis proceeds, the HF content of the melt is renewed by adding dry gas from cylinders." [1]

Dichlorine (Cl_2)

The Castner-Kellner process, invented jointly by Hamilton Castner and Karl Kellner in the 1890's is the earliest industrial process for the extraction of dichlorine (Cl_2).

The Castner-Kellner Chlor-alkali electrolysis cell
A=graphite anode, C=iron cathode, F=fulcrum system, M=mercury cathode, N=NaOH solution, S=NaCl solution, W=slate wall

In the diagram above there are two types of cells shown, one in the centre and two outer cells. They are separated by slate walls (W) that dip into a pool of liquid mercury (M). The outer cells have a solution a sodium chloride (S), a graphite anode (A) and mercury cathode. The inner cell has a solution of sodium hydroxide (N), an iron cathode (C) and here the mercury acts as the anode. The mercury is able to move between the three cells aided by a rocking mechanism (F), but the solutions are kept separated by the slate walls.

The overall processes are given by the following equations:

$2Cl^- \rightarrow Cl_2 + 2e^-$
$2Na^+ + 2e^- \rightarrow 2Na$ (amalgam)
and
$2Na$ (amalgam) $\rightarrow 2Na^+ + 2e^-$
$2H_2O + 2e^- \rightarrow 2OH^- + H_2$

As the electrolysis proceeds the concentration of sodium chloride in the outside cells decreases and the concentration of sodium hydroxide in the center cell increases. When this reaches a concentration of about 50% some of this sodium hydroxide solution is removed from center cell to be replaced with water. Sodium chloride is added to the outside cells to replace that used up. Dihydrogen and dichlorine are collected as gases in high purity. An animation of the working of a modern plant can be see at Euro-Chlor, Chlorine Online

The large scale use of mercury has raised numerous environmental issues and many of these industrial plants have been decommissioned and the sites cleaned up, those that remain are expected to wind up operation by 2020. According to Euro Chlor "In 2007, emissions for all mercury cells across Western Europe reached an all-time low of 0.97 grammes per tonne of chlorine capacity."

Apart from the mercury cell process, two others are in operation and these require less electricity and do not use mercury. They are the "membrane cell process" and the diaphragm cell process".

Dibromine (Br_2)

Internationally, bromine reserves are found in Arkansas, USA, the waters of the Dead Sea, Israel and Shandong Province, China. In 2007, approximately 556,000 metric tonnes (worth around US$2.5 billion) of bromine were produced predominantly by these three countries and this equated to a sixfold increase since the 1960s.

The extraction involves treating the bromide-rich brines with chlorine gas then flushing through with air. In this treatment, bromide anions are oxidized to bromine by the chlorine gas.

$2\ Br^- + Cl_2 \rightarrow 2\ Cl^- + Br_2$

Diiodine (I_2)

Chilean Caliche

In the Atacama Desert in northern Chile, there are vast deposits of a mixture, often referred to as caliche, composed of gypsum, sodium chloride, plus other salts and sand, associated to Salitre ("Chile Saltpeter"). Salitre, in turn, is a composite of sodium nitrate ($NaNO_3$) and potassium nitrate (KNO_3) and was an important source of export revenue for Chile until World War I, when both nitrates began to be industrially produced in large quantities in Europe.

These deposits are the largest known natural source of nitrates in the world, containing up to 25% sodium nitrate and 3% potassium nitrate, as well as **iodate minerals**, sodium chloride, sodium sulfate, and sodium borate (borax). The caliche beds are from 0.2 to 5 meters thick, and they are mined and refined to produce a variety of products, including sodium nitrate (for agriculture or industry uses), potassium nitrate, sodium sulfate, iodine, and iodine derivatives. The discovery of the iodate impurity in the Chilean saltpetre dates from 1840 and led to the large scale extraction process that saw Chile as the largest producer of iodine worldwide in 2007, followed by Tokyo, Japan and Oklahoma, USA where the iodine was recovered from brine solutions.

$2IO_3^- + 5HSO_3^- \rightarrow 3HSO_4^- + 2SO_4^{2-} + H_2O + I_2$

The Halogens - Properties and Uses

Difluorine (F_2), is a highly toxic, colorless gas, and is highly reactive. It is so reactive that it even forms compounds with Kr, Xe, and Rn, elements once considered inert. Due to its high reactivity it is difficult to find a container in which it can be stored. F_2 attacks both glass and quartz, for example, and causes most metals to burst into flame. It has to be handled in equipment built from alloys of copper and nickel where even though it still reacts with these alloys, it forms a layer of fluoride salt on the surface that protects the metal from further reaction.

Fluorine is such a powerful oxidizing agent that it can convert other elements into unusually high oxidation numbers, as in AgF_2, PtF_6, and IF_7.

portion of Teflon

Fluorine is used in the manufacture of Teflon or PTFE poly(tetrafluoroethylene), $(C_2F_4)_n$. Teflon was first prepared in 1938 by accident, since the intended product was a new refrigerant. The first non-stick frying pan was developed in France in 1954 and in the USA in 1961. Another important use is for lining of valves and gaskets that are inert to chemical reactions. This is needed in Uranium enrichment involving UF_6.

Natural uranium is 99.284% ^{238}U isotope, with ^{235}U only constituting about 0.711% of its weight. Isotope enrichment of ^{235}U is difficult because the two isotopes have nearly identical chemical properties, and can only be separated gradually using small mass differences. (^{235}U is only 1.26% lighter than ^{238}U). Gaseous diffusion was the first successful technology used to produce enrich uranium by forcing gaseous uranium hexafluoride through semi-permeable membranes. This produced a slight separation between the molecules containing ^{235}U and ^{238}U.

Large amounts of fluorine were consumed each year to make the "Freons" (such as Freon-12, CCl_2F_2) used in refrigerators. CFCs (chlorofluorocarbons) and HCFCs hydrochlorofluorocarbons) were produced by halogen exchange starting from chlorinated methanes and ethanes. For example, the synthesis of chlorodifluoromethane from chloroform:

$CHCl_3 + 2HF \rightarrow HCF_2Cl + 2HCl$

2010 marks the year when the production of CFC's is to cease in developing countries, having already been phased out in 2000 in developed countries under the Montreal Protocol, since they are deplete stratospheric ozone. Recycling will then be the only source of CFC's. HCFC's are not regarded as suitable replacements, since although they start degrading before reaching the ozone layer, a proportion still reaches the stratosphere and chlorine buildup was found to be higher than originally predicted. HFC's (hydrofluorocarbons) are considered suitable since they have a shorter lifetime in the lower atmosphere. HFO-1234yf, (CH_2=$CFCF_3$) or 2,3,3,3-Tetrafluoropropene is proposed as a refrigerant for automobiles. It has a boiling point of -30 °C.

Fluoridation of water supplies was introduced in many countries in the mid-1900's as a preventative measure against dental decay. The fluorides used include: H_2SiF_6 and Na_2SiF_6. Due to the possibility of an increased risk of cancer this practise has been reduced but fluoridation of toothpaste (NaF or monofluorophosphates) has increased as an alternative.

Chlorine (Cl_2) is a highly toxic gas with a pale yellow-green color and is a very strong oxidizing agent.

Chlorine useage in Europe, 2008 (/kt) [6]	PVC - door and window frames, piping etc, (34.2%) Isocyanates and Oxygenates - upholstery, insulation, pesticides, (29.1%) Inorganics - disinfectants, water treatment, (13.7%) Organics - detergents, herbicides, insecticides, (7.0%) Chloromethanes - silicon rubbers, decaffeination, paint strippers, cosmetics, (5.9%) Epichlorohydrin - epoxy resins, printed circuits, sports boats, (5.4%) Solvents - metal degreasing, adhesives, (4.7%)

PVC is the third most widely used plastic material in the world, after polyethylene and polypropylene. At the global level, demand for PVC exceeds 35 million tonnes per annum and it is in constant growth (+5% on global average), with higher growth rates in the developing countries. PVC is durable, easy to clean, stain resistant, lightweight, corrosion resistant and needs no maintenance. [7]

Chlorine has been used commercially as a disinfectant and as a bleaching agent. Chlorine was first used as a disinfectant for drinking water in the late 19th century as a means of controlling the spread of water-borne diseases such as typhoid, cholera, dysentery and gastro-enteritis. In the USA in 1900, annual deaths from cholera totalled 25,000 but following the introduction of chlorination, this figure had fallen to fewer than 20 by 1960! In 1991, a misinterpretation of US law resulted in the Peruvian government voluntarily suspending chlorination of water supplies. The resulting cholera epidemic spread to neighbouring countries causing an estimated 1 million cases of cholera and more than 10,000 deaths.[6]

Chemical pulp bleaching aims to remove coloured residual lignin from the pulp and increase its brightness, brightness stability and cleanliness while preserving the strength (cellulose integrity) and carbohydrate yield (cellulose and hemicellulose) of the unbleached fibre, with due regard for potential effects on the environment. [8]

World use of bleached pulp, 1990-2007 (/Mt) [9]	ECF - Elemental Chlorine-Free (ECF) pulp, bleached with chlorine dioxide. TCF - Totally Chlorine-Free pulp, a small 5% niche market. other - this includes dichlorine

ECF, using ClO_2, accounts for 99% of the bleached chemical pulp production in the USA, while dichlorine was essentially phased out in 2001 in compliance with rules from the Environmental Protection Agency. Cl_2 was found to contribute to the formation of perchlorodibenzodioxins PCDD and perchlorodibenzofurans PCDF. A number of these are highly toxic, persistent (lasting for years or even decades before degrading into less dangerous forms), highly volatile and liable to accumulate in fatty tissue, hence they are called persistent organic pollutants (POP).

For example, tetrachlorodibenzodioxin and hexachlorodibenzofuran

Some 85% of pharmaceuticals contain or are manufactured using chlorine, including products to treat Aids, allergies, arthritis, cancer, depression, diabetes, heart disease, hypertension, infections, pneumonia and ulcers. An example is the natural antibiotic

vancomycin, an effective medicine in fighting hospital Staphylococcus infections.[6]

Bromine (Br_2) is a reddish-orange liquid with an unpleasant, choking odor. The name of the element is derived from the Greek stem *bromos*, "stench." Bromine is used to prepare flame retardants, fire-extinguishing agents, sedatives and insecticides.

There are approximately 75 different brominated flame retardants (BFRs) of which Deca-BDE, TBBPA and HBCD are the three main commercial products.
Deca-BDE 1,2,3,4,5-pentabromo-6-(2,3,4,5,6-pentabromophenoxy)benzene is a highly effective brominated flame retardant which is used to prevent fires in plastics for electrical and electronic equipment as well as in contract textiles.
TBBPA 2,2',6,6'-Tetrabromo-4,4'-isopropylidenediphenol is the largest BFR in terms of production. 70% is used as a reacted flame retardant in polymers like epoxy resins in electrical and electronic equipment and 20% is used as an additive to plastics.
HBCD 1,2,5,6,9,10-hexabromocyclododecane has been used for many years mainly in thermal polystyrene insulation foams and applied in the back-coating of textiles for upholstered furniture. [10]

Marine organisms are the main source of naturally occuring organobromine compounds. Perhaps the most famous example and certainly oldest of these is a dyestuff that has been used by humans since the 18th century BC, Tyrian purple. The dye, Tyrian purple - 6,6'-dibromoindigo was extracted from the the marine gastropods Murex brandaris and the purple silks produced were a status symbol of the Byzantium imperial court.

Iodine is an intensely colored solid with an almost metallic luster. The solid is relatively volatile, and it sublimes when heated to form a violet-colored gas. Iodine has been used for many years as a disinfectant in "tincture of iodine." Iodine compounds are used as catalysts, drugs, and dyes. Silver iodide (AgI) played an important role in the photographic process and in attempts to seed clouds to make rain. Iodide is also added to salt to protect against goiter, an iodine deficiency disease characterized by a swelling of the thyroid gland.

Among dyes that have a high iodine content is erythrosine B (food red-colour additive E127 (Federal Food, Drug and Cosmetic Act, Red #3)

More on the Properties of Halogens

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17.3A: NMR Active Nuclei and Isotopes as Tracers

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17.4A: Difluorine

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17.4B: Dichlorine, Dibromine, and Diiodine

Iodine

Iodine was discovered by French chemist Bernard Courtois in 1811. His father was a manufacturer of saltpeter (a vital part of gunpowder) and at the time of the French Napoleonic Wars, saltpeter was in great demand. Saltpeter produced from French niter beds required sodium carbonate, which could be isolated from seaweed collected on the coasts of Normandy and Brittany. To isolate the sodium carbonate, the seaweed was burned and the ash washed with water. The remaining waste was destroyed by adding sulfuric acid. Courtois once added excessive sulfuric acid and a cloud of purple vapour rose. He noted that the vapour crystallized on cold surfaces, making dark crystals. Courtois suspected that this was a new element but lacked the funds to pursue it further.

Samples of the material reached Humphry Davy and Joseph Louis Gay-Lussac and in early December 1813 both claimed that they had identified a new element. Arguments erupted between them over who had identified iodine first, but both scientists acknowledged Courtois as the first to isolate the element.

Iodine is found on Earth mainly as the highly water-soluble iodide ion I^-, concentrated in oceans and brine pools. Like the other halogens, free iodine occurs mainly as a diatomic molecule I_2. In the universe and on Earth, iodine's high atomic number makes it a relatively rare element. However, its presence in ocean water has given it a role in biology. It is the heaviest essential element widely utilized by life in biological functions.

Under standard conditions, iodine is a bluish-black solid that sublimes to form a noxious violet-pink gas. It melts at 113.7 °C (386.85 K) and forms compounds with many elements but is less reactive than the other halogens, and has some metallic light reflectance.

Elemental iodine is slightly soluble in water, with one gram dissolving in 3450 ml at 20 °C and 1280 ml at 50 °C; potassium iodide may be added to increase solubility via formation of triiodide ions (I_3^-). Nonpolar solvents such as hexane and carbon tetrachloride provide a higher solubility.

Iodine normally exists as a diatomic molecule with an I-I bond length of 270 pm, one of the longest single bonds known. The I_2 molecules tend to interact via weak London dispersion forces, and this interaction is responsible for the higher melting point compared to more compact halogens, which are also diatomic. Since the atomic size of iodine is larger, its melting point is higher.

The I-I bond is relatively weak, with a bond dissociation energy of 151 $kJmol^{-1}$, and most bonds to iodine are weaker than for the

lighter halides. One consequence of this weak bonding is the relatively high tendency of I_2 molecules to dissociate into atomic iodine.

orthorhombic structure of I_2
a= 0.72701, b= 0.97934, c= 0.47900 nm

The halogens, Cl_2, Br_2, and I_2 adopt similar orthorhombic structures in which diatomic molecules lie in layers:
Cl a= 0.624 b= 0.826 c= 0.448 nm
Br a= 0.667 b= 0.872 c= 0.448 nm
I a= 0.72701, b= 0.97934, c= 0.47900 nm

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17.4C: Charge Transfer Complexes

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17.4D: Clathrates

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17.5: Hydrogen Halides

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17.6: Metal Halides - Structures and Energetics

Simple binary salts

When considering the structures of simple binary salts only a small number of types are important. The simplest are for crystals with formula MX and include NaCl, CsCl and ZnS where the CN of the anion and cation are the same and may be 6, 8 or 4.

Compounds with formulae of MX_2 or M_2X will have different CN's for the cation and anion. The most important of these are the fluorite and rutile structures.

For the MX case, one reason why a substance might favour one form over another is due to the geometry of the packing of the spheres. What is needed is to be able to maximise the interactions of oppositely-charged ions while at the same time minimise the interactions of similarly-charged ions.
The larger the difference in the sizes of the ions affects the packing of the larger ions around the smaller ions. It is relatively easy to calculate the radius ratio (r+/r-) and from this determine the limits for the various CN's.
For the ZnS type structure with CN 4:4 the radius ratio is predicted to be in the range 0.22 - 0.41 while for the NaCl type structure with CN 6:6 it is predicted that the radius ratio will be within the range of 0.41 - 0.73. For CsCl structures with CN 8:8, the radius ratio is expected to be greater than 0.73. The Table below shows the values for a number of alkali halides. Experimentally it is found that the only examples under normal conditions of temperature and pressure to adopt the CsCl structure are CsCl, CsBr and CsI whereas several other salts were predicted to have this structure based on their radius ratios.

Among the other factors that might influence the final structure is the interaction between ions in addition to the nearest neighbours. However the energies involved would not seem to be sufficient to alter the results as shown by the Madelung constants for NaCl and CsCl which are 1.74756 and 1.76267 respectively.

Radius ratio values for alkali halides

X- / M+	Li	Na	K	Rb	Cs
F	0.44	0.70	0.98	0.92	0.81
Cl	0.33	0.52	0.73	0.82	0.93
Br	0.31	0.49	0.68	0.76	0.87
I	0.28	0.44	0.62	0.69	0.78

Transition Metal Halides

The only stable **pentahalide** is VF_5, which is readily hydrolysed and a strong Lewis acid. In the solid state it exists as an infinite chain polymer with *cis*-bridging fluorides but in the vapour phase it has a trigonal-bipyramid monomeric structure. M.P. 19.5° and B.P. 48.3°C.

Tetrahalides are formed by Ti and V. The Ti tetrahalides are fairly unreactive in redox and halogenation chemistry, unlike the V compounds. VCl_4 and VBr_4 dissociate spontaneously under ambient conditions to VX_3 and X_2. They also tend to halogenate organic material.

All **trihalides** of the elements from Ti to Cr are known. Mn(III) and Co(III) are too oxidising to coexist with any halide except F- under ambient conditions, whereas Ti(III) and V(III) are moderately strongly reducing. Chromium(III) is fairly stable toward both reduction or oxidation. There is a marked tendency toward decreasing ionic character on passing from left to right across the period and from the fluorides to the heavier halides. Ferric chloride and bromide show essentially covalent behaviour such as low MPs and solubility in donor organic solvents.

Many trihalides can be prepared by direct combination of the elements. In those cases where direct combination gives a higher oxidation state, trihalides can be produced by either thermal dissociation, disproportionation of the higher halide or by reduction- for example $TiCl_3$ can be prepared by reduction of $TiCl_4$ with H_2 at high temperatures.

All these trihalides adopt structures in which the metal is six-coordinate, either octahedral or distorted octahedral. Many of the lattices are complicated, but can be represented as $CrCl_3$ or BiI_3 types. In some cases it becomes even more complicated since some salts exist in more than one form. For example, at low temperature (below 240K) $CrCl_3$ exists in the rhombohedral form mentioned above, but at room temperature it is monoclinic.

All the first row transition metal elements form **dihalides** with all the halogens, with the exceptions of TiF_2 and CuI_2. The instability of TiF_2 is probably due to easy disproportionation to Ti and TiF_3 whereas the oxidising power of Cu^{2+} (reducing power of I^-) explains the lack of the copper salt. Anhydrous dihalides can generally be synthesised by reaction of the pure metal with hydrogen halide or, for labile metal ions, by dehydration of hydrated salts with a covalent halogen compound e.g. $SOCl_2$.

The difluorides commonly have rutile structures, for example MnF_2, the dichlorides $CdCl_2$ structures and the diiodides CdI_2 structures. Dibromides have either $CdCl_2$ or CdI_2 structures or both. Dihalides are all ionic and typically dissolve in water to give aquo complexes or mixed aquo-halo-complexes. The solutions of Ti(II), V(II) and Cr(II) are very strongly reducing. They react extremely rapidly with O_2, and Ti(II) even rapidly reduces water to liberate hydrogen. Solutions of Fe(II) undergo slow oxidation in air, but in acid or neutral solution Mn(II), Co(II), Ni(II), and Cu(II) are quite stable to oxygen.

CuI adopts the Zinc Blende cubic close packed structure.

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SECTION OVERVIEW

17.7: Interhalogen Compounds and Polyhalogen Ions

Topic hierarchy

17.7A: Interhalogen Compounds

17.7B: Bonding in \([XY_2]^-\) Ions

17.7C: Polyhalogen Cations

17.7D: Polyhalide Anions

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17.7A: Interhalogen Compounds

Some selected properties of the hydrogen halides (HX) are given in the table below [1].

Property of HX	HF	HCl	HBr	HI
Physical appearance at 298K	Colorless gas	Colorless gas	Colorless gas	Colorless gas
Melting point /K	189	159	186	222
Boiling point /K	293	188	207	237.5
Liquid Range /K	104	29	21	15.5
ΔfusH°(mp) / kJ mol^{-1}	4.6	2	2.4	2.9
ΔvapH°(bp) / kJ mol^{-1}	34	16.2	18	19.8
ΔfH°(298 K) / kJ mol^{-1}	-273.3	-92.3	-36.3	+26.5
ΔfG°(298 K) / kJ mol^{-1}	-275.4	-95.3	-53.4	+1.7
Bond dissociation energy / kJ mol^{-1}	570	432	366	298
Bond length /pm	92	127.5	141.5	161
Dipole moment /D	1.83	1.11	0.83	0.45
predicted pKa's	1.4	-9.3	-11.7	-12.4

At room temperature, all of the halogen halides are gases and have sharp, acid smells. They can be prepared by direct combination of the halogens with H_2 or by the action of a concentrated acid (nonoxidising for HBr and HI) on metal halides.

$$CaF_{2(s)} + H_2SO_{4(l)} \rightarrow CaSO_{4(s)} + 2HF_{(g)} \tag{17.7A.1}$$

The reaction is exothermic so to optimise yields it is done at 473-523 °K for 30-60 minutes. Sulfuric acid is too strong an oxidising agent to be used in the generation of HBr and HI resulting in partial oxidation, for example:

$$2HBr + H_2SO_4 \rightarrow Br_2 + 2H_2O + SO_2 \tag{17.7A.2}$$

Phosphoric acid can be used instead though:

$$3NaBr_{(s)} + H_3PO_4 \rightarrow Na_3PO_{4(s)} + 3HBr_{(g)} \tag{17.7A.3}$$

Aqueous solutions of HX are generally referred to as hydohalic acids and we will look at some chemistry of both the anhydrous hydrogen halides and the hydrohalic acids.

Commercial production of anhydrous **Hydrogen Fluoride** began in the 1930's and by the 1980's at least 16 countries were involved in generating over 1 million tonnes worldwide. Initially the HF was used in making refrigerants and for synthetic cryalite Na_2AlF_6 for aluminium production as well as in uranium processing. A small amount is used in glass etching. Hydrofluoric acid attacks glass by reaction with silicon dioxide to form gaseous or water soluble silicon fluorides. The dissolution process proceeds as follows:

$$SiO_2 + 4HF \rightarrow SiF_{4(g)} + 2H_2O \tag{17.7A.4}$$

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \tag{17.7A.5}$$

This property has been known since the 17th century, even before a general procedure for the preparation of large quantities of hydrofluoric acid had been devised by Scheele in 1771. Small quantities of HF(aq) are shipped in TEFLON or polyethylene-lined containers with which it does not react.



***Figure 1**: Edged glass from the Bankfield Museum, Halifax, West Yorkshire, England. (53.43'.57".N; 1.51'.48".W.). from Wikipedia.*

HF is miscible with water in all proportions and phase diagrams show several distinct species including

- $HF.H_2O$ (mp 237.7 °K)
- $2HF.H_2O$ (mp 197.7 °K)
- $4HF.H_2O$ (mp 172.8 °K).

An interesting high-tech application of HF/DF is in High-Energy Lasers as weapons which were first demonstrated in the 1970's and have now reached the level of being mobile and capable of shooting down incoming missiles. The construction of a deuterium fluoride laser resembles a rocket engine. In the combustion chamber, ethylene is burned in nitrogen trifluoride. This reaction produces free excited fluorine radicals. Just after the nozzle, the mixture of helium and hydrogen or deuterium gas is injected to the exhaust stream; the hydrogen or deuterium reacts with the fluorine radicals, producing excited molecules of deuterium or hydrogen fluoride. The excited molecules then undergo stimulated emission in the optical resonator region of the laser.

Deuterium fluoride lasers have found military applications: the MIRACL laser, the Pulsed Energy Projectile and the Tactical High Energy Lasers are of the deuterium fluoride type. The HF laser is somewhat cheaper and operates at 2.7-2.9 μm and this is affected by the atmosphere. The DF laser operates at 3.8 μm and so is considered more useful for terrestrial applications.

Hydrogen chloride

Hydrogen chloride is one of the the largest volume chemicals to be manufactured as either the gas or aqueous acid. Total world production is estimated at 20 Mt/year. When a cheap source of NaCl was available the two-stage Leblanc process, developed during the Industrial Revolution of the 1700's, was used:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \tag{17.7A.6}$$

$$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl \tag{17.7A.7}$$

Here salt is converted to sodium sulfate, using sulfuric acid, giving hydrogen chloride as by-product. Initially, this gas was released to the air, but the Alkali Act of 1863 in the UK prohibited such release, the manufacturers then absorbed the HCl waste gas in water, producing hydrochloric acid on an industrial scale. Modern production of HCl is still as a byproduct that is recovered from large scale processes but now more likely to be from an Industrial Organic Scheme.

Commercial HCl is available up to about 40%, above which the evaporation rate makes it too unstable. Industrially it is usually sold at 30-35% in strength and its major use is for cleaning iron surfaces, where 18% is used. Pickling or removal of rust (iron oxide scale) from steel involves the following reaction:

$$Fe_2O - 3 + Fe + 6HCl \rightarrow 3FeCl_2 + 3H_2O \tag{17.7A.8}$$

The HCl is then regenerated via a closed loop reaction scheme that has been developed so that Fe_2O_3 is recovered as a by-product as well. When high-purity HCl is required, then burning of dihydrogen in dichlorine is used. This is a highly exothermic reaction. High quality HCl is used in the food and pharmaceutical industry as well as for water treatment.

The acid in our stomachs (gastric acid) consists mainly of HCl (around 0.5%), and large quantities of potassium chloride and sodium chloride. The pH is usually around 1-2.

The infrared spectrum of gaseous hydrogen chloride consists of a number of sharp absorption lines grouped around 2886 cm^{-1} and for deuterium chloride vapor this has shifted to 2090 cm^{-1}. These classic molecular spectra can be analyzed to provide information about both rotational and vibrational energies of the molecules. The absorption lines shown involve transitions from the ground to the first excited vibrational state of HCl/DCL, but also involve changes in the rotational states. The rotational angular momentum changes by 1 during such transitions. The splitting of the lines shows the difference in rotational inertia of the two chlorine isotopes ^{35}Cl (75.5%) and ^{37}Cl (24.5%). Calculation of the bond length for H-^{35}Cl for example gives a value of 131 pm, close to the accepted value of 127 pm.

Both HBr and HI can be produced by direct combination, using platinum catalysts and elevated temperatures. An alternate method for the production of HI is the quantitative reaction of iodine with hydrazine.

$$2I_2 + N_2H_4 \rightarrow 4HI + N_2 \tag{17.7A.9}$$

Hydrogen Bromide is very water soluble and aqueous HBr becomes saturated at around 69% by weight at room temperature. A constant boiling point mixture exists at about 47.6% and this boils at 124.3 °C. Boiling more dilute solutions will evaporate some of the water first to eventually arrive at a concentration of 47%.

Hydrogen iodide is extremely soluble in water (425 dm^{-3} in 1 dm^{-3}, which is roughly equivalent to only 4 water molecules per HI molecule). The hydroiodic acid produced is the strongest acid in the series, pka ~-10.

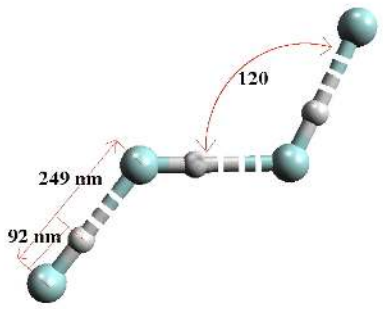
$$HI_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + I^-_{(aq)} \text{ pKa} \sim -10$$

$$HBr_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Br^-_{(aq)} \text{ pKa} \sim -9$$

$$HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \text{ pKa} \sim -8$$

Melting and Boiling Points

As with the dihalogens, it is expected that with increasing size and polarizability the MP's and BP's should increase. The position of HF though needs further explanation.



There is extensive H-bonding in HF in all states and this explains why HF has such a high boiling point (293 °K), even higher than the much heavier HI. Solid HF exists as an H-bonded polymer.

Acidic properties

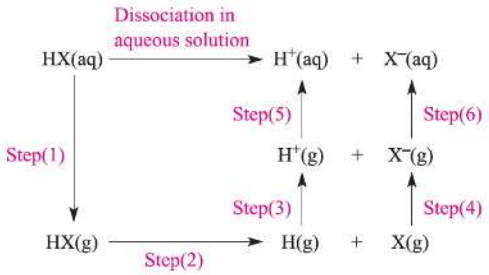
In water, the hydrohalic acids are formed by reaction with the gaseous hydrogen halides and apart from HF these are completely dissociating strong acids. In the case of HF, where there is a short, strong bond, (bond dissociation energy of 570 kJ mol^{-1}) only a weak acid is formed (pKa=3.45). A qualitative explanation for this behavior is related to the tendency of HF to hydrogen-bond and form ion-pair clusters such as $[H_3O^+F^-]$

$$H_2O + HF \rightarrow [H_3O^+F^-] \rightarrow H_3O^+ + F^- \tag{17.7A.10}$$

The first step is thought to lie well to the right, but the 2nd step perhaps only 15%. The reaction representing the pK is given by:

$HX(aq) \rightarrow H^+(aq) + X^-(aq)$
$\Delta G° = -RT\ln(K)$
$\Delta G° = \Delta H° - T\Delta S°$

The factors that influence the degree of dissociation can not all be readily measured but can be simplified as the following 6 steps in the Hess cycle. [1]



Step 1 must be predicted since it is based on having undissociated HX(aq), and apart from HF the hydrogen halides are completely dissociated in aqueous solution. Step 2 is the cleavage of the HX bond. Steps 3 and 5 are independent of the halide and are for the ionisation and hydration of the H+ ion. Step 4 is related to the Electron Affinity and step 6 is the hydration of the gaseous X- ion.

A plot of the energies of steps 1,2,4 and 6 shows little variation for the heavier halides so that it appears that considering only the ΔH terms is not sufficient to explain the trend and it is only when the TΔS terms are considered as well that the ΔG° for HF is predicted to be positive whereas the others are all negative. The predicted value for HF is 1.4 but experimentally the value is found to be 3.45, the trend is accurately predicted but there is clearly much room for improvement!

Safety

In contrast to the weak acidicity of dilute aqueous HF solutions, in concentrated hydrogen fluoride solution, F- ions form a $[HF_2]^-_{(aq)}$ complex by addition to HF molecules. HF molecules remain ionised to compensate the loss of F- ions. More H^+ ions are thus formed, making concentrated HF an effectively strong acid. Anhydrous hydrogen fluoride is an extremely strong acid comparable in strength to anhydrous sulfuric acid.

The fact that it is a weak acid in dilute solutions does not mean it is any less of a hazard and the poorly dissociated HF actually penetrates tissue more quickly than typical acids. Symptoms of exposure to hydrofluoric acid may not be immediately evident and unfortunately any delay in treatment can lead to serious consequences. The severe pain that comes on is thought to be caused by dissolution of Ca in the bone to form insoluble CaF_2 and it is has been found necessary in some cases to amputate affected limbs.

Interhalogens

Some properties of interhalogen compounds are listed below. They are all prepared by direct combination of the elements although since in some cases more than one product is possible the conditions may vary by altering the temperature and relative proportions. For example under the same conditions difluorine reacts with dichlorine to give ClF with dibromine to give BrF_3 but with diiodine to give IF_5.[1]

Compound	ClF	BrF	BrCl	ICl	IBr	ClF_3	BrF_3	IF_3	I_2Cl_6	ClF_5	BrF_5	IF_5	IF_7
Appearance at 298K	Colorless gas	Pale brown gas	impure	Red solid	Black solid	Colorless gas	Yellow liquid	Yellow solid	Orange solid	Colorless gas	Colorless liquid	Colorless liquid	Colorless gas
Stereochemistry	linear	linear	linear	linear	linear	T-shaped	T-shaped	T-shaped	planar	square-based pyramid	square-based pyramid	square-based pyramid	pentagonal bipyramid
Melting point /K	117	~240	dissoc.	300(a)	313	197	282	245 (dec)	337 (sub)	170	212.5	282.5	278 (sub)
Boiling point /K	173	~293	~278	~373	389	285	399	-	-	260	314	373	-
$\Delta fH°(298\ K)$ /kJ mol^{-1}	-50.3	-58.5	14.6	-23.8	-10.5	-163.2	-300.8	~-500	-89.3	-255	-458.6	-864.8	-962
Dipole moment for gas-phase molecule /D	0.89	1.42	0.52	1.24	0.73	0.6	1.19	-	0	-	1.51	2.18	0
Bond distances in gas-phase molecules except for IF_3 and I_2Cl_6 / pm	163	176	214	232	248.5	160 (eq), 170 (ax)	172 (eq), 181 (ax)	187 (eq), 198 (ax)	238 (terminal) 268 (bridge)	172 (basal), 162 (apical)	178 (basal), 168 (apical)	187 (basal), 185 (apical)	186 (eq), 179 (ax)

Valence-shell electron-pair repulsion theory, VSEPR

The premise of the VSEPR is that the valence electron pairs surrounding an atom mutually repel each other, and will therefore adopt an arrangement that minimizes this repulsion, thus determining the molecular geometry. The number of electron pairs surrounding an atom, both bonding and nonbonding, is called its **steric number**. The VSEPR theory thus provides a simple model for predicting the shapes of such species, in particular for main group compounds. The model combines original ideas of Sidgwick and Powell (1940's) with extensions developed by Nyholm and Gillespie (1950's).

- Each valence shell electron pair of the central atom E in a molecule EX_n containing E-X single bonds is stereochemically significant, and repulsions between them determine the molecular shape.

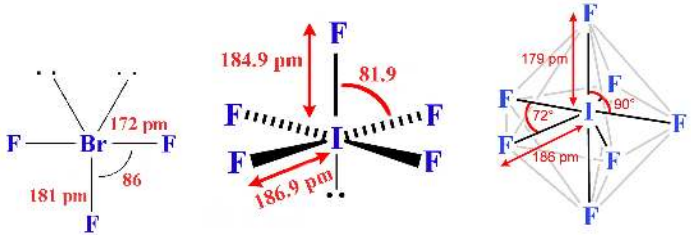
- Electron-electron repulsions **decrease** in the sequence: **lone pair-lone pair** > **lone pair-bonding pair** > **bonding pair-bonding pair**.
- Where the central atom E is involved in multiple bond formation to atoms X, electron-electron repulsions **decrease** in the order: **triple bond-single bond** > **double bond-single bond** > **single bond-single bond**.
- Repulsions between the bonding pairs in EX_n depend on the difference between the electronegativities of E and X; electron-electron repulsions are less the more the E.X bonding electron density is drawn away from the central atom E.

The VSEPR theory works best for simple halides of the p-block elements, but may also be applied to species with other substituents. However, the model does not take steric factors (i.e. the relative sizes of substituents) into account.+

Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs
2	linear			
3	trigonal planar	bent		
4	tetrahedral	trigonal pyramid	bent	
5	trigonal bipyramid	seesaw	**T-shaped**	linear
6	octahedral	**square pyramid**	square planar	
7	**pentagonal bipyramid**	pentagonl pyramid		

Structure of the Interhalogens

The structures found for the various interhalogens conform to what would be expected based on the VSEPR model. For XY_3 the shape can be described as T-shaped with 2 lone pairs sitting in equatorial positions of a trigonal bipyramid. For XY_5 the shape is a square pyramid with the unpaired electrons sitting in an axial position of an octahedral and XY_7 is a pentagonal bipyramid.



XY diatomic interhalogens

The interhalogens with formula XY have physical properties intermediate between those of the two parent halogens. The covalent bond between the two atoms has some ionic character, the larger element, X, becoming oxidised and having a partial positive charge. Most combinations of F, Cl, Br and I are known, but not all are stable.

- Chlorine monofluoride (ClF), the lightest interhalogen, is a colorless gas with a boiling point of 173 °K.
- Bromine monofluoride (BrF) has not been obtained pure - it dissociates into the trifluoride and free bromine. Similarly, iodine monofluoride is unstable - iodine reacts with fluorine to form a pentafluoride.
- Iodine monofluoride (IF) is unstable and disproportionates rapidly and irreversibly at room temperature: $5IF \rightarrow 2I_2 + IF_5$. However, its molecular properties have been determined by spectroscopy: the iodine-fluorine distance is 190.9 pm and the I-F bond dissociation energy is around 277 kJ mol^{-1}. $\Delta Hf° = -95.4$ kJ mol^{-1} and $\Delta Gf° = -117.6$ kJ mol^{-1}, both at 298 K.
  IF can be generated, by the following reactions:
  $I_2 + F_2 \rightarrow 2IF$ at -45 °C in CCl_3F;
  $I_2 + IF_3 \rightarrow 3IF$ at -78 °C in CCl_3F;
  $I_2 + AgF \rightarrow IF + AgI$ at 0 °C.
- Bromine monochloride (BrCl) is an unstable red-brown gas with a boiling point of 5 °C.

- Iodine monochloride (ICl) consists of red transparent crystals which melt at 27.2 °C to form a choking brownish liquid (similar in appearance and weight to bromine). It reacts with HCl to form the strong acid $HICl_2$. The crystal structure of iodine monochloride consists of puckered zig-zag chains, with strong interactions between the chains.
- Iodine monobromide (IBr) is made by direct combination of the elements to form a dark red crystalline solid. It melts at 42 °C and boils at 116 °C to form a partially dissociated vapor.

XY_3 interhalogens

- Chlorine trifluoride (ClF_3) is a Colorless gas that condenses to a green liquid, and freezes to a white solid. It is made by reacting chlorine with an excess of fluorine at 250° C in a nickel tube. It reacts more violently than fluorine, often explosively. The molecule is planar and T-shaped.
- Bromine trifluoride (BrF_3) is a yellow green liquid that conducts electricity - it ionises to form $[BrF_2^+]$ + $[BrF_4^-]$. It reacts with many metals and metal oxides to form similar ionised entities; with some others it forms the metal fluoride plus free bromine and oxygen. It is used in organic chemistry as a fluorinating agent. It has the same molecular shape as chlorine trifluoride.
- Iodine trifluoride (IF_3) is a yellow solid which decomposes above -28 °C. It can be synthesised from the elements, but care must be taken to avoid the formation of IF_5. F_2 attacks I_2 to yield IF_3 at -45 °C in CCl_3F. Alternatively, at low temperatures, the fluorination reaction $I_2 + 3XeF_2 \rightarrow 2IF_3 + 3Xe$ can be used. Not much is known about iodine trifluoride as it is so unstable.
- Iodine trichloride (ICl_3) forms lemon yellow crystals which can be melted under pressure to a brown liquid. It can be made from the elements at low temperature, or from iodine pentoxide and hydrogen chloride. It reacts with many metal chlorides to form tetrachloriodides, and hydrolyses in water. The molecule is a planar dimer, with each iodine atom surrounded by four chlorine atoms. In the melt it is conductive, which may indicate dissociation:

$$I_2Cl_6 \rightarrow ICl_2^+ + ICl_4^- \tag{17.7A.11}$$

Chlorine trifluoride, ClF_3 was first reported in 1931 and it is primarily used for the manufacture of uranium hexafluoride, UF_6 as part of nuclear fuel processing and reprocessing, by the reaction:

$$U + 3ClF_3 \rightarrow UF_6 + 3ClF \tag{17.7A.12}$$

U isotope separation is difficult because the two isotopes have very nearly identical chemical properties, and can only be separated gradually using small mass differences. (^{235}U is only 1.26% lighter than ^{238}U.) A cascade of identical stages produces successively higher concentrations of ^{235}U. Each stage passes a slightly more concentrated product to the next stage and returns a slightly less concentrated residue to the previous stage.

There are currently two generic commercial methods employed internationally for enrichment: gaseous diffusion (referred to as first generation) and gas centrifuge (second generation) which consumes only 6% as much energy as gaseous diffusion. These both make use of the volatility of UF_6. ClF_3 has been investigated as a high-performance storable oxidizer in rocket propellant systems. Handling concerns, however, prevented its use.

Note: ClF_3 is Hypergolic

Hypergolic means explode on contact with no need for any activator. One observer made the following comment about ClF_3:

> It is, of course, extremely toxic, but that's the least of the problem. It is hypergolic* with every known fuel, and so rapidly hypergolic that no ignition delay has ever been measured. It is also hypergolic with such things as cloth, wood, and test engineers, not to mention asbestos, sand, and water with which it reacts explosively. It can be kept in some of the ordinary structural metals-steel, copper, aluminium, etc.-because of the formation of a thin film of insoluble metal fluoride which protects the bulk of the metal, just as the invisible coat of oxide on aluminium keeps it from burning up in the atmosphere. If, however, this coat is melted or scrubbed off, and has no chance to reform, the operator is confronted with the problem of coping with a metal-fluorine fire. For dealing with this situation, I have always recommended a good pair of running shoes."[3]

It is believed that prior to and during World War II, ClF_3 code named N-stoff ("substance N") was being stockpiled in Germany for use as a potential incendiary weapon and poison gas. The plant was captured by the Russians in 1944, but there is no evidence that the gas was actually ever used during the war.

XY5 interhalogens

- Chlorine pentafluoride (ClF_5) is a Colorless gas, made by reacting chlorine trifluoride with fluorine at high temperatures and high pressures. It reacts violently with water and most metals and nonmetals.
- Bromine pentafluoride (BrF_5) is a Colorless fuming liquid, made by reacting bromine trifluoride with fluorine at 200° C. It is physically stable, but reacts violently with water and most metals and nonmetals.
- Iodine pentafluoride (IF_5) is a Colorless liquid, made by reacting iodine pentoxide with fluorine, or iodine with silver fluoride. It is highly reactive, even slowly with glass. It reacts with elements, oxides and carbon halides. The molecule has the form of a tetragonal pyramid.
- Primary amines react with iodine pentafluoride to form nitriles after hydrolysis with water.

$$R-CH_2-NH_2 \rightarrow R-CN \tag{17.7A.13}$$

XY7 interhalogens [3]

- Iodine heptafluoride (IF_7) is a Colorless gas. It is made by reacting the pentafluoride with fluorine. IF_7 is chemically inert, having no lone pair of electrons in the valency shell; in this it resembles sulfur hexafluoride. The molecule is a pentagonal bipyramid. This compound is the only interhalogen compound possible where the larger atom is carrying seven of the smaller atoms.
- All attempts to form bromine heptafluoride have met with failure; instead, bromine pentafluoride and fluorine gas are produced.

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1. "Inorganic Chemistry" - C. Housecroft and A.G. Sharpe, Prentice Hall, 3rd Ed., Dec 2007, ISBN13: 978-0131755536, ISBN10: 0131755536, Chapter 17.
2. "Chemistry of the Elements", Greenwood and Earnshaw,Elsevier.

Contributors and Attributions

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17.10: Aqueous Solution Chemistry

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CHAPTER OVERVIEW

18: The Group 18 Elements

The noble gases (Group 18) are located in the far right of the periodic table and were previously referred to as the "inert gases" due to the fact that their filled valence shells (octets) make them extremely nonreactive. The noble gases were characterized relatively late compared to other element groups.

Topic hierarchy

- 18.1: Introduction
- 18.2: Occurrence, Extraction, and Uses
  - 18.2A: Occurrence
  - 18.2B: Extraction
  - 18.2C: Uses
- 18.3: Physical Properties
  - 18.3A: NMR Active Nuclei
- 18.4: Compounds of Xenon
  - 18.4A: Fluorides
  - 18.4B: Chlorides
  - 18.4C: Oxides
  - 18.4D: Oxofluorides and Oxochlorides
  - 18.4E: Other Compounds of Xenon
- 18.5: Compounds of Argon, Krypton, and Radon
- 18.6: Group 18 Elemental Solids

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18.1: Introduction

Introduction

Until comparatively recently, it was believed that the noble gases "had no chemistry". The observation that dioxygen reacts with platinum hexafluoride lead N. Bartlett to attempt a similar reaction with Xe in the early '60's. His attempt was prompted by his recognition that the first ionization enthalpy of Xe was almost identical to that of O_2 (going to O_2^+).

> $O_2 + PtF_6$  $[O_2]^+[PtF_6]^-$
> $Xe + PtF_6$  $"[Xe]^+[PtF_6]^-"$

The compound actually formed with xenon was subsequently found to have a more complicated structure, but nevertheless, the way was paved for an exhaustive investigation of the chemistry of the noble gases.

The Chemistry of Xenon

The known compounds with fluorine and oxygen are listed in Table 21-2: A detailed study of this topic is not necessary for chem 242. There are also a few compounds containing a Xe-C bond, for example:

> $XeF_2 + B(C_6H_5)_3$  $[C_6H_5Xe]^+[F_3B(C_6H_5)]^-$ + other products

Other Noble Gas Chemistry

Krypton forms only the unstable KrF_2. Radon probably has a chemistry more extensive than xenon, but because of its radioactivity, has not been very much studied.

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SECTION OVERVIEW

18.2: Occurrence, Extraction, and Uses

Topic hierarchy

18.2A: Occurrence

18.2B: Extraction

18.2C: Uses

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18.2A: Occurrence

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18.3A: NMR Active Nuclei

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SECTION OVERVIEW

18.4: Compounds of Xenon

Topic hierarchy

18.4A: Fluorides

18.4B: Chlorides

18.4C: Oxides

18.4D: Oxofluorides and Oxochlorides

18.4E: Other Compounds of Xenon

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18.4A: Fluorides

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18.4B: Chlorides

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18.4D: Oxofluorides and Oxochlorides

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18.4E: Other Compounds of Xenon

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18.5: Compounds of Argon, Krypton, and Radon

It was initially believed that the noble gases could not form compounds due to their full valence shell of electrons that rendered them very chemically stable and unreactive. All noble gases have full s and p outer electron shells (except helium, which has no p sublevel), and so do not form chemical compounds easily. Because of their high ionization energy and almost zero electron affinity, they were not expected to be reactive.

The heavier noble gases have more electron shells than the lighter ones. Hence, the outermost electrons experience a shielding effect from the inner electrons that makes them more easily ionized, since they are less strongly attracted to the positively charged nucleus. This results in an ionization energy low enough to form stable compounds with the most electronegative elements, fluorine and oxygen, and even with less electronegative elements such as nitrogen and carbon under certain circumstances. These compounds are listed in order of decreasing order of the atomic weight of the noble gas, which generally reflects the priority of their discovery, and the breadth of available information for these compounds.

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18.6: Group 18 Elemental Solids

Once cooled below their respective melting points, the Group 18 elements form an ordered solid. Group 18 elemental solids are useful in providing a place for electrons to become trapped or reactions to take place. Some examples include the use of solid argon to study highly reactive molecules, and solid neon to allow reaction and formation of xenon hydrides.

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- Jordan Boothe, University of California Davis, Pharmaceutical Chemistry

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CHAPTER OVERVIEW

19: d-Block Metal Chemistry - General Considerations

Isomers are classified into 1) stereoisomers which have different spatial orientations, and 2) constitutional isomers where atoms are connected in different orders.

Topic hierarchy

19.1: Topic Overview
19.2: Ground State Electronic Configurations
- 19.2A: d-block Metals Versus Transition Elements
- 19.2B: Electronic Configurations

19.3: Physical Properties
19.4: The Reactivity of the Metals
19.5: Characteristic Properties - A General Perspective
- 19.5A: Color
- 19.5B: Paramagnetism
- 19.5C: Complex Formation
- 19.5D: Variable Oxidation States

19.6: Electroneutrality Principle
19.7: Coordination Numbers and Geometries
- 19.7A: The Kepert Model
- 19.7B: Coordination Numbers in the Solid State
- 19.7C: Coordination Number 2
- 19.7D: Coordination Number 3
- 19.7E: Coordination Number 4
- 19.7F: Coordination Number 5
- 19.7G: Coordination Number 6
- 19.7H: Coordination Number 7
- 19.7I: Coordination Number 8
- 19.7J: Coordination Number 9
- 19.7K: Coordination Numbers of 10 and Above

19.8: Isomerism in d-block Metal Complexes
- 19.8A: Structural Isomerism - Ionization Isomers
- 19.8B: Structural Isomerism - Hydration Isomers
- 19.8C: Structural Isomerism - Coordination Isomerism
- 19.8D: Structural Isomerism - Linkage Isomerism
- 19.8E: Stereoisomerism - Diastereomers
- 19.8F: Stereoisomerism - Enantiomers

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19.1: Topic Overview

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SECTION OVERVIEW

19.2: Ground State Electronic Configurations

Topic hierarchy

19.2A: d-block Metals Versus Transition Elements

19.2B: Electronic Configurations

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19.2A: d-block Metals Versus Transition Elements

The elements of the second and third rows of the Periodic Table show gradual changes in properties across the table from left to right as expected. Electrons in the outer shells of the atoms of these elements have little shielding effects resulting in an increase in effective nuclear charge due to the addition of protons in the nucleus. Consequently, the effects on atomic properties are: smaller atomic radius, increased first ionization energy, enhanced electronegativity and more nonmetallic character. This trend continues until one reaches calcium (Z=20). There is an abrupt break at this point. The next ten elements called the first transition series are remarkably similar in their physical and chemical properties. This general similarity in properties has been explained in terms of their relatively small difference in effective nuclear charge over the series. This occurs because each additional electron enters the penultimate 3d shell providing an effective shield between the nucleus and the outer 4s shell.
Thus, the transition elements can be defined as those in which the d electron shells are being filled and so we generally ignore Sc and Zn where Sc(III) is d^0 and Zn(II) is d^{10}.

Summary of Physical Properties

It is useful, at the beginning, to identify the physical and chemical properties of transition elements which differ from main group elements (s-block) such as Calcium.

Transition elements:

- have large charge/radius ratio;
- are hard and have high densities;
- have high melting and boiling points;
- form compounds which are often paramagnetic;
- show variable oxidation states;
- form coloured ions and compounds;
- form compounds with profound catalytic activity;
- form stable complexes.

The following table summarises some of the physical properties of transition elements:

Element	Group	density /g cm^{-3}	m. p. / °C	b.p. / °C	radius / pm	free atom configuration	ionization energy / kJ mol^{-1}	Uses
Sc	3	2.99	1541	2831	164	[Ar] $3d^1 4s^2$	631	
Ti	4	4.50	1660	3287	147	[Ar]$3d^2 4s^2$	658	-engines/aircraft industry-density is 60% of iron
V	5	5.96	1890	3380	135	[Ar]$3d^3 4s^2$	650	-stainless steel, 19% Cr, 9% Ni the rest Fe
Cr	6	7.20	1857	2670	129	[Ar]$3d^5 4s^1$	653	-alloys eg with C steel, the most significant use
Mn	7	7.20	1244	1962	137	[Ar]$3d^5 4s^2$	717	-alloys eg with Cu
Fe	8	7.86	1535	2750	126	[Ar]$3d^6 4s^2$	759	-alloys eg with C steel, the most significant use
Co	9	8.90	1495	2870	125	[Ar]$3d^7 4s^2$	758	-alloys eg with Cr and W for hardened drill bits
Ni	10	8.90	1455	2730	125	[Ar]$3d^8 4s^2$	737	-alloys Fe/Ni armour plating, resists corrosion
Cu	11	8.92	1083	2567	128	[Ar]$3d^{10} 4s^1$	746	-high electrical conductivity (2nd to Ag), wiring
Zn	12	7.14	420	907	137	[Ar]$3d^{10} 4s^2$	906	

Densities and metallic radii

The transition elements are much denser than the s-block elements and show a gradual increase in density from scandium to copper. This trend in density can be explained by the small and irregular decrease in metallic radii coupled with the relative increase in atomic mass.

Melting and boiling points

The melting points and the molar enthalpies of fusion of the transition metals are both high in comparison to main group elements. This arises from strong metallic bonding in transition metals which occurs due to delocalization of electrons facilitated by the availability of both d and s electrons.

Ionization Energies

In moving across the series of metals from scandium to zinc a small change in the values of the first and second ionization energies is observed. This is due to the build-up of electrons in the immediately underlying d-sub-shells that efficiently shields the 4s electrons from the nucleus and minimizing the increase in effective nuclear charge from element to element. The increases in third and fourth ionization energy values are more rapid. However, the trends in these values show the usual discontinuity half way along the series. The reason is that the five d electrons are all unpaired, in singly occupied orbitals. When the sixth and subsequent electrons enter, the electrons have to share the already occupied orbitals resulting in inter-electron repulsions, which would require less energy to remove an electron. Hence, the third ionization energy curve for the last five elements is identical in shape to the curve for the first five elements, but displaced upwards by about 580 kJ mol^{-1}.

Electronic Configurations

The electronic configuration of the atoms of the first row transition elements are basically the same. It can be seen in the Table above that there is a gradual filling of the 3d orbitals across the series starting from scandium. This filling is, however, not regular, since at chromium and copper the population of 3d orbitals increase by the acquisition of an electron from the 4s shell. This illustrates an important generalization about orbital energies of the first row transition series. At chromium, both the 3d and 4s orbitals are occupied, but neither is completely filled in preference to the other. This suggests that the energies of the 3d and 4s orbitals are relatively close for atoms in this row.

In the case of copper, the 3d level is full, but only one electron occupies the 4s orbital. This suggests that in copper the 3d orbital energy is lower than the 4s orbital. Thus the 3d orbital energy has passed from higher to lower as we move across the period from potassium to zinc. However, the whole question of preference of an atom to adopt a particular electronic configuration is not determined by orbital energy alone. In chromium it can be shown that the 4s orbital energy is still below the 3d which suggests a configuration [Ar] $3d^4 4s^2$. However due to the effect of electronic repulsion between the outer electrons the actual configuration becomes [Ar]$3d^5 4s^1$ where all the electrons in the outer orbitals are unpaired. It should be remembered that the factors that determine electronic configuration in this period are indeed delicately balanced.

Redox Couple	E°/V
Mn^{2+}(aq.)/Mn(s)	-1.18
H^+(aq.)/H_2(g)	0.00

This shows that elemental Mn is a stronger reductant than dihydrogen and hence should be able to displace hydrogen gas from 1 mol dm^{-3} hydrochloric acid.

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19.2B: Electronic Configurations

To be able to use Crystal Field Theory (CFT) successfully, it is essential that you can determine the **electronic configuration** of the central metal ion in any complex.
This requires being able to recognise all the entities making up the complex and knowing whether the ligands are neutral or anionic, so that you can determine the **oxidation number** of the metal ion.



In many cases the oxidation number for first row transition metal ions will be either (II) or (III), but in any case you may find it easier to start with the M(II) from which you can easily add or subtract electrons to get the final electronic configuration.

A simple procedure exists for the M(II) case.

First write out all the first row transition metals with their symbols and atomic numbers:

22	23	24	25	26	27	28	29
Ti	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**

To see the number of electrons in the 3d orbitals then cross off the first 2, hence:

2	3	4	5	6	7	8	9

So, the electronic configuration of **Ni(II) is d^8** and the electronic configuration of **Mn(II) is d^5**.

What is the electronic configuration of Fe(III)?
Well, using the above scheme, Fe(II) would be d^6, by subtracting a further electron to make the ion more positive, the configuration of **Fe(III) will be d^5**.

This simple procedure works fine for first row transition metal ions, but sorry it is no good for 2nd or 3rd row elements!

Note: For all final Chemistry examinations, a Periodic Table is provided in the inside back cover of the examination booklets. A Periodic Table may NOT necessarily be provided for course tests.

Oxidation Numbers and their Relative Stabilities

The IUPAC definition of the oxidation number in a coordination compound is:

> *the charge a central atom in a coordination entity would bear if all the ligands were removed along with the electron pairs that were shared with the central atom. It is represented by a Roman numeral.*

The transition metals show a wide range of oxidation numbers. The reason for this is the closeness of 3d and 4s energy states as discussed above. The Table below summarizes known oxidation numbers of the first row transition elements. The most prevalent oxidation numbers are shown in **bold** and those in blue are likely to be met in this course.

Known Oxidation Numbers of First Row Transition Elements*

21	22	23	24	25	26	27	28	29	30
Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
	I	I	I	I	I	I	I	**I**	
	II	**II**	**II**	**II**	**II**	**II**	**II**	**II**	**II**
III	**III**	**III**	**III**	**III**	**III**	**III**	III	III	
	IV	**IV**	IV	**IV**	IV	IV	IV		
		V	V	V	V	V			
			VI	**VI**	VI				
				VII					

* The oxidation number zero usually assigned to the elemental state has been omitted from the Table. The elements Cr to Co form several metal carbonyl compounds where the metals are considered to have an oxidation number of zero.

A number of important conclusions can be drawn from this Table.
1. There is an increase in the number of oxidation numbers from Sc to Mn. All seven oxidation numbers are exhibited by Mn. The oxidation number of VII represents the formal loss of all seven electrons from 3d and 4s orbitals. In fact all of the elements in the series can utilize all the electrons in their 3d and 4s orbitals.
2. There is a decrease in the number of oxidation states from Mn to Zn.
This is because the pairing of d-electrons occurs after Mn (Hund's rule) which in turn decreases the number of available unpaired electrons and hence, the number of oxidation states.
3. The stability of higher oxidation states decreases in moving from Sc to Zn. Mn(VII) and Fe(VI) are powerful oxidizing agents and the higher oxidation states of Co, Ni and Zn are unknown.
4. The relative stability of the +2 state with respect to higher oxidation states, particularly the +3 state increases in moving from left to right. This is justifiable since it will be increasingly difficult to remove the third electron from the d orbitals.
5. There is a tendency of intermediate oxidation states to disproportionate. For example, Mn(VI) → Mn(IV) + Mn(VII)
Cu(I) → Cu(0) + Cu(II).

6. The lower oxidation numbers are usually found in ionic compounds and higher oxidation numbers tend to be involved in covalent compounds.

The relative stability of oxidation numbers is an extremely important topic in transition metal chemistry and is usually discussed in terms of the standard reduction potential (E°) values. Thermodynamically E° values are equated to ΔG° values by the relationship: $\Delta G^\circ = -nFE^\circ$ where n = number of electrons involved and F = Faraday of electricity. Hence, the E° values indicate the possibility of spontaneous change from one oxidation state to the other. This value however, does not give any information about the reaction rate. Predictions regarding the stability of a particular oxidation state of an element can be made from the Tables of Redox values found in any standard text book or online.

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19.3: Physical Properties

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19.4: The Reactivity of the Metals

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SECTION OVERVIEW

19.5: Characteristic Properties - A General Perspective

Topic hierarchy

19.5A: Color

19.5B: Paramagnetism

19.5C: Complex Formation

19.5D: Variable Oxidation States

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19.5A: Color

Introduction to the colour and magnetism of 1st row transition metal complexes

Before beginning a more detailed examination of the spectroscopy and magnetism of transition meal complexes, it is worth while reviewing how far a simple CFT approach will take us.

When electromagnetic radiation is absorbed by atoms or molecules it promotes them to an excited state. Microwave and infrared radiation correspond to lower energy quanta and so initiate rotational and vibrational excitation. Visible and UV light have much higher frequencies and can cause excitations characterstic of electronic excitation: the promotion of an electron from one orbital to another. We expect therefore that molecules will absorb light when the energy corresponds to the energy differences between occupied and unoccupied orbitals. For transition metal ions, the simplest case is Ti(III), solutions of which appear violet.

Absorption of light of frequency ~20,000 cm^{-1} excites the electron from the t2g subset to the eg subset. This is described as a $e_g \leftarrow t_{2g}$ transition.
Absorption of green light, i.e. transmission of blue and red, gives a purple solution
ν ~20,000 cm^{-1}
λ_{max} ~ 500 nm
$E = h\nu = hc/\lambda$
Δ ~ 240 kJ mol^{-1}

Rough guide to absorbance and colour

Wavelength Absorbed (nm)	Frequency (cm^{-1})	Colour of Light Absorbed	Colour of Complex
410	24,400	violet	lemon-yellow
430	23,300	indigo	yellow
480	20,800	blue	orange
500	20,000	blue-green	red
530	18,900	green	purple
560	17,900	lemon-yellow	violet
580	17,200	yellow	indigo
610	16,400	orange	blue
680	14,700	red	blue-green

In spectroscopy it is usual to measure either the amount of light that is absorbed or transmitted through the sample. For UV/Vis, absorbance is given by the Beer-Lambert expression:

$A = \varepsilon c l$

where A is the Absorbance
ε is the molar absorbance (extinction coefficient)

c is the concentration
and l is the path length of the cell

The most common (and cheapest) sample cells have a 1 cm path length and since A is unitless then we can see that the units of ε are mol^{-1} l cm^{-1}. To move this to an acceptable SI set of units requires converting ε to units of m^2 mol^{-1} and this involves a factor of 1/10.

Thus an ε of 5 mol^{-1} l cm^{-1} is equivalent to ε of 0.5 m^2 mol^{-1}.

Given that the separation between the t_{2g} and e_g levels is Δ then whether there is 1 d electron or several d electrons the simple Crystal Field Theory model would suggest that there is only 1 energy gap hence all spectra should consist of 1 peak. That this is not found in practise means that the theory is not sophisticated enough. What is required is an extension of the theory that allows for multi-electron systems where the energy levels are modified to include electron-electron interactions. This can be achieved by looking at the various quantum numbers for each of the electrons involved and using a system called the Russell-Saunders coupling scheme to describe an electronic state that can adequately describe the energy levels available to a group of electrons that includes these interactions.

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19.5B: Paramagnetism

Magnetism

In CHEM1902 (C10K) we introduced the formula used to relate the magnetic moment to the number of unpaired spins in a transition metal complex.

$\mu_{s.o.} = \sqrt{\{4S(S+1)\}}$ B.M.

During the laboratory session you will carry out a measurement of the magnetic susceptibility which is a measure of the force exerted by the magnetic field on a unit mass of the sample under investigation. This is related to the number of unpaired electrons per unit weight and hence per mole and in the simplest picture we consider that this is solely dependent on the presence of unpaired electrons.

For a Ti(III) complex with 1 unpaired electron this corresponds to:

$\mu_{s.o.} = 2 \sqrt{(1/2\ (1/2 + 1))}$ B.M
$\mu_{s.o.} = \sqrt{(3)}$ B.M.
$\mu_{s.o.} = 1.73$ Bohr Magneton

We will see later that while the spin-only approximation works in many cases, for a more complete analysis it is necessary to consider the contribution made by the orbital motion of the electron as well.

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19.5C: Complex Formation

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19.5D: Variable Oxidation States

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19.6: Electroneutrality Principle

Pauling's principle of electroneutrality states that each atom in a stable substance has a charge close to zero. It was formulated by Linus Pauling in 1948 and later revised. The principle has been used to predict which of a set of molecular resonance structures would be the most significant, to explain the stability of inorganic complexes and to explain the existence of π-bonding in compounds and polyatomic anions containing silicon, phosphorus or sulfur bonded to oxygen; it is still invoked in the context of coordination complexes. However, modern computational techniques indicate many stable compounds have a greater charge distribution than the principle predicts (they contain bonds with greater ionic character).

Contributor

- Wikipedia

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SECTION OVERVIEW

19.7: Coordination Numbers and Geometries

Topic hierarchy

19.7A: The Kepert Model

19.7B: Coordination Numbers in the Solid State

19.7C: Coordination Number 2

19.7D: Coordination Number 3

19.7E: Coordination Number 4

19.7F: Coordination Number 5

19.7G: Coordination Number 6

19.7H: Coordination Number 7

19.7I: Coordination Number 8

19.7J: Coordination Number 9

19.7K: Coordination Numbers of 10 and Above

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19.7A: The Kepert Model

The **Kepert model** is a modification of VSEPR theory used to predict the 3-dimensional structures of transitional metal complexes. In the Kepert model, the ligands attached to the metal are considered to repel each other the same way that point charges repel each other in VSEPR theory. Unlike VSEPR theory, the Kepert model does not account for non-bonding electrons. Therefore, the geometry of the coordination complex is independent of the electronic configuration of the metal center. Thus $[ML_n]^{m+}$ has the same coordination geometry as $[ML_n]^{m-}$. The Kepert model cannot explain the formation of square planar complexes or distorted structures.

The Kepert model predicts the following geometries for coordination numbers of 2 through 6:

2. Linear
3. Trigonal planar
4. Tetrahedral
5. Trigonal bipyramidal or Square pyramidal
6. Octahedral

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19.7B: Coordination Numbers in the Solid State

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19.7C: Coordination Number 2

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19.7K: Coordination Numbers of 10 and Above

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SECTION OVERVIEW

19.8: Isomerism in d-block Metal Complexes

There are several types of this isomerism frequently encountered in coordination chemistry and the following represents some of them. Isomers that contain the same number of atoms of each kind but differ in which atoms are bonded to one another are called structural isomers, which differ in structure or bond type. For inorganic complexes, there are three types of structural isomers: *ionization*, *coordination*, and *linkage* and two types of stereoisomers: *geometric and optical*.

Topic hierarchy

19.8A: Structural Isomerism - Ionization Isomers

19.8B: Structural Isomerism - Hydration Isomers

19.8C: Structural Isomerism - Coordination Isomerism

19.8D: Structural Isomerism - Linkage Isomerism

19.8E: Stereoisomerism - Diastereomers

19.8F: Stereoisomerism - Enantiomers

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19.8A: Structural Isomerism - Ionization Isomers

Coordination isomerism is a form of structural isomerism in which the composition of the complex ion varies. In a coordination isomer the total ratio of ligand to metal remains the same, but the ligands attached to a specific metal ion change. Ionization isomers can be thought of as occurring because of the formation of different ions in solution.

Introduction

Ionization isomers are identical except for a ligand has exchanged places with an anion or neutral molecule that was originally outside the coordination complex. The central ion and the other ligands are identical. For example, an octahedral isomer will have five ligands that are identical, but the sixth will differ. The non-matching ligand in one compound will be outside of the coordination sphere of the other compound. Because the anion or molecule outside the coordination sphere is different, the chemical properties of these isomers is different.

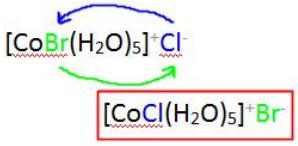


Figure 19.8A.1: Two Ionization isomers. The two isomers differ only which ligands are actually bound to the center metal. These two isomers are called pentaaqua**bromo**cobaltate(II) **chloride** and pentaaqua**chloro**cobaltate(II) **bromide**.

The difference between the ionization isomers can be viewed within the context of the ions generated when each are dissolved in solution.

For example, when pentaaquabromocobaltate(II)chloride is dissolved in water, Cl^- ions are generated:

$$CoBr(H_2O)_5Cl(s) \rightarrow CoBr(H_2O)_5^+(aq) + Cl^+(aq)$$

whereas when pentaaquachlorocobaltate(II)bromide is dissolved, Br^- ions are generated:

$$CoCl(H_2O)_5Br(s) \rightarrow CoCl(H_2O)_5^+(aq) + Br^+(aq).$$

Note

If one dissolved $[PtBr(NH_3)_3]NO_2$ and $[Pt(NO_2)(NH_3)_3]Br$ into solution, then two different set of ions will be general.

- Dissolving $[Pt(NO_2)(NH_3)_3]Br$ in aqueous solution would have the following reaction

$$[PtBr(NH_3)_3]NO_2(s) \rightarrow [PtBr(NH_3)_3]^+(aq) + NO_2^-(aq) \tag{19.8A.1}$$

- Dissolving of $[Pt(NO_2)(NH_3)_3]Br$ in aqueous solution would be

$$[Pt(NO_2)(NH_3)_3]Br(s) \rightarrow [Pt(NO_2)(NH_3)_3]^+(aq) + Br^-(aq) \tag{19.8A.2}$$

Notice that these two ionization isomers differ in that one ion is directly attached to the central metal, but the other is not.

Equations 19.8A.1 and 19.8A.2 are valid under the assumption that the platinum-ligand bonds of the complexes are stable (i.e., not labile). Otherwise, they may break and other ligands (e.g., water) may bind.

Example 19.8A.1

Are $[Cr(NH_3)_5(OSO_3)]Br$ and $[Cr(NH_3)_5Br]SO_4$ coordination isomers?

Solution

First, we need confirm that each compound has the same number of atoms of the respective elements (this requires viewing both cations and anions of each compound).

Element	number of atoms in $[Cr(NH_3)_5(OSO_3)]Br$	number of atoms in $[Cr(NH_3)_5Br]SO_4$
Cr	1	1
N	5	5
H	15	15
O	4	4
S	1	1
Br	1	1

Now, let's look at what these two compounds look like (Figure 19.8A.2). The sulfate group is a ligand with a dative bond to the chromium atom and the bromide counter ion ($[Cr(NH_3)_5(OSO_3)]Br$). For $[Cr(NH_3)_5Br]SO_4$, this is the the reverse.

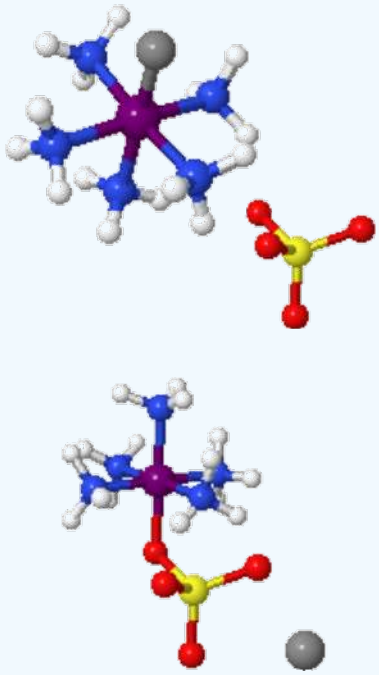


Figure 19.8A.2: $[Cr(NH_3)_5(OSO_3)]Br$ (left) and $[Cr(NH_3)_5Br]SO_4$ (right) are coordination isomers.

Yes, $[Cr(NH_3)_5(OSO_3)]Br$ and $[Cr(NH_3)_5Br]SO_4$ are coordination isomers.

? Exercise 19.8A.1

Are $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$ ionization isomers?

Solution

In the first isomer, SO_4 is attached to the Cobalt and is part of the complex ion (the cation), with Br as the anion. In the second isomer, Br is attached to the cobalt as part of the complex and SO_4 is acting as the anion.

A hydrate isomer is a specific kind of ionization isomer where a water molecule is one of the molecules that exchanges places.

Solvate or Hydrate Isomerization: A Special kind of Ionization Isomer

A very similar type of isomerism results from replacement of a coordinated group by a solvent molecule (*Solvate Isomerism*). In the case of water, this is called *Hydrate isomerism*. The best known example of this occurs for chromium chloride "$CrCl_3.6H_2O$" which may contain 4, 5, or 6 coordinated water molecules.

- $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$: bright-green colored
- $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$: grey-green colored
- $[Cr(H_2O)_6]Cl_3$: violet colored

These isomers have very different chemical properties and on reaction with $AgNO_3$ to test for Cl^- ions, would find 1, 2, and 3 Cl^- ions in solution respectively.

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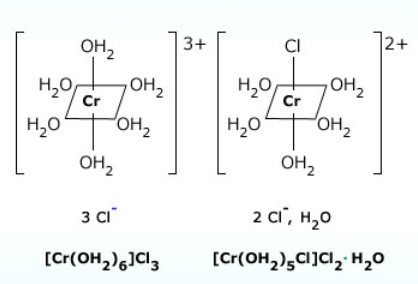
19.8B: Structural Isomerism - Hydration Isomers

A very similar type of isomerism results from replacement of a coordinated group by a solvent molecule (*Solvate Isomerism*), which in the case of water is called *Hydrate Isomerism*. The best known example of this occurs for chromium chloride ($CrCl_3 \cdot 6H_2O$) which may contain 4, 5, or 6 coordinated water molecules (assuming a coordination number of 6). The dot here is used essentially as an expression of ignorance to indicate that, though the parts of the molecule separated by the dot are bonded to one another in some fashion, the exact structural details of that interaction are not fully expressed in the resulting formula. Using Alfred Werner's coordination theory that indicates that several of the water molecules are actually bonded directly (via coordinate covalent bonds) to the central chromium ion. In fact, there are several possible compounds that use the brackets to signify bonding in the complex and the the dots to signify "water molecules that are not bound to the central metal, but are part of the lattice:

- $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$: bright-green colored
- $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$: grey-green colored
- $[Cr(H_2O)_6]Cl_3$: violet colored

These isomers have very different chemical properties and on reaction with $AgNO_3$ to test for Cl^- ions, would find 1, 2, and 3 Cl^- ions in solution, respectively.

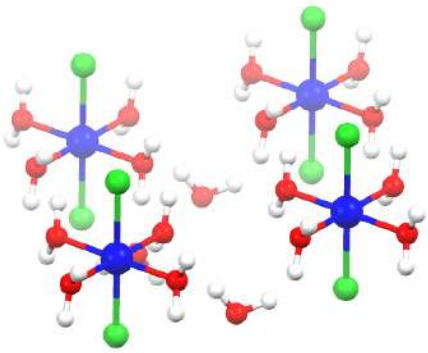
Upon crystallization from water, many compounds incorporate water molecules in their crystalline frameworks. These "waters of crystallization" refers to water that is found in the crystalline framework of a metal complex or a salt, which is **not directly bonded** to the metal cation. In the first two hydrate isomers, there are water molecules that are artifacts of the crystallization and occur inside crystals. These water of crystallization is the total weight of water in a substance at a given temperature and is mostly present in a definite (stoichiometric) ratio.



The $[Cr(H_2O)_6]Cl_3$ hydrate isomer (left) is violet colored and the $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ hydrate isomer is green-grey colored.

What are "Waters of Crystallization"?

A compound with associated water of crystallization is known as a hydrate. The structure of hydrates can be quite elaborate, because of the existence of hydrogen bonds that define polymeric structures. For example, consider the aquo complex $NiCl_2 \cdot 6H_2O$ that consists of separated *trans*-[$NiCl_2(H_2O)_4$] molecules linked more weakly to adjacent water molecules. Only four of the six water molecules in the formula are bound to the nickel (II) cation, and the remaining two are waters of crystallization as the crystal structure resolves.



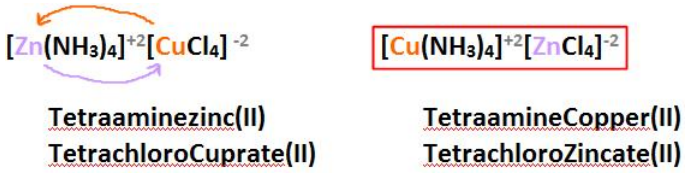
Structure of $NiCl_2 \cdot 6H_2O$ salt with chlorine atoms (green), water molecules (red), and Ni metals (blue) indicated. (CC BY-SA 4.0; Smokefoot).

Water is particularly common solvent to be found in crystals because it is small and polar. But *all* solvents can be found in some host crystals. Water is noteworthy because it is reactive, whereas other solvents such as benzene are considered to be chemically innocuous.

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19.8C: Structural Isomerism - Coordination Isomerism

Coordination isomerism occurs in compounds containing complex anionic and cationic parts and can be viewed as the interchange of one or more ligands between the cationic complex ion and the anionic complex ion. For example, $[Co(NH_3)_6][Cr(CN)_6]$ is a coordination isomer with $[Cr(NH_3)_6][Co(CN)_6]$. Alternatively, coordination isomers may be formed by switching the metals between the two complex ions like $[Zn(NH_3)_4][CuCl_4]$ and $[Cu(NH_3)_4][ZnCl_4]$.



? Exercise 19.8C.1

Are $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$ coordination isomers?

Solution

Here, both the cation and anion are complex ions. In the first isomer, NH_3 is attached to the copper and the Cl^- are attached to the platinum. In the second isomer, they have swapped.

Yes, they are coordination isomers.

? Exercise 19.8C.2

What is one coordination isomer of $[Co(NH_3)_6]$ $[Cr(C_2O_4)_3]$?

Solution

Coordination isomers involve swapping the species from the inner coordination sphere to one metal (e.g, cation) to inner coordination sphere of a different metal (e.g., the anion) in the compound. One isomer is completely swapping the ligand sphere, e.g, $[Co(C_2O_4)_3]$ $[Cr(NH_3)_6]$.

Alternative coordination isomers are $[Co(NH_3)_4(C_2O_4)]$ $[Cr(NH_3)_2(C_2O_4)_2]$ and $[Co(NH_3)_2(C_2O_4)_2]$ $[Cr(NH_3)_4(C_2O_4)]$.

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19.8D: Structural Isomerism - Linkage Isomerism

Linkage isomerism occurs with *ambidentate* ligands that are capable of coordinating in more than one way. The best known cases involve the monodentate ligands: SCN^-/NCS^- and NO_2^-/ONO^-. The only difference is what **atoms the molecular ligands bind to the central ion**. The ligand(s) must have more than one donor atom, but bind to ion in only one place. For example, the (NO_2^-) ion is a ligand can bind to the central atom through the nitrogen or the oxygen atom, but cannot bind to the central atom with both oxygen and nitrogen at once, in which case it would be called a *polydentate* rather than an *ambidentate* ligand.

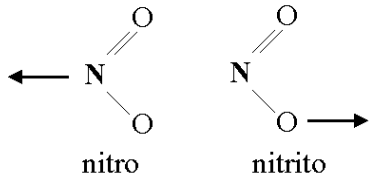
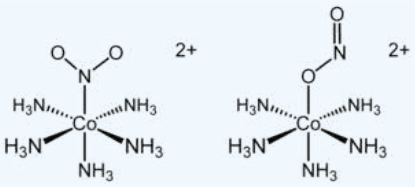


Figure 19.8D.1: Linkage Isomerism in the NO_2 ligand. This occurs when a particular ligand is capable of coordinating to a metal in two different and distinct ways. from Angel C. de Dios.

The names used to specify the changed ligands are changed as well. For example, the (NO_2^-) ion is called *nitro* when it binds with the N atom and is called *nitrito* when it binds with the O atom.

Example 19.8D.1: Nitro- vs. Nitrito- Linkage Isomers

The cationic cobalt complex $[Co(NH_3)_5(NO_2)]Cl_2$ exists in two separable linkage isomers of the complex ion: $(NH_3)_5(NO_2)]^{2+}$.



(left) The nitro isomer (Co-NO_2) and (right) the nitrito isomer (Co-ONO)

When donation is from nitrogen to a metal center, the complex is known as a *nitro*- complex and when donation is from one oxygen to a metal center, the complex is known as a *nitrito*- complex. An alternative formula structure to emphasize the different coordinate covalent bond for the two isomers

- $[Co(ONO)(NH_3)_5]Cl$: the *nitrito* isomer -O attached
- $[Co(NO_2)(NH_3)_5]Cl$: the *nitro* isomer - N attached.

The formula of the complex is unchanged, but the properties of the complex may differ.

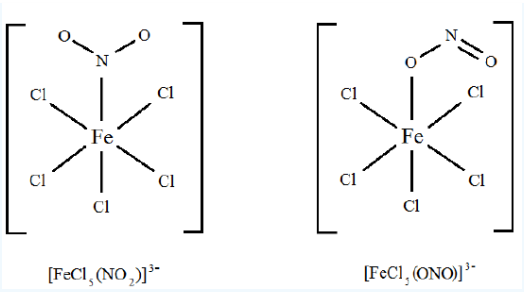
Another example of an ambidentate ligans is thiocyanate, SCN^-, which can attach at either the sulfur atom or the nitrogen atom. Such compounds give rise to linkage isomerism. Polyfunctional ligands can bond to a metal center through different ligand atoms to form various isomers. Other ligands that give rise to linkage isomers include selenocyanate, $SeCN^-$ – isoselenocyanate, $NCSe^-$ and sulfite, SO_3^{2-}.

Exercise 19.8D.1

Are $[FeCl_5(NO_2)]^{3-}$ and $[FeCl_5(ONO)]^{3-}$ linkage isomers?

Solution

Here, the difference is in how the ligand bonds to the metal. In the first isomer, the ligand bonds to the metal through an electron pair on the nitrogen. In the second isomer, the ligand bonds to the metal through an electron pair on one of the oxygen atoms. It's easier to see it:



Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

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19.8E: Stereoisomerism - Diastereomers

Isomers are classified into 1) stereoisomers which have different spatial orientations, and 2) constitutional isomers where atoms are connected in different orders. There are two types of stereoisomers: enantiomers and diastereomers.

Enantiomers

One of the stereoisomeric types is enantiomers where two compounds look like mirror images, but those are not superimposable. It is a kind of mirror-image stereoisomers, but the image and mirror images are not superimposable like left and right hand. For this reason, such structures are also called chiral molecules. On the other hand, there are superimposable structures which are called achiral molecules. As shown in Figure 2, an enantiomeric compound pair is non-superimposable and therefore two are not identical.

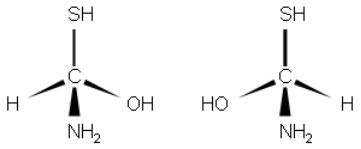


Figure 2: An example of enantiomers (faculty.clintoncc.suny.edu)

Like the figure above, chiral molecules have a centric atom called a stereocenter or an asymmetric atom in their structures. For instance, the example in Figure 2 has an asymmetric carbon in its center and it is connected to other substituent groups. Due to the symmetry of enantiomers, an enantiomer pair has most chemical and physical properties such as melting and boiling points, densities, and energy contents.

Diastereomers

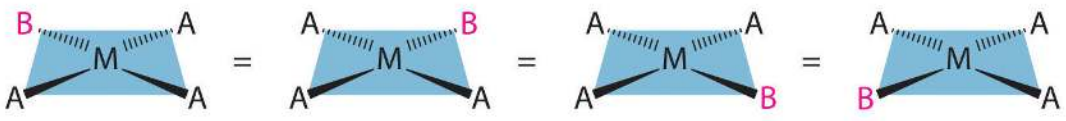
Diastereomers are non-enantiomeric where two compounds of the same stereoisomers do not look like mirror images. Figure 2 shows an example of diastereomers. Unlike enantiomeric compounds, two compounds of a diastereomer pair have different chemical and physical properties.

The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. Recall that in many cases more than one structure is possible for organic compounds with the same molecular formula; examples discussed previously include n-butane versus isobutane and cis-2-butene versus trans-2-butene. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique.

Planar Isomers

Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called geometrical isomers. They are most important for square planar and octahedral complexes.

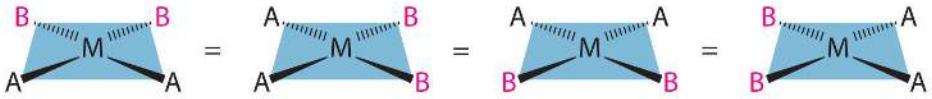
Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar MA_3B complex; hence only a single geometrical isomer is possible in this case (and in the analogous MAB_3 case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:



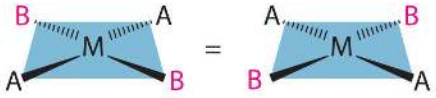
MA_3B square planar complex

https://chem.libretexts.org/@go/page/2553

For an MA_2B_2 complex, there are two possible isomers: either the A ligands can be adjacent to one another (cis), in which case the B ligands must also be cis, or the A ligands can be across from one another (trans), in which case the B ligands must also be trans. Even though it is possible to draw the cis isomer in four different ways and the trans isomer in two different ways, all members of each set are chemically equivalent:

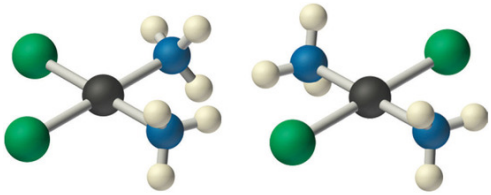


MA_2B_2 square planar complex, *cis* isomer



MA_2B_2 square planar complex, *trans* isomer

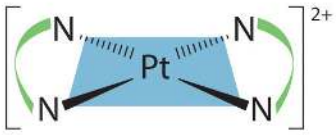
Because there is no way to convert the cis structure to the trans by rotating or flipping the molecule in space, they are fundamentally different arrangements of atoms in space. Probably the best-known examples of cis and trans isomers of an MA_2B_2 square planar complex are cis-$Pt(NH_3)_2Cl_2$, also known as cisplatin, and trans-$Pt(NH_3)_2Cl_2$, which is actually toxic rather than therapeutic.



cis-$Pt(NH_3)_2Cl_2$ *trans*-$Pt(NH_3)_2Cl_2$

The anticancer drug cisplatin and its inactive trans isomer. Cisplatin is especially effective against tumors of the reproductive organs, which primarily affect individuals in their 20s and were notoriously difficult to cure. For example, after being diagnosed with metastasized testicular cancer in 1991 and given only a 50% chance of survival, Lance Armstrong was cured by treatment with cisplatin.

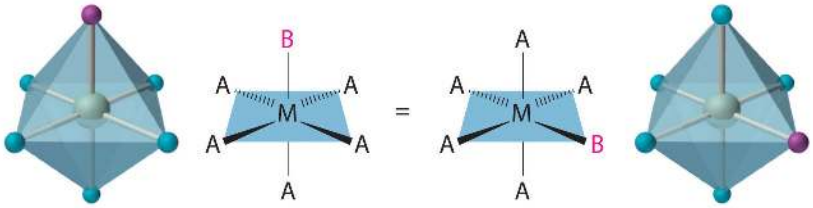
Square planar complexes that contain symmetrical bidentate ligands, such as $[Pt(en)_2]^{2+}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:



$[Pt(en)_2]^{2+}$

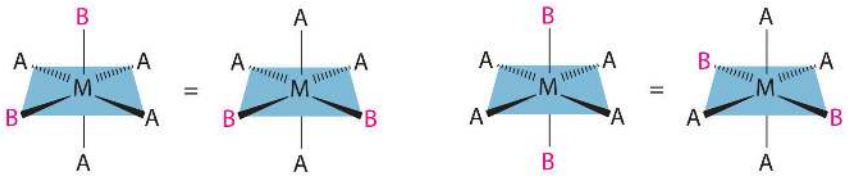
Octahedral Isomers

Octahedral complexes also exhibit cis and trans isomers. Like square planar complexes, only one structure is possible for octahedral complexes in which only one ligand is different from the other five (MA_5B). Even though we usually draw an octahedron in a way that suggests that the four “in-plane” ligands are different from the two “axial” ligands, in fact all six vertices of an octahedron are equivalent. Consequently, no matter how we draw an MA_5B structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an MA_5B structure are as follows:



MA_5B octahedral complex

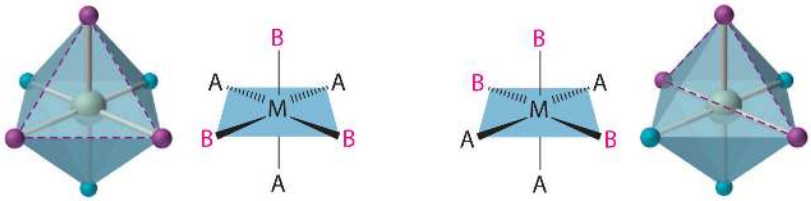
If two ligands in an octahedral complex are different from the other four, giving an MA_4B_2 complex, two isomers are possible. The two B ligands can be cis or trans. Cis- and trans-$[Co(NH_3)_4Cl_2]Cl$ are examples of this type of system:



MA_4B_2 octahedral complex, *cis* isomer

MA_4B_2 octahedral complex, *trans* isomer

Replacing another A ligand by B gives an MA_3B_3 complex for which there are also two possible isomers. In one, the three ligands of each kind occupy opposite triangular faces of the octahedron; this is called the fac isomer (for facial). In the other, the three ligands of each kind lie on what would be the meridian if the complex were viewed as a sphere; this is called the mer isomer (for meridional):



MA_3B_3 octahedral complex, *fac* isomer

MA_3B_3 octahedral complex, *mer* isomer

Example 19.8*E*.1

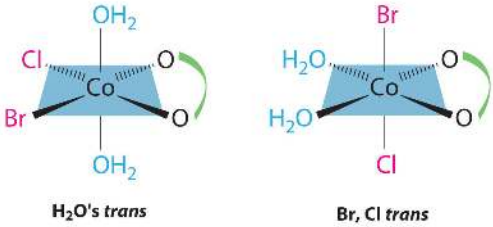
Draw all the possible geometrical isomers for the complex $[Co(H_2O)_2(ox)BrCl]^-$, where ox is $^-O_2CCO_2^-$, which stands for oxalate.

Given: formula of complex

Asked for: structures of geometrical isomers

Solution

This complex contains one bidentate ligand (oxalate), which can occupy only adjacent (cis) positions, and four monodentate ligands, two of which are identical (H_2O). The easiest way to attack the problem is to go through the various combinations of ligands systematically to determine which ligands can be trans. Thus either the water ligands can be trans to one another or the two halide ligands can be trans to one another, giving the two geometrical isomers shown here:

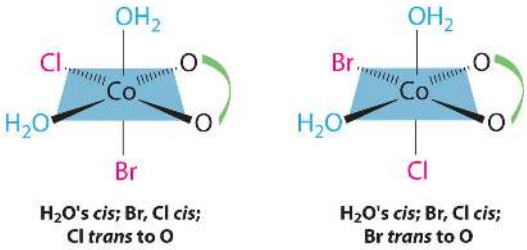


H_2O's *trans*

Br, Cl *trans*

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In addition, two structures are possible in which one of the halides is trans to a water ligand. In the first, the chloride ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens. Exchanging the chloride and bromide ligands gives the other, in which the bromide ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens:

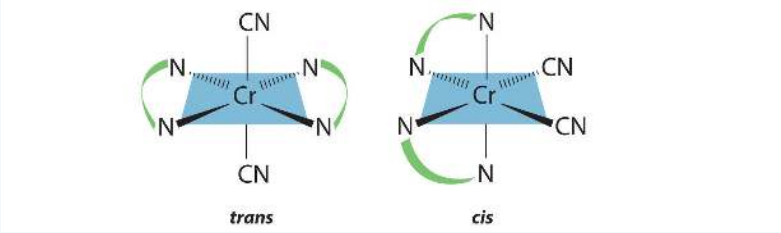


This complex can therefore exist as four different geometrical isomers.

Exercise 19.8E.1

Draw all the possible geometrical isomers for the complex $[Cr(en)_2(CN)_2]^+$.

Answer



Two geometrical isomers are possible: trans and cis.

Summary

Many metal complexes form isomers, which are two or more compounds with the same formula but different arrangements of atoms. Structural isomers differ in which atoms are bonded to one another, while geometrical isomers differ only in the arrangement of ligands around the metal ion. Ligands adjacent to one another are cis, while ligands across from one another are trans.

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19.8F: Stereoisomerism - Enantiomers

Optical activity refers to whether or not a compound has optical isomers. A coordinate compound that is optically active **has** optical isomers and a coordinate compound that is not optically active does **not have** optical isomers. As we will discuss later, optical isomers have the unique property of rotating light. When light is shot through a polarimeter, optical isomers can rotate the light so it comes out in a different direction on the other end. Armed with the knowledge of symmetry and mirror images, optical isomers should not be very difficult. There are two ways optical isomers can be determined: using mirror images or using planes of symmetry.

Optical isomers do not exhibit symmetry and do not have identical mirror images. Let's go through a quick review of symmetry and mirror images. A *mirror image* of an object is that object flipped or the way the object would look in front of a mirror. For example, the mirror image of your left hand would be your right hand. Symmetry on the other hand refers to when an object looks exactly the same when sliced in a certain direction with a plane. For example imagine the shape of a square. No matter in what direction it is sliced, the two resulting images will be the same.

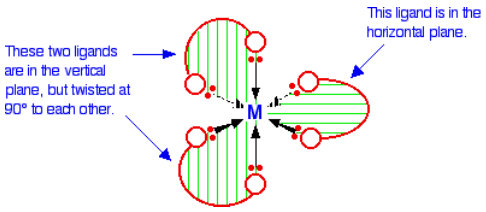
Method 1: The "Mirror Image Method"

The mirror images method uses a mirror image of the molecule to determined whether optical isomers exist or not. If the mirror image **can** be rotated in such a way that it looks identical to the original molecule, then the molecule is said to be superimposable and has no optical isomers. On the other hand, if the mirror image **cannot** be rotated in any way such that it looks identical to the original molecule, then the molecule is said to be non-superimposable and the molecule has optical isomers. Once again, if the mirror image is superimposable, then no optical isomers but if the mirror image is non-superimposable, then optical isomers exist.

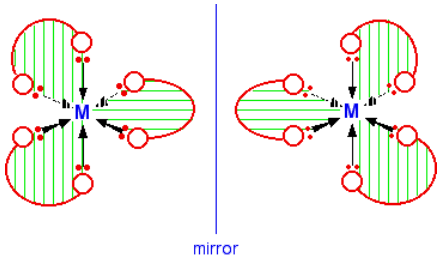
Definition: Non-superimposable

Non-superimposable means the structure cannot be rotated in a way that one can be put on top of another. This means that no matter how the structure is rotated, it cannot be put on top of another with all points matching. An example of this is your hands. Both left and right hands are identical, but they cannot be put on top of each other with all points matching.

The examples you are most likely to need occur in octahedral complexes which contain bidentate ligands - ions like $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ or $[Cr(C_2O_4)_3]^{3-}$. The diagram below shows a simplified view of one of these ions. Essentially, they all have the same shape - all that differs is the nature of the "headphones".



A substance with *no plane of symmetry is going to have optical isomers* - one of which is the mirror image of the other. One of the isomers will rotate the plane of polarization of plane polarised light clockwise; the other rotates it counter-clockwise. In this case, the two isomers are:



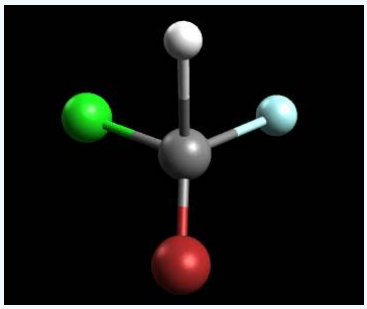
You may be able to see that there is no way of rotating the second isomer in space so that it looks exactly the same as the first one. As long as you draw the isomers carefully, with the second one a true reflection of the first, the two structures will be different.

Method 2: The "Plane of Symmetry Method"

The plane of symmetry method uses symmetry, as it's name indicates, to identify optical isomers. In this method, one tries to see if such a plane exists which when cut through the coordinate compound produces two exact images. In other words, one looks for the existence of a plane of symmetry within the coordinate compound. If a plane of symmetry exists, then no optical isomers exist. On the other hand, if there is no plane of symmetry, the coordinate compound has optical isomers. Furthermore, if a plane of symmetry exists around the central atom, then that molecule is called **achiral** but if a plane of symmetry does not exist around the central molecule, then that molecule has chiral center.

Example $19.8F.1$: CHBrClF

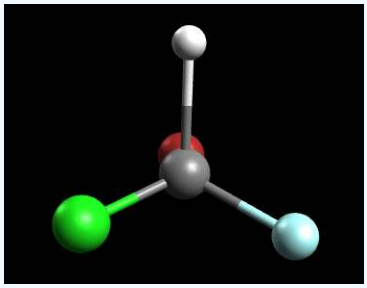
Consider the tetrahedral molecule, CHBrClF (note the color scheme: grey=carbon, white=hydrogen, green=chlorine, blue=fluorine, red=bromine)



Is this molecule optically active? In other words, does this molecule have optical isomers?

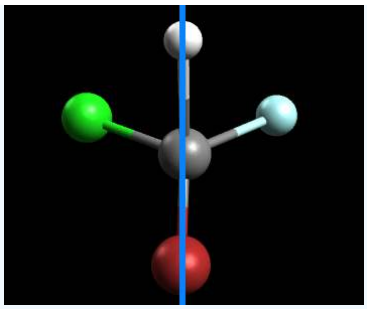
Solution

First take the Mirror-image method. The mirror image of the molecule is:



Note that this mirror image is not superimposable. In other words, the mirror image above cannot be rotated in any such way that it looks identical to the original molecule. Remember, if the mirror image is not superimposable, then optical isomers exist. Thus we know that this molecule has optical isomers.

Let's try approaching this problem using the symmetry method. If we take the original molecule and draw an axis or plane of symmetry down the middle, this is what we get:



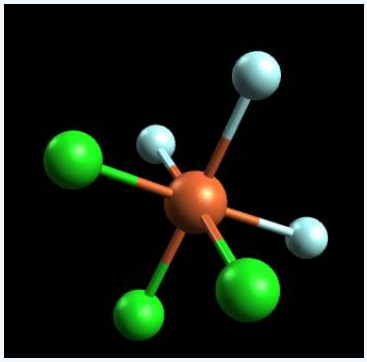
Since the left side is not identical to the right, this molecule does not have a symmetrical center and thus can be called chiral.Additionally, because it does not have a symmetrical center, we can conclude that this molecule has optical isomers. In general, when dealing with a tetrahedral molecule that has 4 different ligands, optical isomers will exist most of the time.

No matter which method you use, the answer will end up being the same.

Optical isomers because they have no plane of symmetry. In the organic case, for tetrahedral complexes, this is fairly easy to recognize the possibility of this by looking for a center atom with **four** different things attached to it. Unfortunately, this is not quite so easy with more complicated geometries!

Example 19.8F.1: $PFeCl_3F_3$

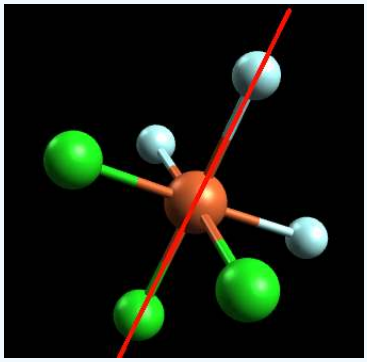
This time we will be analyzing the octahedral compound $FeCl_3F_3$. Is this molecule optically active?



(note the color scheme: orange=iron, blue=fluorine, green=chlorine):

Solution

If we try to attempt this problem using the mirror image method, we notice that the mirror image is essentially identical to the original molecule. In other words, the mirror image can be placed on top of the original molecule and is thus superimposable. Since the mirror image is superimposable, this molecule does not have any optical isomers. Let's attempt this same problem using the symmetry method. If we draw an axis or plane of symmetry, this is what we get:



Since the left side is identical to the right side, this molecule has a symmetrical center and is an achiral molecule. Thus, it has no optical isomers.

What is a Polarimeter?

A polarimeter is a scientific instrument used to measure the angle of rotation caused by passing polarized light through an optically active substance. Some chemical substances are optically active, and polarized (uni-directional) light will rotate either to the left (counter-clockwise) or right (clockwise) when passed through these substances. The amount by which the light is rotated is known as the *angle of rotation*. The angle of rotation is basically known as observed angle.

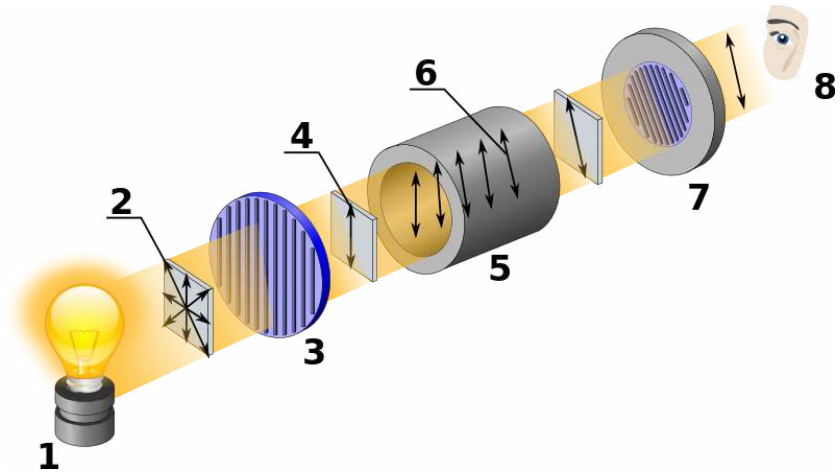


Figure 19.8*F*.1: Schematic of a polarimeter showing the principles behind it's operation. Unpolarized light is passed through a polarizing filter before traveling through a sample. The degree of rotation of polarization is determined by a second, rotatable filter. (CC AS 3.0; Kaidor).

The polarimeter is made up of a polarizer (#3 on Figure 19.8*F*.1) and an analyzer (#7 on Figure 19.8*F*.1). The polarizer allows only those light waves which move in a single plane. This causes the light to become plane polarized. When the analyzer is also placed in a similar position it allows the light waves coming from the polarizer to pass through it. When it is rotated through the right angle no waves can pass through the right angle and the field appears to be dark. If now a glass tube containing an optically active solution is placed between the polarizer and analyzer the light now rotates through the plane of polarization through a certain angle, the analyzer will have to be rotated in same angle.

Nomenclature of Optical Isomers

Various methods have been used to denote the absolute configuration of optical isomers such as R or S, Λ or Δ, or C and A. The IUPAC rules suggest that for general octahedral complexes C/A scheme is convenient to use and that for bis and tris bidentate complexes the absolute configuration be designated Lambda Λ (left-handed) and Delta Δ (right-handed).

Priorities are assigned for mononuclear coordination systems based on the standard sequence rules developed for enantiomeric carbon compounds by Cahn, Ingold and Prelog (CIP rules). These rules use the coordinating atom to arrange the ligands into a priority order such that the highest atomic number gives the highest priority number (smallest CIP number). For example the hypothetical complex [Co Cl Br I NH_3 NO_2 SCN]$^{2-}$ would assign the I- as 1, Br as 2, Cl as 3, SCN as 4, NO_2 as 5 and NH_3 as 6.

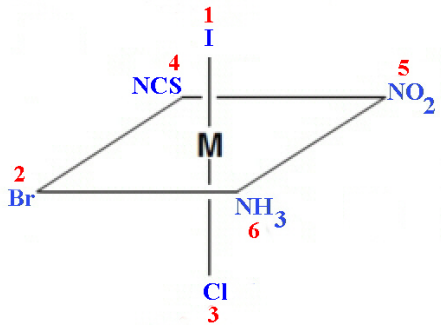
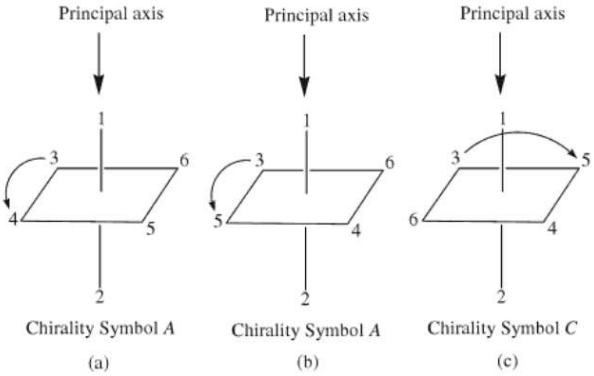


Figure 19.8*F*.2***:*** *Here is one isomer where the I and Cl, and Br and NO_2 were found to be trans- to each other.*

The reference axis for an octahedral center is that axis containing the ligating atom of CIP priority 1 and the trans ligating atom of lowest possible priority (highest numerical value). The atoms in the coordination plane perpendicular to the reference axis are viewed from the ligand having that highest priority (CIP priority 1) and the clockwise and anticlockwise sequences of priority numbers are compared. The structure is assigned the symbol C or A, according to whether the clockwise (C) or anticlockwise (A) sequence is lower at the first point of difference. In the example shown above this would be C.



The two optical isomers of $[Co(en)_3]^{3+}$ have identical chemical properties and just denoting their absolute configuration does NOT give any information regarding the direction in which they rotate plane-polarised light. This can ONLY be determined from measurement and then the isomers are further distinguished by using the prefixes (-) and (+) depending on whether they rotate left or right.

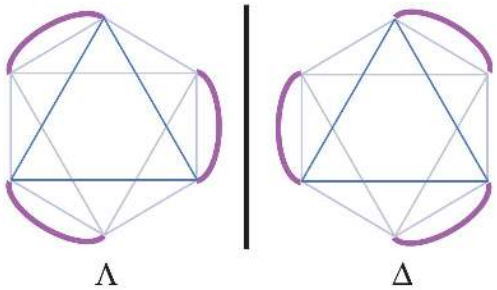


Figure 19.8*F*.3: left-handed Λ isomer (left) and right-handed Δ isomer (right)

To add to the confusion, when measured at the sodium D line (589 nm), the tris(1,2-diaminoethane)M(III) complexes (M= Rh(III) and Co(III)) with **IDENTICAL** absolute configuration, rotate plane polarized light in **OPPOSITE** directions! The left-handed (Λ)-$[Co(en)_3]^{3+}$ isomer gives a rotation to the right and therefore corresponds to the (+) isomer. Since the successful resolution of an entirely inorganic ion (containing no C atoms) (hexol) only a handful of truly inorganic complexes have been isolated as their optical isomers e.g. $(NH_4)_2Pt(S_5)_3.2H_2O$.

For tetrahedral complexes, R and S would be used in a similar method to tetrahedral Carbon species and although it is predicted that tetrahedral complexes with 4 different ligands should be able to give rise to optical isomers, in general they are too labile and can not be isolated.

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)
- Jim Clark (Chemguide.co.uk)

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20.2A: Hybridization Schemes

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20.3B: Crystal Field Stabilization Energy - High- and Low-spin Octahedral Complexes

A consequence of Crystal Field Theory is that the distribution of electrons in the d orbitals may lead to net stabilization (decrease in energy) of some complexes depending on the specific ligand field geometry and metal d-electron configurations. It is a simple matter to calculate this stabilization since all that is needed is the electron configuration and knowledge of the splitting patterns.

Definition: Crystal Field Stabilization Energy

The Crystal Field Stabilization Energy is defined as the energy of the electron configuration in the ligand field minus the energy of the electronic configuration in the isotropic field.

$$CFSE = \Delta E = E_{\text{ligand field}} - E_{\text{isotropic field}} \tag{20.3B.1}$$

The CSFE will depend on multiple factors including:

- Geometry (which changes the d-orbital splitting patterns)
- Number of d-electrons
- Spin Pairing Energy
- Ligand character (via Spectrochemical Series)

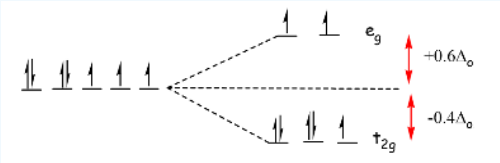
For an octahedral complex, an electron in the more stable t_{2g} subset is treated as contributing $-2/5\Delta_o$ whereas an electron in the higher energy e_g subset contributes to a destabilization of $+3/5\Delta_o$. The final answer is then expressed as a multiple of the crystal field splitting parameter Δ_o. If any electrons are paired within a single orbital, then the term P is used to represent the spin pairing energy.

Example $20.3B.1$: CFSE for a high Spin d^7 complex

What is the Crystal Field Stabilization Energy for a high spin d^7 octahedral complex?

Solution

The splitting pattern and electron configuration for both isotropic and octahedral ligand fields are compared below.



The energy of the isotropic field ($E_{\text{isotropic field}}$) is

$$E_{\text{isotropic field}} = 7 \times 0 + 2P = 2P$$

The energy of the octahedral ligand field $E_{\text{ligand field}}$ is

$$E_{\text{ligand field}} = (5 \times -2/5\Delta_o) + (2 \times 3/5\Delta_o) + 2P = -4/5\Delta_o + 2P$$

So via Equation 20.3B.1, the CFSE is

$$\begin{aligned} CFSE &= E_{\text{ligand field}} - E_{\text{isotropic field}} \\ &= (-4/5\Delta_o + 2P) - 2P \\ &= -4/5\Delta_o \end{aligned}$$

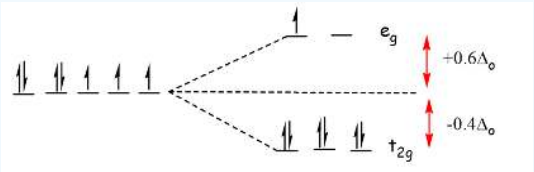
Notice that the Spin pairing Energy falls out in this case (and will when calculating the CFSE of high spin complexes) since the number of paired electrons in the ligand field is the same as that in isotropic field of the free metal ion.

Example $20.3B.2$: CFSE for a Low Spin d^7 complex

What is the Crystal Field Stabilization Energy for a low spin d^7 octahedral complex?

Solution

The splitting pattern and electron configuration for both isotropic and octahedral ligand fields are compared below.



The energy of the isotropic field is the same as calculated for the high spin configuration in Example 1:

$$E_{\text{isotropic field}} = 7 \times 0 + 2P = 2P$$

The energy of the octahedral ligand\) field $E_{\text{ligand field}}$ is

$$\begin{aligned} E_{\text{ligand field}} &= (6 \times -2/5\Delta_o) + (1 \times 3/5\Delta_o) + 3P \\ &= -9/5\Delta_o + 3P \end{aligned}$$

So via Equation 20.3B.1, the CFSE is

$$\begin{aligned} CFSE &= E_{\text{ligand field}} - E_{\text{isotropic field}} \\ &= (-9/5\Delta_o + 3P) - 2P \\ &= -9/5\Delta_o + P \end{aligned}$$

Adding in the pairing energy since it will require extra energy to pair up one extra group of electrons. This appears more a more stable configuration than the high spin d^7 configuration in Example $20.3B.1$, but we have then to take into consideration the Pairing energy P to know definitely, which varies between $200 - 400\ kJ\ mol^{-1}$ depending on the metal.

Table $20.3B.1$: Crystal Field Stabilization Energies (CFSE) for high and low spin octahedral complexes

Total d-electrons	Isotropic Field	Octahedral Complex				Crystal Field Stabilization Energy	
		High Spin		Low Spin			
	$E_{\text{isotropic field}}$	Configuration	$E_{\text{ligand field}}$	Configuration	$E_{\text{ligand field}}$	High Spin	Low Spin
d^0	0	$t_{2g}0e_g0$	0	$t_{2g}^0e_g^0$	0	0	0
d^1	0	$t_{2g}1e_g0$	-2/5 Δ_o	$t_{2g}^1e_g^0$	-2/5 Δ_o	-2/5 Δ_o	-2/5 Δ_o
d^2	0	$t_{2g}2e_g0$	-4/5 Δ_o	$t_{2g}^2e_g^0$	-4/5 Δ_o	-4/5 Δ_o	-4/5 Δ_o
d^3	0	$t_{2g}3e_g0$	-6/5 Δ_o	$t_{2g}^3e_g^0$	-6/5 Δ_o	-6/5 Δ_o	-6/5 Δ_o
d^4	0	$t_{2g}3e_g1$	-3/5 Δ_o	$t_{2g}^4e_g^0$	-8/5 Δ_o + P	-3/5 Δ_o	-8/5 Δ_o + P
d^5	0	$t_{2g}3e_g2$	0 Δ_o	$t_{2g}^5e_g^0$	-10/5 Δ_o + 2P	0 Δ_o	-10/5 Δ_o + 2P
d^6	P	$t_{2g}4e_g2$	-2/5 Δ_o + P	$t_{2g}^6e_g^0$	-12/5 Δ_o + 3P	-2/5 Δ_o	-12/5 Δ_o + P
d^7	2P	$t_{2g}5e_g2$	-4/5 Δ_o + 2P	$t_{2g}^6e_g^1$	-9/5 Δ_o + 3P	-4/5 Δ_o	-9/5 Δ_o + P
d^8	3P	$t_{2g}6e_g2$	-6/5 Δ_o + 3P	$t_{2g}^6e_g^2$	-6/5 Δ_o + 3P	-6/5 Δ_o	-6/5 Δ_o
d^9	4P	$t_{2g}6e_g3$	-3/5 Δ_o + 4P	$t_{2g}^6e_g^3$	-3/5 Δ_o + 4P	-3/5 Δ_o	-3/5 Δ_o
d^{10}	5P	$t_{2g}6e_g4$	0 Δ_o + 5P	$t_{2g}^6e_g^4$	0 Δ_o + 5P	0	0

P is the spin pairing energy and represents the energy required to pair up electrons within the same orbital. For a given metal ion P (pairing energy) is constant, but it does not vary with ligand and oxidation state of the metal ion).

Octahedral Preference

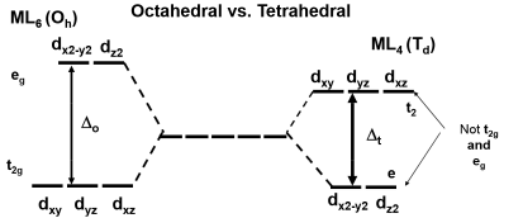
Similar CFSE values can be constructed for non-octahedral ligand field geometries once the knowledge of the d-orbital splitting is known and the electron configuration within those orbitals known, e.g., the tetrahedral complexes in Table 20.3B.2. These energies geoemtries can then be contrasted to the octahedral CFSE to calculate a thermodynamic preference (Enthalpy-wise) for a metal-ligand combination to favor the octahedral geometry. This is quantified via a Octahedral Site Preference Energy defined below.

Definition: Octahedral Site Preference Energies

The Octahedral Site Preference Energy (OSPE) is defined as the difference of CFSE energies for a non-octahedral complex and the octahedral complex. For comparing the preference of forming an octahedral ligand field vs. a tetrahedral ligand field, the OSPE is thus:

$$OSPE = CFSE_{(oct)} - CFSE_{(tet)} \tag{20.3B.2}$$

The OSPE quantifies the preference of a complex to exhibit an octahedral geometry vs. a tetrahedral geometry.



Note: the conversion between Δ_o and Δ_t used for these calculations is:

$$\Delta_t \approx \frac{4}{9}\Delta_o \tag{20.3B.3}$$

which is applicable for comparing octahedral and tetrahedral complexes that involve same ligands only.

Table 20.3B.2: Octahedral Site Preference Energies (OSPE)

Total d-electrons	**CFSE(Octahedral)**		**CFSE(Tetrahedral)**		**OSPE (for high spin complexes)****
	High Spin	Low Spin	Configuration	**Always High Spin***	
d^0	0 Δ_o	0 Δ_o	e^0	0 Δ_t	0 Δ_o
d^1	-2/5 Δ_o	-2/5 Δ_o	e^1	-3/5 Δ_t	-6/45 Δ_o
d^2	-4/5 Δ_o	-4/5 Δ_o	e^2	-6/5 Δ_t	-12/45 Δ_o
d^3	-6/5 Δ_o	-6/5 Δ_o	$e^2t_2^1$	-4/5 Δ_t	-38/45 Δ_o
d^4	-3/5 Δ_o	-8/5 Δ_o + P	$e^2t_2^2$	-2/5 Δ_t	-19/45 Δ_o
d^5	0 Δ_o	-10/5 Δ_o + 2P	$e^2t_2^3$	0 Δ_t	0 Δ_o
d^6	-2/5 Δ_o	-12/5 Δ_o + P	$e^3t_2^3$	-3/5 Δ_t	-6/45 Δ_o
d^7	-4/5 Δ_o	-9/5 Δ_o + P	$e^4t_2^3$	-6/5 Δ_t	-12/45 Δ_o
d^8	-6/5 Δ_o	-6/5 Δ_o	$e^4t_2^4$	-4/5 Δ_t	-38/45 Δ_o
d^9	-3/5 Δ_o	-3/5 Δ_o	$e^4t_2^5$	-2/5 Δ_t	-19/45 Δ_o
d^{10}	0	0	$e^4t_2^6$	0 Δ_t	0 Δ_o

P is the spin pairing energy and represents the energy required to pair up electrons within the same orbital.

> Tetrahedral complexes are always high spin since the splitting is appreciably smaller than P (Equation 20.3B.3).

After conversion with Equation 20.3B.3. The data in Tables $20.3B.1$ and $20.3B.2$ are represented graphically by the curves in Figure $20.3B.1$ below for the high spin complexes only. The low spin complexes require knowledge of P to graph.

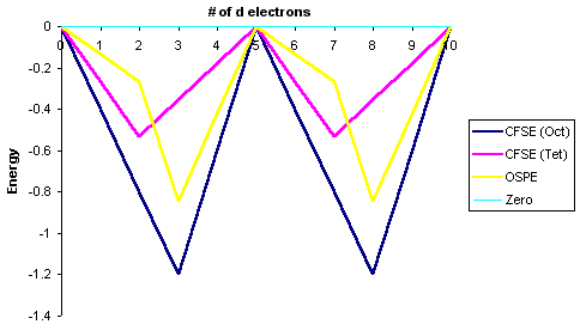


Figure $20.3B.1$***:*** *Crystal Field Stabilization Energies for both octahedral fields ($CFSE_{oct}$) and tetrahedral fields ($CFSE_{tet}$). Octahedral Site Preference Energies (OSPE) are in yellow. This is for high spin complexes.*

From a simple inspection of Figure $20.3B.1$, the following observations can be made:

- The OSPE is *small* in d^1, d^2, d^5, d^6, d^7 complexes and other factors influence the stability of the complexes including steric factors
- The OSPE is *large* in d^3 and d^8 complexes which strongly favor octahedral geometries

Applications

The "double-humped" curve in Figure $20.3B.1$ is found for various properties of the first-row transition metals, including Hydration and Lattice energies of the M(II) ions, ionic radii as well as the stability of M(II) complexes. This suggests that these properties are somehow related to Crystal Field effects.

In the case of Hydration Energies describing the complexation of water ligands to a bare metal ion:

$$M^{2+}(g) + H_2O \rightarrow [M(OH_2)_6]^{2+}(aq)$$

Table $20.3B.3$ and Figure $20.3B.1$ shows this type of curve. Note that in any series of this type not all the data are available since a number of ions are not very stable in the M(II) state.

Table $20.3B.3$: Hydration energies of M^{2+} ions

M	ΔH°/kJmol^{-1}	M	ΔH°/kJmol^{-1}
Ca	-2469	Fe	-2840
Sc	no stable 2+ ion	Co	-2910
Ti	-2729	Ni	-2993
>V	-2777	Cu	-2996
Cr	-2792	Zn	-2928
Mn	-2733		

Graphically the data in Table 2 can be represented by:

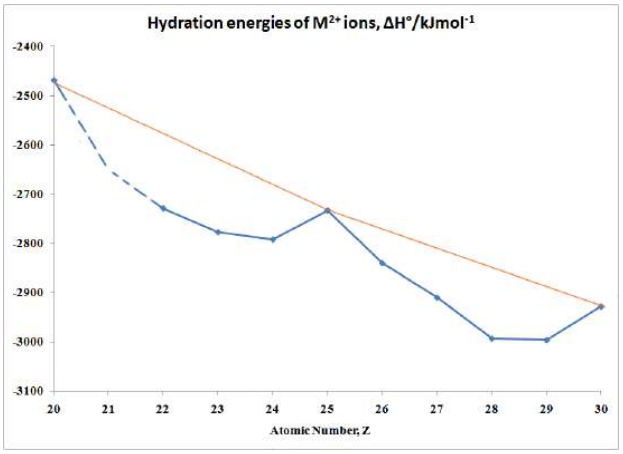


Figure $20.3B.2$***:*** hydration energies of M^{2+} ions

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5.07: Jahn-Teller effect

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20.3D: The Tetrahedral Crystal Field

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SECTION OVERVIEW

20.4: Molecular Orbital Theory - Octahedral Complexes

Topic hierarchy

20.4A: Complexes with no Metal-Ligand \(\pi\)-bonding

20.4B: Complexes with Metal-Ligand \(\pi\)-bonding

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20.4A: Complexes with no Metal-Ligand π -bonding

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20.4B: Complexes with Metal-Ligand π -bonding

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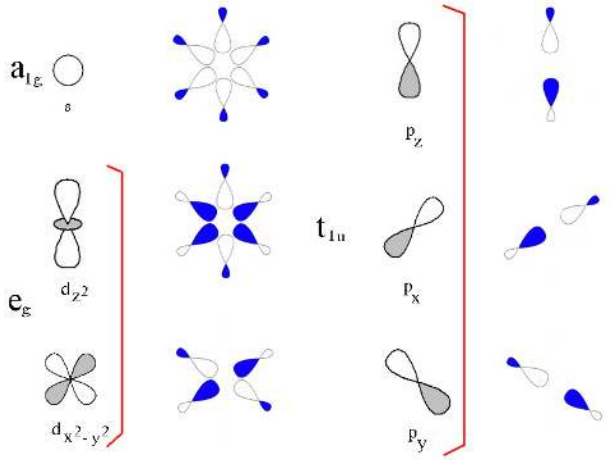
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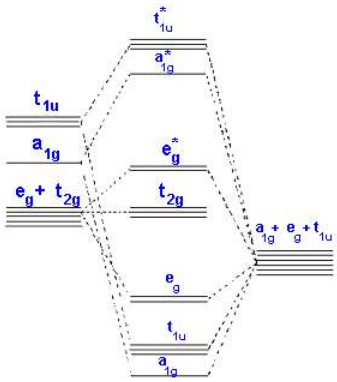
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20.5: Ligand Field Theory

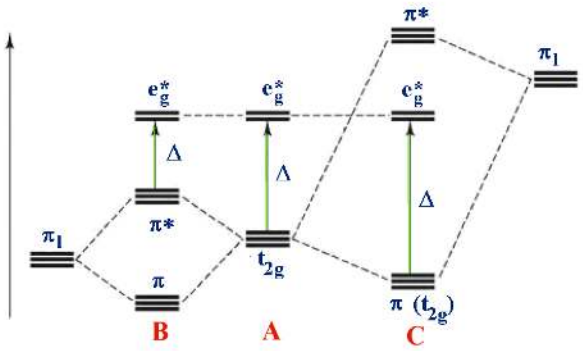
Ligand Field Theory can be considered an extension of Crystal Field Theory such that all levels of covalent interactions can be incorporated into the model. Treatment of the bonding in LFT is generally done using Molecular Orbital Theory. A qualitative approach that can be used for octahedral metal complexes is given in the following 3 diagrams.



In the first diagram, the 3d, 4s and 4p metal ion atomic orbitals are shown together with the ligand group orbitals that would have the correct symmetry to be able to overlap with them. The symmetry adapted linear comination of ligand orbitals are generated by taking 6 sigma orbitals from the ligands, designated as σ_x, σ_{-x}, σ_y, σ_{-y}, σ_z, σ_{-z} and then combining them to make 6 ligand group orbitals. (labelled e_g, a_{1g}, t_{1u})



In the second diagram only sigma bonding is considered and it shows the combination of the metal 3d, 4s and 4p orbitals with OCCUPIED ligand group orbitals (using 1 orbital from each ligand). The result is that that the metal electrons would be fed into t2g and eg* molecular orbitals which is similar to the CFT model except that the eg orbital is now eg*.



For example: B - $[M(II)I_6]^{4-}$ A - $[M(II)(H_2O)_6]^{2+}$ C - $[M(II)(CN)_6]^{4-}$

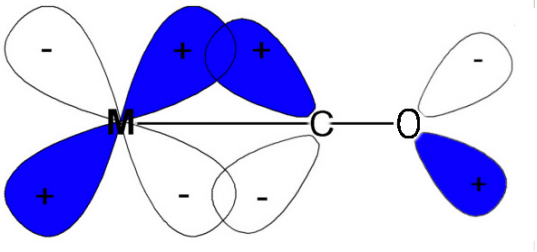
In the third diagram, π (pi) bonding is considered. In general π bonds are weaker than σ (sigma) bonds and so the effect is to modify rather than dramatically alter the description. 2 orbitals from each ligand are combined to give a total of 12 which are subdivided into four sets with three ligand group orbitals in each set. These are labelled t_{1g}, t_{1u}, t_{2g} and t_{2u}. The metal t_{2g} orbital is the most suitable for interaction and this is shown in the 2 cases above.
Case A is the same as above, ignoring π interactions.

- For case B, the ligand π orbitals are full and at lower energy than the metal t_{2g}. This causes a decrease in the size of Δ.
- For case C, the ligand π orbitals are empty and at higher energy than the metal t_{2g}. This causes an increase in the size of Δ.

Returning to the problem of correctly placing ligands in the Spectrochemical series, the halides are examples of case A and groups like CN- and CO are examples of case B. It is possible then to explain the Spectrochemical series once covalent effects are considered.

Some convincing arguments for covalency and effects on Δ come from a study of the IR spectra recorded for simple carbonyl compounds e.g. $M(CO)_6$.

- The CO molecule has a strong triple bond which in the IR gives rise to a strong absorption at ~2140 cm^{-1}. For the series $[Mn(CO)_6]^+$, $[Cr(CO)_6]$ and $[V(CO)_6]^-$, which are isoelectronic, the IR bands for the CO have shifted to 2090, 2000 and 1860 cm^{-1} respectively. Despite the fact that the metals have the same number of electrons (isoelectronic) the frequency of force constant of the CO bond is seen to vary $Mn^+ > Cr > V^-$.
- This can not be explained on an ionic basis but is consistent with the π bonding scheme since the greater the positive charge on the metal, the less readily the metal can delocalize electrons back into the π^* orbitals of the CO group.



Note that the IR values we are dealing with relate to the CO bond and not the M-C so when the CO frequency gets less then it is losing triple bond character and becoming more like a double bond. This is expected if electrons are pushed back from the metal into what were empty π^* antibonding orbitals.

Contributors and Attributions

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SECTION OVERVIEW

20.6: Decribing Electrons in Multi-Electron Systems

Topic hierarchy

20.6A: Quantum Number \(L\) and \(M_L\) for Multi-electron Species

20.6B: Quantum Numbers \(S\) and \(M_S\) for Multi-electron Species

20.6C: Microstates and Term Symbols

20.6D: The Quantum Numbers \(J\) and \(M_J\)

20.6E: Ground States of Elements with Z = 1-10

20.6F: The d^2 Configuration

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20.6A: Quantum Number L and M_L for Multi-electron Species

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20.6B: Quantum Numbers S and M_S for Multi-electron Species

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20.6C: Microstates and Term Symbols

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20.6D: The Quantum Numbers J and M_J

Learning Objectives

- Compate two spin-orbit coupling schemes that couple the total spin angular momenta and total orbital angular momenta of a multi-electron spectra

We need to be able to identify the electronic states that result from a given electron configuration and determine their relative energies. An electronic state of an atom is characterized by a specific energy, wavefunction (including spin), electron configuration, total angular momentum, and the way the orbital and spin angular momenta of the different electrons are coupled together. There are two descriptions for the coupling of angular momentum. One is called **j-j coupling**, and the other is called **L-S coupling**. The j-j coupling scheme is used for heavy elements (z > 40) and the L-S coupling scheme is used for the lighter elements. Only L-S coupling is discussed below.

L-S Coupling of Angular Momenta

L-S coupling also is called R-S or Russell-Saunders coupling. In L-S coupling, the orbital and spin angular momenta of all the electrons are combined separately

$$L = \sum_i l_i \tag{20.6D.1}$$

$$S = \sum_i s_i \tag{20.6D.2}$$

The total angular momentum vector then is the sum of the total orbital angular momentum vector and the total spin angular momentum vector.

$$J = L + S \tag{20.6D.3}$$

The total angular momentum quantum number parameterizes the total angular momentum of a given particle, by combining its orbital angular momentum and its intrinsic angular momentum (i.e., its spin). Due to the spin-orbit interaction in the atom, the orbital angular momentum no longer commutes with the Hamiltonian, nor does the spin.

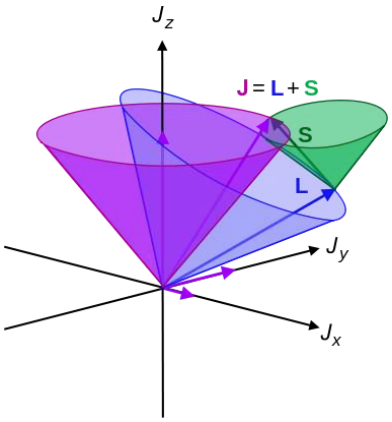


Figure 8.9.1 : "Vector cones" of total angular momentum J (purple), orbital L (blue), and spin S (green). The cones arise due to quantum uncertainty between measuring angular momentum components (see vector model of the atom). (Public Domain; Maschen).

However the total angular momentum J does commute with the Hamiltonian and so is a constant of motion (does not change in time). The relevant definitions of the angular momenta are:

Orbital Angular Momentum

$$|\vec{L}| = \hbar\sqrt{\ell(\ell+1)}$$

with its projection on the z-axis

$$L_z = m_\ell \hbar$$

Spin Angular Momentum

$$|\vec{S}| = \hbar\sqrt{s(s+1)}$$

with its projection on the z-axis

$$S_z = m_s \hbar$$

Total Angular Momentum

$$|\vec{J}| = \hbar\sqrt{j(j+1)}$$

with its projection on the z-axis

$$J_z = m_j \hbar$$

where

- l is the azimuthal quantum number of a single electron,
- s is the spin quantum number intrinsic to the electron,
- j is the total angular momentum quantum number of the electron,

The quantum numbers take the values:

$$m_\ell \in \{-\ell, -(\ell-1) \cdots \ell-1, \ell\}, \quad \ell \in \{0, 1 \cdots n-1\} \tag{20.6D.4}$$
$$m_s \in \{-s, -(s-1) \cdots s-1, s\}, \tag{20.6D.5}$$
$$m_j \in \{-j, -(j-1) \cdots j-1, j\}, \tag{20.6D.6}$$
$$m_j = m_\ell + m_s, \quad j = |\ell + s| \tag{20.6D.7}$$

and the magnitudes are:

$$|\mathbf{J}| = \hbar\sqrt{j(j+1)} \tag{20.6D.8}$$
$$|\mathbf{J}_1| = \hbar\sqrt{j_1(j_1+1)} \tag{20.6D.9}$$
$$|\mathbf{J}_2| = \hbar\sqrt{j_2(j_2+1)} \tag{20.6D.10}$$

in which

$$j \in \{|j_1 - j_2|, |j_1 - j_2| - 1 \cdots j_1 + j_2 - 1, j_1 + j_2\}$$

This process may be repeated for a third electron, then the fourth etc. until the total angular momentum has been found.

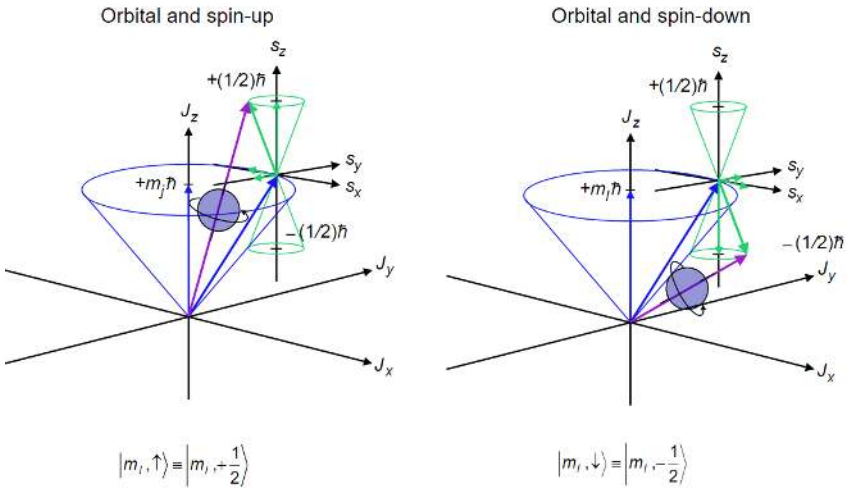


Figure 8.9.2 : Vector model of total angular momentum: spin and orbital coupling (spin-1/2 particles). (Public Domain; Maschen).

The result of these vector sums is specified in a code that is called a Russell-Saunders term symbol, and each term symbol identifies an energy level of the atom. Consequently, the energy levels also are called terms. A term symbol has the form $^{2s+1}L_J$ where the code letter that is used for the total orbital angular momentum quantum number L = 0, 1, 2, 3, 4, 5 is S, P, D, F, G, H, respectively. Note how this code matches that used for the atomic orbitals. The superscript $2S + 1$ gives the spin multiplicity of the state, where S is the total spin angular momentum quantum number. The spin multiplicity is the number of spin states associated with a given electronic state. In order not to confuse the code letter S for the orbital angular momentum with the spin quantum number S, you must examine the context in which it is used carefully. In the term symbol, the subscript J gives the total angular momentum quantum number. Because of spin-orbit coupling, only J and M_j are valid quantum numbers, but because the spin-orbit coupling is weak L, M_l, S, and m_s still serve to identify and characterize the states for the lighter elements.

For example, the ground state, i.e. the lowest energy state, of the hydrogen atom corresponds to the electron configuration in which the electron occupies the 1s spatial orbital and can have either spin α or spin β. The term symbol for the ground state is $^2S_{1/2}$, which is read as “doublet S 1/2”. The spin quantum number is 1/2 so the superscript 2S+1 = 2, which gives the spin multiplicity of the state, i.e. the number of spin states equals 2 corresponding to α and β. The S in the term symbol indicates that the total orbital angular momentum quantum number is 0 (For the ground state of hydrogen, there is only one electron and it is in an s-orbital with $l = 0$). The subscript ½ refers to the total angular momentum quantum number. The total angular momentum is the sum of the spin and orbital angular momenta for the electrons in an atom. In this case, the total angular momentum quantum number is just the spin angular momentum quantum number, ½, since the orbital angular momentum is zero. The ground state has a degeneracy of two because the total angular momentum can have a z-axis projection of $+\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$, corresponding to m_J = +1/2 or -1/2 resulting from the two electron spin states α and β. We also can say, equivalently, that the ground state term or energy level is two-fold degenerate.

? Exercise 8.9.1

Write the term symbol for a state that has 0 for both the spin and orbital angular momentum quantum numbers.

? Exercise 8.9.2

Write the term symbol for a state that has 0 for the spin and 1 for the orbital angular momentum quantum numbers

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20.6E: Ground States of Elements with Z = 1-10

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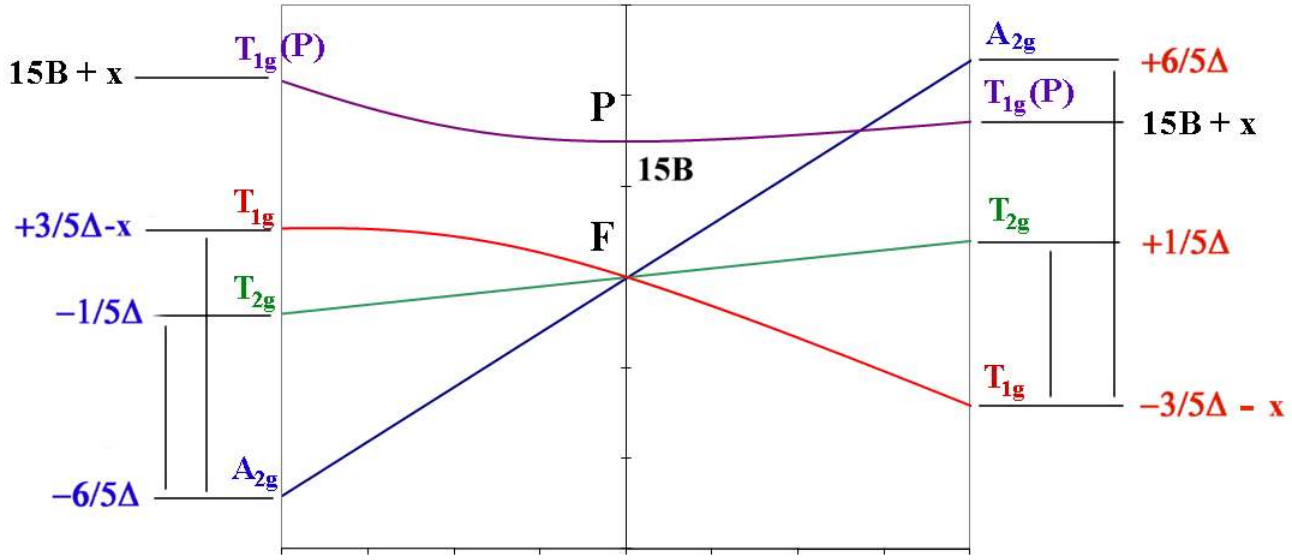
20.6F: The d² Configuration

We have already looked at Transition metal ion complexes with D ground states which accounts for the d^1, d^4, d^6 and d^9 configurations.
We turn now to d^2, d^3, d^7 and d^8 configurations for which the ground state of the free ions are given by Russell-Saunders F terms.

In octahedral and tetrahedral crystal fields, the F state is split into $A_{2(g)}$, $T_{1(g)}$ and $T_{2(g)}$ terms, while the P term generates an additional $T_{1(g)}$ term. Once again we can make use of the analogy to the splitting of orbitals in a crystal field so in this case we can look at how the f-orbitals lose their 7-fold degeneracy in an octahedral field.

It should be noted that whenever the ground state is an F term there will be a P term found at higher energy with the same spin multiplicity. The separation of these terms in the free ion is measured in terms of the B Racah parameter and is equivalent to 15B (where B is usually around 1000 cm^{-1}).

Once again, one approach taken to aid in the interpretation of these spectra is to use an Orgel diagram. The relevant Orgel diagram for the F ground state is given below:

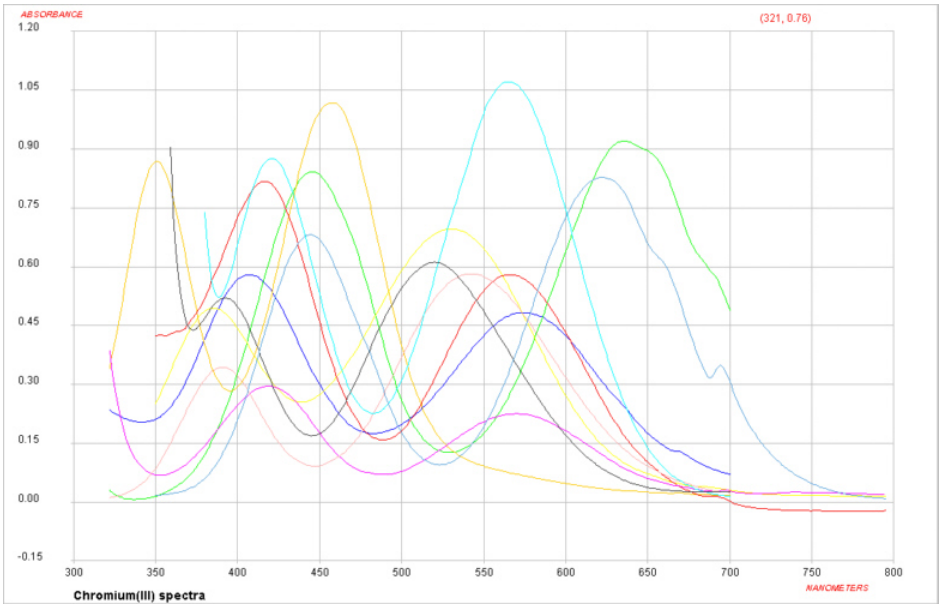


oct d^3,d^8 tet d^2,d^7 ←----------→ oct d^2,d^7 tet d^3,d^8

$\nu_1 = \Delta$ (T2g ← A2g)	$\nu_1 = 4/5\,\Delta + x$ (T2g ← T1g)
$\nu_2 = 9/5\,\Delta - x$ (T1g ← A2g)	$\nu_2 = 9/5\,\Delta + x$ (A2g ← T1g) **OR** $\nu_2 = 3/5\,\Delta + 15B + 2x$ (T1g(P) ← T1g)
$\nu_3 = 6/5\,\Delta + 15B + x$ (T1g(P) ← A2g)	$\nu_3 = 3/5\,\Delta + 15B + 2x$ (T1g(P) ← T1g) **OR** $\nu_3 = 9/5\,\Delta + x$ (A2g ← T1g)

The lines showing the A_2 and T_2 terms are linear and depend solely on Δ. The "**non-crossing rule**" results in the lines for the two T_1 terms being curved to avoid each other and as a result this introduces a "configuration interaction" in the transition energy equations.

That is, whenever there are lines with equivalent Russell-Saunders terms on the Orgel diagram they are not allowed to cross and are found to diverge. All other lines are expected to be linear.



Visible spectra of some Cr(III) complexes

For Cr(III) complexes, we would start by writing the free ion electronic configuration as d^3 and in an octahedral crystal field this would be described as $t_{2g}^3\ e_g^0$.
The Russell-Saunders scheme that takes into account the electron-electron interactions would be described by a free ion ground state of ^4F. To decide which side of the F Orgel diagram should be applied to the interpretation can be quickly determined by looking at the electronic configuration and noting that the ground state is singly degenerate (i.e. we need the left-hand-side where the lowest term is A_2).

It is expected then that there should be 3 absorption bands found in the electronic spectrum. The energy of the first transition corresponds directly to Δ and the transition is written as $4T_{2g} \leftarrow 4A_{2g}$.

If we now consider the d^2 electronic configuration, then the Russell-Saunders free ion ground term state is a ^3F. For an octahedral complex, the lowest energy state is a triplet which tells us that we need to be using the right-hand-side of the F Orgel diagram.

The first transition is written as $3T_{2g} \leftarrow 3T_{1g}$ and the energy of this transition does NOT correspond directly to Δ. **It should be carefully noted that when using this side of the F-Orgel diagram none of the expected transitions correspond exactly to Δ** . Interpretation of d^2 spectra are made even more complicated since as we increase the size of Δ we note that at some point the $3T_{1g}(P)$ and $3A_{2g}$ lines cross. To determine the sequence of the transitions (that is whether we are on the left-hand-side or right-hand-side of the intersection) normally requires that all 3 absorption bands can be observed. This is often not the case and an alternative approach to interpretation of these spectra is needed. One such approach makes use of what are known as Tanabe-Sugano diagrams.

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SECTION OVERVIEW

20.7: Electronic Spectra - Absorption

Topic hierarchy

20.7A: Spectral Features

20.7B: Charge Transfer Absorptions

20.7C: Selection Rules

20.7D: Electronic Absorption Spectra of Octahedral and Tetrahedral Complexes

20.7E: Interpretation of Electronic Absorption Spectra - Use of Racah Parameters

20.7F: Interpretation of Electronic Absorption Spectra - Tanabe-Sugano Diagrams

20.7G: Help on using Tanabe-Sugano diagrams

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20.7A: Spectral Features

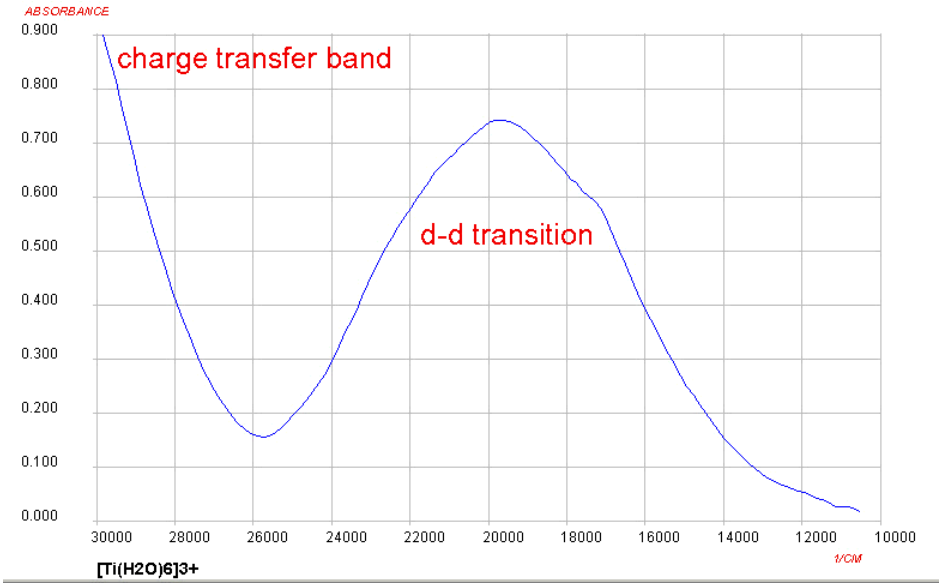
Crystal Field Theory copes reasonably well for d^1 (d^9) systems but not for multi-electron systems, which are the more common. To deal with these systems we need to introduce a new concept, that of the electronic state. Electronic configurations refer to the way in which the electrons occupy the d orbitals, so for Ti(III) we write an electronic configuration of [Ar] $3d^1$ and in an octahedral crystal field the lowest energy configuration would be written as $t_{2g}^1\ e_g^0$.

The electronic state refers to energy levels available to a group of electrons. This is much more complex than the single electron case since not only is it necessary to consider the crystal field effects of the repulsion of the metal electrons by the ligand electrons, but it is necessary to include the interactions between the electrons themselves.
When describing electronic configurations, lower case letters are used, thus t_{2g}^1 etc.

For electronic states, upper case (CAPITAL) letters are used and by analogy, a T state is triply degenerate. Subscripts 1 and 2 are used to distinguish states of like degeneracy and g and u subscripts indicate the presence of a center of symmetry eg. T_{1g}, T_{2g}, T_{1u} and T_{2u}.

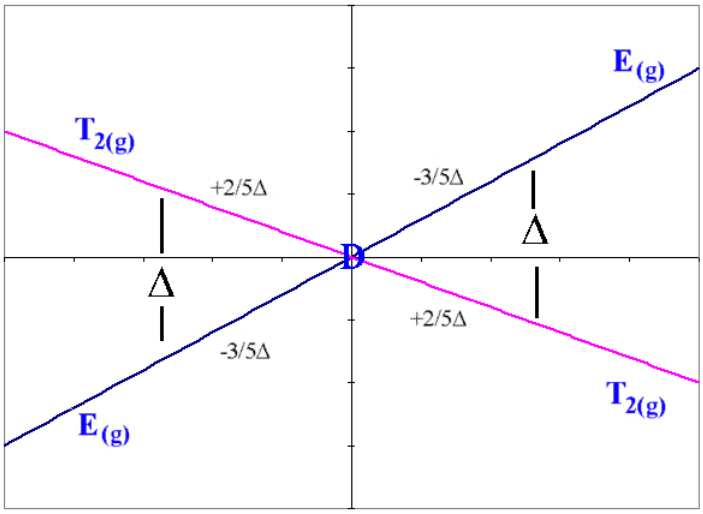
These symbols are further modified to show the spin multiplicity of the electronic state using the Russell-Saunders Notation.
If we consider the Ti(III) case, the electronic configuration is d^1. In an octahedral crystal field this would give rise to a t_{2g}^1 arrangement and the excitation of the low lying electron to the higher level would then give an e_g^1 arrangement.

Only one d-d transition is expected and this roughly corresponds to what is observed for Ti(III) complexes, although it is somewhat more complicated due to Jahn-Teller considerations. At the high energy end of the spectrum, the presence of a charge transfer band should be noted as well. The origin of this will not be covered in detail in this course.



One approach taken when we consider the Russell-Saunders scheme with the various electronic states makes use of what are called Orgel diagrams. The relevant Orgel diagram for the D ground state is given below:

Orgel Diagram for D free ion ground state



oct 4,9 tet 1,6 <----------> oct 1,6 tet 4,9

For a Fe(II) high spin octahedral complex we would write the free ion electronic configuration as d^6 and in the octahedral crystal field it would be described as $t_{2g}^4\ e_g^2$.

The Russell-Saunders scheme that takes into account the electron-electron interactions would be described by a free ion ground state of ^5D. In octahedral and tetrahedral crystal fields, this D state is split into $E_{(g)}$ and $T_{2(g)}$ terms. To decide which side of the D Orgel diagram should be applied to the interpretation can be quickly determined by looking at the electronic configuration and noting that the ground state is triply degenerate and the excited state is doubly degenerate (i.e. we must use the right-hand-side).
It is expected then that there should be 1 absorption band found in the electronic spectrum and that the energy of the transition corresponds directly to Δ. The transition is written in a notation that is read from right to left, which in this case is $5E_g \leftarrow 5T_{2g}$.

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20.7B: Charge Transfer Absorptions

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20.7D: Electronic Absorption Spectra of Octahedral and Tetrahedral Complexes

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20.7E: Interpretation of Electronic Absorption Spectra - Use of Racah Parameters

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20.7F: Interpretation of Electronic Absorption Spectra - Tanabe-Sugano Diagrams

For ALL octahedral complexes, except high spin d^5, simple CFT would predict that only 1 band should appear in the electronic spectrum and that the energy of this band should correspond to the absorption of energy equivalent to Δ. In practice, ignoring spin-forbidden lines, this is only observed for those ions with D free ion ground terms i.e., d^1, d^9 as well as d^4, d^6.

The observation of 2 or 3 peaks in the electronic spectra of d^2, d^3, d^7 and d^8 high spin octahedral complexes requires further treatment involving electron-electron interactions. Using the Russell-Saunders (LS) coupling scheme, these free ion configurations give rise to F free ion ground states which in octahedral and tetrahedral fields are split into terms designated by the symbols $A_{2(g)}$, $T_{2(g)}$ and $T_{1(g)}$.

To derive the energies of these terms and the transition energies between them is beyond the needs of introductory level courses and is not covered in general textbooks[10,11]. A listing of some of them is given here as an Appendix. What is necessary is an understanding of how to use the diagrams, created to display the energy levels, in the interpretation of spectra.

In the laboratory component of the course we will measure the absorption spectra of some typical chromium(III) complexes and calculate the spectrochemical splitting factor, Δ. This corresponds to the energy found from the first transition below and as shown in Table 1 is generally between 15,000 cm^{-1} (for weak field complexes) and 27,000 cm^{-1} (for strong field complexes).

For the d^3 octahedral case, 3 peaks can be predicted and these would correspond to the following transitions and energies:

1. $^4T_{2g} \leftarrow {}^4A_{2g}$ transition energy = Δ
2. $^4T_{1g}(F) \leftarrow {}^4A_{2g}$ transition energy = 9/5 * Δ - C.I.
3. $^4T_{1g}(P) \leftarrow {}^4A_{2g}$ transition energy = 6/5 * Δ + 15B' + C.I.

where C.I. is the configuration interaction arising from the "non-crossing rule".

Table 1. Peak positions for some octahedral Cr(III) complexes (in cm^{-1}).

Complex	v1	v2	v3	v2/ v1	v1/ v2	Δ/B	Ref
Cr^{3+} in emerald	16260	23700	37740	1.46	0.686	20.4	13
K_2NaCrF_6	16050	23260	35460	1.45	0.690	21.4	13
$[Cr(H_2O)_6]^{3+}$	17000	24000	37500	1.41	0.708	24.5	This work
Chrome alum	17400	24500	37800	1.36	0.710	29.2	4
$[Cr(C_2O_4)_3]^{3-}$	17544	23866	?	1.37	0.735	28.0	This work
$[Cr(NCS)_6]^{3-}$	17800	23800	?	1.34	0.748	31.1	4
$[Cr(acac)_3]$	17860	23800	?	1.33	0.752	31.5	This work
$[Cr(NH_3)_6]^{3+}$	21550	28500	?	1.32	0.756	32.6	4
$[Cr(en)_3]^{3+}$	21600	28500	?	1.32	0.758	33.0	4
$[Cr(CN)_6]^{3-}$	26700	32200	?	1.21	0.829	52.4	4

For octahedral Ni(II) complexes the transitions would be:

1. $^3T_{2g} \leftarrow {}^3A_{2g}$ transition energy = Δ
2. $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ transition energy = 9/5 * Δ - C.I.
3. $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ transition energy = 6/5 * Δ + 15B' + C.I.

where C.I. again is the configuration interaction and as before the first transition corresponds exactly to Δ.

For M(II) the size of Δ is much less than for M(III) and typical values for Ni(II) are 6500 to 13000 cm^{-1} as shown in Table 2.

Table 2. Peak positions for some octahedral Ni(II) complexes (in cm^{-1}).

Complex	v1	v2	v3	v1	v1/ v2	Δ/B	Ref
$NiBr_2$	6800	11800	20600	1.74	0.576	5	13
$[Ni(H_2O)_6]^{2+}$	8500	13800	25300	1.62	0.616	11.6	13
$[Ni(gly)_3]^-$	10100	16600	27600	1.64	0.608	10.6	13
$[Ni(NH_3)_6]^{2+}$	10750	17500	28200	1.63	0.614	11.2	13
$[Ni(en)_3]^{2+}$	11200	18350	29000	1.64	0.610	10.6	3
$[Ni(bipy)_3]^{2+}$	12650	19200	?	1.52	0.659	17	3

For d^2 octahedral complexes, few examples have been published. One such is V^{3+} doped in Al_2O_3 where the vanadium ion is generally regarded as octahedral, Table 3.

Table 3. Peak positions for some octahedral V(III) complexes (in cm^{-1}).

Complex	v1	v2	v3	v2/ v1	v1/v2	Δ/B	Ref
V^{3+} in Al_2O_3	17400	25200	34500	1.448	0.6906	30.90	13
$[VCl_3(MeCN)_3]$	14400	21400	?	1.486	0.6729	28.68	4
$K_3[VF_6]$	14800	23250	?	1.571	0.6365	24.78	4

Interpretation of the spectrum highlights the difficulty of using the right-hand side of the Orgel diagram as previously noted. For d^2 cases where none of the transitions correspond exactly to Δ often only 2 of the 3 transitions are clearly observed and hence the calculations will have three unknowns (Δ, B and C.I.) but only 2 energies to use in the the analysis.

The first transition can be unambiguously assigned as:

$^3T_{2g} \leftarrow {}^3T_{1g}$ transition energy = 4/5 * Δ + C.I.

But, depending on the size of the ligand field (Δ) the second transition may be due to:

$^3A_{2g} \leftarrow {}^3T_{1g}$ transition energy = 9/5 * Δ + C.I.

for a weak field or

$^3T_{1g}(P) \leftarrow {}^3T_{1g}$ transition energy = 3/5 * Δ + 15B' + 2 * C.I.

for a strong field.

The transition energies of these terms are clearly different and it is often necessary to calculate (or estimate) values of B, Δ and C.I. for both arrangements and then evaluate the answers to see which fits better.

The difference between the $^3A_{2g}$ and the $^3T_{2g}$ (F) lines should give Δ. In this case Δ is equal to either:
25200 - 17400 = 7800 cm^{-1}
or 34500 - 17400 = 17100 cm^{-1}.
Given that we expect Δ to be greater than 15000 cm^{-1} then we must interpret the second transition as to the $^3T_{2g}(P)$ and the third to $^3A_{2g}$. Further evaluation of the expressions then gives C.I. as 3720 cm^{-1} and B' as 567 cm^{-1}.

Solving the equations like this for the three unknowns can ONLY be done if the three transitions are observed. When only two transitions are observed, a series of equations[14] have been determined that can be used to calculate both B and Δ. This approach still requires some evaluation of the numbers to ensure a valid fit. For this reason, Tanabe-Sugano diagrams become a better method for interpreting spectra of d^2 octahedral complexes.

Using Tanabe-Sugano diagrams

The use of Orgel diagrams allows a qualitative description of the spin-allowed electronic transitions expected for states derived from D and F ground terms. Only 2 diagrams are needed for high spin d^2-d^9 and both tetrahedral and octahedral ions are covered.

Tanabe-Sugano diagrams were developed in the 1950's to give a semi-quantitative approach and include both high and low spin ions and not only the spin-allowed transitions are shown but the spin-forbidden transitions are displayed as well.

At first glance they can appear quite daunting, but in practice they are much easier to use for interpreting spectra and provide much more information. The obvious differences are the presence of the additional lines and that the ground state is shown as the base line along the X axis rather than as a straight line or curve originating from the Y axis.

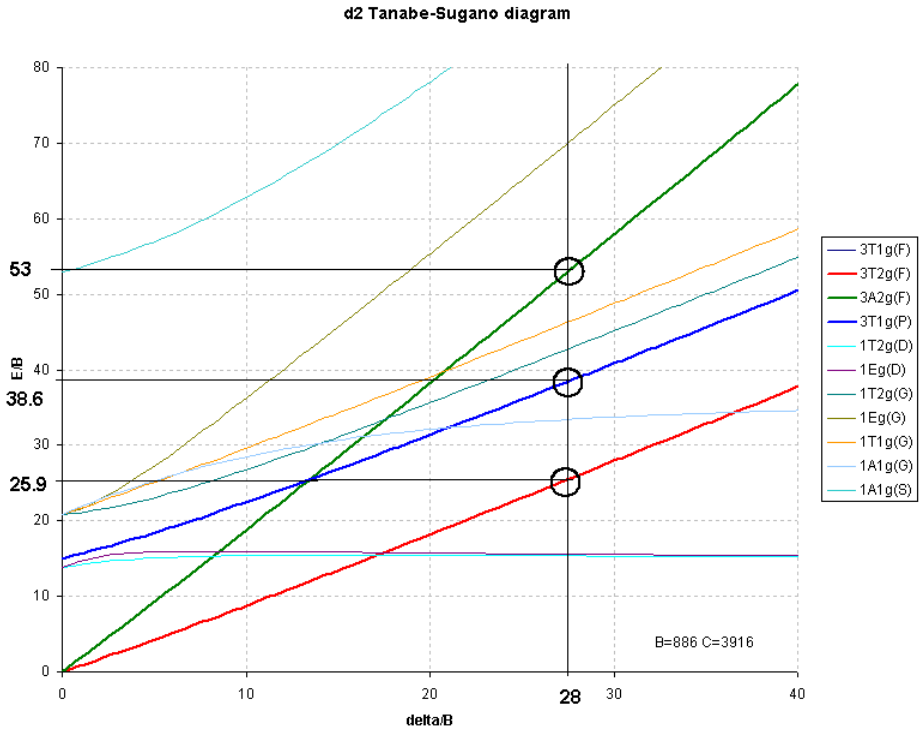
On the X axis Δ/B' is plotted while on the Y axis E/B' is plotted, where B' is the modified Racah B parameter that exists in the complex.

A separate diagram is needed for each electronic configuration d^2-d^9 and for the d^4-d^7 cases both the high spin and low spin electronic configurations are shown. The high spin is on the left-hand-side of the vertical line on the diagram.

For the d2 case where it is difficult to use an Orgel diagram, the TS diagram is shown below. The ground state is $^3T_{1g}$ which is plotted along the base line.
Note that the transitions that occur are dependent on the sizes of Δ and B and the A_{2g} term may be either higher or lower than the T_{1g} (P) term (depending on whether Δ/B' is greater than about 15).

For the V(III) aqua ion, transitions are observed at 17,200 and 25,600 cm^{-1} which are assigned to the $3T_{2g} \leftarrow 3T_{1g}$ and $3T_{1g}(P) \leftarrow 3T_{1g}$ (F) respectively.
Interpretation requires taking the ratio of these frequencies and then finding the position on the diagram where the height of the $3T_{1g}(P) / 3T_{2g}$ exactly matches that ratio.

For a ratio of 1.49, this is found on the diagram below at Δ/B' of 28.0.



Reading off the position on the Y axis for the three spin-allowed lines gives E/B' values of 25.9, 38.6 and 53 ($3T_{2g}$, $3T_{1g}$ and $3A_{2g}$)

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To determine the value of Δ and B' is now relatively straightforward since from the first transition energy of 17,200 cm^{-1} and the value of E/B' of 25.9 we can equate B' as:
B' = 17,200/ 25.9 or B' = 665 cm^{-1}
Alternatively from the second transition energy of 25,600 cm^{-1} and the value of E/B' of 38.6 we can equate B' as:
B' = 25,600/ 38.6 or B' = 663 cm^{-1} which is in excellent agreement with the value found from the first transition.

The value of Δ can then be determined from the Δ/B' ratio of 28.0 and the value just calculated for B' of 665 cm^{-1}.
This gives Δ as 28.0 x 665 = 18,600 cm^{-1}

The transition $^3A_{2g} \leftarrow 3T_{1g}$ would be predicted to occur at 53 x 665 that is 35,245 cm^{-1} (or 284 nm) which is in the UV region and not observed. (Possibly obscured by charge transfer bands).

The values of Δ and B' can be compared to similar V(III) complexes and it should be noted that in general for M(III) ions the Δ value is often about 3/2 times the value expected for M(II) ions.

The free ion value of B for a V(III) ion is 860 cm^{-1} and the reduction of this value noted for the observed B' is a measure of what is described as the Nephelauxetic Effect.

The Nephelauxetic Effect

The Racah repulsion parameters for a metal complex vary as the ligand is changed

- As the complex becomes more covalent the electrons are to some extent spread over the ligands so the electron-electron repulsion is reduced
- This reduction in repulsion as covalency increases is called the nephelauxetic effect (literally "cloud expanding")

A nephelauxetic series can be set up based on the variation of the Racah parameter.
A large reduction in B (free ion) indicates a strong **Nephelauxetic Effect**.

{B(free ion)- B'(Complex)} / B(free ion)

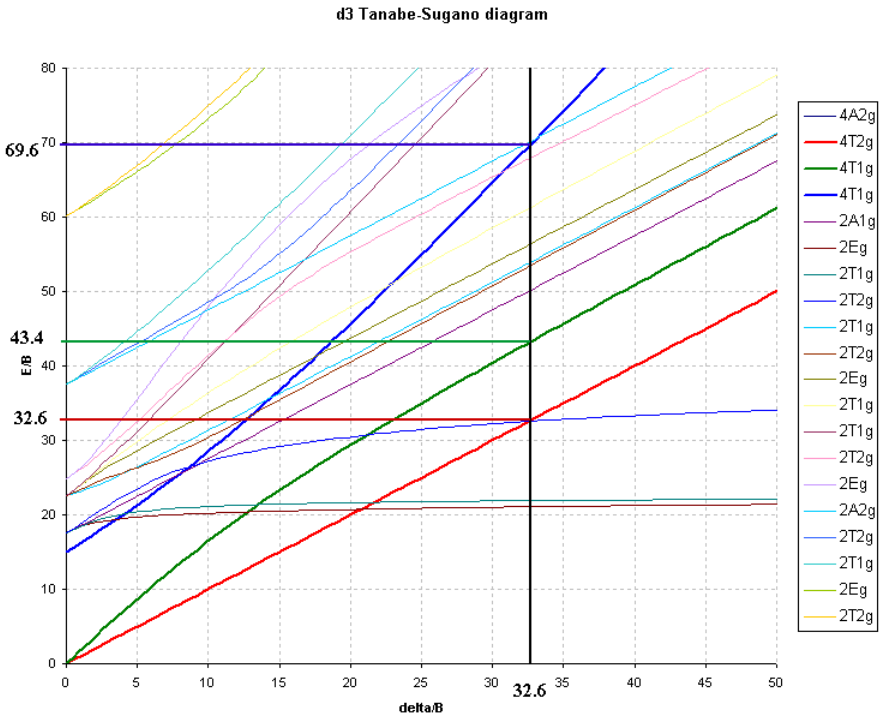
The Nephelauxetic Series is given by:

$$F^- < H_2O < urea < NH_3 < en \sim C_2O_4^{2-} < NCS^- < Cl^- \sim CN^- < Br^- < S^{2-} \sim I^-$$

This series is consistent with fluoride complexes being the most ionic and giving a small reduction in B while covalently bonded ligands such as I- give a large reduction of B.

N.B. The order of the nephelauxetic series is NOT the same as the spectrochemical series as one is an indication of B and the other of Δ

As an example of a Cr(III) complex, using the observed peaks found for $[Cr(NH_3)_6]^{3+}$ in Table 1 above, namely ν_1 = 21550 cm^{-1} and ν_2 = 28500 cm^{-1} the ratio of ν_2/ν_1 = 1.32.
The value of Δ is obtained directly from the first transition so Δ/B' is equal to ν_1/B' and finding B' is now relatively straightforward since from the first transition energy of 21,550 cm^{-1} and the value of Δ/B' (ν1/B') of 32.6 we get:
B' = 21,550/ 32.6 or B' = 661 cm^{-1}
The third peak can then be predicted to occur at 69.64 * 661 = 46030 cm^{-1} or 217 nm (well in the UV region and probably hidden by charge transfer or solvent bands).

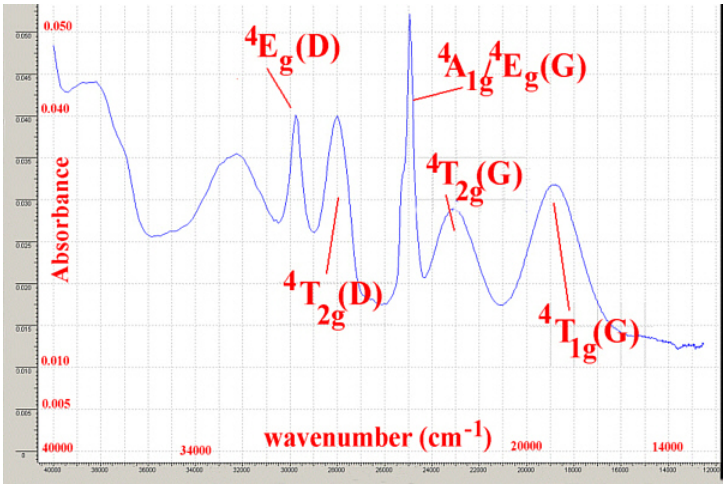


It is important to remember that for spectra recorded in solution the width of the peaks may be as large as 1-2000 cm^{-1} so as long as it is possible to unambiguously assign peaks, the techniques are valuable.

high-spin octahedral d^5 case and low-spin complexes

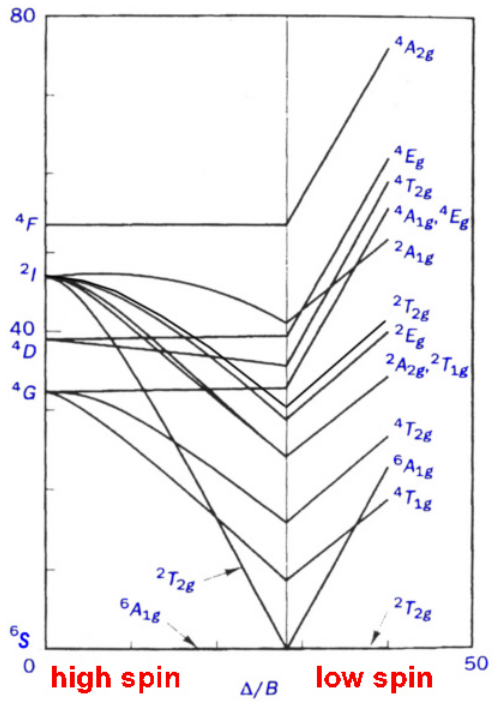
For Mn(II) and other d^5 cases, the ground state is ^6S and higher states include, ^4G, ^4D, ^4P ^4F etc.

It is expected that since there are NO spin-allowed transitions possible, the electronic spectrum should only contain very weak bands. For the other electronic configurations spin-forbidden bands are rarely observed since they are hidden by the more intense spin-allowed transitions. Since there are now no spin-allowed transitions, by amplifying the signal and using concentrated solutions, a number of weak peaks can be seen.



The Tanabe-Sugano diagram can be used to interpret these bands by once again calculating the ratio of the energies of 2 peaks and finding that position on the diagram.

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20.7G: Help on using Tanabe-Sugano diagrams

To make use of the Tanabe-Sugano diagrams provided in textbooks, it would be expected that they should at least be able to cope with typical spectra for d^3, d^8 octahedral and d^2, d^7 tetrahedral systems since these are predicted to be the most favoured from Crystal Field Stabilisation calculations. **This is not the case**. All the diagrams presented are impractical, being far too small and for chromium(III) actually stop before the region of interest of many simple coordination complexes.

If we ignore spin-forbidden transitions, where the energy of the states depend on both the B and C Racah parameter, then it should be possible to use the d^n, d^{10-n} relationship between octahedral and tetrahedral for interpretation of the spin-allowed transitions. This is because, for example, the d^3 octahedral and d^7 tetrahedral states have the same energy dependencies on Δ/B. When using the Tanabe-Sugano diagram in this way the major difference is that the size of Δ tetrahedral is only roughly 4/9 times that of Δ octahedral and so all complexes are high spin and the area of interest is moved closer to the left hand side of the diagram.

Procedure

- Record the UV/Vis spectrum of your sample.
- Tabulate peak information in wavelengths (nm) and convert to wavenumbers (cm^{-1}), $\{\nu = 10^7 / \lambda\}$
- calculate the extinction coefficients based on the concentration
- calculate the experimental ratio of v_2 / v_1
- use the appropriate Tanabe-Sugano diagram to locate where the ratio of the second to first peak matches that of the experimental value above.

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For d^2 (oct), d^8 (tet) and d^3, d^8 (oct) d^2, d^7 (tet) JAVA applets and spreadsheets are available which perform these calculations.

- Tabulate the values of v_1 / B', v_2 / B', v_3 / B' from the Y-intercepts and Δ/B' from the X-intercept.
- Using your experimental values of v_1 and v_2 (v_3 if seen), calculate an average value of B' from these Y intercept values.
- Calculate Δ based on your value of Δ/B'.
- Assign all the spin-allowed transitions you observed.
- Comment on the size of the experimental B' compared to the free-ion value.
- Do you observe any peaks that might be spin-forbidden transitions? If so, can you assign them?
- Comment on the size of your calculated extinction coefficients and relate this to the relevant selection rules.

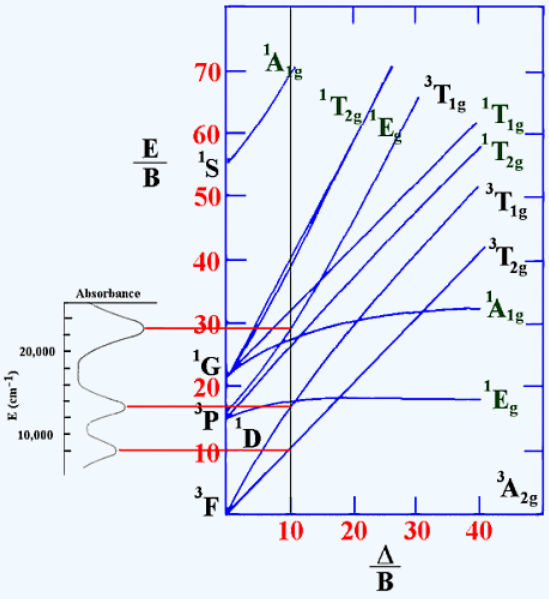
The expected values should be compared to the following rough guide.

- For M^{2+} complexes, expect Δ= 7500 - 12500 cm^{-1}.
- For M^{3+} complexes, expect Δ= 14000 - 25000 cm^{-1}.

B for first-row transition metal free ions is around 1000 cm^{-1}. Depending on the position of the ligand in the nephelauxetic series, this can be reduced to as low as 60% in the complex. Extinction coefficients for octahedral complexes are expected to be around 50-100 times smaller than for tetrahedral complexes. For a typical spin-allowed but Laporte (orbitally) forbidden transition in an octahedral complex, expect $\varepsilon < 10$ m^2mol^{-1}.

Example 20.7G.1:

For an octahedral Ni(II) complex, three peaks were observed at 8000, 13200 and 22800 cm^{-1}. From the ratio v_2/v_1 of 1.65 this gives a value of Δ/B' of 10.0. This can be shown in the following diagram.



Since v1= Δ in this case (and equals 8000 cm^{-1}) then B' can be evaluated to be 800 cm^{-1}. The spin-forbidden lines that would be between v_2 and v_3 in energy are not observed in the spectrum nor are any lines seen at higher energy.

References

1. Ligand Field Theory and its Applications, B.N. Figgis and M.A. Hitchman, Wiley-VCH, New York, 2000.
2. Inorganic Chemistry, J.E. Huheey, 3rd Edition, Harper & Row Publishers, New York 1983.

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20.8: Electronic Spectra - Emission

Overview

- To introduce the concept of absorption and emission line spectra and describe the Balmer equation to describe the visible lines of atomic hydrogen.

The first person to realize that white light was made up of the colors of the rainbow was Isaac Newton, who in 1666 passed sunlight through a narrow slit, then a prism, to project the colored spectrum on to a wall. This effect had been noticed previously, of course, not least in the sky, but previous attempts to explain it, by Descartes and others, had suggested that the white light became colored when it was refracted, the color depending on the angle of refraction. Newton clarified the situation by using a second prism to reconstitute the white light, making much more plausible the idea that the white light was composed of the separate colors. He then took a monochromatic component from the spectrum generated by one prism and passed it through a second prism, establishing that no further colors were generated. That is, light of a single color did not change color on refraction. He concluded that white light was made up of all the colors of the rainbow, and that on passing through a prism, these different colors were refracted through slightly different angles, thus separating them into the observed spectrum.

Atomic Line Spectra

The spectrum of hydrogen *atoms*, which turned out to be crucial in providing the first insight into atomic structure over half a century later, was first observed by Anders Ångström in Uppsala, Sweden, in 1853. His communication was translated into English in 1855. Ångström, the son of a country minister, was a reserved person, not interested in the social life that centered around the court. Consequently, it was many years before his achievements were recognized, at home or abroad (most of his results were published in Swedish).

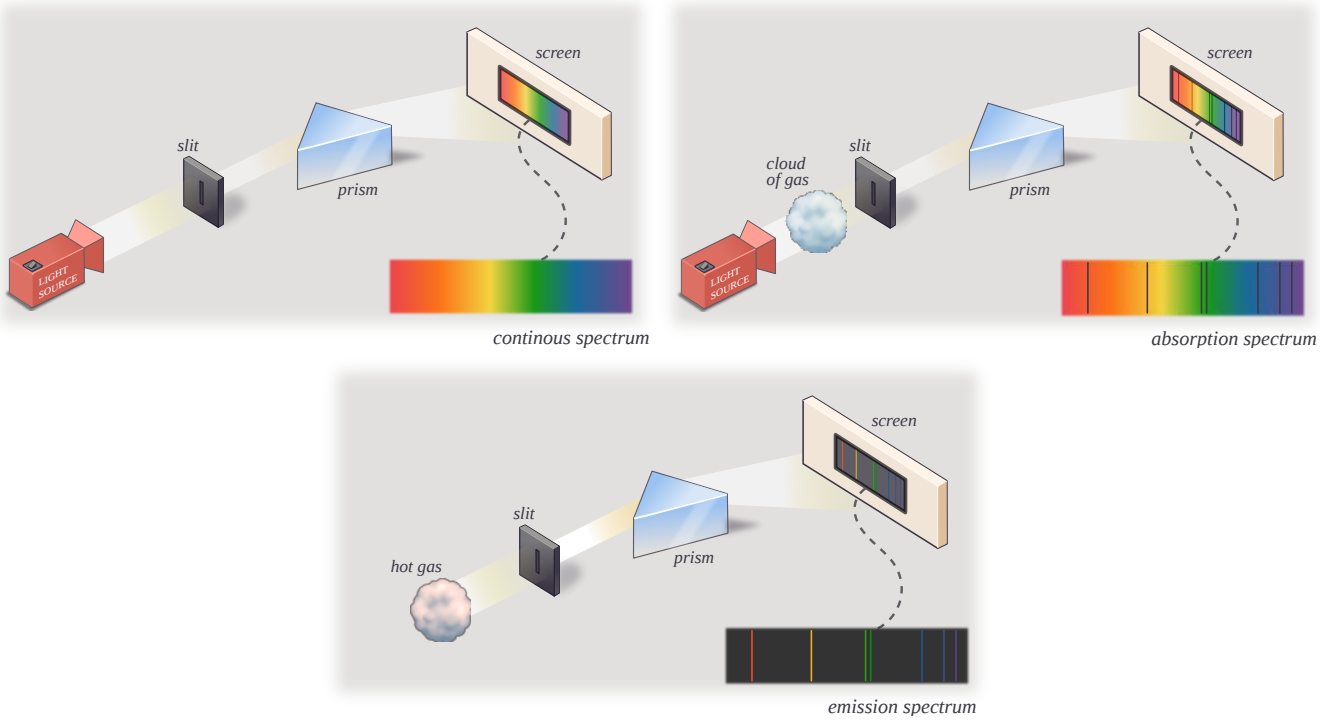


Figure 1.4.1 : Three Kinds of Spectra. When we see a lightbulb or other source of continuous radiation, all the colors are present. When the continuous spectrum is seen through a thinner gas cloud, the cloud's atoms produce absorption lines in the continuous spectrum. When the excited cloud is seen without the continuous source behind it, its atoms produce emission lines. We can learn which types of atoms are in the gas cloud from the pattern of absorption or emission lines. (CC BY-NC; Ümit Kaya via LibreTexts).

Most of what is known about atomic (and molecular) structure and mechanics has been deduced from spectroscopy. Figure 1.4.1 shows two different types of spectra. A continuous spectrum can be produced by an incandescent solid or gas at high pressure (e.g., blackbody radiation is a continuum). An emission spectrum can be produced by a gas at low pressure excited by heat or by collisions with electrons. An absorption spectrum results when light from a continuous source passes through a cooler gas, consisting of a series of dark lines characteristic of the composition of the gas.

Fraunhofer Lines

In 1802, William Wollaston in England had discovered that the solar spectrum had tiny gaps - there were many thin dark lines in the rainbow of colors. These were investigated much more systematically by Joseph von Fraunhofer, beginning in 1814. He increased the dispersion by using more than one prism. He found an "almost countless number" of lines. He labeled the strongest dark lines A, B, C, D, etc. Frauenhofer between 1814 and 1823 discovered nearly 600 dark lines in the solar spectrum viewed at high resolution and designated the principal features with the letters A through K, and weaker lines with other letters (Table 1.4.1). Modern observations of sunlight can detect many thousands of lines. It is now understood that these lines are caused by absorption by the outer layers of the Sun.

Table 1.4.1 : Major Fraunhofer lines and the elements they are associated with.

Designation	Element	Wavelength (nm)
y	O_2	898.765
Z	O_2	822.696
A	O_2	759.370
B	O_2	686.719
C	H	656.281
a	O_2	627.661
D_1	Na	589.592
D_2	Na	588.995
D_3 or d	He	587.5618

The Fraunhofer lines are typical spectral absorption lines. These dark lines are produced whenever a cold gas is between a broad spectrum photon source and the detector. In this case, a decrease in the intensity of light in the frequency of the incident photon is seen as the photons are absorbed, then re-emitted in random directions, which are mostly in directions different from the original one. This results in an *absorption line*, since the narrow frequency band of light initially traveling toward the detector, has been turned into heat or re-emitted in other directions.

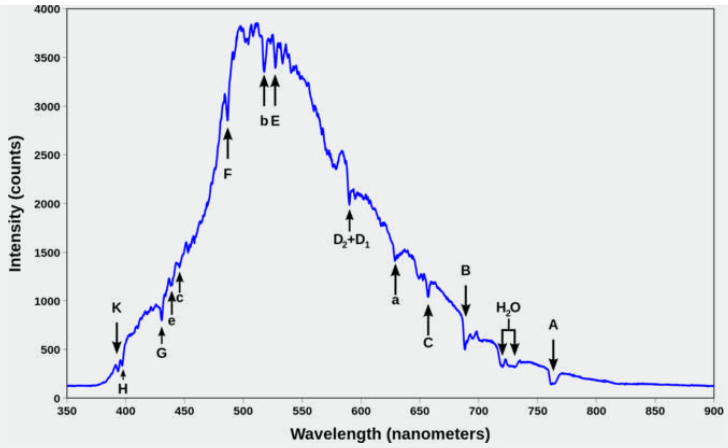


Figure 1.4.2 : Spectrum of blue sky. Dips are present at the Fraunhofer line wavelengths. (CC BY-SA 4.0; Eric Bajart via Wikipedia).

By contrast, if the detector sees photons emitted directly from a glowing gas, then the detector often sees photons emitted in a narrow frequency range by quantum emission processes in atoms in the hot gas, resulting in an *emission line*. In the Sun, Fraunhofer lines are seen from gas in the outer regions of the Sun, which are too cold to directly produce emission lines of the elements they represent.

Gases heated to incandescence were found by Bunsen, Kirkhoff and others to emit light with a series of sharp wavelengths. The emitted light analyzed by a spectrometer (or even a simple prism) appears as a multitude of narrow bands of color. These so called *line spectra* are characteristic of the atomic composition of the gas. The line spectra of several elements are shown in Figure 1.4.3 .

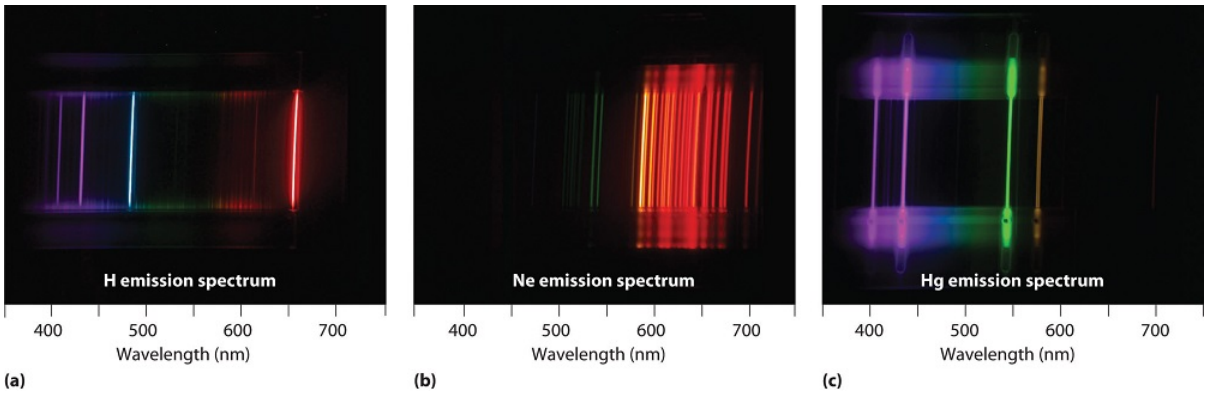


Figure 1.4.3 : The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest lines in the mercury spectrum are at 181 and 254 nm, also in the UV; these are not shown. (CC BY-SA-NC; Anonymous by request).

The Balmer Series of Hydrogen

Obviously, if any pattern could be discerned in the spectral lines for a specific atom (in contract to the mixture that Fraunhofer lines represent), that might be a clue as to the internal structure of the atom. One might be able to build a model. A great deal of effort went into analyzing the spectral data from the 1860's on. The big breakthrough was made by Johann Balmer, a math and Latin teacher at a girls' school in Basel, Switzerland. Balmer had done no physics before and made his great discovery when he was almost sixty.

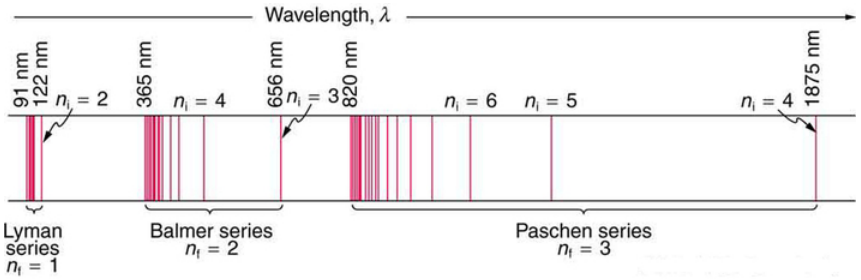


Figure 1.4.4 : A schematic of the hydrogen spectrum shows several series named for those who contributed most to their determination. Part of the Balmer series is in the visible spectrum, while the Lyman series is entirely in the UV, and the Paschen series and others are in the IR. Values of n_f and n_i are shown for some of the lines (CC BY-SA; OpenStax).

Balmer decided that the most likely atom to show simple spectral patterns was the lightest atom, hydrogen. Ångström had measured the four visible spectral lines to have wavelengths 656.21, 486.07, 434.01 and 410.12 nm (Figure 1.4.4). Balmer concentrated on just these four numbers, and found they were represented by the phenomenological formula:

$$\lambda = b\left(\frac{n_2^2}{n_2^2 - 4}\right) \tag{20.8.1}$$

where b = 364.56 nm and $n_2 = 3, 4, 5, 6$.

The first four wavelengths of Equation 20.8.1 (with n_2 = 3, 4, 5, 6) were in excellent agreement with the experimental lines from Ångström (Table 1.4.2). Balmer predicted that other lines exist in the ultraviolet that correspond to $n_2 \geq 7$ and in fact some of them had already been observed, unbeknown to Balmer.

Table 1.4.2 : The Balmer Series of Hydrogen Emission Lines

n_2	3	4	5	6	7	8	9	10
λ	*656*	*486*	*434*	*410*	397	389	383	380
color	*red*	*teal*	*blue*	*indigo*	violet	not visible	not visible	not visible

The n_2 integer in the Balmer series extends theoretically to infinity and the series represents a monotonically increasing energy (and frequency) of the absorption lines with increasing n_2 values. Moreover, the energy difference between successive lines decreased as n_2 increases (1.4.4). This behavior converges to a highest possible energy as Example 1.4.1 demonstrates. If the lines are plot according to their λ on a linear scale, you will get the appearance of the spectrum in Figure 1.4.4 ; these lines are called the **Balmer series**.

Balmer's general formula (Equation 20.8.1) can be rewritten in terms of the inverse wavelength typically called the *wavenumber* ($\tilde{\nu}$).

$$\tilde{\nu} = \frac{1}{\lambda} \tag{20.8.2}$$

$$= R_H\left(\frac{1}{4} - \frac{1}{n_2^2}\right) \tag{20.8.3}$$

where $n_2 = 3, 4, 5, 6$ and R_H is the Rydberg constant (discussed in the next section) equal to 109,737 cm^{-1}.

He further conjectured that the 4 could be replaced by 9, 16, 25, … and this also turned out to be true - but these lines, further into the infrared, were not detected until the early twentieth century, along with the ultraviolet lines.

The Wavenumber as a Unit of Frequency

The relation between wavelength and frequency for electromagnetic radiation is

$$\lambda\nu = c$$

In the SI system of units the wavelength, (λ) is measured in meters (m) and since wavelengths are usually very small one often uses the nanometer (nm) which is 10^{-9} m. The frequency (ν) in the SI system is measured in reciprocal seconds 1/s − which is

called a Hertz (after the discover of the photoelectron effect) and is represented by Hz.

It is common to use the reciprocal of the wavelength in centimeters as a measure of the frequency of radiation. This unit is called a wavenumber and is represented by ($\tilde{\nu}$) and is defined by

$$\begin{aligned}\tilde{\nu} &= \frac{1}{\lambda} \\ &= \frac{\nu}{c}\end{aligned}$$

Wavenumbers is a convenient unit in spectroscopy because it is directly proportional to energy.

$$\begin{aligned}E &= \frac{hc}{\lambda} \\ &= hc \times \frac{1}{\lambda} \\ &= hc\tilde{\nu} \\ &\propto \tilde{\nu}\end{aligned}$$

Example 1.4.1 : Balmer Series

Calculate the longest and shortest wavelengths (in nm) emitted in the Balmer series of the hydrogen atom emission spectrum.

Solution

From the behavior of the Balmer equation (Equation 20.8.1 and Table 1.4.2), the value of n_2 that gives the longest (i.e., greatest) wavelength (λ) is the smallest value possible of n_2, which is (n_2=3) for this series. This results in

$$\begin{aligned}\lambda_{longest} &= (364.56\ nm)\left(\frac{9}{9-4}\right) \\ &= (364.56\ nm)\,(1.8) \\ &= 656.2\ nm\end{aligned}$$

This is also known as the H_α line of atomic hydrogen and is bright red (Figure 20.8.3a).

For the shortest wavelength, it should be recognized that the shortest wavelength (greatest energy) is obtained at the limit of greatest (n_2):

$$\lambda_{shortest} = \lim_{n_2\to\infty}(364.56\ nm)\left(\frac{n_2^2}{n_2^2-4}\right)$$

This can be solved via L'Hôpital's Rule, or alternatively the limit can be expressed via the equally useful energy expression (Equation 20.8.3) and simply solved:

$$\begin{aligned}\tilde{\nu}_{greatest} &= \lim_{n_2\to\infty} R_H\left(\frac{1}{4}-\frac{1}{n_2^2}\right) \\ &= \lim_{n_2\to\infty} R_H\left(\frac{1}{4}\right) \\ &= 27,434\ cm^{-1}\end{aligned}$$

Since $\frac{1}{\tilde{\nu}} = \lambda$ in units of cm, this converts to 364 nm as the shortest wavelength possible for the Balmer series.

The Balmer series is particularly useful in astronomy because the Balmer lines appear in numerous stellar objects due to the abundance of hydrogen in the universe, and therefore are commonly seen and relatively strong compared to lines from other elements.

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SECTION OVERVIEW

20.9: Evidence for Metal-Ligand Covalent Bonding

Topic hierarchy

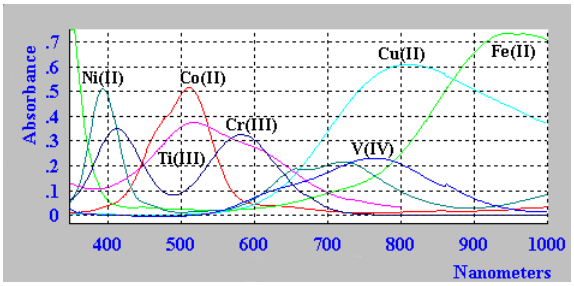
20.9A: The Nephelauxetic Effect

20.9B: EPR Spectroscopy

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20.9A: The Nephelauxetic Effect

The spectra of the aqua ions for some first row transition metal ions are shown below.



For a much more detailed description of the interpretation of the spectra of first row transition metal ion complexes see the notes on the use of Tanabe-Sugano diagrams.

Cr(III) - an example in more detail

For \9d^3\), d^8 octahedral and d^2, d^7 tetrahedral complexes, the above diagrams can be used to interpret the observed electronic absorption spectra.

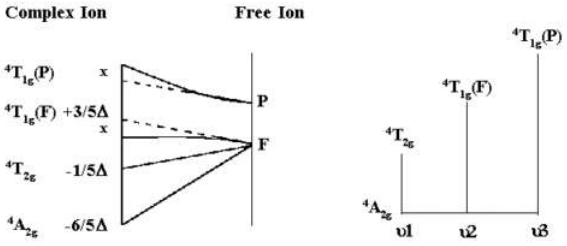


Figure 2

Take for example the Cr^{3+} aquo-ion $[Cr(H_2O)_6]^{3+}$. From the simplified Orgel diagram in Figure 2, three absorptions transitions are expected. In practice, the spectrum is found to contain three bands which occur at 17,000 cm^{-1}, 24,000 cm^{-1} and 37,000 cm^{-1}. Of which only two are shown in Figure 1.

μ_1 corresponds exactly to Δ (Delta) and since the lowest band is found at 17,000 cm^{-1} then this enables us to measure Δ directly from the spectrum.

The next band is found at 24,000 cm^{-1} and this can be equated to:

$$\mu_2 = 9/5\Delta - x \tag{20.9A.1}$$

where x is the *configuration interaction* between the T(F) state and the T(P) state of the same symmetry.

Since Δ is 17,000 and μ2 is observed at 24,000 then x must be 6,600 cm^{-1}.

The last band is seen at 37,000 cm^{-1} and here

$$\mu_3 = 6/5\Delta + 15B + x \tag{20.9A.2}$$

where B is one of the **RACAH parameters**.

Solving Equation 20.9A.2 for B gives a value of $B = 667\,cm^{-1}$.

For the free Cr3+ ion, B is ~1030 cm^{-1} so that in the complex this term is reduced by ~2/3 of the free ion value.

A large reduction in B indicates a strong **Nephelauxetic Effect**. The Nephelauxetic Series is given by:

$$\begin{aligned} F^- > H_2O > \text{urea} > NH_3 > \text{en}\sim\ C_2O_{42}{}^- > NCS^- \\ > Cl^- \quad CN^- > Br^- > S_2{}^- \quad I^- \end{aligned} \tag{20.9A.3}$$

Ionic ligands such as F^- give a small reduction in B, while covalently bonded ligands such as I^- give a large reduction of B.

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20.9B: EPR Spectroscopy

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SECTION OVERVIEW

20.10: Magnetic Properties

Topic hierarchy

20.10A: Magnetic Susceptibility and the Spin-only Formula

20.10B: Spin and Orbital Contributions to the Magnetic Moment

20.10C: The Effects of Temperature on Magnetic Moment

20.10D: Spin Crossover

20.10E: Ferromagnetism, Antiferromagnetism, and Ferrimagnetism

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20.10A: Magnetic Susceptibility and the Spin-only Formula

Complexes that contain unpaired electrons are paramagnetic and are attracted into magnetic fields. Diamagnetic compounds are those with no unpaired electrons are repelled by a magnetic field. All compounds, including transition metal complexes, posses some diamagnetic component which results from paired electrons moving in such a way that they generate a magnetic field that opposes an applied field. The magnitude of paramagnetism is measured in terms of the magnetic moment, μ, where the larger the magnitude of μ, greater the paramagnetism of the compound.

Magnetic Susceptibility

The magnetic susceptibility measures the strength of interaction on placing the substance in a magnetic field. For chemical applications the molar magnetic susceptibility (χ_{mol}) is the preferred quantity and is measured in $m^3 \cdot mol^{-1}$ (SI) or $cm^3 \cdot mol^{-1}$ (CGS) and is defined as

$$\chi_{\text{mol}} = M\chi_v/\rho \tag{20.10.1}$$

where ρ is the density in $kg \cdot m^{-3}$ (SI) or $g \cdot cm^{-3}$ (CGS) and M is molar mass in $kg \cdot mol^{-1}$ (SI) or $g \cdot mol^{-1}$ (CGS). There are multiple methods for measuring magnetic susceptibilities, including, the Gouy, Evans, and Faraday methods. These all depend on measuring the force exerted upon a sample when it is placed in a magnetic field. The more paramagnetic the sample, the more strongly it will be drawn toward the more intense part of the field.

Origin of Paramagnetism

Electrons in most atoms exist in pairs, with each electron spinning in an opposite direction. Each spinning electron causes a magnetic field to form around it. In most materials, the magnetic field of one electron is cancelled by an opposite magnetic field produced by the other electron in the pair. The atoms in materials materials such as iron, cobalt and nickel have unpaired electrons, so they don't cancel the electrons' magnetic fields. As result, each atom of these elements acts like very small magnets.

There are three origins of paramagnetism in complexes:

1. **Nuclear spin** (μ_n)**:** Some nuclei, such as a hydrogen atom, have a net spin, which creates a magnetic field.
2. **Electron spin** (μ_s)**:** An electron has two intrinsic spin states (similar to a top spinning) which we call up (α) and down (β).
3. **Electron orbital motion** (μ_l)**:** There is a magnetic field due to the electron moving around the nucleus.

Each of these magnetic moments interact with one another and/or with external magnetic fields to generate interesting physics. However, some of these interactions are stronger than others and can be (tentatively) ignored. For example, the nuclear spin magnetic moment (#1 above), which is central to NMR spectroscopy, is appreciably weaker than the other two moments and we can ignore it for this discussion and focus on the electronic moments.

The classical theory of magnetism was well developed before quantum mechanics with (see Lenz Law). From a quantum mechanical picture, for an individual electron in a molecule or atom, we can identify the orbital angular momentum l and spin angular momentum s. For multi-electron systems, the total orbital angular momentum (L) and total spin angular momentum (S) are sum of the constituent electron spins.

$$L = l_1 + l_2 + l_3 + ... \tag{20.10.2}$$

and

$$S = s_1 + s_2 + s_3 + ... \tag{20.10.3}$$

The total magnetic susceptibility from both orbital and spin angular momenta is

$$\mu_{L+S} = \sqrt{4S(S+1) + L(L+1)}\,\mu_B \tag{20.10.4}$$

where μ_B is the Bohr Magneton ($9.274 \times 10^{-24} J/T$).

nuclear magneton vs. Bohr magneton

The associated the nuclear magneton μ_N attributed to nuclear spin magnetic moments is ~2000 fold smaller than the Bohr magneton. This is why we can ignore the nuclear spin components for this discussion.

That is, the rotation of electrons about the nucleus is restricted which leads to

$$L = 0 \tag{20.10.5}$$

and

$$\mu_s = \sqrt{4S(S+1)}\,\mu_B \tag{20.10.6}$$

Equation 20.10.3 can be simplified to

$$S = n(1/2) = n/2 \tag{20.10.7}$$

where n is the number of unpaired electrons in the complex. Hence

$$\mu_s = \sqrt{4S(S+1)}\,\mu_B \tag{20.10.8}$$

$$= \sqrt{4(n/2)(n/2+1)}\,\mu_B \tag{20.10.9}$$

$$= \sqrt{n(n+2)}\,\mu_B \tag{20.10.10}$$

Equation 20.10.10 is called *Spin-Only Formula*. For transient metal complexes, the magnetic properties arise primarily from the exposed d-orbitals that are perturbed by ligands. Hence, experimentally measured magnetic moment can provide some important information about the compounds themselves including: (1) number of unpaired electrons present, (2) high-spin vs. low-spin states, (3). spectral behavior, and (4) even structure of the complexes (Table 20.10.1).

Table 20.10.1: Predicted Spin only Magnetic Moment

Ion	Number of unpaired electrons	μ_s	observed moment /μ_B
Ti^{3+}	1	$\sqrt{3} \approx 1.73\,\mu_B$	1.73
V^{4+}	1	$\sqrt{3} \approx 1.73\,\mu_B$	1.68–1.78
Cu^{2+}	1	$\sqrt{3} \approx 1.73\,\mu_B$	1.70–2.20
V^{3+}	2	$\sqrt{8} \approx 2.83\,\mu_B$	2.75–2.85
Ni^{2+}	2	$\sqrt{8} \approx 2.83\,\mu_B$	2.8–3.5
V^{2+}	3	$\sqrt{15} \approx 3.87\,\mu_B$	3.80–3.90
Cr^{3+}	3	$\sqrt{15} \approx 3.87\,\mu_B$	3.70–3.90
Co^{2+}	3	$\sqrt{15} \approx 3.87\,\mu_B$	4.3–5.0
Mn^{4+}	3	$\sqrt{15} \approx 3.87\,\mu_B$	3.80–4.0
Cr^{2+}	4	$\sqrt{24} \approx 4.90\,\mu_B$	4.75–4.90
Fe^{2+}	4	$\sqrt{24} \approx 4.90\,\mu_B$	5.1–5.7
Mn^{2+}	5	$\sqrt{35} \approx 5.92\mu_B$	5.65–6.10
Fe^{3+}	5	$\sqrt{35} \approx 5.92\mu_B$	5.7–6.0

The small deviations from the spin-only formula for these octahedral complexes can result from the neglect of orbital angular momentum or of spin-orbit coupling. Tetrahedral d^3, d^4, d^8 and d^9 complexes tend to show larger deviations from the spin-only

formula than octahedral complexes of the same ion because quenching of the orbital contribution is less effective in the tetrahedral case.

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20.10B: Spin and Orbital Contributions to the Magnetic Moment

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20.10C: The Effects of Temperature on Magnetic Moment

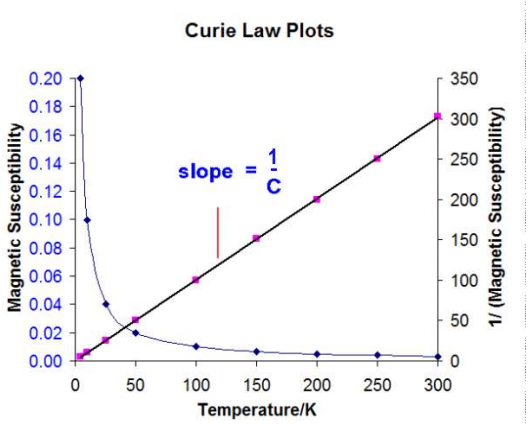
Normal paramagnetic substances obey the **Curie Law**

$$\chi = \frac{C}{T} \tag{20.10.1}$$

where C is the Curie constant. Thus a plot of 1/ χ versus T should give a straight line of slope 1/C passing through the origin (0 K). Whereas many substances do give a straight line it often intercepts just a little above 0 K and these are said to obey the Curie-Weiss Law:

$$\chi = \frac{C}{T + \Phi} \tag{20.10.2}$$

where Φ is known as the Weiss constant.



Quantum Mechanics Approach

A similar expression (where χ is inversely proportional to Temperature) is obtained but now the constant C is given by the **Langevin expression**, which relates the susceptibility to the magnetic moment:

$$\chi_m = \frac{N\mu^2}{3kT} \tag{20.10.3}$$

where

- N is Avogadro's number
- k is the Boltzmann constant and
- T the absolute temperature

rewriting this gives the magnetic moment as

$$\mu = 2.828\sqrt{\chi_m T}B.M. \tag{20.10.4}$$

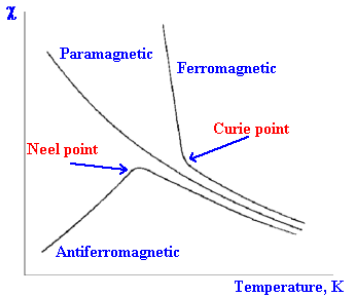
There are two main types of magnetic compounds, those that are diamagnetic (compounds that are repelled by a magnetic field) and those that are paramagnetic (compounds that are attracted by a magnetic field). All substances possess the property of diamagnetism due to the presence of closed shells of electrons within the substance. Note that diamagnetism is a weak effect while paramagnetism is a much stronger effect.

Paramagnetism derives from the spin and orbital angular momenta of electrons. This type of magnetism occurs only in compounds containing unpaired electrons, as the spin and orbital angular momenta is canceled out when the electrons exist in pairs. Compounds in which the paramagnetic centers are separated by diamagnetic atoms within the sample are said to be magnetically dilute.

If the diamagnetic atoms are removed from the system then the paramagnetic centers interact with each other. This interaction leads to ferromagnetism (in the case where the neighboring magnetic dipoles are aligned in the same direction) and antiferromagnetism

(where the neighboring magnetic dipoles are aligned in alternate directions).

These two forms of paramagnetism show characteristic variations of the magnetic susceptibility with temperature.



In the case of ferromagnetism, above the Curie point the material displays "normal" paramagnetic behavior. Below the Curie point the material displays strong magnetic properties.

- Ferromagnetism is commonly found in compounds containing iron and in alloys.
- For antiferromagnetism, above the Neel point the material displays "normal" paramagnetic behavior. Below the Neel point the material displays weak magnetic properties which at lower and lower temperatures can become essentially diamagnetic. Antiferromagnetism is more common and is found to occur in transition metal halides and oxides, such as $TiCl_3$ and VCl_2.

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20.10D: Spin Crossover

Octahedral complexes with between 4 and 7 d electrons can be either high-spin or low-spin depending on the size of Δ When the ligand field splitting has an intermediate value such that the two states have similar energies, then the two states can coexist in measurable amounts at equilibrium. Many "crossover" systems of this type have been studied, particularly for iron complexes.

The change in spin state is a transition from a low spin (LS) ground state electron configuration to a high spin (HS) ground state electron configuration of the metal's d atomic orbitals (AOs), or vice versa. The magnitude of the ligand field splitting along with the pairing energy of the complex determines whether it will have a LS or HS electron configuration. A LS state occurs because the ligand field splitting (Δ) is greater than the pairing energy of the complex (which is an unfavorable process).

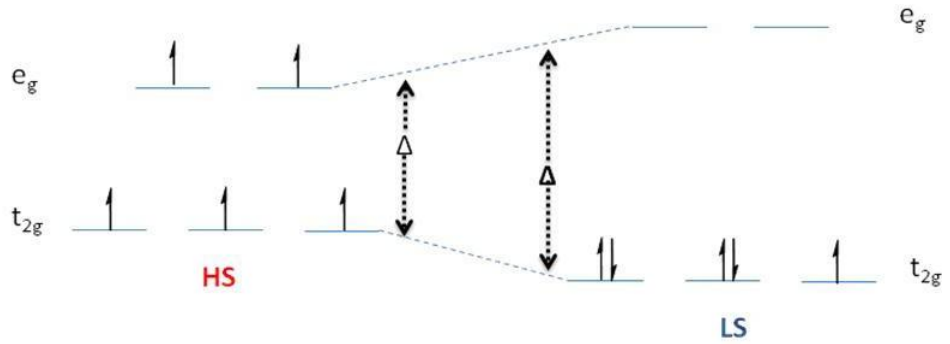
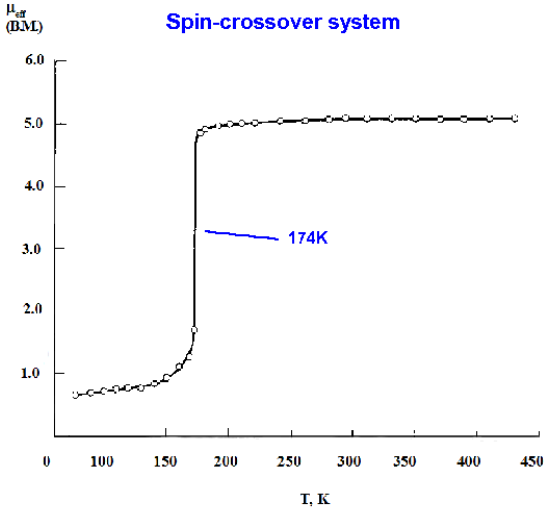


Figure 20.10.1: Diagram illustrating the dependence of the HS or LS state on Δ of the octahedral ligand field splitting and the corresponding electron configuration.

Figure 20.10.1 is a simplified illustration of the metal's d orbital splitting in the presence of an octahedral ligand field. A large splitting between the t_{2g} and e_g AOs requires a substantial amount of energy for the electrons to overcome the energy gap (Δ) to comply with Hund's Rule. Therefore, electrons will fill the lower energy t_{2g} orbitals completely before populating the higher energy e_g orbitals. Conversely, a HS state occurs with weaker ligand fields and smaller orbital splitting. In this case the energy required to populate the higher levels is substantially less than the pairing energy and the electrons fill the orbitals according to Hund's Rule by populating the higher energy orbitals before pairing with electrons in the lower lying orbitals. An example of a metal ion that can exist in either a LS or HS state is Fe^{3+} in an octahedral ligand field. Depending on the ligands that are coordinated to this complex the Fe^{3+} can attain a LS or a HS state, as in Figure 20.10.1.

In the d^6 case of $Fe(phen)_2(NCS)_2$, the crossover involves going from S=2 to S=0.



At the higher temperature the ground state is $^5T_{2g}$ while at low temperatures it changes to $^1A_{1g}$. The changeover is found at about 174 K. In solution studies, it is possible to calculate the heat of conversion from the one isomer to the other.

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20.10E: Ferromagnetism, Antiferromagnetism, and Ferrimagnetism

6.7: Ferro-, ferri- and antiferromagnetism

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SECTION OVERVIEW

20.11: Thermodynamic Aspects - Ligand Field Stabilization Energies (LFSE)

Topic hierarchy

20.11A: Trends in LFSE

20.11B: Lattice Energies and Hydration Energies of \(M^{n+}\) Ions

20.11C: Octahedral Versus Tetrahedral Coordination - Spinels

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20.11A: Trends in LFSE

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20.11B: Lattice Energies and Hydration Energies of $M\ n$ + Ions

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20.11C: Octahedral Versus Tetrahedral Coordination - Spinels

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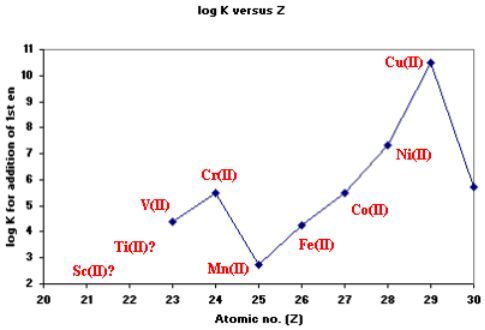
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20.12: Thermodynamic Aspects - The Irving-Williams Series

The general stability sequence of high spin octahedral metal complexes for the replacement of water by other ligands is:

$$\mathrm{Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)}$$

This trend is essentially independent of the ligand. In the case of 1,2-diaminoethane (en), the first step-wise stability constants ($\log K_1$) for M(II) ions are shown below.



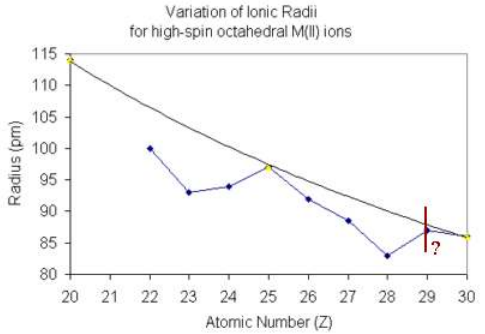
The Irving-Williams sequence is generally quoted ONLY for Mn(II) to Zn(II) since there is little data available for the other first row transition metal ions because their M(II) oxidation states are not very stable. The position of Cu(II) is considered out-of-line with predictions based on Crystal Field Theory and is probably a consequence of the fact that Cu(II) often forms Jahn-Teller distorted octahedral complexes.

One explanation

Crystal Field Theory is based on the idea that a purely electrostatic interaction exists between the central metal ion and the ligands. This suggests that the stability of the complexes should be related to the ionic potential; that is, the **charge to radius ratio**. In the Irving-Williams series, the trend is based on high-spin M(II) ions, so what needs to be considered is how the ionic radii vary across the d-block.

For free metal ions in the gaseous phase it might be expected that the ionic radius of each ion on progressing across the d-block should show a gradual decrease in size. This would come about due to the incomplete screening of the additional positive charge by the additional electron, as is observed in the Lanthanide Contraction.

For high-spin octahedral complexes it is essential to consider the effect of the removal of the degeneracy of the d-orbitals by the crystal field. Here the d-electrons will initially add to the lower t_{2g} orbitals before filling the e_g orbitals since for octahedral complexes, the t_{2g} subset are directed in between the incoming ligands whilst the e_g subset are directed towards the incoming ligands and cause maximum repulsion.



For d^1-d^3 (and d^6-d^8) the addition of the electrons to the t_{2g} orbitals will mean that the screening of the increasing attractive nuclear charge is not very effective and the radius should be smaller than for the free ion.

The position of d^4 and d^9 on the plot is difficult to ascertain with certainty since six-coordinate complexes are expected to be distorted due to the Jahn-Teller Theorem. Cr(II) is not very stable so few measurements are available. For Cu(II) however, most complexes are found to have 4 short bonds and 2 long bonds although 2 short and 4 long bonds is feasible. The radii are expected to show an increase over the d^3 and d^8 situation since electrons are being added to the e_g subset. The reported values have been found to lie on both sides of the predicted value.

For d^0, d^5 and d^{10} the screening expected is essentially that of a spherical arrangement equivalent to the absence of a crystal field. The plot above shows that these points return to the line drawn showing a gradual decrease of the radius on moving across the d-block.

Once the decrease in radius with Z pattern is understood, it is a small step to move to a pattern for q/r since this only involves taking the reciprocal of the radius and holding the charge constant. The radius essentially decreases with increasing Z, therefore 1/r must increase with increasing Z.

For the sequence Mn(II) to Zn(II), the crystal field (q/r) trend expected would be

$$\mathrm{Mn(II)} < \mathrm{Fe(II)} < \mathrm{Co(II)} < \mathrm{Ni(II)} > \mathrm{Cu(II)} > \mathrm{Zn(II)}$$

Apart from the position of Cu(II), this corresponds to the Irving-Williams series (Eqution 1). The discrepancy is once again accounted for by the fact that copper(II) complexes are often distorted or not octahedral at all. When this is taken into consideration, it is seen that the Irving-Williams series can be explained quite well using Crystal Field Theory.

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

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20.13: Thermodynamic Aspects - Oxidation States in Aqueous Solutions

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21.1: Introduction

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21.2: Occurrence, Extraction, and Uses

Occurrence

Manganese is the 12th most abundant element and 3rd most abundant transition metal (cf. Fe, Ti). A number of forms of manganese occur in nature (~ 300 minerals) giving an overall abundance of 0.106%. 12 of these minerals are economically viable including: pyrolusite (MnO_2), manganite ($Mn_2O_3.H_2O$), hausmannite (Mn_3O_4) rhodochrosite ($MnCO_3$) and Mn-nodules. The main deposits are found in South Africa and the Ukraine (> 80%) and other important manganese deposits are in China, Australia, Brazil, Gabon, India, and Mexico.

Extraction

The metal is obtained by reduction with Al, or in a Blast furnace. The metal resembles iron in being moderately reactive and at high temperatures reacts vigorously with a range of non-metals. For example it burns in N_2 at 1200 °C to form Mn_3N_2 and roasting in air gives Mn_3O_4

Uses

85-90% of the Manganese produced goes in to the fabrication of ferromanganese alloys. The 1 and 2 Euro coins contain manganese since there it is more abundant and cheaper than nickel. Manganese dioxide has been used in the cathodes of dry cell batteries and is used in newer alkaline batteries as well. Manganese salts have been used in glass making since the Eygyptian and Roman times and found in paints from as early as 17,000 years ago. Its use in glass is either to add color or to reduce the effect iron impurities have on the color of glass, see below.

Manganese in Biology

Manganese is an essential trace element for all forms of life. It accumulates in mitochondria and is essential for their function. The manganese transport protein, transmanganin, is thought to contain Mn(III). Several metalloenzymes are known: arginase, pyruvate carboxylase and superoxide dismutase. Humans excrete roughly 10 kg of urea per year, this results from the hydrolysis of arginine by the enzyme arginase found on the liver which is the final step of the urea cycle. This reaction allows for the disposal of nitrogenous waste from the breakdown of proteins.

In mammalian arginases I and II, binuclear manganese clusters are present at the active site. In the structure 1rla the Manganese nearest neighbours were identifed as: Asp124, Asp128, Asp232, Asp234, His101, His126.

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21.3: Physical Properties - An Overview

Now given in more detail in individual pages covering each Transition Metal

Ti	V	Cr	Mn	Fe	Co	Ni	Cu

Halides

Titanium

Titanium(IV) Halides

Formula	Color	MP	BP	Structure
TiF_4	white	-	284	fluoride bridged
$TiCl_4$	Colorless	-24	136.5	-
$TiBr_4$	yellow	38	233.5	hcp I- but essentially monomeric cf. SnI_4
TiI_4	violet-black	155	377	hcp I- but essentially monomeric cf. SnI_4

Preparations:

They can all be prepared by direct reaction of Ti with halogen gas (X_2). All are readily hydrolysed.
They are all expected to be diamagnetic.

Titanium(III) halides

Formula	Color	MP	BP	μ (BM)	Structure
TiF_3	blue	950d	-	1.75	-
$TiCl_3$	violet	450d	-	-	BiI_3
$TiBr_3$	violet	-	-	-	BiI_3
TiI_3	violet-black	-	-	-	-

Preparations:

They can be prepared by reduction of TiX_4 with H_2.

Vanadium

Vanadium(V) halides

Formula	Color	MP	BP	μ (BM)	Structure
VF_5	white	19.5	48.3	0	trigonal bipyramid in gas phase

Preparations:

Prepared by reaction of V with F_2 in N_2 or with BrF_3 at 300C.
In the solid state it is an infinite chain polymer with *cis*-fluoride bridging.

Vanadium(IV) halides

Formula	Color	MP	BP	μ (BM)	Structure
VF_4	lime-green	100 [a]	-	1.68	-
VCl_4	red-brown	-25.7	148	1.61	tetrahedral (monomeric)
VBr_4	purple	-23d	-	-	-

[a] sublimes with decomposition at 100 C.

Preparations:

VCl_4 is prepared by reaction of V with chlorinating agents such as Cl_2, $SOCl_2$, $COCl_2$ etc.
Reaction of VCl_4 with HF in CCl_3F at -78C gives VF_4.

Chromium

Chromium(III) halides

Formula	Color	MP	M-X (pm)	μ (BM) [b]	Structure
CrF_3	green	1404	190	-	-
$CrCl_3$	red-violet	1152	238	-	$CrCl_3$
$CrBr_3$	green-black	1130	257	-	BiI_3
CrI_3	black	>500d	-	-	-

[b] all 3.7-4.1 BM.

Preparations:

CrX_3 are prepared from Cr with X_2, dehydration of $CrCl_3.6H_2O$ requires $SOCl_2$ at 650C.

Chromium(II) halides

Formula	Color	MP	μ (BM)	Structure
CrF_2	green	894	4.3	distorted rutile
$CrCl_2$	white	820-824	5.13	distorted rutile
$CrBr_2$	white	844	-	-
CrI_2	red-brown	868	-	-

Preparations:

Reduction of CrX_3 with H_2/HX gives CrX_2.

Manganese

Manganese(II) halides

Formula	Color	MP	BP	μ (BM)	Structure
MnF_2	pale-pink	920	-	-	rutile
$MnCl_2$	pink	652	1190	5.73	$CdCl_2$
$MnBr_2$	rose	695	-	5.82	-
MnI_2	pink	613	-	5.88	CdI_2

Preparations:

Prepared from $MnCO_3$ + HX -> MnX_2 + CO_2 + H_2O

Iron

Iron(III) halides

Formula	Color	MP	Structure
FeF_3	green	1000 sublimes	-
$FeCl_3$	black	306 sublimes	BiI_3
$FeBr_3$	dark-red-brown	-	BiI_3

Preparations:

Prepared by reaction of Fe + X_2 -> FeX_3.
Note that $FeBr_3$.aq when boiled gives $FeBr_2$.

Iron(II) halides

Formula	Color	MP	BP	Structure
FeF_2	white	1000	1100	rutile
$FeCl_2$	pale yellow-grey	670-674	-	$CdCl_2$
$FeBr_2$	yellow-green	684	-	CdI_2
FeI_2	grey	red heat	-	CdI_2

Preparations:

Fe +HX at red heat -> FeX_2 for X=F,Cl and Br
Fe + I_2 -> FeI_2

Cobalt

Cobalt(II) halides

Formula	Color	MP	μ (BM)	Structure
CoF_2	pink	1200	-	rutile
$CoCl_2$	blue	724	5.47	$CdCl_2$
$CoBr_2$	green	678	-	CdI_2
CoI_2	blue-black	515	-	CdI_2

Preparations:

Co or $CoCO_3$ + HX -> CoX_2.aq -> CoX_2

Nickel

Nickel(II) halides

Formula	Color	MP	μ (BM)	Structure
NiF_2	yellow	1450	2.85	tetragonal rutile
$NiCl_2$	yellow	1001	3.32	$CdCl_2$
$NiBr_2$	yellow	965	3.0	$CdCl_2$
NiI_2	Black	780	3.25	$CdCl_2$

Preparations:

$Ni + F_2$ 55 C /slow -> NiF_2
$Ni + Cl_2$ EtOH/ 20 C -> $NiCl_2$
$Ni + Br_2$ red heat -> $NiBr_2$
$NiCl_2 + 2NaI -> NiI_2 + 2NaCl$

Copper

Copper(II) halides

Formula	Color	MP	BP	μ (BM)	Structure
CuF_2	white	950d	-	1.5	
$CuCl_2$	brown	632	993d	1.75	$CdCl_2$
$CuBr_2$	black	498	-	1.3	

Preparations:

Copper(II) halides are moderate oxidising agents due to the Cu(I)/ Cu(II) couple. In water, where the potential is largely that of the aquo-complexes, there is not a great deal of difference between them, but in non-aqueous media, the oxidising (halogenating) power increases in the sequence: $CuF_2 << CuCl_2 << CuBr_2$.

$Cu + F_2 -> CuF_2$
$Cu + Cl_2$ 450 C -> $CuCl_2$
$Cu + Br_2 -> CuBr_2$
or from CuX_2.aq by heating -> CuX_2

Copper(I) halides

Formula	Color	MP	BP	Structure
CuCl	white	430	1359	-
CuBr	white	483	1345	-
CuI	white	588	1293	Zinc Blende

Preparations:

Reduction of CuX_2 -> CuX except for F which has not been obtained pure.
Note that $Cu(II)I_2$ can not be isolated due reduction to CuI.

Oxides and Aquo Species

Titanium

Titanium oxides

Formula	Color	MP	μ (BM)	Structure
TiO_2	white	1892	diam.	rutile - Refractive Index 2.61-2.90 cf. Diamond 2.42

Preparations:

obtained from hydrolysis of TiX_4 or Ti(III) salts.

TiO_2 reacts with acids and bases.
In Acid:
$TiOSO_4$ formed in H_2SO_4 (Titanyl sulfate)
In Base:
$MTiO_3$ metatitanates (eg Perovskite, $CaTiO_3$ and ilmenite, $FeTiO_3$)
M_2TiO_4 orthotitanates.

Peroxides are highly Colored and can be used for Colorimetric analysis.
pH <1 $[TiO_2(OH)(H_2O)x]+$
pH 1-2 $[(O_2)Ti\text{-}O\text{-}Ti(O_2)](OH)_x^{2-x}$; x=1-6

$[Ti(H_2O)_6]^{3+}$ -> $[Ti(OH)(H_2O)_5]^{2+}$ + [H+] pK=1.4
$TiO^{2+} + 2H^+ + e^-$ -> $Ti^{3+} + H_2O$ E=0.1V

Vanadium

Vanadium oxides

Formula	Color	Common name	Oxidation State	MP	V-O distance (pm)
V_2O_5	brick-red	pentoxide	V^{5+}	658	158.5-202
V_2O_4	blue	dioxide	V^{4+}	1637	176-205
V_2O_3	grey-black	sesquioxide	V^{3+}	1967	196-206

Preparations:
V_2O_5 is the final product of the oxidation of V metal, lower oxides etc.

Aqueous Chemistry very complex:

In alkaline solution,

$$VO_4^{3-} + H^+ \rightarrow HVO_4^{2-}$$
$$2HVO_4^{2-} \rightarrow V_2O_7^{4-} + H_2O$$
$$HVO_4^{2-} + H^+ \rightarrow H_2VO_4^-$$
$$3H_2VO_4^- \rightarrow V_3O_9^{3-} + 3H_2O$$
$$4H_2VO_4^- \rightarrow V_3O_{12}^{4-} + 4H_2O$$

In acidic solution,

$$10V_3O_9^{3-} + 15H^+ \rightarrow 3HV_{10}O_{28}^{5-} + 6H_2O$$
$$H_2VO_4^- + H^+ \rightarrow H_2VO_4$$
$$HV_{10}O_{28}^{5-} + H^+ \rightarrow H_2V_{10}O_{28}^{4-}$$
$$H_3VO_4 + H^+ \rightarrow VO_2^+ + 2H_2O$$
$$H_2V_{10}O_{28}^{4-} + 14H^+ \rightarrow 10VO_2^+ + 8H_2O$$

$VO(H_2O)_4SO_4$

The crystal structure of this salt was first determined in 1965. The V=O bond length was 159.4 pm, the aquo group trans to this had the longest V-O bond length (228.4pm) and the equatorial bond lengths were in the range 200.5-205.6 pm. Note that SO_4^{2-} was coordinated in an equatorial position.

The IR stretching frequency for the V=O in vanadyl complexes generally occurs at 985 +/- 50 cm^{-1}.

Redox properties of oxovanadium ions:

> $VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O \quad E=1.0v$
>
> $VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O \quad E=0.34V$

Chromium

Chromium oxides

Formula	Color	Oxidation State	MP
CrO_3	deep red	Cr^{6+}	197d
Cr_3O_8	-	intermediate	-
Cr_2O_5	-	-	-
Cr_5O_{12} etc	-	-	-
CrO_2	brown-black	Cr^{4+}	300d
Cr_2O_3	green	Cr^{3+}	2437

Dichromate and chromate equilibria is pH dependent:

> $HCrO_4^- \rightarrow CrO_4^{2-} + H^+ \quad K=10^{-5.9}$
> $H_2CrO_4 \rightarrow HCrO_4^- + H^+ \quad K=10^{+0.26}$
>
> $Cr_2O_7^{2-} + H_2O \rightarrow 2HCrO_4^- \quad K=10^{-2.2}$
> $HCr_2O_7^- \rightarrow Cr_2O_7^{2-} + H^+ \quad K=10^{+0.85}$

CrO_3

> *pH > 8 CrO_4^{2-} yellow*
> *2-6 $HCrO_4^-$ & $Cr_2O_7^{2-}$ orange-red*
> *< 1 $H_2Cr_2O_7$*
>
> $[Cr(H_2O)_6]^{3+} \rightarrow [Cr(H_2O)_5(OH)]^{2+} \rightarrow [(H_2O)_4Cr\ Cr(H_2O)_4]^{4+}$ *pK=4 etc.*

Manganese

Manganese oxides

Formula	Color	Oxidation State	MP
Mn_2O_7	green oil	Mn^{7+}	5.9
MnO_2	black	Mn^{4+}	535d
Mn_2O_3	black	Mn^{3+}	1080d
Mn_3O_4 - Haussmanite	black	$Mn^{2/3+}$	1705
MnO	grey-green	Mn^{2+}	1650

Preparations:

Mn_3O_4 is prepared from the other oxides by heating in air. MnO is prepared from the other oxides by heating with H_2 at temperatures below 1200 C

Redox properties of $KMnO_4$.

```
strong base
MnO4- + e-      →  MnO4 2-      E=0.56V (RAPID)
MnO4 2-  + 2H2O  + e-  →  MnO2  + 4OH-  E=0.60V (SLOW)
moderate base
MnO4- + 2H2O  + 3e- →  MnO2  + 4OH-    E=0.59V
dil. H2SO4
MnO4- + 8H2O  + 5e- →  Mn2+  + 4H2O    E=1.51V
```

Iron

Iron oxides

Formula	Color	Oxidation State	MP	Structure / comments
Fe_2O_3	red brown	Fe^{3+}	1560d	α-form Haematite, β-form used in cassettes
Fe_3O_4	black	$Fe^{2+/3+}$	1538d	magnetite/lodestone
FeO	black	Fe^{2+}	1380	pyrophoric

Preparations:
α-Fe_2O_3 is obtained by heating alkaline solutions of Fe(III) and dehydrating the solid formed.

```
FeO,Fe3O4, γ-Fe2O3 ccp
α-Fe2O3   hcp
```

The Fe(III) ion is strongly acidic:

```
[Fe(H2O)6]3+    + H2O   -> [Fe(H2O)5(OH)]2+ + H3O+   K=10-3.05
[Fe(OH)(H2O)5]2+ +  H2O -> [Fe(OH)2(H2O)4]+ + H3O+   K=10-3.26
```

olation

```
2Fe(H2O)6 3+ + 2H2O  ->  [Fe2(OH)2(H2O)8]4+ + 2H3O+   K=10-2.91
```

The Fe^{2+} ion is barely acidic:

$Fe(H_2O)_6^{2+} + H_2O \rightarrow [Fe(OH)(H_2O)_5]^+ + H_3O+ \quad K=10\text{-}9.5$

The Redox chemistry of Iron is pH dependent:

$Fe(H_2O)_6^{3+} + e- \rightarrow Fe(H_2O)_6^{2+} \quad E=0.771V$

$E=E-RT/nF \ \ Ln[Fe^{2+}]/[Fe^{3+}]$
at precipitation
$[Fe^{2+}].[OH-]^2 \sim 10^{-14}$
$[Fe^{3+}].[OH-]^3 \sim 10^{-36}$

or for OH- =1M then $[Fe^{2+}]/[Fe^{3+}] = 10^{22}$

$E = 0.771 - 0.05916 \log10(10^{22})$
$= 0.771 - 1.301$
$= -0.530v$

thus in base the value of E is reversed and the susceptibility of Fe^{2+} to oxidation increased. In base it is a good reducing agent and will reduce Cu(II) to Cu(0) etc. Note the implications for rust treatment.

Cobalt

Cobalt oxides

Formula	Color	Oxidation State	MP	Structure / comments
Co_2O_3		Co^{3+}		
Co_3O_4	black	$Co^{2+/3+}$	900-950d	normal spinel
CoO	olive green	Co^{2+}	1795	NaCl -antiferromag. < 289 K

Preparations:

Co_2O_3 is formed from oxidation of $Co(OH)_2$.
CoO when heated at 600-700 converts to Co_3O_4
Co_3O_4 when heated at 900-950 reconverts back to CoO.

no stable $[Co(H_2O)_6]^{3+}$ or $[Co(OH)_3$ exist.
$[Co(H_2O)_6]^{2+}$ not acidic

Nickel

Nickel oxides

Formula	Color	Oxidation State	MP	Structure / comments
NiO	green powder	Ni^{2+}	1955	NaCl

thermal decomposition of $Ni(OH)_2$, $NiCO_3$, or $NiNO_3$ gives NiO.
$[Ni(H_2O)_6]^{2+}$ not acidic

Copper

Copper oxides

Formula	Color	Oxidation State	MP
CuO	black	Cu^{2+}	1026d
Cu_2O	red	Cu^{+}	1230

$[Cu(H_2O)_6]^{2+}$ not acidic

Preparations:

Cu_2O is prepared from thermal decomposition of $CuCO_3$, $Cu(NO_3)_2$ or $Cu(OH)_2$. The Fehling's test for reducing sugars also gives rise to red Cu_2O. It is claimed that 1 mg of dextrose produces sufficient red Color for a positive test.

The Redox chemistry of Copper:

$$Cu^{2+} + e^- \rightarrow Cu^{+} \quad E=0.15V$$
$$Cu^{+} + e^- \rightarrow Cu \quad E=0.52V$$
$$Cu^{2+} + 2e^- \rightarrow Cu \quad E=0.34V$$

By consideration of this data, it will be seen that any oxidant strong enough to covert Cu to Cu^{+} is more than strong enough to convert Cu^{+} to Cu^{2+} (0.52 cf 0.14V). It is not expected therefore that any stable Cu^{+} salts will exist in aqueous solution.
Disproportionation can also occur:

$$2Cu^{+} \rightarrow Cu^{2+} + Cu \quad E=0.37V \text{ or } K=10^6$$

Representative Coordination Complexes

Titanium

$TiCl_4$ is a good Lewis acid and forms adducts on reaction with Lewis bases such as;

$$2PEt_3 \rightarrow TiCl_4(PEt_3)_2$$
$$2MeCN \rightarrow TiCl_4(MeCN)_2$$
$$bipy \rightarrow TiCl_4(bipy)$$

Solvolysis can occur if ionisable protons are present in the ligand;

$$2NH_3 \rightarrow TiCl_2(NH_2)_2 + 2HCl$$
$$4H_2O \rightarrow TiO_2.aq + 4HCl$$
$$2EtOH \rightarrow TiCl_2(OEt)_2 + 2HCl$$

$TiCl_3$ has less Lewis acid strength but can form adducts also;

$$3pyr \rightarrow TiCl_3pyr_3$$

Vanadium

The Vanadyl ion (eg. from $VO(H_2O)_4SO_4$ retains the V=O bond when forming complexes.

$$VO^{2+} + 2acac \rightarrow VO(acac)_2$$

Vanadyl complexes are often 5 coordinate square pyramidal and are therefore coordinately unsaturated. They can take up another ligand to become octahedral, eg;

$$VO(acac)_2 + pyr \rightarrow VO(acac)_2pyr$$

The V=O stretching frequency in the IR can be monitored to see the changes occurring during these reactions. It generally is found at 985 cm^{-1} but will shift to lower wavenumbers when 6-coordinate, since the bond becomes weaker.

Chromium

The Chromium(III) ion forms many stable complexes which being inert are capable of exhibiting various types of isomerism. "$CrCl_3.6H_2O$" exists as hydrate isomers, including:

$$trans\text{-}[Cr(H_2O)_4Cl_2]Cl.2H_2O \text{ etc}$$

$CrCl_3$ anhydrous reacts with pyridine only in the presence of Zinc powder. This allows a small amount of Cr(II) to be formed, which is very labile.

$$CrCl_3 + pyr/Zn \rightarrow CrCl_3pyr_3$$

$[Cr_2(OAc)_4].2H_2O$ is an example of a Cr(II) complex which is reasonably stable in air once isolated. Each Cr(II) ion has 4 d electrons but the complex is found to be diamagnetic which is explained by the formation of a quadruple bond between the two metal ions. The Cr-Cr bond distance in a range of these quadruply bonded species has been found to vary between 195-255 pm.

Manganese

Octahedral complexes of Mn(III) are expected to show Jahn-Teller distortions. It was of interest therefore to compare the structures of $Cr(acac)_3$ with $Mn(acac)_3$ since the Cr(III) ion is expected to give a regular octahedral shape. In fact the Mn-O bond distances were all found to be equivalent.

An unusual Mn complex is obtained by the reaction of $Mn(OAc)_2$ with $KMnO_4$ in HOAc. This gives $[MnO(OAc)_6\ 3H_2O]$ OAc. It is used as an industrial oxidant for the conversion of toluene to phenol.

Iron

An important Fe complex which is used in Actinometry since it is photosensitive is $K_3[Fe(C_2\ O_4)_3.3H_2O$.
It can be prepared from:
$Fe(C_2O_4)$ in $K_2C_2O_4$ by reacting with H_2O_2 in $H_2C_2O_4$ to give green crystals. It is high spin m =5.9 BM at 300K and has been resolved into its two optical isomers, although they racemise in less than 1 hour.

In light the reaction is:

$$K_3Fe(C_2O_4)3.3H_2O \rightarrow 2Fe(C_2O_4) + 2CO_2 +$$

Another important complex is used as a redox indicator since the Fe(II) and Fe(III) complexes are both quite stable and have different Colors:

$$Fe(phen)_33+ + e- \rightarrow Fe(phen)_32+ \quad E=1.12V$$
$$\text{blue} \qquad\qquad \text{red}$$

The ligand is 1,10 phenanthroline and the indicator is called ferroin.

Cobalt

The Cobalt(III) ion forms many stable complexes, which being inert, are capable of exhibiting various types of isomerism. The preparation and characterisation of many of these complexes dates back to the pioneering work of Werner and his students.
Coordination theory was developed on the basis of studies of complexes of the type:

Werner Complexes

$[Co(NH_3)_6]Cl_3$	yellow
$[CoCl(NH_3)_5]Cl_2$	red
trans-$[CoCl_2(NH_3)_4]Cl$	green
cis-$[CoCl_2(NH_3)_4]Cl$	purple

Another important complex in the history of coordination chemistry is HEXOL. This was the first complex that could be resolved into its optical isomers that did not contain Carbon atoms. Since then, only three or four others have been found.

An interesting complex which takes up O_2 from the air reversibly is Cosalen. This has been used as an emergency oxygen carrier in jet aircraft.

Nickel

The Nickel(II) ion forms many stable complexes. Whilst there are no other important oxidation states to consider, the Ni(II) ion can exist in a wide variety of CN's which complicates its coordination chemistry.
For example, for CN=4 both tetrahedral and square planar complexes can be found,
for CN=5 both square pyramid and trigonal bipyramid complexes are formed.
The phrase "anomalous nickel" has been used to describe this behaviour and the fact that equilibria often exist between these forms.
Some examples include:
(a) addition of ligands to square planar complexes to give 5 or 6 coordinate species
(b) monomer/polymer equilibria
(c) square-planar/ tetrahedron equilibria
(d) trigonal-bipyramid/ square pyramid equilibria.

- (a) substituted acacs react with Ni^{2+} to give green dihydrates (6 Coord) by heating the waters are removed to give tetrahedral species. The unsubstituted acac complex, $Ni(acac)_2$ normally exists as a trimer.
  Lifschitz salts containing substituted ethylenediamines can be isolated as either 4 or 6 coordinate species depending on the presence of coordinated solvent.
- (b) $Ni(acac)_2$ is only found to be monomeric at temperatures around 200 C in non-coordinating solvents such as n-decane. 6-coordinate monomeric species are formed at room temperature in solvents such as pyridine but in the solid state $Ni(acac)_2$ is a trimer, where each Ni atom is 6-coordinate. Note that $Co(acac)_2$ actually exists as a tetramer.
- (c) Complexes of the type NiL_2X_2 where L are phosphines can give rise to either tetrahedral or square planar complexes. It has been found that:

$L=P(aryl)_3$	are tetrahedral
$L=P(alkyl)_3$	are square planar

L= mixed aryl and alkyl phosphines, both stereochemistries can occur in the same crystalline substance. The energy of activation for conversion of one form to the other has been found to be around 50 kJ mol^{-1}. Similar changes have been observed with variation of the X group:

$Ni(PPh_3)_2Cl_2$	green	tetrahedral	μ = 2.83 BM
$Ni(PPh_3)_2(SCN)_2$	red	sq. planar	μ = 0.

Ni^{2+} reacts with CN- to give $Ni(CN)_2.nH_2O$ (blue-green) which on heating at 180-200 is dehydrated to yield $Ni(CN)_2$. Reaction with excess KCN gives $K_2Ni(CN)_4.H_2O$ (orange crystals) which can be dehydrated at 100C. Addition of strong concentrations of KCN produces red solutions of $[Ni(CN)_5]^{3-}$.

The crystal structure of the double salt prepared by addition of $[Cr(en)_3]^{3+}$ to $[Ni(CN)_5]^{3-}$ showed that two types of Ni stereochemistry were present in the crystals in approximately equal proportions;
50% as square pyramid and 50% as trigonal bipyramid .

Copper

The Copper(II) ion forms many stable complexes which are invariably described as either 4 coordinate or distorted 6 coordinate species.
$Cu(OH)_2$ reacts with NH_3 to give a solution which will dissolve cellulose. This is exploited in the industrial preparation of Rayon. The solutions contain tetrammines and pentammines. With pyridine, only tetramines are formed eg $Cu(py)_4\ SO_4$.
A useful reagent for the analytical determination of Cu^{2+} is the sodium salt of N,N-diethyldithiocarbamate. In dilute alcohol solutions, the presence of trace levels of Cu^{2+} is indicated by a yellow Color which can be measured by a spectrometer and the concentration determined from a Beer's Law plot. The complex is $Cu(Et_2dtc)_2$ which can be isolated as a brown solid.

Contributors and Attributions

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Transition Metal Oxides

The **high oxidation state oxides** are good oxidising agents with $V_2O_5 < CrO_3 < Mn_2O_7$ becoming progressively more acidic as well.

Mixed oxidation state species M(II)M(III) $_2O_4$ are formed by a number of elements, many of which adopt the spinel structure. The Normal Spinel structure, named after a mineral form of $MgAl_2O_4$ and of generic formula AB_2O_4 may be approximated as a cubic close packed lattice of oxide ions with one-eighth of the tetrahedral holes occupied by the A(II) ions and one-half of the octahedral holes occupied by the B(III) ions. Closely related is the Inverse Spinel structure where there is a site change between the A(II) ions and half of the B(III) ions. Given the fact that this occurs, it is evident that the energy factors directing the two different ions to the different sites are not overwhelmingly large, and it is not surprising that such structures are highly susceptible to defects in actual crystals. One factor that may influence this site selectivity is the crystal field stabilisation energy of transition metal ions.

Another ternary oxide structural type that is found is perovskite ($CaTiO_3$). Again, the oxygens can be considered as cubic close packed.

All the elements from Ti to Fe give stable M_2O_3 oxides with corundum-type structures. These oxides are all ionic and predominantly basic. In air the M_2O_3 is the most stable oxide for Cr, Mn and Fe.

Dioxides-The elements Ti,V,Cr and Mn give MO_2 oxides with rutile or distorted rutile structures. Note that CrO_2 is ferromagnetic and used in the production of magnetic tapes.

All of the 3d elements from Ti to Cu form a **monoxide**, either by direct combination of the elements or by reduction of a higher oxide by the metal. Most of these have the NaCl structure and are basic. With the exception of TiO, they all dissolve in mineral acids to give stable salts or complexes of M^{2+} ions. The Ti^{2+} ion liberates hydrogen from aqueous acid and so dissolution of TiO gives Ti^{3+} and hydrogen.

The monoxides show a variety of physical properties. Thus Ti and V are quasi-metallic, CrO is marginal but Mn to Cu are typical ionic insulators (or more precisely, semiconductors).

Summary of ionic lattice structures

Fraction of holes occupied by cations	Sequence of close packed anionic layers		Formula	CN of M and X
	hcp (ABAB..)	ccp (ABCABC..)		
all octahedral	NiAs	NaCl	MX	6:6
1/2 octahedral - all in alternate layers	CdI_2	$CdCl_2$	MX_2	6:3
1/3 octahedral - 2/3 in alternate layers	BiI_3	$CrCl_3$	MX_3	6:2
1/2 tetrahedral	ZnS - wurtzite	ZnS - zinc blende	MX	4:4
all tetrahedral	-	CaF_2- fluorite	MX_2	8:4

For further details on the structures of some of these salts see The Virtual Museum of Minerals and Molecules.

Contributors and Attributions

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SECTION OVERVIEW

21.4: Group 3 - Scandium

Topic hierarchy

21.4A: Scandium Metal

21.4B: Scandium(III)

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21.4A: Scandium Metal

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SECTION OVERVIEW

21.5: Group 4 - Titanium

Topic hierarchy

21.5A: Titanium Metal

21.5B: Titanium(IV)

21.5C: Titanium(III)

21.5D: Low Oxidation States

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21.5A: Titanium Metal

The discovery of titanium in 1791 is attributed to William Gregor, a Cornish vicar and amateur chemist. He isolated an impure oxide from ilmenite ($FeTiO_3$) by treatment with HCl and H_2SO_4. Titanium is the second most abundant transition metal on Earth (6320 ppm) and plays a vital role as a material of construction because of its: Excellent Corrosion Resistance, High Heat Transfer Efficiency, and Superior Strength-To-Weight Ratio. For example, when it's alloyed with 6% aluminum and 4% vanadium, titanium has half the weight of steel and up to four times the strength.

While a biological function in man is not known, it has excellent biocompatibility--that is the ability to be ignored by the human body's immune system--and an extreme resistance to corrosion. Titanium is now the metal of choice for hip and knee replacements.

Properties of titanium

Extraction of Titanium - the Kroll process

Wilhelm J. Kroll (Born November 24, 1889 - Died March 30, 1973) developed the process in Luxemburg around the mid 1930's and then after moving to the USA extended it to enable the extraction of Zirconium as well.

Titanium ores, mainly rutile (TiO_2) and ilmentite ($FeTiO_3$), are treated with carbon and chlorine gas to produce titanium tetrachloride.

$$\mathrm{TiO_2 + Cl_2 \ \rightarrow TiCl_4 + CO_2} \tag{21.5A.1}$$

Fractionation

Titanium tetrachloride is purified by distillation (BP 136.4) to remove iron chloride.

Reduction

Purified titanium tetrachloride is reacted with molten magnesium under argon to produce a porous “titanium sponge”.

$$\mathrm{TiCl_4 + 2\,Mg \longrightarrow Ti + 2\,MgCl_2} \tag{21.5A.2}$$

Melting

Titanium sponge is melted under argon to produce ingots.

The Kroll process (ISIS Draw .skc file)

Titanium Halides

Titanium(IV) Halides

Formula	Color	MP	BP	Structure
TiF_4	white	-	284	fluoride bridged
$TiCl_4$	Colorless	-24	136.4	-
$TiBr_4$	yellow	38	233.5	hcp I- but essentially monomeric cf. SnI_4
TiI_4	violet-black	155	377	hcp I- but essentially monomeric cf. SnI_4

Preparations:

They can all be prepared by direct reaction of Ti with halogen gas (X_2). All are readily hydrolysed.
They are all expected to be diamagnetic.

Titanium(III) halides

Formula	Color	MP	BP	m (BM)	Structure
TiF_3	blue	950d	-	1.75	-
$TiCl_3$	violet	450d	-	-	BiI_3
$TiBr_3$	violet	-	-	-	BiI_3
TiI_3	violet-black	-	-	-	-

Preparations:

They can be prepared by reduction of TiX_4 with H_2.

Titanium Oxides and Aqueous Chemistry

Titanium oxides

Formula	Color	MP	m (BM)	Structure
TiO_2	white	1892	diam.	rutile - Refractive Index 2.61-2.90 cf. Diamond 2.42

Preparations:

obtained from hydrolysis of TiX_4 or Ti(III) salts.

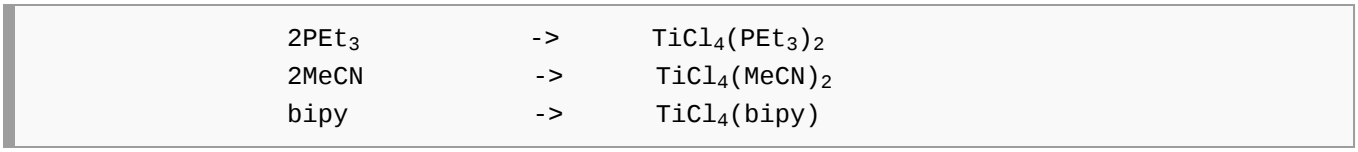
TiO_2 reacts with acids and bases.
In Acid:
$TiOSO_4$ formed in H_2SO_4 (Titanyl sulfate)
In Base:
$MTiO_3$ metatitanates (eg Perovskite, $CaTiO_3$ and ilmenite, $FeTiO_3$)
M_2TiO_4 orthotitanates.

Peroxides are highly Colored and can be used for Colorimetric analysis.
pH <1 $[TiO_2(OH)(H_2O)x]+$
pH 1-2 $[(O_2)Ti\text{-}O\text{-}Ti(O_2)](OH)_x^{2-x}$; x=1-6

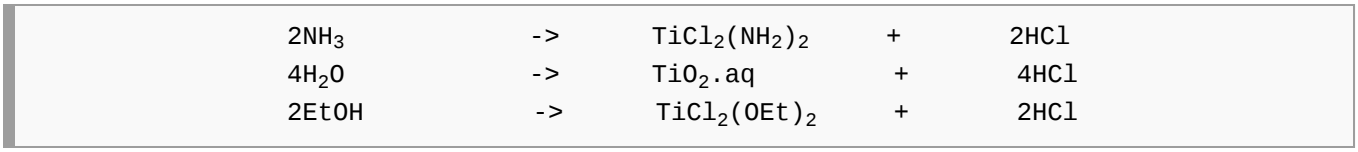
$[Ti(H_2O)_6]^{3+}$ -> $[Ti(OH)(H_2O)_5]^{2+}$ + [H+] pK=1.4
$TiO^{2+} + 2H^+ + e^-$ -> $Ti^{3+} + H_2O$ E=0.1V

Representative complexes

$TiCl_4$ is a good Lewis acid and forms adducts on reaction with Lewis bases such as;



Solvolysis can occur if ionisable protons are present in the ligand;



$TiCl_3$ has less Lewis acid strength but can form adducts also;



References

1. "Complexes and First-Row Transition Elements", D. Nicholls
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21.5D: Low Oxidation States

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SECTION OVERVIEW

21.6: Group 5 - Vanadium

Topic hierarchy

21.6A: The Metal

21.6B: Vanadium(V)

21.6C: Vanadium(IV)

21.6D: Vanadium(III)

21.6E: Vanadium(II)

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21.6A: The Metal

The discovery of vanadium is attributed to Andres Manuel del Rio (a Spanish mineralogist working in Mexico City) who prepared a number of salts from a material contained in "brown lead" around 1801. Unfortunately, the French chemist Collett-Desotils incorrectly declared that del Rio's new element was only impure Chromium. Del Rio thought himself to be mistaken and withdrew his claim. The element was rediscovered in 1830 by the Swedish chemist Nils Gabriel Sefström who named it after the Norse goddess Vanadis, the goddess of beauty and fertility.

Metallic vanadium was not isolated until 1867 when Sir Henry Enfield Roscoe (1833-1915), Professor of Chemistry at Owens College (later the University of Manchester) from 1857 to 1885, reduced vanadium chloride (VCl_5) with gaseous hydrogen to give vanadium metal and HCl.

Properties of vanadium

An excellent site for finding the properties of the elements, including vanadium is at WebElements periodic table

Introduction

Vanadium has been found to play a number of roles in biological systems. It is present in certain vanadium dependent haloperoxidase and nitrogenase enzymes.



A tunicate (*Clavelina Puertosecensis*) discovered near Discovery Bay, Jamaica

Many sea squirts, such as *Ciona Intestinalis* accumulate vanadium in very high concentration, although the reason is not known.



The mushroom *Amanita muscaria* accumulate vanadium in the form of a coordination complex called amavadin, whose function is still unknown.
A number of vanadium complexes have been shown to alleviate many of the symptoms of diabetes in both in vitro and in vivo (in rats and mice) studies. These complexes are being studied as potential alternatives to insulin therapy.

Vanadium Halides

Vanadium(V) halides

Formula	Colour	MP	BP	m (BM)	Structure
VF_5	white	19.5	48.3	0	trigonal bipyramid in gas phase

Preparations:

Prepared by reaction of V with F_2 in N_2 or with BrF_3 at 300C.
In the solid state it is an infinite chain polymer with *cis*-fluoride bridging.

Vanadium(IV) halides

Formula	Colour	MP	BP	m (BM)	Structure
VF_4	lime-green	100 [(a)]	-	1.68	-
VCl_4	red-brown	-25.7	148	1.61	tetrahedral (monomeric)
VBr_4	purple	-23d	-	-	-

[(a)] sublimes with decomposition at 100 C.
Preparations:

VCl_4 is prepared by reaction of V with chlorinating agents such as Cl_2, $SOCl_2$, $COCl_2$ etc.
Reaction of VCl_4 with HF in CCl_3F at -78C gives VF_4.

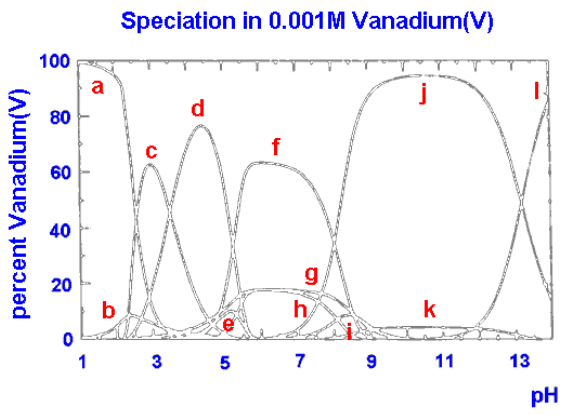
Vanadium Oxides and Aqueous Chemistry

Vanadium oxides

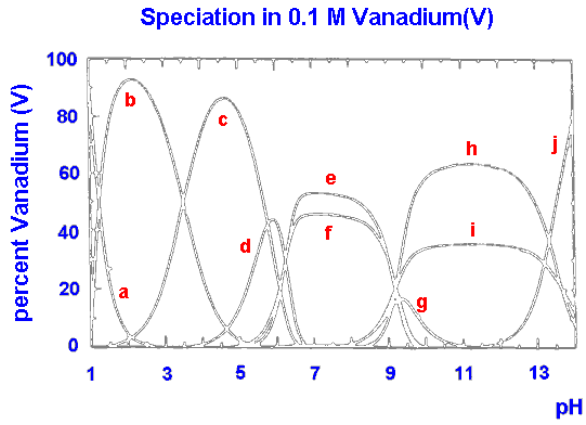
Formula	Colour	Common name	Oxidation State	MP	V-O distance (pm)
V_2O_5	brick-red	pentoxide	V^{5+}	658	158.5-202
V_2O_4	blue	dioxide	V^{4+}	1637	176-205
V_2O_3	grey-black	sesquioxide	V^{3+}	1967	196-206

Preparations:
V_2O_5 is the final product of the oxidation of V metal, lower oxides etc.

Aqueous Chemistry very complex:



a VO_2^+
b $VO(OH)_3$
c $V_{10}O_{26}(OH)_2^{4-}$
d $V_{10}O_{27}(OH)^{5-}$
e $V_{10}O_{28}^{6-}$
f $V_3O_9^{3-}$
g $VO_2(OH)_2^-$
h $V_4O_{12}^{4-}$
i $V_2O_6(OH)^{3-}$
j $VO_3(OH)^{2-}$
k $V_2O_7^{4-}$
l VO_4^{3-}



a VO_2^+
b $V_{10}O_{26}(OH)_2^{4-}$
c $V_{10}O_{27}(OH)^{5-}$
d $V_{10}O_{28}^{6-}$
e $V_4O_{12}^{4-}$
f $V_3O_9^{3-}$
g $V_2O_6(OH)^{3-}$
h $V_2O_7^{4-}$
i $VO_3(OH)^{2-}$
j VO_4^{3-}

In alkaline solution,

$$VO_4^{3-} + H^+ \rightarrow HVO_4^{2-}$$
$$2HVO_4^{2-} \rightarrow V_2O_7^{4-} + H_2O$$
$$HVO_4^{2-} + H^+ \rightarrow H_2VO_4^-$$
$$3H_2VO_4^- \rightarrow V_3O_9^{3-} + 3H_2O$$
$$4H_2VO_4^- \rightarrow V_3O_{12}^{4-} + 4H_2O$$

In acidic solution,

$$10V_3O_9^{3-} + 15H^+ \rightarrow 3HV_{10}O_{28}^{5-} + 6H_2O$$
$$H_2VO_4^- + H^+ \rightarrow H_2VO_4$$
$$HV_{10}O_{28}^{5-} + H^+ \rightarrow H_2V_{10}O_{28}^{4-}$$
$$H_3VO_4 + H^+ \rightarrow VO_2^+ + 2H_2O$$
$$H_2V_{10}O_{28}^{4-} + 14H^+ \rightarrow 10VO_2^+ + 8H_2O$$

$VO(H_2O)_4SO_4$

The crystal structure of this salt was first determined in 1965. The V=O bond length was 159.4 pm, the aquo group trans to this had the longest V-O bond length (228.4pm) and the equatorial bond lengths were in the range 200.5-205.6 pm. Note that SO_4^{2-} was coordinated in an equatorial position.

The IR stretching frequency for the V=O in vanadyl complexes generally occurs at 985 +/- 50 cm^{-1}.

Redox properties of oxovanadium ions:

> $VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O \; E=1.0 \; V$
>
> $VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O \; E=0.34 \; V$

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1. "Inorganic Chemistry", 3rd Edition, Catherine Housecroft, Alan G. Sharpe, Publisher: Prentice Hall
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21.6B: Vanadium(V)

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21.6E: Vanadium(II)

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SECTION OVERVIEW

21.7: Group 6 - Chromium

Topic hierarchy

21.7A: Chromium Metal

21.7B: Chromium(VI)

21.7C: Chromium(V) and Chromium(IV)

21.7D: Chromium(III)

21.7E: Chromium(II)

21.7F: Chromium-Chromium Multiple Bonds

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21.7A: Chromium Metal

Discovered in 1797 by the French chemist Louis Nicolas Vauquelin, it was named chromium (Greek chroma, "color") because of the many different colors characteristic of its compounds. Chromium is the earth's 21st most abundant element (about 122 ppm) and the 6th most abundant transition metal. The principal and commercially viable ore is chromite, $FeCr_2O_4$, which is found mainly in southern Africa (with 96% of the worlds reserves), the former U.S.S.R and the Philippines. Less common sources include crocoite, $PbCrO_4$, and chrome ochre, \(\ce{Cr2O3}\), while the gemstones emerald and ruby owe their colors to traces of chromium.

Extraction

Chromite ($FeCr_2O_4$) is the most commercially useful ore, and is extensively used for extraction of chromium. Chromium is produced in two forms:

a. Ferrochrome by the reduction of chromite with coke in an electric arc furnace. A low-carbon ferrochrome can be produced by using ferrosilicon instead of coke as the reductant. This iron/chromium alloy is used directly as an additive to produce chromium-steels which are "stainless" and hard.
b. Chromium metal by the reduction of Cr_2O_3. This is obtained by aerial oxidation of chromite in molten alkali to give sodium chromate, Na_2CrO_4, which is leached out with water, precipitated and then reduced to the Cr(III) oxide by carbon. The oxide can be reduced by aluminum (aluminothermic process) or silicon:

$$Cr_2O_3 + 2\,Al \rightarrow 2\,Cr + Al_2O_3 \tag{21.7A.1}$$

$$2\,Cr_2O_3 + 3\,Si \rightarrow 4\,Cr + 3\,SiO_2 \tag{21.7A.2}$$

The main use of the chromium metal so produced is in the production of nonferrous alloys, the use of pure chromium being limited because of its low ductility at ordinary temperatures. Alternatively, the Cr_2O_3 can be dissolved in sulfuric acid to give the electrolyte used to produce the ubiquitous chromium-plating which is at once both protective and decorative. The sodium chromate produced in the isolation of chromium is itself the basis for the manufacture of all industrially important chromium chemicals. World production of chromite ores approached 12 million tonnes in 1995.

Chromium Compounds

Most compounds of chromium are colored (why is $Cr(CO)_6$ white?); the most important are the chromates and dichromates of sodium and potassium and the potassium and ammonium chrome alums. The dichromates are used as oxidizing agents in quantitative analysis, also in tanning leather. Other compounds are of industrial value; lead chromate is chrome yellow, a valued pigment. Chromium compounds are used in the textile industry as mordants, and by the aircraft and other industries for anodizing aluminium.

Halides

CrX_3 are prepared from Cr with X_2, dehydration of $CrCl_3.6H_2O$ requires $SOCl_2$ at 650C.

Table 1: Chromium(III) halides

Formula	Color	MP	M-X (pm)	μ(BM) (b)	Structure
CrF_3	green	1404	190	-	-
$CrCl_3$	red-violet	1152	238	-	$CrCl_3$
$CrBr_3$	green-black	1130	257	-	BiI_3
CrI_3	black	>500decomp	-	-	-

(b) all 3.7-4.1 BM.

Reduction of CrX_3 with H_2/HX gives CrX_2.

Table 2: Chromium(II) halides

Formula	Color	MP	μ (BM)	Structure
CrF_2	green	894	4.3	distorted rutile
$CrCl_2$	white	820-824	5.13	distorted rutile
$CrBr_2$	white	844	-	-
CrI_2	red-brown	868	-	-

Oxides

Table 3: Chromium oxides

Formula	Color	Oxidation State	MP	Magnetic Moment
CrO_3	deep red	Cr^{6+}	197decomp	-
Cr_3O_8	-	intermediate	-	-
Cr_2O_5	-	-	-	-
Cr_5O_{12} etc	-	-	-	-
CrO_2	brown-black	Cr^{4+}	300decomp	-
Cr_2O_3	green	Cr^{3+}	2437	-antiferromagnetic < 35 C

Dichromate and chromate equilibria is pH dependent:

$$HCrO_4^- \longrightarrow CrO_{42}^- + H^+ \quad K = 10^{-5.9} \tag{21.7A.3}$$

$H_2CrO_4 \rightarrow HCrO_4^- + H^+$ $K=10^{+0.26}$

$Cr_2O_7^{2-} + H_2O \rightarrow 2HCrO_4^-$ $K=10^{-2.2}$
$HCr_2O_7^- \rightarrow Cr_2O_7^{2-} + H^+$ $K=10^{+0.85}$

Hence the variation found for solutions of CrO_3 are:

- pH > 8 CrO_4^{2-} yellow
- pH 2-6 $HCrO_4^-$ and $Cr_2O_7^{2-}$ orange-red
- pH < 1 $H_2Cr_2O_7$

One of the most obvious characteristics of Cr(III) is that it is acidic i.e it has a tendency to hydrolyse and form polynuclear complexes containing OH^- bridges in a process known as OLATION. This is thought to occur by the loss of a proton from coordinated water, followed by coordination of the OH^- to a second cation:

$[Cr(H_2O)_6]^{3+} \rightarrow [Cr(H_2O)_5(OH)]^{2+} \rightarrow$

H
O
/ \
$[(H_2O)_4Cr\ Cr(H_2O)_4]^{4+}$ pK=4 etc.
\ /
O
H

The ease with which the proton is removed can be judged by the fact that the hexaaquo ion (pKa ~ 4) is almost as strong as acetic acid. Further deprotonation and polymerization can occur and, as the pH is raised, the final product is hydrated chromium(III) oxide or "chromic hydroxide".

Representative Complexes

The Chromium(III) ion forms many stable complexes and since they are inert are capable of exhibiting various types of isomerism.



anhydrous $CrCl_3$ and hydrated "$CrCl_3.6H_2O$",

Hydrated chromium chloride, "$CrCl_3.6H_2O$", exists as hydrate isomers, including:

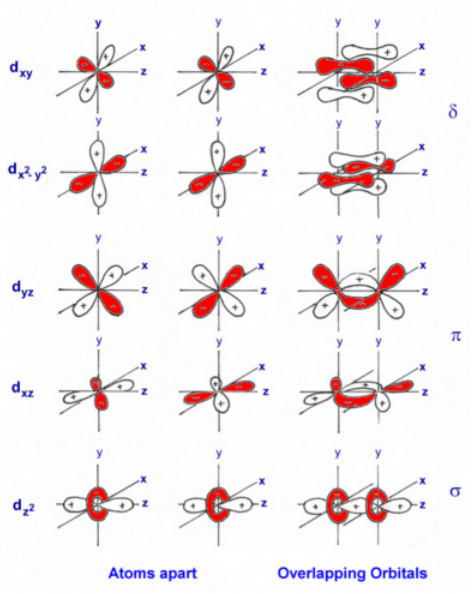
- the violet $[Cr(H_2O)_6]Cl_3$
- the dark green *trans*-$[CrCl_2(H_2O)_4]Cl.2H_2O$ salt shown above, etc.
- the pale green $[CrCl(H_2O)_5]Cl_2.H_2O$

Anhydrous $CrCl_3$ reacts with pyridine only in the presence of Zinc powder. This allows a small amount of the Cr(II) ion to be formed, which is very labile but unstable with respect to oxidation back to Cr(III).

$$CrCl_3 + pyr/Zn \rightarrow CrCl_3pyr_3 \tag{21.7A.4}$$

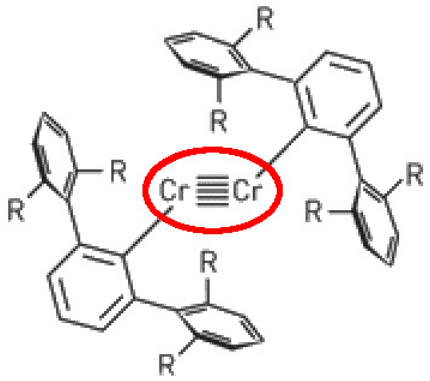
See the laboratory manual for this course for a range of other Cr(III) complexes for which you should know the structure.

$[Cr_2(OAc)_4].2H_2O$ is an example of a Cr(II) complex which is reasonably stable in air once isolated. Each Cr(II) ion has 4 d electrons but the complex is found to be diamagnetic which is explained by the formation of a quadruple bond between the two metal ions. The Cr-Cr bond distance in a range of these quadruply bonded species has been found to vary between 195-255 pm.



Cr(II) acetate complex.

In case you think that quadruple bonds are as far as it goes.... a recent report describes the structure of a Cr complex with a quintuple bond between two Cr(I) ions.

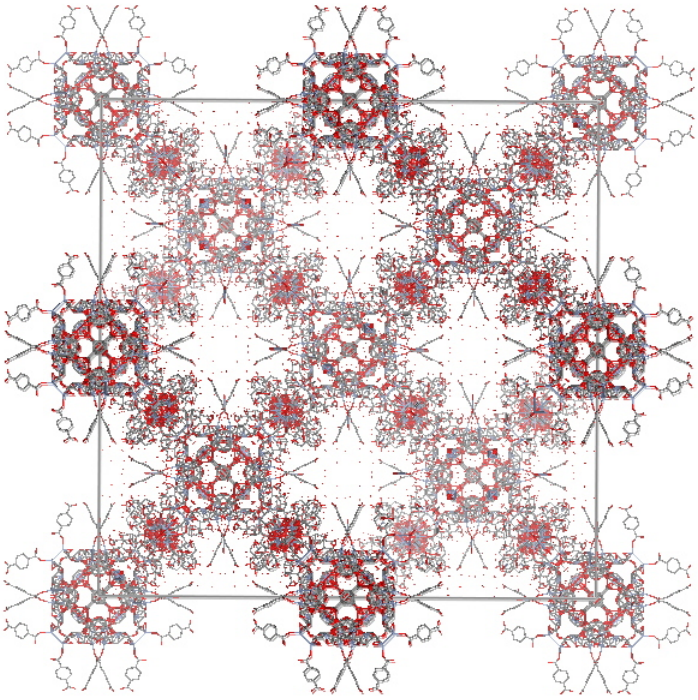


Cr(I) - Cr(I) quintuple bonded structure.

The compound Ar'CrCrAr' (R = isopropyl) was very air and moisture sensitive and crystallised as dark red crystals. X-ray diffraction revealed a Cr-Cr bond length of about 184 pm and a planar, trans-bent core geometry. Published in Science by P Power et. al., UC Davis, 22 September 2005 [DOI: 10.1126/science.1116789].

Another recent innovation is the formation of "zeolite-type" architectures from Metal-Organic-Frameworks (MOF's). The synthesis of MIL-101 consists of the hydrothermal reaction of 1,4-benzene dicarboxylate, H_2BDC (166 mg, 1 mmol) with $Cr(NO_3)_3.9H_2O$ (400 mg, 1 mmol), hydrofluoric acid (1 mmol), and 4.8 mL of H_2O (265 mmol) for 8 h at 220 °C, producing a pure and highly crystallized green powder of the chromium terephthalate with formula $Cr_3F(H_2O)_2O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3.nH_2O$ (n=25), based on chemical analysis.

https://chem.libretexts.org/@go/page/34440



MIL 101 Chromium MOF structure. "First Direct Imaging of Giant Pores of the Metal-Organic Framework MIL-101" Millange and co-workers Chem. Mater. 2005, 17, 6525-6527

Uses

More than half the production of chromium goes into metallic products, and about another third is used in refractories. It is an ingredient in several important catalysts. The chief use of chromium is to form alloys with iron, nickel, or cobalt. The addition of chromium imparts hardness, strength, and corrosion resistance to the alloy. In the stainless steels, chromium makes up 10 percent or more of the final composition. Because of its hardness, an alloy of chromium, cobalt, and tungsten is used for high-speed metal-cutting tools. When deposited electrolytically, chromium provides a hard, corrosion-resistant, lustrous finish. For this reason it is widely used as body trim on automobiles and other vehicles. The extensive use of chromite as a refractory is based on its high melting point, its moderate thermal expansion, and the stability of its crystalline structure.

In chromites and chromic salts, chromium has a valence of +3. Most of these compounds are green, but some are red or blue. Chromic oxide (Cr_2O_3) is a green solid. In chromates and dichromates, chromium has a valence of +6. Potassium dichromate ($K_2Cr_2O_7$) is a red, water-soluble solid that, mixed with gelatin, gives a light-sensitive surface useful in photographic processes. The chromates are generally yellow, the best known being lead chromate ($PbCrO_4$), an insoluble solid widely used as a pigment called chrome yellow. Chrome green is a mixture of chrome yellow and Prussian blue.

Chromium is used to harden steel, to manufacture stainless steel, and to form many useful alloys. Much is used in plating to produce a hard, beautiful surface and to prevent corrosion. Chromium gives glass an emerald green color and is widely used as a catalyst. The refractory industry has found chromite useful for forming bricks and shapes, as it has a high melting point, moderate thermal expansion, and stability of crystalline structure.

Health

Chromium is an essential trace element in mammalian metabolism. In addition to insulin, it is responsible for reducing blood glucose levels, and is used to control certain cases of diabetes. It has also been found to reduce blood cholesterol levels by diminishing the concentration of (bad) low density lipoproteins "LDLs" in the blood. It is supplied in a variety of foods such as

Brewer's yeast, liver, cheese, whole grain breads and cereals, and broccoli. It is claimed to aid in muscle development, and as such dietary supplements containing chromium picolinate (its most soluble form), is very popular with body builders.

mer- isomer of Cr(III) picolinate complex.

Ammonium Reineckate, $NH_4(Cr(NH_3)_2(SCN)_4).H_2O$, is used to test for the presence of dihydromorphinone and other substances generally found in persons involved in substance abuse.

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21.7B: Chromium(VI)

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21.7C: Chromium(V) and Chromium(IV)

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21.7D: Chromium(III)

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21.7F: Chromium-Chromium Multiple Bonds

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21.8: Group 7 - Manganese

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21.8A: The Metal

Oxides

Table 21.8A.1: Manganese oxides

Formula	Color	Oxidation State	MP °C
Mn_2O_7	green oil	Mn^{7+}	5.9
MnO_2	black	Mn^{4+}	535d
Mn_2O_3	black	Mn^{3+}	1080d
Mn_3O_4 - Haussmanite	black	$Mn^{2/3+}$	1705
MnO	grey-green	Mn^{2+}	1650

Preparations

- Mn_3O_4 is prepared from the other oxides by heating in air at 1000 °C
- MnO is prepared from the other oxides by heating with H_2 at temperatures below 1200 °C above that Mn metal is produced.
- MnO_2 has been used for many years to decolorise commercial glass. When added to molten glass a small amount of red-brown Mn(III) results that masks the blue-green color from iron impurities. That is, by adding a reagent with the complimentary color of the impurity, the resultant effect is to balance out and give a clear glass.
- MnO_2 is used as an oxidant for the conversion of aniline to hydroquinone.
- Mn_2O_7 is dangerously explosive above 3 °C. It is thought that some accidents have occurred when instead of adding conc HCl to solid $KMnO_4$ to produce Cl_2 the wrong bottle is selected and conc H_2SO_4 was used leading to the formation of a green oil that explodes.

High Oxidation State Oxide Salts

Fusion of MnO_2 with an alkali metal hydroxide and an oxidizing agent such as KNO_3 produces very dark-green manganate(VI) salts (manganates) which are stable in strongly alkaline solution but which disproportionate readily in neutral or acid solution.

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O \tag{21.8A.1}$$

The deep-purple manganate(VII) salts (permanganates) may be prepared in aqueous solution by oxidation of manganese(II) salts with very strong oxidizing agents such as PbO_2 or $NaBiO_3$. They are manufactured commercially by alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate(VI):

$$2MnO_2 + 4KOH + O2 \rightarrow 2K_2MnO_4 + 2H_2O \tag{21.8A.2}$$

$$2K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + 2KOH + H_2 \tag{21.8A.3}$$

The most important manganate(VII) is $KMnO_4$ and the very intense purple color is due to a charge transfer band and not a d-d transition. It is a well-known oxidizing agent; the usual conditions for its use are 0.02 M $KMnO_4$ and 1.5 M H_2SO_4.

Redox properties of $KMnO_4$

- **strong base**

$$MnO_4^- + e^- \rightarrow MnO_4^{2-} \quad \text{(RAPID)} \tag{21.8A.4}$$

with $E = 0.56\,V$

$$MnO_4^{2-} + 2H_2O + e^- \rightarrow MnO_2 + 4OH^- \quad \text{(SLOW)} \tag{21.8A.5}$$

with $E = 0.60\,V$

- **moderate base**

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^- \quad (21.8A.6)$$

with $E = 0.59\,V$

- **dil. H_2SO_4**

$$MnO_4^- + 8H_2O + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad (21.8A.7)$$

with $E = 1.51\,V$

In the industrial production of saccharin and benzoic acid, $KMnO_4$ is the oxidant, medically, it has been used as a disinfectant. It is gaining in use for water purification, since it has an advantage over chlorine that it does not affect the taste, and has the bonus that the MnO_2 produced acts as a coagulant for colloidal impurities.

Table 21.8A.2: Manganese(II) halides

Formula	Color	MP °C	BP °C	m (BM)	Structure
MnF_2	pale-pink	920	-	-	rutile
$MnCl_2$	pink	652	1190	5.73	$CdCl_2$
$MnBr_2$	rose	695	-	5.82	-
MnI_2	pink	613	-	5.88	CdI_2

Preparations:

Prepared from

$$MnCO_3 + HX \rightarrow MnX_2 + CO_2 + H_2O \quad (21.8A.8)$$

Manganese complexes

Octahedral complexes of Mn(III) are expected to show Jahn-Teller distortions. It was of interest therefore to compare the structures of $Cr(acac)_3$ with $Mn(acac)_3$ since the Cr(III) ion is expected to give a regular octahedral shape. In fact the Mn-O bond distances were all found to be equivalent. An unusual Mn complex is obtained by the reaction of $Mn(OAc)_2$ with $KMnO_4$ in HOAc. This gives $[Mn_3O(OAc)_6\ 3H_2O]OAc$. It is used as an industrial oxidant for the conversion of toluene to phenol.

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21.8B: Manganese(VII)

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21.8F: Manganese(III)

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21.8G: Manganese(II)

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21.8H: Manganese(I)

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21.9: Group 8 - Iron

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21.9A: The Metal

Iron is the most abundant transition metal on Earth (62000 ppm).

Extraction of Iron

Iron is generally extracted in a Blast furnace.

Iron Halides

Iron(III) halides

Formula	Color	MP	Structure
FeF_3	green	1000 sublimes	
$FeCl_3$	black	306 sublimes	BiI_3
$FeBr_3$	dark-red-brown	decomposes above 200°C	BiI_3

Preparations:

Prepared by reaction of $Fe + X_2 \rightarrow FeX_3$.
Note that $FeBr_3$.aq when boiled gives $FeBr_2$.

An important application of the chloride is as an etching material for copper electrical printed circuits.

Iron(II) halides

Formula	Color	MP	BP	Structure
FeF_2	white	1000	1100	rutile
$FeCl_2$	pale yellow-grey	670-674	-	$CdCl_2$
$FeBr_2$	yellow-green	684	-	CdI_2
FeI_2	grey	red heat	-	CdI_2

Preparations:

Fe +HX at red heat $\rightarrow FeX_2$ for X=F,Cl and Br
$Fe + I_2 \rightarrow FeI_2$

Iron Oxides and Aqueous Chemistry

Iron oxides

Formula	Color	Oxidation State	MP	Structure / comments
Fe_2O_3	red brown	Fe^{3+}	1560d	α-form Haematite, β-form used in cassettes
Fe_3O_4	black	$Fe^{2+/3+}$	1538d	magnetite/lodestone
FeO	black	Fe^{2+}	1380	pyrophoric

Preparations

$\alpha - Fe_2O_3$ is obtained by heating alkaline solutions of Fe(III) and dehydrating the solid formed.

FeO, Fe_3O_4, γ-Fe_2O_3 ccp, α-Fe_2O_3 hcp

The Fe(III) ion is strongly acidic:

$$[Fe(H_2O)_6]^{3+} + H_2O \rightarrow [Fe(H_2O)_5(OH)]^{2+} + H_3O^+ \quad K = 10^{-3.05} \tag{1}$$

$$[Fe(OH)(H_2O)_5]^{2+} + H_2O \rightarrow [Fe(OH)_2(H_2O)_4]^{+} + H_3O^+ \quad K = 10^{-3.26} \tag{2}$$

olation

$$2Fe(H_2O)_6^{3+} + 2H_2O \rightarrow [Fe_2(OH)_2(H_2O)_8]^{4+} + 2H_3O^+ \quad K = 10^{-2.91} \tag{3}$$

The Fe^{2+} ion is barely acidic:

$$Fe(H_2O)_6^{2+} + H_2O \rightarrow [Fe(OH)(H_2O)_5]^{+} + H_3O^+ \quad K = 10^{-9.5} \tag{4}$$

Rusting of Iron

The economic importance of rusting is such that it has been estimated that the cost of corrosion is over 1% of the world's economy. (25% of the annual steel production in the USA goes towards replacement of material that has corroded.) Rusting of iron consists of the formation of hydrated oxide, $Fe(OH)_3$ or FeO(OH), and is an electrochemical process which requires the presence of water, oxygen and an electrolyte - in the absence of any one of these rusting does not occur to any significant extent. In air, a relative humidity of over 50% provides the necessary amount of water and at 80% corrosion is severe.

The process is complex and will depend in detail on the prevailing conditions, for example, in the presence of a small amount of O_2,

- the anodic oxidation will be:

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{5}$$

- and the cathodic reduction:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{6}$$

- i.e. overall:

$$Fe + 2H_2O \rightarrow H_2 + Fe^{2+} + 2OH^- \tag{7}$$

i.e $Fe(OH)_2$ and this precipitates to form a coating that slows further corrosion.

If **both water and air are present**, then the corrosion can be severe with oxygen now as the oxidant

- the anodic oxidations:

$$2Fe \rightarrow 2Fe^{2+} + 4e^- \tag{8}$$

- and the cathodic reduction:

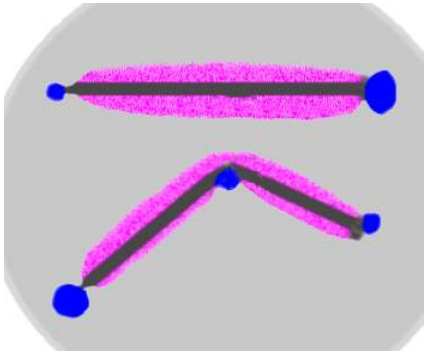
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{9}$$

- i.e. overall:

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2 \tag{10}$$

with limited O_2, magnetite is formed (Fe_3O_4), otherwise the familiar red-brown Fe_2O_3 H_2O “rust” is found.

The presence of an electrolyte is required to provide a pathway for the current and, in urban areas, this is commonly iron(II) sulfate formed as a result of attack by atmospheric SO_2 but, in seaside areas, airborne particles of salt are important. The anodic oxidation of the iron is usually localized in surface pits and crevices which allow the formation of adherent rust over the remaining surface area.



The illustration above shows 2 nails immersed in an agar gel containing phenolphthalein and $[Fe(CN)_6]^{3-}$. The nails can be seen to have started to corrode since the Prussian blue formation indicates the formation of Fe(II) (the Anodic sites which correspond to the end of the nails and the bend in the middle). The phenolphthalein (change to pink in presence of base) shows the build up of OH^- and shows that essentially the whole length of the nail is acting as the cathode.

Eventually the lateral extension of the anodic area undermines the rust to produce loose flakes. Moreover, once an adherent film of rust has formed, simply painting over gives but poor protection. This is due to the presence of electrolytes such as iron(II) sulfate in the film so that painting merely seals in the ingredients for anodic oxidation. It then only requires the exposure of some other portion of the surface, where cathodic reduction can take place, for rusting beneath the paint to occur.

The protection of iron and steel against rusting takes many forms, including: simple covering with paint; coating with another metal such as zinc (galvanizing) or tin; treating with "inhibitors" such as chromate(VI) or (in the presence of air) phosphate or hydroxide, all of which produce a coherent protective film of Fe_2O_3. Another method uses sacrificial anodes, most usually Mg or Zn which, being higher than Fe in the electrochemical series, are attacked preferentially. In fact, the Zn coating on galvanized iron is actually a sacrificial anode.

Rust prevention

Galvanised iron is the name given to iron that has been dipped into molten zinc (at about 450°C) to form a thin covering of zinc oxide. One level of rust prevention occurs through a purely mechanical method since it is more difficult for water and oxygen to reach the iron. Even if the layer becomes somewhat worn though another reason corrosion is inhibited is that the anodic processes are affected.

The E° for zinc oxidation (0.76V) is considerably more positive that E° for iron oxidation (0.44V) so the zinc metal is oxidized before the iron. Zn^{2+} is lost to the solution and the zinc coating is called a ***sacrificial anode***.

Foodstuffs are often distributed in "tin cans" and it has generally been easier to coat the iron with a layer of tin than with zinc. Another benefit is that tin is less reactive then zinc so does not react as readily with the contents. However the electrode oxidation potential for Sn/Sn^{2+} is 0.14V so once again iron becomes the anode and rust will occur once the coating is worn or punctured.

Another technique is to treat the iron surface with dichromate solution.

$$2Fe + 2Na_2CrO_4 + 2H_2O \rightarrow > Fe_2O_3 + Cr_2O_3 + 4NaOH \qquad (21.9A.1)$$

The iron oxide coating formed has been found to be impervious to water and oxygen so no further corrosion can occur.

The Fe(III)/Fe(II) Couples

A selection of standard reduction potentials for some iron couples is given below, from which the importance of the participating ligand can be judged. Thus Fe(III), being more highly charged than Fe(II) is stabilized (relatively) by negatively charged ligands such as the anions of edta and derivatives of 8-hydroxyquinoline, whereas Fe(II) is favoured by neutral ligands which permit some charge delocalization in π-orbitals (e.g. bipy and phen).

Table 1: E° at 25°C for some FeIII/FeII couples in acid solution

FeIII		FeII	E°/V
$[Fe(phen)_3]^{3+}$	+ e^- →	$[Fe(phen)_3]^{2+}$	1.12
$[Fe(bipy)_3]^{3+}$	+ e^- →	$[Fe(bipy)_3]^{2+}$	0.96
$[Fe(H_2O)_6]^{3+}$	+ e^- →	$[Fe(H_2O)_6]^{2+}$	0.77
$[Fe(CN)_6]^{3-}$	+ e^- →	$[Fe(CN)_6]^{4-}$	0.36
$[Fe(C_2O_4)_3]^{3-}$	+ e^- →	$[Fe(C_2O_4)_2]^{2-}$ + $(C_2O_4)^{2-}$	0.02
$[Fe(edta)]^-$	+ e^- →	$[Fe(edta)]^{2-}$	-0.12
$[Fe(quin)_3]$	+ e^- →	$[Fe(quin)_2]$ + quin-	-0.30
where quin- = 5-methyl-8-hydroxyquinolinate,			

The value of E° for the couple involving the simple aquated ions, shows that Fe(II)(aq) is thermodynamically stable with respect to hydrogen; which is to say that Fe(III)(aq) is spontaneously reduced by hydrogen gas. However, under normal circumstances, it is not hydrogen but atmospheric oxygen which is important and, for the process $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$, E° = 1:229 V, i.e. oxygen gas is sufficiently strong an oxidizing agent to render $[Fe(H_2O)_6]^{2+}$ (and, indeed, all other Fe(II) species in the Table) unstable with respect to atmospheric oxidation. In practice the oxidation in acidic solutions is slow and, if the pH is increased, the potential for the Fe(III)/Fe(II) couple remains fairly constant until the solution becomes alkaline and hydrous Fe_2O_3 (considered here for convenience to be $Fe(OH)_3$) is precipitated. But here the change is dramatic, as explained below.

The Redox chemistry of Iron is pH dependent:

$$Fe(H_2O)_6^{3+} + e^- \rightarrow Fe(H_2O)_6^{2+} \quad E°= 0.771V \tag{X}$$

The actual potential E of the couple is given by the Nernst equation,

where E= E° when all activities are unity. However, once precipitation occurs, the activities of the iron species are far from unity; they are determined by the solubility products of the 2 hydroxides. These are:

$$[Fe(III)][OH^-]^2 \sim 10^{-14} \text{ (mol dm}^{-3})^3$$

and

$$[Fe(III)][OH^-]^3 \sim 10^{-36} \text{ (mol dm}^{-3})^4$$

Therefore when $[OH^-]$ =1 mol dm^{-3}; $[Fe(II)]/[Fe(III)] \sim 10^{22}$

Hence $E \sim 0.771 - 0.05916 \log_{10}.(10^{22}) = 0.771 - 1.301 = -0.530$ V

Thus by making the solution alkaline the sign of E has been reversed and the susceptibility of Fe(II)(aq) to oxidation (i.e. its reducing power) enormously increased. In base the white, precipitated $Fe(OH)_2$ and $FeCO_3$ is a good reducing agent and samples are rapidly darkened by aerial oxidation and this explains why Fe(II) in alkaline solution will reduce nitrates to ammonia and copper(II) salts to metallic copper.

Representative complexes

An important Fe complex which is used in Actinometry since it is photosensitive is $K_3[Fe(C_2O_4)_3 \cdot 3H_2O$. It can be prepared from $Fe(C_2O_4)$ in $K_2C_2O_4$ by reacting with H_2O_2 in $H_2C_2O_4$ to give green crystals. It is high spin μ =5.9 BM at 30 0K and has been resolved into its two optical isomers, although they racemize in less than 1 hour.

In light, the photodissociation reaction is:

$$K_3Fe(C_2O_4)_3 \cdot 3H_2O \xrightarrow{h\nu} 2Fe(C_2O_4) + 2CO_2 + 3K_2C_2O_4 \tag{10}$$

Another important complex is used as a redox indicator since the Fe(II) and Fe(III) complexes are both quite stable and have different colors

$$\underset{\text{blue}}{Fe(phen)_3^{3+}} + e^- \rightarrow \underset{\text{red}}{Fe(phen)_3^{2+}} \quad E° = 1.12\ V \tag{11}$$

The ligand is 1,10 phenanthroline and the indicator is called ferroin. An interesting example of how acetates can bind to metal ions is seen in what has been described as a "molecular ferric wheel". The structure was determined in 1990 and contains $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$. see J. Amer. Chem. Soc., 1990, 112, 9629.

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21.9B: Iron(VI), Iron(V), and Iron(IV)

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21.9E: Iron in Low Oxidation States

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21.10: Group 9 - Cobalt

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21.10A: The Metal

The origin of the name Cobalt is thought to stem from the German kobold for "evil spirits or goblins", who were superstitiously thought to cause trouble for miners, since the cobalt minerals contained arsenic that injured their health and the cobalt ores did not yield metals when treated using the normal methods. The name could also be derived from the Greek kobalos for "mine". Cobalt was discovered in 1735 by the Swedish chemist Georg Brandt.

Occurrence

The principal ores of Cobalt are cobaltite, [(Co,Fe)AsS], erythrite, [$Co_3(AsO_4)_2.8(H_2O)$], glaucodot, [(Co,Fe)AsS], and skutterudite, [$CoAs_3$]. World production of cobalt has steadily increased in recent years, almost trebling since 1993. The dominance of African copper-cobalt producers has been replaced by a more even spread of output between leading producing countries, with Canada, Norway and more recently Australia, together with exports from Russia, replacing lost production in the Democratic Republic of Congo (Zaire). The strongest growth in production of cobalt has come from Finland, where output grew at over 16% between 1990 and 2002.

Extraction

Not covered in this course.

Uses

- Alloys, such as:
  Superalloys, for parts in gas turbine aircraft engines.
  Corrosion- and wear-resistant alloys. Estimated as about 20% of production in 2003
- High-speed steels.
- Cemented carbides (also called hard metals) and diamond tools.
- Magnets and magnetic recording media.
- Catalysts for the petroleum and chemical industries.
- electroplating because of its appearance, hardness, and resistance to oxidation.
- Drying agents for paints, varnishes, and inks.
- Ground coats for porcelain enamels.
- Pigments (cobalt blue, known in ancient times, and Cobalt green).
- Battery sector (e.g. electrodes) estimated as about 11% of production in 2003.
- Steel-belted radial tires.
- Cobalt-60 has multiple uses as a gamma ray source:
  * It is used in radiotherapy.
  * It is used in radiation treatment of foods for sterilization (cold pasteurization).
  * It is used in industrial radiography to detect structural flaws in metal parts.

Cobalt compounds

Oxides

Table 1: Cobalt oxides

Formula	Color	Oxidation State	MP	Structure / comments
Co_2O_3		Co^{3+}		
Co_3O_4	black	$Co^{2+/3+}$	900-950decomp	normal spinel
CoO	olive green	Co^{2+}	1795	NaCl -antiferromag. < 289 K

Preparations

- Co_2O_3 is formed from oxidation of $Co(OH)_2$.
- CoO when heated at 600-700°C converts to Co_3O_4
- Co_3O_4 when heated at 900-950°C reconverts back to CoO.

$$Co^{3+} + e^- \leftrightharpoons Co^{2+} \quad 1.81\,V \tag{21.10.1}$$

$$Co^{2+} + 2e^- \leftrightharpoons Co \quad -0.28\,V \tag{21.10.2}$$

no stable $[Co(H_2O)_6]^{3+}$ or $[Co(OH)_3$ exist since these convert to CoO(OH).

$[Co(H_2O)_6]^{2+}$ not acidic and a stable carbonate exists.

Cobalt Blue

One of the earliest uses of cobalt was in the coloring of glass by the addition of cobalt salts.



The cobalt blue pigment is based on the spinel $CoAl_2O_4$ and in the laboratory can be readily synthesized by pyrolysis of a mixture of $AlCl_3$ and $CoCl_2$.

Halides

Cobalt(II) halides

Formula	Color	MP	μ(BM)	Structure
CoF_2	pink	1200	-	rutile
$CoCl_2$	blue	724	5.47	$CdCl_2$
$CoBr_2$	green	678	-	CdI_2
CoI_2	blue-black	515	-	CdI_2

Preparations:

Co or $CoCO_3$ + HX → CoX_2.aq → CoX_2

Cobalt complexes

The Cobalt(III) ion forms many stable complexes, which being inert, are capable of exhibiting various types of isomerism. The preparation and characterization of many of these complexes dates back to the pioneering work of Werner and his students. Coordination theory was developed on the basis of studies of complexes of the type:

Werner Complexes

$[Co(NH_3)_6]Cl_3$	yellow
$[CoCl(NH_3)_5]Cl_2$	red
trans-$[CoCl_2(NH_3)_4]Cl$	green
cis-$[CoCl_2(NH_3)_4]Cl$	purple

Another important complex in the history of coordination chemistry is hexol. This was the first complex that could be resolved into its optical isomers that did not contain carbon atoms. Since then, only three or four others have been found.

Recently a structure that Werner apparently misassigned has been determined to be related to the original hexol although in this case the complex contains 6 Co atoms, i.e. is hexanuclear. The dark green compound is not resolvable into optical isomers.

☐ Highlight Co-O ON/OFF	☐ Highlight Co-O ON/OFF

Werner's hexol and "2nd hexol"

A noticeable difference between chromium(III) and cobalt(III) chemistry is that cobalt complexes are much less susceptible to hydrolysis, though limited hydrolysis, leading to polynuclear cobaltammines with bridging OH- groups, is well known. Other commonly occurring bridging groups are NH_2^-, NH^{2-} and NO_2^-, which give rise to complexes such as the bright-blue amide bridged $[(NH_3)_5Co\text{-}NH_2\text{-}Co(NH_3)_5]^{5+}$.

In the preparation of cobalt(III) hexaammine salts by the oxidation in air of cobalt(II) in aqueous ammonia it is possible to isolate blue $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5]^{4+}$. This is moderately stable in concentrated aqueous ammonia and in the solid state but readily decomposes in acid solutions to Co(II) and O_2, while oxidizing agents such as $(S_2O_8)^{2-}$ convert it to the green, paramagnetic $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5]^{5+}$ (μ_{300} = 1.7 B.M.).

In the brown compound both cobalt atoms are Co(III) and are joined by a peroxo group, O_2^{2-}, this fits with the observed diamagnetism; in addition the stereochemistry of the central Co-O-O-Co group is similar to that of H_2O_2. The green compound is less straightforward. Werner thought that it too involved a peroxo group but in this instance bridging between Co(III) and Co(IV) atoms.

This could account for the paramagnetism, but EPR evidence shows that the 2 cobalt atoms are equivalent, and X-ray evidence shows the central Co-O-O-Co group to be planar with an O-O distance of 131 pm, which is very close to the 128 pm of the superoxide, O_2^-, ion.

A more satisfactory formulation therefore is that of 2 Co(III) atoms joined by a superoxide bridge.

A range of Co(II) dioxygen complexes are known, some of which are able to reversibly bind O_2 from the air. During WWII, some US aircraft carriers are reported to have used these complexes as a solid source for oxy-acetylene welding. By slightly warming the solid complex the oxygen was released and when cooled again oxygen would be coordinated again. Unlike an oxygen cylinder, the solid would not explode if hit by a stray bullet!

[CosalenO_2]

A laboratory experiment designed to measure the uptake of dioxygen by Cosalen is available online.

$Co(acac)_3$ is a green octahedral complex of Co(III). In the case of Co(II) a comparison can be made to the Ni(II) complexes. $Ni(acac)_2$ is only found to be monomeric at temperatures around 200C in non-coordinating solvents such as n-decane. 6-coordinate monomeric species are formed at room temperature in solvents such as pyridine, but in the solid state $Ni(acac)_2$ is a trimer, where each Ni atom is 6-coordinate. Note that $Co(acac)_2$ actually exists as a tetramer.

$[Ni(acac)_2]_3$ $[Co(acac)_2]_4$

Cobalt(II) halide complexes with pyridine show structural isomerism. Addition of pyridine to cobalt(II) chloride in ethanol can produce blue, purple or pink complexes each having the composition "$CoCl_2pyr_2$". The structures are 4, 5 and 6 coordinate with either no bridging chlorides or mono- or di- bridged chlorides.

blue-$[CoCl_2pyr_2]$ CN=4 pink-$[CoCl_2pyr_2]$ CN=6

See the notes on isomerism for examples of Co(III) compounds that show linkage and structural isomerism.

Health

see the notes at The University of Bristol on Vitamin B12 and other Cobalt species essential for good health.

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21.10B: Cobalt(IV)

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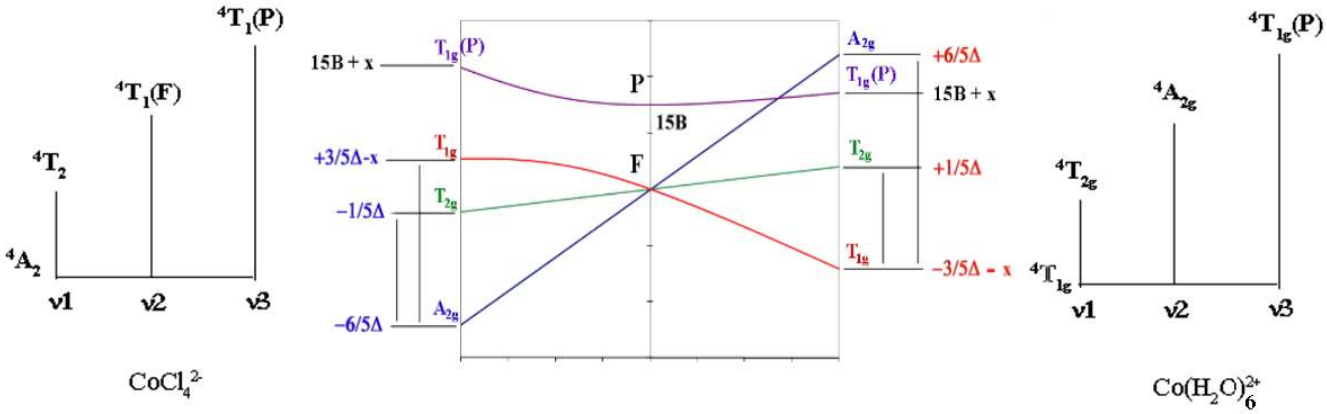
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21.10D: Cobalt(II)

The color of Co(II) complexes has interested chemists for many years and the pale-pink, octahedral to bright-blue, tetrahedral colour change is seen in such devices as weather guides and in the dye in silica gel desiccant used in the laboratory. Assignment of the bands for these spectra can present some problems however where the different stereochemistries are interpreted on each side of an F Orgel diagram.



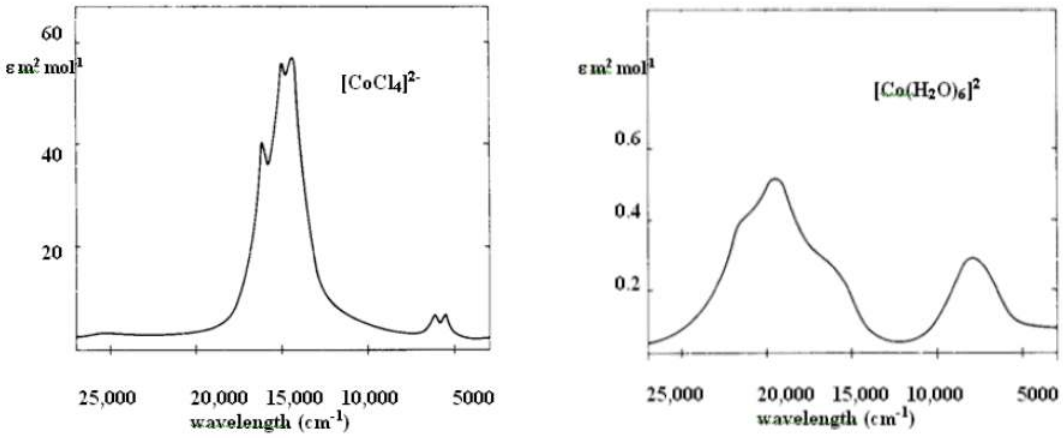
For a typical tetrahedral complex, $[CoCl_4]^{2-}$ and assuming $\Delta t = 4/9\ \Delta o$ where Δo is around 9000 cm^{-1} then we can predict that the transition

$^4T_2 \leftarrow {}^4A_2$ should be observed below 4000 cm^{-1}. Only 1 band is seen in the visible region at 15,000 cm^{-1} although a full scan from the IR through to the UV reveals an additional band at 5,800 cm^{-1}. (ε value for the 15,000 band is ~60 $m^2\ mol^{-1}$). The lower energy band must therefore correspond to $^4T_1(F) \leftarrow {}^4A_2$ and the other to $^4T_1(P) \leftarrow {}^4A_2$ (which shows splitting thought to arise from spin-orbit coupling).

The Octahedral aqua ion

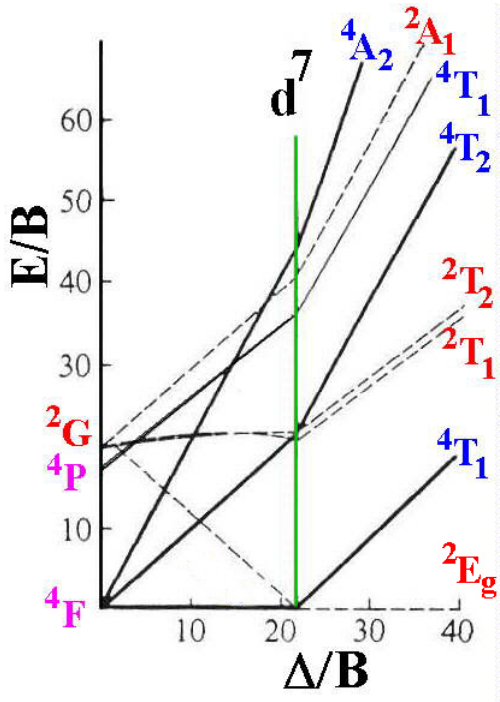
For the octahedral aqua ion, a band is observed at around 8000 cm^{-1} and a broad band centrrd around 20,000 cm^{-1} (ε for these bands is less than 1 $m^2\ mol^{-1}$).

The lowest energy band must correspond to:
$^4T_{2g} \leftarrow {}^4T_{1g}$ which leaves the bands at 16,000, 19,400 and 21,600 cm^{-1} to be assigned.
A tentative assignment puts the $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ transition at 19,400 and hence the 16,000 band is due to $^4A_{2g} \leftarrow {}^4T_{1g}$.
The band at 21,600 cm^{-1} is believed to come from spin-orbit effects.
From this $\Delta \sim 9000\ cm^{-1}$ and $B \sim 900\ cm^{-1}$.



https://chem.libretexts.org/@go/page/34463

Low spin Co(II) complexes



The ground term for the low spin case is 2Eg and looking at the right hand side of the TS diagram where Δ is quite large then it can be seen there are numerous doublet excited states. The quartets would now correspond to spin-forbidden states and be the weaker bands in the spectrum.

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21.11: Group 10 - Nickel

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21.11A: Chromium Metal

Nickel had been in use centuries before its actual discovery and isolation. As far back as 3500 BC Syrian bronzes contained a small amount of the element. In 235 BC, coins in China were minted from nickel. However there was no real documentation of the element until thousands of years later. In the 17thcentury, German miners discovered a red colored ore they believed to contain copper. They discovered upon analysis that there was no copper but that a useless, smelly material was actually present. Thinking the ore was evil they dubbed it "Kupfernickel" or Old Nick's Copper, which meant false or bad copper. Swedish scientist Baron Axel Frederich Cronstedt in 1751 finally isolated nickel from an ore closely resembling kupfernickel. Hence, he named this new element after the traditional mineral.

At the time of its discovery nickel was thought to be useless but over time as its valuable properties came to light the demand for the metal dramatically increased. The usefulness of nickel as a material in alloys was eventually appreciated since it added to the strength, corrosion resistance and hardness of the other metals. In the 1800s, the technique of silver plating was developed with a nickel-copper-zinc alloy being utilised in the process. Today, stainless steel, another nickel containing alloy, is recognised as one of the most valuable materials of the 20th and 21st centuries.

Occurrence

Nickel is the earth's 22nd most abundant element and the 7th most abundant transition metal. It is a silver white crystalline metal that occurs in meteors or combined with other elements in ores. Two important groups of ores are:

1. Laterites: oxide or silicate ores such as garnierite, $(Ni,Mg)_6\ Si_4O_{10}(OH)_8$ which are predominantly found in tropical areas such as New Caledonia, Cuba and Queensland.
2. Sulphides: these are ores such as pentlandite, $(Ni,Fe)_9S_8$ which contain about 1.5%, nickel associated with copper, cobalt and other metals. They are predominant in more temperate regions such as Canada, Russia and South Africa.

Canada is the world's leading nickel producer and the Sudbury Basin of Ontario contains one of the largest nickel deposits in the world.

Extraction of Nickel

In 1899 Ludwig Mond developed a process for extracting and purifying nickel. The so-called "Mond Process" involves the conversion of nickel oxides to pure nickel metal. The oxide is obtained from nickel ores by a series of treatments including concentration, roasting and smelting of the minerals.

In the first step of the process, nickel oxide is reacted with water gas, a mixture of H_2 and CO, at atmospheric pressure and a temperature of 50 °C. The oxide is thus reduced to impure nickel. Reaction of this impure material with residual carbon monoxide gives the toxic and volatile compound, nickel tetracarbonyl, $Ni(CO)_4$. This compound decomposes on heating to about 230 °C to give pure nickel metal and CO, which can then be recycled.

The actual temperatures and pressures used in this process may very slightly from one processing plant to the next. However the basic process as outlined is common to all.

The process can be summarised as follows:

50°C 230°C
$Ni + 4CO \rightarrow Ni(CO)_4 \rightarrow Ni + 4CO.$
(impure) (pure)

Properties

Nickel is a hard silver white metal, which occurs as cubic crystals. It is malleable, ductile and has superior strength and corrosion resistance. The metal is a fair conductor of heat and electricity and exhibits magnetic properties below 345°C. Five isotopes of nickel are known.

In its metallic form nickel is chemically unreactive. It is insoluble in cold and hot water and ammonia and is unaffected by concentrated nitric acid and alkalis. It is however soluble in dilute nitric acid and sparingly soluble in dilute hydrochloric and sulphuric acids.

Nickel Compounds

Nickel is known primarily for its divalent compounds since the most important oxidation state of the element is +2. There do exist however certain compounds in which the oxidation state of the metal is between -1 to +4. Blue and green are the characteristic colors of nickel compounds and they are often hydrated.

Nickel hydroxide usually occurs as green crystals that can be precipitated when aqueous alkali is added to a solution of a nickel (II) salt. It is insoluble in water but dissolves readily in acids and ammonium hydroxide.

Nickel oxide is a powdery green solid that becomes yellow on heating.
It is difficult to prepare this compound by simply heating nickel in oxygen and it is more conveniently obtained by heating nickel hydroxide, carbonate or nitrate. Nickel oxide is readily soluble in acids but insoluble in hot and cold water.

Formula	color	Oxidation State	MP	Structure / comments
NiO	green powder	Ni^{2+}	1955	NaCl

Thermal decomposition of $Ni(OH)_2$, $NiCO_3$, or $NiNO_3$ gives NiO.

Nickel sulfides consist of NiS_2, which has a pyrite structure, and Ni_3S_4, which has a spinel structure.

All the nickel dihalides are known to exist. These compounds are usually yellow to dark brown in color. Preparation directly from the elements is possible for all except NiF_2, which is best prepared from reaction of F_2 on $NiCl_2$ at 350°C. Most are soluble in water and crystallisation of the hexahydrate containing the $[Ni(H_2O)_6]^{2+}$ ion can be achieved. NiF_2 however is only slightly soluble in water from which the trihydrate crystallizes. The only nickel trihalide known to exist is an impure specimen of NiF_3.

Nickel(II) halides

Formula	color	MP	μ (BM)	Structure
NiF_2	yellow	1450	2.85	tetragonal rutile
$NiCl_2$	yellow	1001	3.32	$CdCl_2$
$NiBr_2$	yellow	965	3.0	$CdCl_2$
NiI_2	Black	780	3.25	$CdCl_2$

Preparations:

$Ni + F_2$ 55°C /slow → NiF_2
$Ni + Cl_2$ EtOH/ 20°C → $NiCl_2$
$Ni + Br_2$ red heat → $NiBr_2$
$NiCl_2 + 2NaI \rightarrow NiI_2 + 2NaCl$

Nickel carbonate usually occurs as a light green crystalline solid or a brown powder. It dissolves in ammonia and dilute acids but is insoluble in hot water. It exhibits vigorous reaction with iodine, hydrogen sulphide or a mixture of barium oxide and air. It decomposes on heating before melting occurs.

Nickel carbonyl is a colorless, volatile, liquid. It is soluble in alcohol, benzene, and nitric acid but only slightly soluble in water, and insoluble in dilute acids and alkalis. Upon heating or in contact with acid or acid fumes, nickel carbonyl emits toxic carbon monoxide gas, a property exploited in preparation of nickel metal. When exposed to heat or flame the compound explodes and it

can react violently with air, oxygen and bromine.

Identification of nickel compounds can be achieved by employing the use of an organic reagent dimethylglyoxine. This compound forms a red flocculent precipitate on addition to a solution of a nickel compound.

Nickel Complexes

The Nickel (II) ion forms many stable complexes as predicted by the Irving Williams series. Whilst there are no other important oxidation states to consider, the Ni(II) ion can exist in a wide variety of CN's which complicates its coordination chemistry.

For example, for CN=4 both tetrahedral and square planar complexes can be found. For CN=5 both square pyramid and trigonal bipyramid complexes are formed.

The phrase *"**anomalous nickel**"* has been used to describe this behavior and the fact that equilibria often exist between these forms. Some examples include:

a. (a) addition of ligands to square planar complexes to give 5 or 6 coordinate species
b. (b) monomer/polymer equilibria
c. (c) square-planar/ tetrahedron equilibria
d. (d) trigonal-bipyramid/ square pyramid equilibria.

(a) substituted acacs react with Ni^{2+} to give green dihydrates (6 coordinate). On heating, the two coordinated water groups are generally removed to give tetrahedral species. The unsubstituted acac complex, $Ni(acac)_2$ normally exists as a trimer, see below. Lifschitz salts containing substituted 1,2-diaminoethanes can be isolated as either 4 or 6 coordinate species depending on the presence of coordinated solvent.

(b) $Ni(acac)_2$ is only found to be monomeric at temperatures around 200°C in non-coordinating solvents such as n-decane. 6-coordinate monomeric species are formed at room temperature in solvents such as pyridine, but in the solid state $Ni(acac)_2$ is a trimer, where each Ni atom is 6-coordinate. Note that $Co(acac)_2$ actually exists as a tetramer.

$[Ni(acac)_2]_3$ $[Co(acac)_2]_4$

(c) Complexes of the type NiL_2X_2, where L are phosphines, can give rise to either tetrahedral or square planar complexes. It has been found that:
L=P(aryl)3 are tetrahedral
L=P(alkyl)3 are square planar
for L= mixed aryl and alkyl phosphines, both stereochemistries can occur in the same crystalline substance.
The energy of activation for conversion of one form to the other has been found to be around 50kJ mol^{-1}.

Similar changes have been observed with variation of the X group:

$Ni(P\Phi_3)_2Cl_2$	green	tetrahedral	μ =2.83 BM
$Ni(P\Phi_3)_2(SCN)_2$	red	sq. planar	μ =0 BM

where Φ is shorthand for C_6H_5

Ni^{2+} reacts with CN- to give $Ni(CN)_2.nH_2O$ (blue-green) which on heating at 180-200°C is dehydrated to yield $Ni(CN)_2$. Reaction with excess KCN gives $K_2Ni(CN)_4.H_2O$ (orange crystals) which can be dehydrated at 100°C. Addition of strong concentrations of KCN produces red solutions of $Ni(CN)_5^{3-}$.
The crystal structure of the double salt prepared by addition of $Cr(en)_3^{3+}$ to $Ni(CN)_5^{3-}$ showed that two types of Ni stereochemistry were present in the crystals in approximately equal proportions.

50% as square pyramid and 50% as trigonal bipyramid.

Uses of Nickel and its Compounds

The primary use of nickel is in the preparation of alloys such as stainless steel, which accounts for approximately 67% of all nickel used in manufacture. The greatest application of stainless steel is in the manufacturing of kitchen sinks but it has numerous other uses as well.

Other nickel alloys also have important applications. An alloy of nickel and copper for example is a component of the tubing used in the desalination of sea water. Nickel steel is used in the manufacture of armour plates and burglar proof vaults. Nickel alloys are especially valued for their strength, resistance to corrosion and in the case of stainless steel for example, aesthetic value.

Electroplating is another major use of the metal. Nickel plating is used in protective coating of other metals. In wire form, nickel is used in pins, staples, jewellry and surgical wire. Finely divided nickel catalyses the hydrogenation of vegetable oils. Nickel is also used in the coloring of glass to which it gives a green hue.

Other applications of nickel include:

- Coinage
- Transportation and construction
- Petroleum industry
- Machinery and household appliances
- Chemical industry.

Nickel compounds also have useful applications. Ceramics, paints and dyes, electroplating and preparation of other nickel compounds are all applications of these compounds. Nickel oxide for example is used in porcelain painting and in electrodes for fuel cells. Nickel acetate is used as a mordant in the textiles industry. Nickel carbonate finds use in ceramic colors and glazes.

Nickel and Human Health

The first crystallisation of an enzyme was reported in the 1920's. The enzyme was urease which converts urea to ammonia and bicarbonate. One source of the enzyme is the bacterium *Helicobacter Pylori*. The release of ammonia is beneficial to the bacterium since it partially neutralizes the very acidic environment of the stomach (whose function in part helps kill bacteria). In the initial study it was claimed that there were no metals in the enzyme. Fifty years later this was corrected when it was discovered that nickel ions were present and an integral part of the system.

The Nobel Prize in Physiology or Medicine for 2005 was awarded to Barry J. Marshall and J. Robin Warren "for their discovery of the bacterium Helicobacter pylori and its role in gastritis and peptic ulcer disease".

The display below shows the crystal structure found for a *Helicobacter Pylori* urease [published 2001]. The nickel ions can be identified by clicking the approriate button.

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21.11B: Nickel(IV) and Nickel(III)

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SECTION OVERVIEW

21.12: Group 11 - Copper

Topic hierarchy

21.12A: Copper Metal

21.12B: Copper(IV) and Copper(III)

21.12C: Copper(II)

21.12D: Copper(I)

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21.12A: Copper Metal

Information on the history of Copper is available at the Copper Development Association, Inc where they make the point that: "For nearly 5000 years copper was the only metal known to man. Today it is one of the most used and reused of our modern metals." Humans first used copper about 10,000 years ago. A copper pendant discovered in Northern Iraq is thought to date back to around 8700 BC. Prehistoric man probably used copper for weapon making. Ancient Egyptians too seemed to have appreciated the corrosion resistance of the metal. They used copper bands and nails in ship building and copper pipes were used to convey water. Some of these artifacts survive today in good condition. An estimate of the total Egyptian copper output over 1500 years is 10,000 tons.



Years later, copper alloys appeared. Bronzes (copper-tin alloys) came about first followed much later by brass (copper-zinc alloys). The " Bronze Age" saw the extensive use of copper and bronze for arms, coins, household utensils, furniture and other items. The earliest known example of brass use is a Roman coin minted during the reign of Augustus 27 BC- AD 14. Copper later played an important role in the advent of electricity and today is still among our most valued materials.

Usage of copper compounds also dates back to before 4000 BC. Copper sulphate for example was an especially important compound in early times. Ancient Egyptians used it as a mordant in their dyeing process. The compound was also used to make ointments and other such preparations. Later, medicinal use of copper sulphate came about with its prescription for pulmonary diseases. Copper sulphate is still extensively used today and no harmful side effects of its *prescribed* use have been reported.

Occurrence

Copper is the earth's 25th most abundant element, but one of the less common first row transition metals. It occurs as a soft reddish metal that can be found native as large boulders weighing several hundred tons or as sulphide ores. The latter are complex copper, iron and sulphur mixtures in combination with other metals such as arsenic, zinc and silver. The copper concentration in such ores is typically between 0.5-2%.

The commonest ore is chalcopyrite, $CuFeS_2$, a brass yellow ore that accounts for approximately 50% of the world's copper deposits. Numerous other copper ores of varying colors and compositions exist. Examples are malachite, $Cu_2CO_3(OH)_2$, a bright green ore, and the red ore cuprite, Cu_2O.

Copper occurs in biological systems as a part of the prosthetic group of certain proteins. For examples of copper containing proteins see the article originally from the University of Leeds, Department of Biochemistry and Molecular Biology at the Scripps Institute. The red pigment in the softbilled T(o)uraco Bird contains a copper porphyrin complex. The pigment is highly water soluble under alkaline conditions and it was reported in 1952 that attempts by zookeepers to wash a bird resulted in the water becoming tinged with red. T(o)uracos are said to be the only birds to possess true red and green color. Generally, the color you perceive when observing birds, is due to reflections produced by the feather structure. The red and green pigments (turacin and turacoverdin) found in the feathers of the T(o)uraco both contain copper.



Figure 2: The softbilled T(o)uraco Bird

The Extraction of Copper

Copper is extracted from its ore by two principal methods:

1. Pyrometallurgical method
2. Hydrometallurgical method

Pyrometallurgical Method

This technique is often used in the extraction of sulphide ores. There are four main stages:

- Mining and Milling: The ore is crushed and ground into a powder usually containing less than 1% copper. Minerals are concentrated into a slurry that is about 15% copper. Copper minerals are separated from useless material by flotation using froth forming solutions.
- Smelting: Smelting of the copper concentrate and extraction by heat, flux and addition of oxygen. Sulfur, iron and other undesirable elements are removed and the product is called blister copper.
- Refining: This is the final stage in the process for obtaining high grade copper. Fire and electro-refining methods are the techniques used. The latter produces high purity copper fit for electrical uses.

Hydrometallurgical Method -SX/EW

Solvent Extraction / Electrowinning is the most dominant leaching process used today in the recovery of copper from chemical solutions. As the name suggests the method involves two major stages:

- Solvent Extraction- the process by which copper ions are leached or otherwise extracted from the raw ore using chemical agents.
- Electrowinning- electrolysis of a metal ion containing solution such that Cu ions within it are plated onto the cathode and thereafter removed in elemental form.

The process takes place in the following steps:

- A lixivant (leaching solution) is selected for use in leaching Cu ions from the ore. Common reagents are weak acids e.g. H_2SO_4, $H_2SO_4 + Fe_2(SO_4)_3$, acidic chloride solutions e.g. $FeCl_2$, ammonium chloride and ammonium salt compositions.
- When applied to the ore the chosen lixivant dissolves the copper ions present to give a lixivant product called a "pregnant leach solution".
- An organic extractant is then selected to remove Cu ions from the aqueous solution. Preferred organic extractants consist of hydroxyphenyl oximes having the basic chemical formula:
- C_6H_3 (R)(OH) CNOHR*, R= C_9H_{19} or $C_{12}H_{25}$ and R*= H, CH_3, or C_6H_5

Examples of such extractants are 5-nonylsalicylaldoxime and a mixture of this compound and 2-hydroxy-5-nonyl-acetophenone oxime. The commercially available reagents usually contain 5%-10% of the oxime in a 90-95% petroleum dilutant such as kerosene.

Prior to mixing with lixivant product the extractant will contain little or no copper and is at this stage called the "barren organic extractant".

- Copper ions are transferred from the leaching solution to the organic extractant upon mixing of the two reagents. A phase separation takes place to give an aqueous and an organic phase termed the first aqueous and first organic phases respectively.

The first aqueous phase, the "raffinate", is the lixivant stripped of its copper ions while the first organic phase is the "loaded organic extractant" i.e. extractant with copper ions present.

- The raffinate is recycled to the leaching pad while the loaded organic extractant is mixed with an electrolyte solution called the "lean electrolyte" (i.e. containing no copper). Typical electrolytes are acidic solutions such as sulphuric acid, H_2SO_4. The copper ions that were present in the organic extractant thus dissolve in the electrolyte solution to give a copper containing "rich electrolyte." Here again there is a phase separation. The second organic phase is the barren organic extractant while the second aqueous phase is the "rich electrolyte". The barren organic extractant is then recycled for reuse in application to lixivant product.
- The final stage of the process is the electrolysis of the acidic metal ion solution. As a result dissolved copper ions become plated onto the cathode and elemental copper is removed. The recovery process is thus complete.

A Note on Impurities

The presence of suspended contaminants within a SX/EW system can significantly compromise its operating efficiency. Such contaminants may be introduced into the system from the ore or from the surroundings. The system is susceptible to contamination from rain, wind and other environmental forces since the first containment vessel, which stores lixivant product, is typically uncovered and located outdoors. Thus solid waste material in the form of dirt, sand, rock dust, vegetable matter, mineral residue and suspended solids is often introduced into the system in the early stages and persists in the subsequent stages of the process.

The effects of these contaminants are considerable and include:

- increased phase separation time at stages when organic and aqueous solvents are mixed.
- lack of complete phase separation after extraction, this results in loss of expensive organic extractant since much of it remains within the aqueous solution.
- a decrease in the current efficiency and reduction in the purity of the plated copper product in the electrolysis stage.

In most SX/EW systems purification steps have been introduced in order to alleviate this problem. In US patent (number 573341) for example, at least a portion of the second organic phase is filtered to remove solid contaminants before reuse in treating lixivant product. The recycled organic extractant therefore contains little or no impurities dependent on whether a portion or the entire second organic phase was filtered. It has been found that this filtration step considerably improves the operating efficiency, even when only a portion of the extractant is treated.

Uses of copper and its compounds

Copper is second only to iron in its usefulness down the ages. The metal and its compounds are used in every sphere of life from the electrical to medicinal and agricultural industries.

Uses of copper metal

The electrical industry is the beneficiary of most of the world's copper output. The metal is used in the manufacture of electrical apparatus such as cathodes and wires. Other uses include:

- Roofing
- Utensils
- Coins
- Metal work
- Plumbing
- Refrigerator and Air Conditioning coils
- Alloys e.g. bronze, brass

Uses of copper compounds

Copper compounds have their most extensive use in Agriculture. Since the discovery of their toxicity to certain insects, fungi and algae these compounds have been used in insecticides, fungicides and to prevent algal development in potable water reservoirs. They are therefore used in the control of animal and plant diseases. Fertilisers are also often supplemented with copper compounds, e.g. copper sulphate, in order to increase soil fertility and thus boost crop growth. Copper compounds are also used in photography

and as colorants for glass and porcelain.

Copper for Good Health

Copper is one of many trace elements required for good health. It is part of the prosthetic groups of many proteins and enzymes and thus is essential to their proper function. Since the body can not synthesize copper it must be taken in the diet. Nuts, seeds, cereals, meat (e.g. liver) and fish are good sources of copper.

Copper has also found medicinal use. It has been used from early times in the treatment of chest wounds and water purification. It has recently been suggested that copper helps to prevent inflammation associated with arthritis and such diseases. Research continues into medicines containing copper for treatment of this and other conditions.

Copper Compounds

Copper exhibits a variety of compounds, many of which are colored. The two principal oxidation states of copper are +1 and +2 although some +3 complexes are known. Copper(I) compounds are expected to be diamagnetic in nature and are usually colorless, except where color results from charge transfer or from the anion. The +1 ion has tetrahedral or square planar geometry. In solid compounds, copper(I) is often the more stable state at moderate temperatures.

The copper(II) ion is usually the more stable state in aqueous solutions. Compounds of this ion, often called cupric compounds, are usually colored. They are affected by Jahn Teller distortions and exhibit a wide range of stereochemistries with four, five, and six coordination compounds predominating. The +2 ion often shows distorted tetrahedral geometry.

Copper Halides

All of the copper(I) halides are known to exist although the fluoride has not yet been obtained in the pure state. The cuprous chlorides, bromides and iodides are colouless, diamagnetic compounds. They crystallize at ordinary temperatures with the zinc blende structure in which Cu atoms are tetrahedrally bonded to four halogens. The copper(I) chloride and bromide salts are produced by boiling an acidic solution of copper(II) ions in an excess of copper. On dilution, the white CuCl or the pale yellow CuBr is produced. Addition of soluble iodide to an aqueous solution of copper(II) ions results in the formation of a copper(I) iodide precipitate, which rapidly decomposes to Cu(I) and iodine.

The copper(I) halides are sparingly soluble in water and much of the copper in aqueous solution is in the Cu(II) state. Even so, the poor solubility of the copper(I) compounds is increased upon addition of halide ions. The table below shows some properties of copper(I) halides.

Copper(II) halides

Formula	color	MP	BP	m (BM)	Structure
CuF_2	white	950decomp	-	1.5	
$CuCl_2$	brown	632	993decomp	1.75	$CdCl_2$
$CuBr_2$	black	498	-	1.3	

All four copper(II) halides are known although cupric iodide rapidly decomposes to cuprous iodide and iodine. The yellow copper(II) chloride and the almost black copper(II) bromide are the common halides. These compounds adopt a structure with infinite parallel bands of square CuX_4 units. Cupric chlorides and bromides are readily soluble in water and in donor solvents such as acetone, alcohol and pyridine.

Copper(II) halides are moderate oxidising agents due to the Cu(I)/ Cu(II) couple. In water, where the potential is largely that of the aqua-complexes, there is not a great deal of difference between them, but in non-aqueous media, the oxidising (halogenating) power increases in the sequence;

$$CuF_2 \ll CuCl_2 \ll CuBr_2 \quad (21.12A.1)$$

They can be prepared by direct reaction with the respective halogens:

$$Cu + F_2 \longrightarrow CuF_2 \quad (21.12A.2)$$

$$Cu + Cl_2 \ / \ 450\,C \longrightarrow CuCl_2 \quad (21.12A.3)$$

$$Cu + Br_2 \longrightarrow CuBr_2 \quad (21.12A.4)$$

Alternatively they can be prepared from CuX_2.aq by heating -> CuX_2

Copper(I) halides

Formula	color	MP	BP	Structure
CuCl	white	430	1359	-
CuBr	white	483	1345	-
CuI	white	588	1293	Zinc Blende

Prepared by reduction of CuX_2 -> CuX;

except for the F which has not been obtained pure.
Note that CuI_2 has not been isolated because of the ease of reduction to CuI.

Copper Oxides

Copper(I) oxides are more stable than the copper(II) oxides at high temperatures. Copper(I) oxide occurs native as the red cuprite. In the laboratory, the reduction of Fehling's solution with a reducing sugar such as glucose produces a red precipitate. The test is sensitive enough for even 1 mg of sugar to produce the characteristic red color of the compound. Cuprous oxide can also be prepared as a yellow powder by controlled reduction of an alkaline copper(II) salt with hydrazine. Thermal decomposition of copper(II) oxide also gives copper(I) oxide since the latter has greater thermal stability. The same method can be used to prepare the compound from the copper(II) nitrate, carbonate and hydroxide.

Copper(II) oxide occurs naturally as tenorite. This black crystalline solid can be obtained by the pyrolysis of the nitrate, hydroxide or carbonate salts. It is also formed when powdered copper is heated in air or oxygen. The table below shows some characteristics of copper oxides.

Copper oxides

Formula	color	Oxidation State	MP
CuO	black	Cu^{2+}	1026decomp
Cu_2O	red	Cu^{+}	1230

Redox Chemistry of Copper

> *Cu^{2+} + e- → Cu^{+} E=0.15V*
> *Cu^{+} + e- → Cu E=0.52V*
> *Cu^{2+} + 2e- → Cu E=0.34V*

By consideration of this data, it will be seen that any oxidant strong enough to covert Cu to Cu^{+} is more than strong enough to convert Cu^{+} to Cu^{2+} (0.52 cf. 0.14V). It is not expected therefore that any stable Cu^{+} salts will exist in aqueous solution.
Disproportionation can also occur:

> *$2Cu^{+}$ → Cu^{2+} + Cu E=0.37V or $K=10^6$*

Coordination complexes

The reaction of $EDTA^{4-}$ with copper(II) gave a complex where the EDTA was found to be pentadentate NOT hexadentate, unlike other M(II) ions.

$Cu(EDTA)^{2-}$

The structure of the $[Cu(ox)_2]^{2-}$ ion can be described as square planar or as a distorted octahedron when the packing in the crystal lattice is considered. In the case of the sodium salt, the individual units are parallel in the cell with the copper linked to the oxygens coordinated to the copper in the units sitting both above and below, whereas in the potassium salt, the units are not parallel and when looking at three units the central one is almost at right angles to the other two. Here the copper is linked to one of the non-coordinated oxygens in the units above and below it.

Na^+ and K^+ salts of $[Cu(ox)_2]^{2-}$

$Cu(OH)_2$ reacts with NH_3 to give a solution which will dissolve cellulose. This is exploited in the industrial preparation of Rayon. The solutions contain tetrammines and pentammines. With pyridine, only tetramines are formed eg $Cu(py)_4SO_4$.

The reaction of copper(II) with amino-acids has been extensively studied. In nearly all cases the product contains the groups in a *trans* configuration, which is expected to be the more stable. In the case of glycine, the first product precipitated is always the *cis*-isomer which converts to the *trans*- on heating. See the Laboratory Manual for C31L for more details.

Analytical Determination of Copper(II)

A useful reagent for the analytical determination of the copper(II) ion is the sodium salt of N,N-diethyldithiocarbamate. In dilute alcohol solutions the presence of trace levels of Cu^{2+} is indicated by a yellow color, which can be measured by a spectrophotometer, and the concentration determined from a Beer's Law plot. The complex is $Cu(Et_2dtc)_2$, which can be isolated as a brown solid.

$Cu(Et_2dtc)_2$

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21.12B: Copper(IV) and Copper(III)

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21.13: Group 12 - Zinc

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21.13A: The Metal

Occurrence and extraction of zinc from zinc blende

Zinc occurs only in combined state. The important ores of zinc are zinc blende (Zns), calamine etc. These two are the important ores for the extraction of zinc.

Extraction

Zinc blende is crushed, concentrated and heated in air.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \tag{21.13A.1}$$

Zinc oxide formed above is mixed with coke in a fireclay retort. It is fitted with a condenser. The metal distills and condenses in the retort. The metal obtained is purified by electrolysis.

$$ZnO(s) + C(s) \rightarrow Zn + CO(g) \tag{21.13A.2}$$

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21.13B: Zinc(II)

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CHAPTER OVERVIEW

22: d-Block Metal Chemistry - The Heavier Metals

Heavy metals are generally defined as metals with relatively high densities, atomic weights, or atomic numbers. The criteria used, and whether metalloids are included, vary depending on the author and context. In metallurgy, for example, a heavy metal may be defined on the basis of density, whereas in physics the distinguishing criterion might be atomic number, while a chemist would likely be more concerned with chemical behavior. More specific definitions have been published, but none of these have been widely accepted.

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SECTION OVERVIEW

22.1: Introduction to d-Block Metal Chemistry

http://www.t.soka.ac.jp/chem/iwanami...rg/INO_ch6.pdf

http://www.t.soka.ac.jp/chem/iwanami...reo/index.html

https://ocw.mit.edu/courses/chemistr...ns/lecture-27/

Topic hierarchy

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22.2: Occurrence, Extraction, and Uses

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22.3: Physical Properties

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22.3A: Effects of the Lanthanoid Contraction

22.3B: Coordination Numbers

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22.3A: Effects of the Lanthanoid Contraction

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SECTION OVERVIEW

22.4: Group 3 - Yttrium

Group 3 is a group of elements in the periodic table. This group, like other d-block groups, should contain four elements, but it is not agreed what elements belong in the group. Scandium (Sc) and yttrium (Y) are always included, but the other two spaces are usually occupied by lanthanum (La) and actinium (Ac), or by lutetium (Lu) and lawrencium (Lr); less frequently, it is considered the group should be expanded to 32 elements (with all the lanthanides and actinides included) or contracted to contain only scandium and yttrium. When the group is understood to contain all of the lanthanides, its trivial name is the rare-earth metals.

22.4A: The Metal

22.4B: Yttrium(III) Ion

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22.4A: The Metal

In 1787, Carl Axel Arrhenius found a new mineral near Ytterby in Sweden and named it ytterbite, after the village. Johan Gadolin discovered yttrium's oxide in Arrhenius' sample in 1789, and Anders Gustaf Ekeberg named the new oxide yttria. Elemental yttrium was first isolated in 1828 by Friedrich Wöhler.Yttrium is a chemical element with symbol Y and atomic number 39. It is a silvery-metallic transition metal chemically similar to the lanthanides and has often been classified as a "rare-earth element". Yttrium is almost always found in combination with lanthanide elements in rare-earth minerals, and is never found in nature as a free element. 89Y is the only stable isotope, and the only isotope found in the Earth's crust.

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22.4B: Yttrium(III) Ion

As a trivalent transition metal, yttrium forms various inorganic compounds, generally in the oxidation state of +3, by giving up all three of its valence electrons. A good example is yttrium(III) oxide (Y_2O_3), also known as yttria, a six-coordinate white solid.

Yttrium forms a water-insoluble fluoride, hydroxide, and oxalate, but its bromide, chloride, iodide, nitrate and sulfate are all soluble in water. The Y^{3+} ion is colorless in solution because of the absence of electrons in the d and f electron shells. With halogens, yttrium forms trihalides such as yttrium(III) fluoride (YF_3), yttrium(III) chloride (YCl_3), and yttrium(III) bromide (YBr_3) at temperatures above roughly 200 °C.

$$2\,Y\,(s) + 3\,F_2 \rightarrow YF_3\,(s) \tag{22.4B.1}$$

Similarly, carbon, phosphorus, selenium, silicon and sulfur all form binary compounds with yttrium at elevated temperatures.

Water readily reacts with yttrium and its compounds to form Y_2O_3. Concentrated nitric and hydrofluoric acids do not rapidly attack yttrium, but other strong acids do.

Organoyttrium chemistry is the study of compounds containing carbon-yttrium bonds. They are studied in academic research, but have not received widespread use otherwise. These compounds use YCl_3 as a starting material, which is in turn obtained in a reaction of Y_2O_3 with concentrated hydrochloric acid and ammonium chloride.

Hapticity is a term to describe the coordination of a group of contiguous atoms of a ligand bound to the central atom; it is indicated by the Greek character eta, η. Yttrium complexes were the first examples of complexes where carboranyl ligands were bound to a d0-metal center through a η7-hapticity. Vaporization of the graphite intercalation compounds graphite–Y or graphite–Y2O3 leads to the formation of endohedral fullerenes such as Y@C82. Electron spin resonance studies indicated the formation of Y^{3+} and (C82)3− ion pairs. The carbides Y3C, Y2C, and YC2 can be hydrolyzed to form hydrocarbons.

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SECTION OVERVIEW

22.5: Group 4 - Zirconium and Hafnium

Group 4 is a group of elements in the periodic table. It contains the elements titanium (Ti), zirconium (Zr), hafnium (Hf) and rutherfordium (Rf). This group lies in the d-block of the periodic table. The group itself has not acquired a trivial name; it belongs to the broader grouping of the transition metals. Like other groups, the members of this family show patterns in its electron configuration, especially the outermost shells resulting in trends in chemical behavior:

Topic hierarchy

22.5A: Group 4 - Zirconium and Hafnium

22.5B: Zirconium(IV) and Hafnium(IV)

22.5C: Lower Oxidation States of Zirconium and Hafnium

22.5D: Zirconium Clusters

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22.5A: Group 4 - Zirconium and Hafnium

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22.5B: Zirconium(IV) and Hafnium(IV)

As tetravalent transition metals, all three elements form various inorganic compounds, generally in the oxidation state of +4. For the first three metals, it has been shown that they are resistant to concentrated alkalis, but halogens react with them to form tetrahalides. At higher temperatures, all three metals react with oxygen, nitrogen, carbon, boron, sulfur, and silicon. Because of the lanthanide contraction of the elements in the fifth period, zirconium and hafnium have nearly identical ionic radii. The ionic radius of Zr^{4+} is 79 picometers and that of Hf^{4+} is 78 pm.

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22.5C: Lower Oxidation States of Zirconium and Hafnium

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22.5D: Zirconium Clusters

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SECTION OVERVIEW

22.6: Group 5 - Niobium and Tantalum

Topic hierarchy

22.6A: Group 5 - Niobium and Tantalum

22.6B: Niobium(V) and Tantalum(V)

22.6C: Niobium(IV) and Tantalum(IV)

22.6D: Lower Oxidation State Halides

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22.6A: Group 5 - Niobium and Tantalum

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22.6B: Niobium(V) and Tantalum(V)

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22.6C: Niobium(IV) and Tantalum(IV)

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SECTION OVERVIEW

22.7: Group 6 - Molybdenum and Tungsten

Topic hierarchy

22.7A: The Metals

22.7B: Molybdenum(VI) and Tungsten(VI)

22.7C: Molybdenum(V) and Tungsten(V)

22.7D: Molybdenum(IV) and Tungsten(IV)

22.7E: Molybdenum(III) and Tungsten(III)

22.7F: Molybdenum(II) and Tungsten(II)

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22.7A: The Metals

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22.7B: Molybdenum(VI) and Tungsten(VI)

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SECTION OVERVIEW

22.8: Group 7 - Technetium and Rhenium

Topic hierarchy

22.8A: The Metals

22.8B: High Oxidation States of Technetium and Rhenium - M(VII), ,M(VI), and M(V)

22.8C: Technetium(IV) and Rhenium(IV)

22.8D: Technetium(III) and Rhenium(III)

22.8E: Technetium(I) and Rhenium(I)

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22.8A: The Metals

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22.8B: High Oxidation States of Technetium and Rhenium - M(VII), ,M(VI), and M(V)

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22.8C: Technetium(IV) and Rhenium(IV)

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22.8E: Technetium(I) and Rhenium(I)

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SECTION OVERVIEW

22.9: Group 8 - Ruthenium and Osmium

Topic hierarchy

22.9A: The Metals

22.9B: High Oxidation States of Ruthenium and Osmium - M(VIII), M(VII), and M(VI)

22.9C: Ruthenium(V), (IV) and Osmium(V), (IV)

22.9D: Ruthenium(III) and Osmium(III)

22.9E: Ruthenium(II) and Osmium(II)

22.9F: Mixed-valence Ruthenium Complexes

22.9: Group 8 - Ruthenium and Osmium is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

22.9A: The Metals

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22.9B: High Oxidation States of Ruthenium and Osmium - M(VIII), M(VII), and M(VI)

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22.9C: Ruthenium(V), (IV) and Osmium(V), (IV)

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22.9F: Mixed-valence Ruthenium Complexes

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SECTION OVERVIEW

22.10: Group 9 - Rhodium and Iridium

Topic hierarchy

22.10A: The Metals

22.10B: High Oxidation States of Rhodium and Iridium - M(VI) and M(V)

22.10C: Rhodium(IV) and Iridium(IV)

22.10D: Rhodium(III) and Iridium(III)

22.10E: Rhodium(II) and Iridium(II)

22.10F: Rhodium(I) and Iridium(I)

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22.10A: The Metals

Ruthenium is a chemical element with symbol Ru and atomic number 44. It is a rare transition metal belonging to the platinum group of the periodic table. Like the other metals of the platinum group, ruthenium is inert to most other chemicals.

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22.10B: High Oxidation States of Rhodium and Iridium - M(VI) and M(V)

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22.10C: Rhodium(IV) and Iridium(IV)

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SECTION OVERVIEW

22.11: Group 10 - Palladium and Platinum

Topic hierarchy

22.11A: The Metals

22.11B: The Highest Oxidation States - M(VI) and M(V)

22.11C: Palladium(IV) and Platinum(IV)

22.11D: Palladium(III), Platinum(III), and Mixed-valence Complexes

22.11E: Palladium(II) and Platinum(II)

22.11F: Platinum(-II)

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22.11A: The Metals

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22.11B: The Highest Oxidation States - M(VI) and M(V)

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22.11C: Palladium(IV) and Platinum(IV)

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22.11E: Palladium(II) and Platinum(II)

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22.11F: Platinum(-II)

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SECTION OVERVIEW

22.12: Group 11 - Silver and Gold

Topic hierarchy

22.12A: The Metals

22.12B: Gold(V) and Silver(V)

22.12C: Gold(III) and Silver(III)

22.12D: Gold(II) and Silver(II)

22.12E: Gold(I) and Silver(I)

22.12F: Gold(-I) and Silver(-I)

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22.12A: The Metals

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22.12B: Gold(V) and Silver(V)

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22.12C: Gold(III) and Silver(III)

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22.12D: Gold(II) and Silver(II)

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22.12E: Gold(I) and Silver(I)

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SECTION OVERVIEW

22.13: Group 12 - Cadmium and Mercury

Topic hierarchy

22.13A: The Metals

22.13B: Cadmium(II)

22.13C: Mercury(II)

22.13D: Mercury(I)

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22.13A: The Metals

Mercury is a heavy, silvery d-block metal that forms weak bonds and is a liquid at room temperature.

LEARNING OBJECTIVE

- Identify mercury based on its physical properties.

KEY POINTS

- Mercury is the only metal that is liquid at standard conditions for temperature and pressure.
- Mercury is a poor conductor of heat, but a fair conductor of electricity.
- Mercury has a unique electron configuration which strongly resists removal of an electron, making it behave similarly to noble gas elements. As a result, mercury forms weak bonds and is a liquid at room temperature.
- Mercury dissolves to form amalgams with gold, zinc, and many other metals.

TERM

- amalgam

  An alloy containing mercury.

FULL TEXT

Properties of Mercury

Mercury is a dense, silvery d-block element. It is the only metal that is liquid at standard conditions for temperature and pressure. The only other element that is liquid under these conditions is bromine, though metals such as caesium, gallium, and rubidium melt just above room temperature. With a freezing point of −38.83 °C and boiling point of 356.73 °C, mercury has one of the narrowest liquid state ranges of any metal. Mercury occurs in deposits throughout the world mostly as cinnabar (mercuric sulfide), an ore that is highly toxic by ingestion or inhalation. Mercury poisoning can also result from exposure to water-soluble forms of mercury (such as mercuric chloride or methylmercury), inhalation of mercury vapor, or ingestion of seafood contaminated with mercury.

Compared to other metals, mercury is a poor conductor of heat, but a fair conductor of electricity. Mercury has a unique electronic configuration which strongly resists removal of an electron, making mercury behave similarly to noble gas elements. The weak bonds formed by these elements become solids which melt easily at relatively low temperatures.



Mercury

Mercury is a silvery metal that is liquid at standard temperature and pressure (STP).

Reactivity and Amalgams

Mercury does not react with most acids, although oxidizing acids such as concentrated sulfuric acid and nitric acid dissolve it to give sulfate, nitrate, and chloride salts. Like silver, mercury reacts with atmospheric hydrogen sulfide. Mercury even reacts with solid sulfur flakes, which are used in mercury spill kits to absorb mercury vapors.

Mercury dissolves to form amalgams with gold, zinc, and many other metals. Iron is an exception, and iron flasks have been traditionally used to trade mercury. Sodium amalgam is a common reducing agent in organic synthesis, and it is also used in high-pressure sodium lamps. Mercury readily combines with aluminium to form a mercury-aluminium amalgam when the two pure metals come into contact. Since the amalgam destroys the aluminium oxide layer which protects metallic aluminium from oxidizing, even small amounts of mercury can seriously corrode aluminium. For this reason, mercury is not allowed aboard an aircraft under most circumstances because of the risk in forming an amalgam with exposed aluminium parts.

Uses of Mercury

Mercury is used in thermometers, barometers, manometers, float valves, mercury switches, and other devices. Concerns about the element's toxicity have led to mercury thermometers being largely phased out in clinical environments in favor of alcohol-filled

instruments. Mercury is still used in scientific research and as amalgam material for dental restoration. It is also used in lighting—electricity passed through mercury vapor in a phosphor tube produces short-wave ultraviolet light, causing the phosphor to fluoresce and produce visible light.

Boundless

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22.13B: Cadmium(II)

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22.13C: Mercury(II)

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22.13D: Mercury(I)

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CHAPTER OVERVIEW

23: Organometallic chemistry- s-Block and p-Block Elements

Topic hierarchy

23.1: Introduction
- 23.1A: General Methods of preparation
- 23.1B: Structure and bonding
- 23.1C: Characterization of Organometallic Complexes

23.2: Group 1 - Alkali Metal Organometallics

23.3: Group 2 Organometallics
- 23.3A: Beryllium
- 23.3B: Magnesium
- 23.3C: Calcium, Strontium, and Barium

23.4: Group 13
- 23.4A: Boron
- 23.4B: Aluminium
- 23.4C: Gallium, Indium, and Thallium

23.5: Group 14
- 23.5A: Silicon
- 23.5B: Germanium
- 23.5C: Tin
- 23.5D: Lead
- 23.5E: Coparallel and Tilted \(C_5\)-rings in Group 14 Metallocenes

23.6: Group 15
- 23.6A: Bonding Aspects and \(E=E\) Bond Formation
- 23.6B: Arsenic, Antimony, and Bismuth

23.7: Group 16
- 23.7A: Selenium and Tellurium

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23.1: Introduction

Main Group Organometallic Chemistry

Introduction

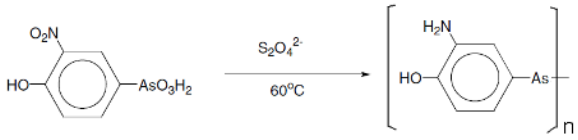
Organometallic compounds have been known and studied for over 250 years. Many of these early compounds were prepared directly from the metal by oxidative addition of alkyl halides. All these metals have strong or moderately negative reduction potentials, with lithium and magnesium being the most reactive. Halide reactivity increases in the order: Cl < Br < I.

In 1757 Louis Claude Cadet de Gassicourt prepared what is believed to be the first synthetic organometallic compound and it was isolated from arseneous oxide (As_2O_3) and potassium acetate. The mixture was named after him "Cadet's fuming liquid" from which came cacodyl oxide.

$4\ KCH_3COO + As_2O_3 \rightarrow As_2(CH_3)_4O + 4\ K_2CO_3 + CO_2 \rightarrow \rightarrow As_2(CH_3)_4$

which disproportionates to produce among other things cacodyl, $As_2(CH_3)_4$. The poisonous garlic-smelling red oily-liquid is unstable undergoing spontaneous combustion in dry air.

Another organoarsenic compound, Salvarsan, was one of the first pharmaceuticals, and earned a Nobel Prize in Medicine for Paul Ehrlich in 1908 (jointly with Ilya Ilyich Mechnikov). Its activity against syphilis was discovered as a result of the first largescale testing of chemicals and had a code name of 606 since it was apparently the 606th chemical that had been tested in Ehrlich's laboratory in his quest for the "magic bullet". The compound was synthesised by reaction of 3-nitro-4- hydroxyphenylarsonic acid with dithionite.



The structure has only recently been characterised as a mixture of polyarsines $(AsR)_n$ n= 3-6, and originally it was proposed that it was a dimer with an As=As double bond.

trimer	pentamer

Edward Frankland prepared the first organozinc compound (diethylzinc) in 1848 from zinc metal and ethyl iodide, he went on to improve the synthesis of diethylzinc by using diethyl mercury as starting material.

$2R\text{-}X + 2Zn \rightarrow R_2Zn + ZnX_2$

Grignard reagents are formed via the action of an alkyl or aryl halide on magnesium metal.

$R\text{-}X + Mg \rightarrow R\text{-}Mg\text{-}X$

Victor Grignard was jointly awarded the 1912 Nobel Prize in Chemistry.

Carl Jacob Lowig (1803-1890) reported the preparation of the first alkyltin and alkyllead compounds in 1852/3. He reacted ethyl iodide and Sn/Na or Pb/Na alloy

Wilhelm Johann Schlenk discovered organolithium compounds around 1917.

$R\text{-}X + 2Li \rightarrow R\text{-}Li + LiX$

He also investigated free radicals and carbanions and discovered (together with his son) that organomagnesium halides are capable of participating in a complex chemical equilibrium, now known as a Schlenk equilibrium.

$2RMgX \rightarrow MgX_2 + MgR_2$

Karl Ziegler

His work with free radicals led him to the organo compounds of the alkali metals. He discovered that ether scission opened a new method of preparing sodium and potassium alkyls; later (1930) he directly synthesized lithium alkyls and aryls from metallic lithium and halogenated hydrocarbons. This important discovery made the lithium compounds as readily available as the familiar Grignard reagents.

Ziegler is perhaps best remembered for his work with Giulio Natta on what are called Ziegler-Natta catalysts. These catalysts are typically based on titanium compounds and organometallic aluminium compounds, such triethylaluminium, $(C_2H_5)_3Al$ and are used to polymerize terminal 1-alkenes.

n CH_2=CHR → -[CH_2-CHR]$_n$-

Together they won the Nobel Prize in Chemistry in 1963.

Classification of organometallic compounds

1	2									12	13	14	15	16	17	18
H																He
Li	Be										B	C	N	O	F	Ne
Na	Mg										Al	Si	P	S	Cl	Ar
K	Ca									Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr									Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba									Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra															

d-block

Examples will be selected from the circled elements.

The organometallic compounds to be considered in this course are those containing a M-C bond, excluding carbonyls (M-CO), cyanides (M-CN) or carbides (M-C). A useful subdivision is by the type of M-C bond:

- ionic - with most Group 1 elements
- covalent - with many Group 12, 13, 14 and 15 elements
- electron deficient - with Li, Be, Mg, B, Al

Ionic

Ionic organometallic compounds are generally formed from elements such as sodium, potassium etc. where the metals are considered electropositive. If the organic groups are able to delocalise the negative charge over several carbon atoms then less electropositive elements like magnesium can also form ionic compounds, eg Cp_2Mg. In this case the charge is considered to be delocalised over each of the five carbon atoms in each ring.

Covalent

The simplest model of the M-C bond is where it consists of essentially a single covalent 2-electron bond. These compounds are often volatile and are comparable to typical organic compounds being soluble in organic solvents.

Electron deficient

Electron deficient organometallic compounds are generally associated with elements that have less than half-filled valence shells and are designated as such because of an insufficient number of valence electrons to allow all the atoms to be linked by traditional two-electron two-centre bonds. The compounds often have bridged or polymeric structures. The methyl derivatives of Li, Be and

Al are found to be 3-D polymers, linear chains and dimeric respectively and despite the increase in RMM of the monomeric unit there is actually an increase in volatility.

Compound	RMM of monomeric unit	Structure	Volatility
LiMe	21.96	3D-polymer	infusible
$BeMe_2$	39.08	Linear chain	sublimes at 473 K
$AlMe_3$	72.08	Dimer	Melts at 288 K

There has been some criticism of the term electron deficient since if a MO approach to the bonding is used then the bonding MO's derived from combination of the available atomic orbitals of suitable energy are generally full. Rundle (who determined the structure of $BeMe_2$) is reported to have made the comment that:

> *There is no such thing as electron deficient compounds, only theory deficient chemists.*

Stability of Organometallic compounds

The M-C bond energies for some methyl derivatives are shown in the Table below. Plotting these values against Atomic Number of the metal shows that there is a decrease down a Group. This behaviour is expected since there should be better orbital overlap between similar valence orbitals and this would decrease for the larger more diffuse elements lower down a Group.

Bond dissociation energies and Heats of Formation

Me_2M	D / kJ mol^{-1}	ΔHf / kJ mol^{-1}	BP /K	Me_3M	D / kJ mol^{-1}	ΔHf / kJ mol^{-1}	BP /K	Me_4M	D / kJ mol^{-1}	ΔHf / kJ mol^{-1}	BP /K
Me_2Be			490.2	Me_3B	364.0	-122.6	251.2	Me_4C	347.3	-167.4	283.2
Me_2Mg				Me_3Al	276.1	-129.7	399.2	Me_4Si	292.9	-238.5	300.2
Me_2Zn	175.7	54.8	317.2	Me_3Ga	246.9	-45	329.2	Me_4Ge	246.9	-71	316.2
Me_2Cd	138.1	109.6	379.2	Me_3In	171.5		409.2	Me_4Sn	217.6	-19.2	350.2
Me_2Hg	121.3	93.3	366.2	Me_3Tl			420.2	Me4Pb	154.8	136.4	383.2
				Me3As	230.1	15.5	325.2				
				Me3Sb	217.6	31.0	352.2				
				Me3Bi	142.3	192.9	383.2				

Thermal Stability

In general terms thermodynamic stability means that the ΔG° is negative i.e. the energy of the products is more stable than that of the starting materials. Since little free energy data is available, it is often assumed that ΔH can be considered as a guide remembering that the entropies of gases are much larger than for liquids, which is again much larger than for solids and this can be taken into account as well.

if we take as an example the thermal decomposition of EtLi:
$EtLi \rightarrow LiH + CH_2{=}CH_2$
ΔHf EtLi = -58.55 kJ mol^{-1}
ΔHf $CH_2{=}CH_2$ = +52.40 kJ mol^{-1}
ΔHf LiH = -90.45 kJ mol^{-1}
so that the overall enthalpy change is: = (RHS - LHS) = 52.40 - 90.45 + 58.55
= +20.50 kJ mol^{-1}

This therefore suggests that the data favours the stability of EtLi over the products. However, given that at room temperature the Entropy of gaseous ethylene (ethene) is high $T\Delta S = +64.4$ kJ mol^{-1} and the entropies for solids will be much smaller, then using $\Delta G = \Delta H - T\Delta S$ it is likely that ΔG will be a sizable NEGATIVE value which would suggest that EtLi should be unstable.

Kinetic Stablity

Calculations of free energy would suggest that many organometallic compounds should be unstable. However, kinetic stability needs to be considered as well since if there is no low activation energy pathway for a reaction to proceed then it may be very slow.

Stability to Oxidation

All organometallic compounds are expected to be thermodynamically unstable with respect to oxidation to give metal oxide, carbon dioxide and water. Some are spectacularly so, being highly pyrophoric. In general organometallic compounds need to be handled under dry nitrogen or some other inert gas to avoid oxidation.

Stability to Hydrolysis

Hydrolysis of organometallic compounds often involves nucleophilic attack by water which is accentuated when there are low-lying empty orbitals on the metal atom. This is seen for Groups I, II and for Zn, Cd, Al, Ga etc and the speed of hydrolysis is dependent on the M-C bond polarity. For "Me_3Al" rapid attack occurs whereas Me_3B is unaffected at room temperature.

Classification of Synthetic Reactions

1. **Elemental Reactions**
a) with organic halides - the most important method
eg $RX + M \rightarrow RM + MX$

b) with hydrocarbons
i)substitution
where the hydrocarbons are acidic
eg $RC{\equiv}C\text{-}H + K \rightarrow RC{\equiv}C\text{-}K + \frac{1}{2}H_2$
eg $R + K \rightarrow RK + \frac{1}{2}H_2$
ii) addition
eg $Na + naphthalene \rightarrow Na^+ naphth^- (C_8H_{10})^-$

c) with other organometallics - transmetallation
eg $M + M'R \rightarrow MR + M'$

2. **Reactions with Element halides or salts**
a) with hydrocarbons
eg $RH + HgX_2 \rightarrow RHgX + HX$

b) with other organometallics
eg $MX + M'R \rightarrow M'X + MR$

3. **Addition and Elimination Reactions**
a) addition
eg $\text{-M-X} + RHC{=}CH_2 \rightarrow \text{M-C-C-X}$
$Ph_3SnH + PhCH{=}CH_2 \rightarrow Ph_3SnCH_2CH_2.Ph$

b) elimination
eg $\text{-M-A-B-C} \rightarrow \text{-M-C} + A{=}B$
$Hg(\text{-OOC-R})_2 + heat \rightarrow HgR_2 + 2CO_2$

References

1. "Inorganic Chemistry" - C. Housecroft and A.G. Sharpe, Prentice Hall, 3rd Ed., Dec 2007, ISBN13: 978-0131755536, ISBN10: 0131755536, Chapter 17.
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23.1A: General Methods of preparation

Learning Objectives

In this lecture you will learn the following

- Various synthetic methodologies to make M—C bonds.
- How to choose an appropriate synthetic method.
- Reaction conditions and the role of solvents.

An organometallic compound contains one or more metal-carbon bonds.

Synthesis

General Methods of Preparation

Most organometallic compounds can be synthesized by using one of four M-C bond forming reactions of a metal with an organic halide, metal displacement, metathesis and hydrometallation.

The net reaction of an electropositive metal M and a halogen-substituted hydrocarbon is



If, one metal atom takes the place of another, it is called transmetallation



Transmetallation is favorable when the displacing metal is higher in the electrochemical series than the displaced metal.

a. Reaction with metal and transmetallation

Metathesis

The metathesis of an organometallic compound MR and a binary halide EX is a widely used synthetic route in organometallic chemistry.



Metathesis reaction can frequently be predicted from electronegativity or hard and soft acid-base considerations.

Hydrocarbon groups tends to bond to the more electronegative element; the halogen favors the formation of ionic compounds with the more electropositive metal.

In brief, the alkyl and aryl group tends to migrate from the less to the more electronegative element [χ = electronegativity].



When the electronegativities are similar, the correct outcome may be predicted, with care*, by considering the combination of the softer element with organic group and harder element with fluoride or chloride.

*An insoluble product or reactant may change the outcome, e.g.;



HgPhBr turns out to be insoluble in THF
Metathesis reactions involving the same central element are often referred to as redistribution reactions.



Al is more electropositive than Ge, this reaction occurs as it is thermodynamically favorable.

Hydrometallation

The net outcome of the addition of a metal hydride to an alkene is an alkylmetal compound.



The reaction is driven by the high strength of E-C bond relative to that of most E-H bonds, and occurs with a wide variety of compounds that contain E-H bonds.

Hydroboration



Hydrosilylation



Ionic and electron-deficient compounds of Group 1, 2

Organometallic derivatives of all Group 1 metals are known. Amongst, the alkyllithium compounds are most thoroughly studied and useful reagents.
Many of them are commercially available.
MeLi is generally handled in ether solution, but RLi compounds with longer chains are soluble in hydrocarbons.

Commercial preparation:



The best method would be:



MeLi exists as a tetrahedral cluster in the solid state and in the solution. Many of its higher homologs exist in solution as hexamers or equilibrium mixture of aggregates ranging up to haxamers.

The larger aggregates can be broken down by Lewis bases, such as, TMEDA.

Common organolithium compounds have one Li per organic group.
Several polylithiated organic molecules containing several lithium atoms per molecule are known.

Ionic and electron-deficient compounds of Group 1, 2 (contd..)

The simplest example is Li_2CH_2, which can be prepared by the pyrolysis of MeLi which crystallizes in a distorted antifulorite* structure. However, the finer details of the orientation of the CH_2 groups are yet to be established.



*the antifluorite structure is the inverse of the fluorite structure in which the locations ofcations and anions are reversed. Look into the structures of CaF_2 (fluorite structure) and K_2O (antifluorite structure). An fcc array of cations and all the tetrahedral holes are filled with anions.

Radical anion salts

Sodium naphthalide is an example of an organometallic salt with a delocalized radical anion, $C_{10}H_8^-$.

Such compounds are readily prepared by reacting an aromatic compound with an alkali metal in a polar aprotic solvent.

Naphthalene dissolved in THF reacts with Na metal to produce a dark green solution of sodium naphthalide.



EPR spectra show that the odd electron is delocalized in an antibonding orbital of $C_{10}H_8$.

Formation of radical anion is more favorable when the π of LUMO of the arene is low in energy.

Simple MOT predicts that the energy of LUMO decreases steadily on going from benzene to more extensively conjugated hydrocarbons.

Sodium naphthalide and similar compounds are highly reactive reducing agents.

They are preferred to sodium because unlike sodium, they are readily soluble in ethers.

Radical anion salts (contd..)

The resulting homogeneous reaction is generally faster and easier to control than a heterogeneous reaction between one reagent in solution and pieces of sodium metal, which are often coated with unreactive sodium oxide or with insoluble reaction products.

The additional advantage is that by proper choice of the aromatic group the reduction potential of the reagent can be chosen to match the requirements of a particular synthetic task.

Alternative route to delocalized anion is the reductive cleavage of acidic C—H bonds by an alkali metal or alkylmetallic compound.

Example:



Problems:

1. Classify the following reactions into, (i) hydrometallation, metal displacement, metathesis OR transmetallation reactions; (ii) give an example for each case in the form of a balanced chemical equation.

   Solution:

   a. M + Mx'R → M' + MR ….Transmetallation
      e.g.: $2Ga + 3CH_3\text{-}Hg\text{-}CH_3 \rightarrow 3Hg + 2Ga(CH_3)_3$
   b. MR + EX → ER + MX ….Metathesis
      e.g.: $Li_4(CH_3)_4 + SiCl_4 \rightarrow 4LiCl + Si(CH_3)_4$ or
      $Al_2(CH_3)_6 + 2BF_3$ à $2AlF_3 + 2B(CH_3)_3$
   c. EH + $H_2C{=}CH_2$ → E—CH_2—CH_3 ….Hydrometallation
      e.g.:  Hydroboration

       Hydrosilylation

Problems:

2. For each of the following compounds, indicate those that may serve as
   (1) a good carbanion nucleophile reagent,
   (2) a mild Lewis acid,
   (3) a mild Lewis base at the central atom,
   (4) a strong reducing agent. (A compound may have more than one of these properties)
   (a) $Li_4(CH_3)_4$, (b) $Zn(CH_3)_2$, (c) $(CH_3)MgBr$, (d) $B(CH_3)_3$, (e) $Al_2(CH_3)_6$, (f) $Si(CH_3)_4$, (g) $As(CH_3)_3$.

   Solution:

   a. $(MeLi)_4$ - good carbanion nucleophile and strong reducing agent
   b. $ZnMe_2$ - reasonable carbanion nucleophile, mild Lewis acid, reducing agent
   c. MeMgBr - good carbanion nucleophile
   d. BMe_3 - mild Lewis acid
   e. Al_2Me_6 - good carbanion nucleophile, strong reducing agent
   f. $SiMe_4$ - mild Lewis acid
   g. $AsMe_3$ - mild Lewis base

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23.1B: Structure and bonding

Learning Objectives

In this lecture you will learn the following

- Solid state structures of nickel-arsenide, alkyl lithium and alkyl aluminium compounds.

Structure and bonding

The slight differences that arise between organometallic compounds and binary hydrogen compounds are mainly due to the tendency of alkyl groups to avoid ionic bonding. The molecular structures of $AlMe_3$and MeLi differ from $AlH_3$and LiH. Even the more ionic MeK crystallizes in the nickel-arsenide structure rather than the rock-salt structure adopted by KCl.

Nickel-arsenide structure is typical of soft-cation, soft-anion combinations.

Electron deficient compounds such as $AlMe_3$contain 3c-2e bonds analogous to the B—H—B bridges in diborane.

The Nickel-Arsenide, NiAs, Structure



MeLi in nonpolar solvents consists of tetrahedron of Li atoms with each face bridged by a methyl group. Similar to Al_2Me_6, the bonding in MeLi consists of a set of localized molecular orbitals. The symmetric combination of three Li 2s orbitals on each face of the Li_4 tetrahedron and one sp^3 hybrid orbital from CH_3 gives an orbital that can accommodate a pair of electron to form a 4c-2e bond.



The lower energy of the C orbital compared with the Li orbitals indicates that the bonding pair of electrons will be associated primarily with the CH_3 group, thus supporting the carbanionic character of the molecule. Some analysis has indicated that about 90% ionic character for the Li-CH_3 interaction.



The interaction between an sp^3 orbital from a methyl group and the three 2s orbitals of the Li atoms in a triangular face of $Li_4(CH_3)_4$ to form a totally symmetric 4c,2e bonding orbital. The next higher orbital is non-bonding and the uppermost is antibonding.

Me_2Be and Me_2Mg exist in a polymeric structure with two 3c,2e-bonding CH_3 bridges between each metal atom.

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23.1C: Characterization of Organometallic Complexes

Learning Objectives

In this lecture you will learn the following

- The characterization techniques of organometallic compounds.
- The NMR analysis of these compounds.
- The IR analysis of these compounds.
- The X-ray single crystal diffraction studies of these compounds.

The characterization of an organometallic complex involves obtaining a complete understanding of the same right from its identification to the assessment of its purity content, to even elucidation of its stereochemical features. Detailed structural understanding of the organometallic compounds is critical for obtaining an insight on its properties and which is achieved based on the structure-property paradigm.

Synthesis and isolation

Synthesis and isolation are two very important experimental protocols in the overall scheme of things of organometallic chemistry and thus these needs to be performed carefully. The isolation of the organometallic compounds is essential for their characterization and reactivity studies. Fortunately, many of the methods of organic chemistry can be used in organometallic chemistry as the organometallic compounds are mostly nonvolatile crystalline solids at room temperature and atmospheric pressure though a few examples of these compounds are known to exist in the liquid [$(CH_3C_5H_4Mn(CO)_3$] and even in the vapor [$Ni(CO)_4$] states. The organometallic compounds are comparatively more sensitive to aerial oxygen and moisture, and because of which the manipulation of these compounds requires stringent experimental skills to constantly provide them with anaerobic environment for their protection. All of these necessities led to the development of the so-called special Schlenk techniques, requiring special glasswares and which in conjunction with a high vacuum line and a dry box allow the lab bench-top manipulation of these compounds. Successful isolation of organometallic compounds naturally points to the need for various spectroscopic techniques for their characterizations and some of the important ones are discussed below.

1H NMR spectroscopy

The ^{1}H NMR spectroscopy is among the extensively used techniques for the characterization of organometallic compounds. Of particular interest is the application of ^{1}H NMR spectroscopy in the characterization of the metal hydride complexes, for which the metal hydride moiety appear at a distinct chemical shift range between 0 ppm to −40 ppm to the high field of tetramethyl silane (TMS). This upfield shift of the metal hydride moiety is attributed to a shielding by metal *d*−electrons and the extent of the upfield shift increases with higher the d^n configuration. Chemical shifts, peak intensities as well as coupling constants from the through-bond couplings between adjacent nuclei like that of the observation of $J_{P\text{-}H}$, if a phosphorous nucleus is present within the coupling range of a proton nucleus, are often used for the analysis of these compounds. The ^{1}H NMR spectroscopy is often successfully employed in studying more complex issues like fluxionality and diastereotopy in organometallic molecules (Figure 1).



Figure 1. Different phosphorous-proton coupling patterns in various iridium hydride complexes. The paramagnetic organometallic complexes show a large range of chemical shifts, for example, $(\eta^6-C_6H_6)_2V$ exhibits proton resonances that extend even up to 290 ppm.

13C NMR spectroscopy

Although the natural abundance of NMR active ^{13}C (I = ½) nuclei is only 1 %, it is possible to obtain a proton decoupled $^{13}C\{^1H\}$ NMR spectra for most of the organometallic complexes. In addition, the off−resonance ^1H decoupled ^{13}C experiments yield $^1J_{C-H}$ coupling constants, which contain vital structural information, and hence are very critical to the ^{13}C NMR spectral analysis. For example, the $^1J_{C-H}$ coupling constants directly correlate with the hybridization of the C−H bonds with *sp* center exhibiting a $^1J_{C-H}$ coupling constant of ~250 Hz, a sp^2 center of 160 Hz and a sp^3 center of 125 Hz. Similar to what is seen in ^1H NMR, a phosphorous−carbon coupling is also observed in a ^{13}C NMR spectrum with the *trans* coupling (~100 Hz) being larger than the *cis* coupling (~10 Hz).

^{31}P NMR spectroscopy

The ^{31}P NMR spectroscopy, which in conjunction with ^1H and ^{13}C NMR spectroscopies, is a useful technique in studying the phosphine containing organometallic complexes. The ^{31}P NMR experiments are routinely run under ^1H decoupled conditions for simplification of the spectral features that allow convenience in spectral analysis. Thus, for this very reason, many mechanistic studies on catalytic cycle are conveniently undertaken by ^{31}P NMR spectroscopy whenever applicable.

IR spectroscopy

Qualitative to semi-quantitative analysis of organometallic compounds using IR spectroscopy are performed whenever possible. In general the signature stretching vibrations for chemical bonds are more conveniently looked at in these studies. The frequency (ν) of a stretching vibration of a covalent bond is directly proportional to the strength of the bond, usually given by the force constant (*k*) and inversely proportional to the reduced mass of the system, which relates to the masses of the individual atoms.



The organometallic compounds containing carbonyl groups are regularly studied using IR spectroscopy, and in which the CO peaks appear in the range between 2100−1700 cm^{-1} as distinctly intense peaks.

Crystallography

The solid state structure elucidation using single crystal diffraction studies are extremely useful techniques for the characterization of the organometallic compounds and for which the X-ray diffraction and neutron diffraction studies are often undertaken. As these methods give a three dimensional structural rendition at a molecular level, they are of significant importance among the various

available characterization methods. The X-ray diffraction technique is founded on Bragg's law that explains the diffraction pattern arising out of a repetitive arrangement of the atoms located at the crystal lattices.

$2d \sin \theta = n\lambda$ A major limitation of the X-ray diffraction is that the technique is not sensitive enough to detect the hydrogen atoms, which appear as weak peaks as opposed to intense peaks arising out of the more electron rich metal atoms, and hence are not very useful for metal hydride compounds. Neutron diffraction studies can detect hydrogens more accurately and thus are good for the analysis of the metal hydride complexes.

Summary

Along with the synthesis, the isolation and the characterization protocols are also integral part of the experimental organometallic chemistry. Because of their air and moisture sensitivities, specialized experimental techniques that succeed in performing the synthesis, isolation and storage of these compounds in an air and moisture-free environment are often used. The organometallic compounds are characterized by various spectroscopic techniques including the ^{1}H NMR, ^{13}C NMR and IR spectroscopies and the X-ray and the neutron diffraction studies.

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23.2: Group 1 - Alkali Metal Organometallics

Learning Objectives

In this lecture you will learn the following

- How to synthesize and handle sodium, lithium compounds.
- Structural features.

Organometallic compounds of alkaline metals

Organic compounds such as terminal alkynes which contain relatively acidic hydrogen atoms form salts with the alkali metals.



NaCp is pyrophoric in air, but air-sensitivity can be lessened by complexing the Na^+ with dme.
In the solid state, [Na(dme)][Cp] is polymeric

**Pyrophoric material: is one that burns spontaneously when exposed to air.*



Organolithium compounds are of particular importance among the group 1 organometallics.

Many of them are commercially available as solutions in hydrocarbon solvents.

Solvent choices for reactions involving organometallics of the alkali metals are critical. For example, ^{n}BuLi is decomposed by Et_2O to give ^{n}BuH, C_2H_4 and LiOEt.

Alkali metal organometallics are extremely reactive and must be handled in air- and moisture-free environments; NaMe, for example, burns explosively in air.

Lithium alkyls are polymeric both in solution and in the solid state.



NMR is very useful in understanding the solution structures; ^{6}Li (I = 1), ^{7}Li (I = ½), ^{13}C (I = ½)

The structures of $(^{t}BuLi)_4$ and $(MeLi)_4$ are similar. $^{n}BuLi$ when mixed with TMEDA, gives a polymeric chain. TMEDA link cubane units together through the formation of Li-N bonds.

Alkyllithium compounds are soluble in organic solvents whereas Na and K salts are insoluble, but are solubilized by the chelating ligand TMEDA. Addition of TMEDA may break down the aggregates of lithium alkyls to give lower nuclearity complexes. E.g. $[^{n}BuLi.TMEDA]_2$

However, detailed studies have revealed that the system is far from simple, and it is possible to isolate crystals of either $[^{n}BULi.TMEDA]_2$ or $[(^{n}BuLi)_4.TMEDA]_\infty$.
In the case of $(MeLi)_4$, the addition of TMEDA does not lead to cluster breakdown, and the X-ray structure confirms the composition $(MeLi)_4.2TMEDA$, the presence of both tetramers and the amine molecules in the crystal lattice.

N. D. R. Barnett et al. *J. Am. Chem. Soc.*, 1993, 115, 1573.

Lithium alkyls and aryls are very useful reagents in organic synthesis and also in making corresponding carbon compounds of main group elements. Lithium alkyls are important catalysts in the synthetic rubber industry for the stereospecific polymerization of alkenes.

Transmetallation:



Organolithium compounds:



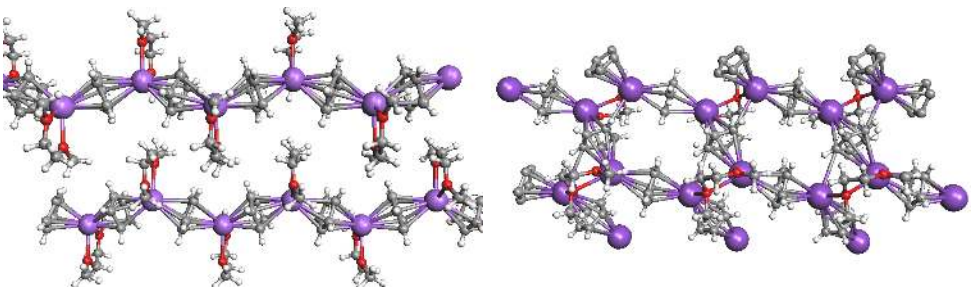
Some typical examples include:
MeLi and nBuLi which depending on solvent may exist as tetramers or hexamers.
(cyclohexyl)Li which exists as a hexamer.
t-BuLi exists as a tetramer and can coordinate diethylether to form a dimer or a bulky diamine like tetraethylethylenediamine (TEEDA) to give a monomer.

n-butyllithium

Sodium forms ionic salts with terminal alkynes and cyclopentadiene:
$2Na^+ + 2\ HC{\equiv}CEt \rightarrow 2\ Na^+[C{\equiv}CEt]^- + H_2$

(in THF) $Cp + NaH \rightarrow Na^+\ Cp^- + H_2$

This salt is pyrophoric but it has been found that when 1,2-dimethoxyethane is added as complexing agent the product is less air-sensitive. Both the Na and K salts have been isolated and their structures determined.



Na(dme)Cp and K(dme)Cp.

The nomenclature used to denote the idea that the 5-carbons of the cp ring are equally attached is by the use of η^5. For the case where only 1-carbon is attached then the designation would be η^1. Here the Greek letter "eta" is used and the term is generally called "hapticity".

Sodium and potassium form intensely coloured salts with aromatic compounds. The alkali metal is oxidised and transfers one electron to the aromatic system and this becomes a paramagnetic radical anion:
$Na + naphthalene \rightarrow Na^+[C_8H_{10}]^-$
In the case of napthalene, the salt is deep blue.

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SECTION OVERVIEW

23.3: Group 2 Organometallics

Topic hierarchy

23.3A: Beryllium

23.3B: Magnesium

23.3C: Calcium, Strontium, and Barium

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23.3A: Beryllium

Learning Objectives

In this lecture you will learn the following

- Organometallic compounds of beryllium and magnesium.
- Structural features of alkyl lithium and beryllium sandwich compounds.

Synthesis

Organoberyllium compounds are best prepared via transmetallation reactions or by reaction of beryllium halides with other organometallic compounds e.g.,

$$\mathrm{HgMe_2 + Be \xrightarrow{383\ K} Me_2Be + Hg} \tag{23.3A.1}$$

$$\mathrm{2\,PhLi + BeCl_2 \xrightarrow{diethyle\ ether} Ph_2Be + 2\,LiCl} \tag{23.3A.2}$$

In the vapor phase $\mathrm{Me_2Be}$ is monomeric with a linear C—Be—C (Be-C = 170 pm), but in the solid state it is polymeric and resembles that of $\mathrm{BeCl_2}$ with a bonding that is considered electron deficient with 3-center-2-electron bonds. With higher alkyls the amount of polymerisation decreases and the tert-butyl derivative is monomeric and linear in both solid and vapour phases.

$$\mathrm{2\,NaCp + BeCl_2 \longrightarrow Cp_2Be + 2\,NaCl} \tag{23.3A.3}$$

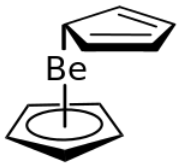
However, ^{1}H NMR spectrum shows that all protons environments are equivalent even at 163 K. Also, the solid state structure shows the Be atom is disordered over two equivalent sites and NMR data can be interpreted in terms of fluxional process in which the Be atom moves between these two sites.

Beryllocene

The reaction of NaCp with beryllium chloride leads to beryllocene ($\mathrm{Cp_2Be}$)

$$\mathrm{2\,K\,[C_5Me_5] + BeCl_2 \xrightarrow[ether/toluene]{388\ K} (C_5Me_5)_2Be + 2\,KCl} \tag{23.3A.4}$$

The solid state structure suggests that the two rings are bound to the Be differently such that 1 is designated η^5 and the other η^1.



Structure of $(\eta^1\mathrm{-Cp})(\eta^5\mathrm{-Cp})\mathrm{Be}$ *also called Beryllocene*

The experimental ^{1}H NMR spectrum adds to the confusion of the bonding since even at 163 K the protons all appear equivalent. This is accounted for by fluxional processes. Some variations of the compound have been prepared to see how general this effect is, for example, 4 protons on each ring replaced by methyl groups and all 5 protons replaced by methyl groups, $(\mathrm{meCp})_2\mathrm{Be}$, and even 4 on one ring and 5 on the other replaced with methyl groups. In the first case the fluxional process was observed down to 183K and in the second case the two rings were found to be coparallel and staggered. (Note that the structure of ferrocene is described as eclipsed when prepared at very low temperatures or in the gas phase but when formed at higher temperatures it is disordered and more staggered and since the barrier to rotation of the two rings is quite low, at 298 K in the solid state there is motion).

However, $\mathrm{Cp^*_2Be}$ possesses a sandwich structure with both the rings are coplanar.



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23.3B: Magnesium

Grignard Reagents

Alkyl and aryl magnesium halides (Grignard reagents, RMgX) are extremely well-known on account of their uses in synthetic chemistry. Over the past 100 years, Gringnard reagents had probably been the most widely used organometallic reagents. The general procedure for their preparation was discovered by Victor Grignard in 1900 and involved the direct reaction of magnesium with organohalides.

$$\mathrm{R{-}X + Mg \longrightarrow R{-}Mg{-}X,\ (X{=}\ Cl, Br, I)} \tag{23.3B.1}$$

When the reaction is performed in diethyl ether or THF and in the absence of air and moisture, the compounds are reasonably stable although they need to be used immediately. Grignard reactions often start slowly. As is common for reactions involving solids and solution, initiation follows an induction period during which reactive magnesium becomes exposed to the organic reagents. After this induction period, the reactions can be highly exothermic.

Transmetallation is useful means of preparing pure Grignard reagents

$$\mathrm{Mg + RHgBr \longrightarrow Hg + RMgBr} \tag{23.3B.2}$$

$$\mathrm{Mg + R_2Hg \ \rightarrow Hg + R_2Mg} \tag{23.3B.3}$$

Two-coordination at Mg in $\mathrm{R_2Mg}$ is observed only when the R groups are sufficiently bulky, e.g. $\mathrm{Mg\{C(SiMe_3)_3\}_2}$. RMgX are generally solvated and Mg center is typically tetrahedral (e.g. $\mathrm{EtMgBr.2Et_2O}$; $\mathrm{PhMgBr.2Et_2O}$); $\mathrm{Cp_2Mg}$ has a staggered sandwich structure.

The composition of ether solutions of Grignards was investigated by the Schlenk's who reported what is now called the **Schlenk Equilibrium**:

$$\mathrm{2\,RMgX \ \rightleftharpoons MgX_2 + MgR_2} \tag{23.3B.4}$$

The notation of RMgX for Grigarnd reacgents is therefore an oversimplification of what truly exists in ether solutions. In diethyl ether, a tendency to form monomeric, dimeric and higher oligomeric species was found and was dependent on the halogen and organic substituents. Figure $23.3B.1$ indicates the percentage of RMgX for a range of Grignard Reagents.

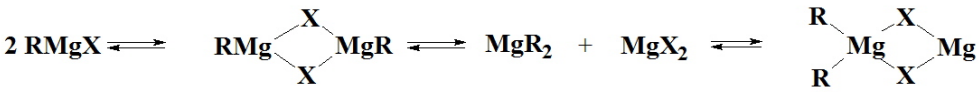


Figure $23.3B.1$***: Composition of solutions of Grignard Reagents in diethyl ether solution at equilibrium. In diethyl ether, a tendency to form monomeric, dimeric and higher oligomeric species was found and was dependent on the halogen and organic substituents.***

Solutions of Grignard reagent may contain several species, e.g. RMgX, $\mathrm{R_2Mg}$, $\mathrm{MgX_2}$, $\mathrm{RMg(\mu\text{-}X)_2MgR}$, which are further complicated by solvation. The position of equilibrium between these species is markedly dependent on concentration, temperature and solvent; strongly donating solvents favor monomeric species in which they coordinate to the metal center.

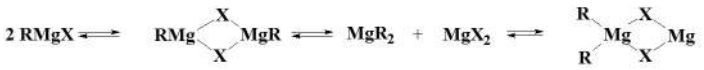


Figure $23.3B.2$: Expanded Schlenk Equilibrium

In tetrahydofuran (THF) the structures were found to be closer to monomeric but it was recognized that the solid state structures may be very different to what exists in solution. For example, when "EtMgCl" is isolated from a THF solution a tetramer was found where the Mg have coordination numbers higher than the expected 4.

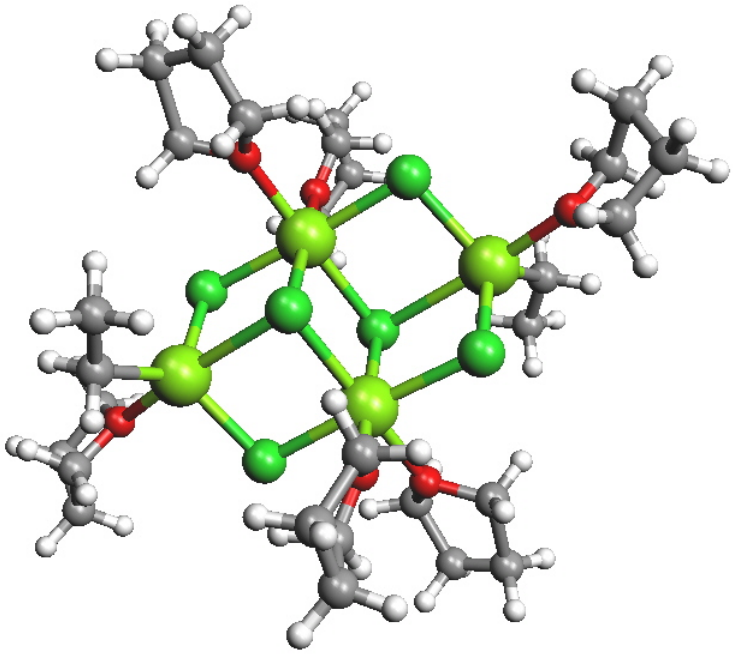


Figure 23.3B.3***:*** EtMgCl isolated from THF.

In the polymeric structures it is generally the halide, rather than the organic group that bridges between the magnesiums.

Reactions of Grignard Reagents

The most common application for the use of Grignard Reagents in Organic Chemistry is for alkylation of aldehydes and ketones, for example:

$$\mathrm{R_1R_2C{=}O + R_3MgX \longrightarrow R_1R_2R_3C{-}OMgX \longrightarrow R_1R_2R_3C{-}OH} \tag{23.3B.5}$$

and more generally:

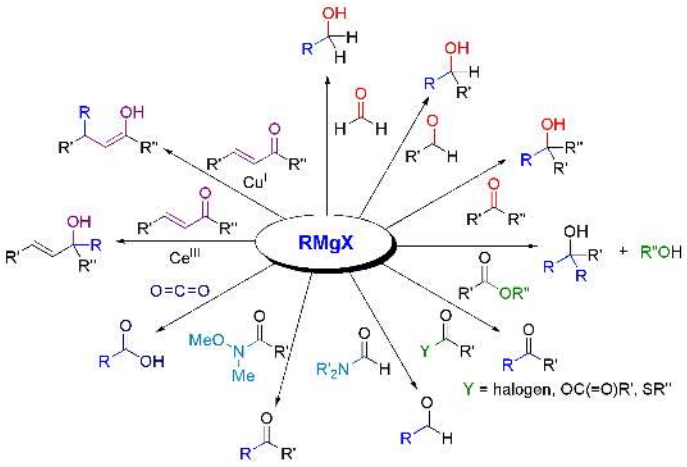


Figure 23.3B.4***:*** Reactions with carbonyls

Other reactions include carbon-carbon coupling which is often affected using a catalyst like transition metal halides.

$$\mathrm{2\,ArMgX + MXn \longrightarrow Ar{-}Ar + MgX_2 + MX_{n-2}} \tag{23.3B.6}$$

and for cross-coupling reactions:

$$\mathrm{ArMgX + RCH{=}CHX \xrightarrow{5\ mol_2} ArCH{=}CHR + MgBrX} \tag{23.3B.7}$$

using, for example, 5 mol% $CoCl_2$ as catalyst and to determine the difference in reactivity of the halides, a series of competitive reactions were performed:

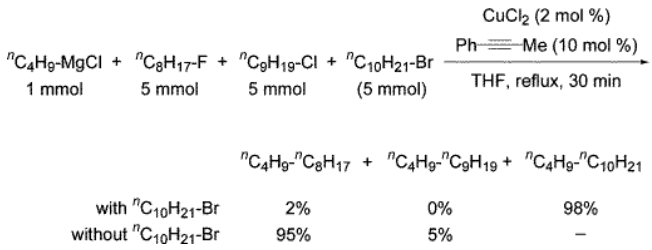


Figure 23.3B.5***:*** Cross-coupling Reactions with Grignard Reagents - 2008 review

Terao and Kambe reported that when they took a mixture of equimolar amounts of n-octyl fluoride, n-nonyl chloride, and n-decyl bromide and added to this $CuCl_2$, 1-phenylpropyne, and a THF solution of n-ButylMgCl, then after the reaction was stirred for 30 min in THF at reflux, GC analysis of the resulting mixture indicated the selective formation of tetradecane in 98% yield along with 2% yield of dodecane. A similar reaction using only alkyl fluorides and chlorides gave dodecane and tridecane in 95% and 5% yields, respectively. These results indicated that the reactivity of alkyl halides was in the order:

$$\text{bromide} > \text{fluoride} > \text{chloride} \tag{23.3B.8}$$

Table 23.3B.1: Transition metal halide catalyzed coupling of phenylmagnesium iodide

metal halide	amt, mol	amt of C_6H_5MgI, mol	yield of biphenyl, %
$FeCl_2$	0.01	0.03	98
$CoBr_2$	0.01	0.03	98
$NiBr_2$	0.03	0.095	100
$RuCl_3$	0.0036	0.0108	99
$RhCl_3$	0.0036	0.013	97.5
$PdCl_2$	0.00566	0.0163	98
$OsCl_3$	0.00275	0.007	53
$IrCl_3$	0.003	0.01	28

Industrial Use

A Grignard reaction that is a key step in an industrial production is shown below, where the target is Tamoxifen. Tamoxifen is an antagonist of the estrogen receptor in breast tissue and it is the standard endocrine (anti-estrogen) therapy for hormone-positive early breast cancer in post-menopausal women.

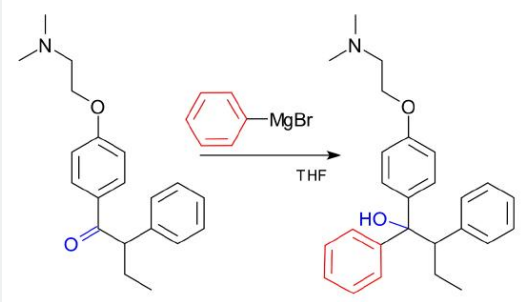


Figure 23.3B.5***:*** *Tamoxifen synthesis using a Grignard Reagent*

Problems

Q1

If a typical Grignard reagent exists as an equilibrium mixture of dialkylmagnesium and magnesium halide, give a method of isolating pure dialkyl magnesium. Your answer should be in the form of balanced chemical equations only.

Solution:



Treatment of equilibrium mixture with dioxane results in the precipitation of, say, $MgCl_2$(dioxane) (if, X = Cl), leaving behind pure R_2Mg in the solution.



Q2

The compound $(Me_3Si)_2C(MgBr)_2.nTHF$ is monomeric. Suggest a value of '*n*' and propose a structure for this Grignard reagent.

Solution:



References

1. "Inorganic Chemistry" - C. Housecroft and A.G. Sharpe, Prentice Hall, 3rd Ed., Dec 2007, ISBN13: 978-0131755536, ISBN10: 0131755536, Chapter 17.
2. "Chemistry of the Elements", Greenwood and Earnshaw, Elsevier.

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23.3C: Calcium, Strontium, and Barium

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23.4A: Boron

Organoboron Compounds

BMe_3 is colorless, gaseous (b.p. -22 °C), and is monomeric. It is pyrophoric but not rapidly hydrolyzed by water.

Alkylboranes can be synthesized by metathesis between BX_3 and organometallic compounds of metals with low electronegativity, such as RMgX or AlR_3.



Why dibutyl ether as a solvent: Has much lower vapor pressure than BMe_3 and as a result the separation by trap-to-trap distillation on a vacuum line is easy.

Also, there is a very weak association between BMe_3 and OBu_2(Me_3B:OBu_2).

Although, trialkyl- and triarylboron compounds are mild Lewis acids, strong carbanion reagents lead to anions of the type $[BR_4]^-$.

Example, $Na[BPh]_4$: The bulky anion hydrolyses very slowly in neutral or basic water and is useful for the preparation of large positive cations.



$K[BPh]_4$ is insoluble, used for the gravimetric estimation (determination) of potassium, an example of the low solubility of large-cation and large-anion salts in water.



Organohaloboron compounds are more reactive than simple trialkylboron compounds.

Preparation



Reactions: (Protolysis reactions with ROH, R_2NH and other reagents)

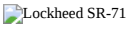


Boron

Most alkyl and aryl organoboron compounds are reasonably stable in water, although they may still be fairly air sensitive even pyrophoric. They are usually monomeric. For example, triethylborane (TEB) is strongly pyrophoric, igniting spontaneously in air. It burns intensely with a very hot flame. The color of the flame is apple-green, which is characteristic for boron compounds. Its vapours may cause flash fires. This was first noted by Frankland in 1860 when he first prepared Et_3B from Et_2Zn by transmetallation.

Et_3B is soluble in tetrahydrofuran and hexane, and is not pyrophoric when in solution. However the solution can slowly react with atmospheric moisture. If the TEB solutions are exposed to air for prolonged time, unstable organic peroxides may form. It has been found to be toxic to the peripheral nervous system, kidneys and testes and is extremely corrosive.

The Lockheed SR-71 strategic reconnaissance aircraft uses as fuel a mixture of hydrocarbons known as JP-7. The very low volatility and relative unwillingness of JP-7 to be ignited required a pyrophoric material like triethylborane (TEB) to be injected into the engine in order to initiate combustion and allow afterburner operation in flight.


Lockheed SR-71

Lockheed SR-71, 'Blackbird'

JP-7 jet fuel was designed to have a relatively high flash point (60 °C) to cope with the heat. In fact, the fuel was used as a coolant and hydraulic fluid in the aircraft before being burned. The fuel also contained fluorocarbons to increase its lubricity, an oxidizing

agent to enable it to burn in the engines, and even a caesium compound, A-50, to help disguise the exhaust's radar signature.

JP-7 is very slippery and extremely difficult to light in any conventional way. The slipperiness was a disadvantage on the ground, because inevitably the aircraft leaked small amounts of fuel when not flying, fortunately JP-7 was not a fire hazard. When the engines of the aircraft were started, puffs of triethylborane (TEB), which ignites on contact with air, were injected into the engines to produce temperatures high enough to ignite the JP-7 initially. The TEB produced a characteristic puff of greenish flame that could often be seen as the engines were ignited. TEB was also used to ignite the afterburners. The aircraft had only 600 ml of TEB on board for each engine, enough for at least 16 injections (a counter advised the pilot of the number of TEB injections remaining), but this was considered more than enough for the requirements of any missions it was likely to carry out.

The triarylborane, BPh_3, is less reactive and forms the salt $Na[BPh_4]$ that is water soluble and is useful as a precipitating agent for large metal ions.

R_2BCl and $RBCl_2$ have been prepared by transmetallation and these have been used to generate species like $R_2B(\mu\text{-}H)_2BR_2$. One example of this is the reagent (9-BBN) that is used for the regioselective reduction of ketone, aldehydes, alkynes and nitriles. Its highly stereoselective addition on olefins allows the preparation of terminal alcohols by subsequent oxidative cleavage with H_2O_2 in aq. KOH. The steric demand of 9-BBN greatly suppresses the formation of the 2-substituted isomer compared to the use of borane.

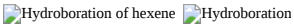
It has been found to be a useful reagent for the Suziki Reaction:



Suzuki Reaction Scheme

Hydroboration

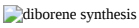
The hydroboration-oxidation reaction is a two-step organic chemical reaction that converts an alkene into a neutral alcohol by the net addition of water across the double bond. The hydrogen and hydroxyl group are added in a syn addition leading to cis stereochemistry. Hydroboration-oxidation is an anti-Markovnikov reaction, with the hydroxyl group attaching to the less-substituted carbon. The reaction was first reported by Herbert C. Brown in the late 1950s and he received the Nobel Prize in Chemistry in 1979. Shown below is the original reaction described in 1957 where hex-1-ene is converted to hexanol.



H. C. Brown reaction of 1957 other hydroboration reactions

Diborene

The first structurally characterized neutral diborene containing a B=B double bond was reported in 2007. It was prepared by the following scheme:



Synthesis of a diborene

According to the authors, the carbene ligands were the key to the ability of boron to form the diborene's B=B bond. The divalent carbon atom of each carbene is able to donate its two free electrons to form a carbon-boron bond, allowing the boron's three valence electrons to form a bond to hydrogen and a σ and a π bond to the other boron.

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23.4B: Aluminium

Learning Objectives

In this lecture you will learn the following

- Preparation and reactivity of organoboron and organo aluminium compounds.
- Influence of Lewis acidity on structural features.

Organoaluminium compounds

With less bulky alkyl groups, dimerization occurs and one of the distinguishing features of alkyl bridge is the small Al-C-Al angle, which is ~ 75°.

The 3c,2e bonds are very weak and tend to dissociate in the pure liquid which increases with increase in the bulkiness of the alkyl group.





Perpendicular orientation of pheynl groups in Al_2Ph_6
Triphenylaluminium exists as a dimer with bridging η^1-phenyl groups lying in a plane perpendicular to the line joining the two Al atoms.



This structure is favored partly on steric grounds and partly by supplementation of the Al-C-Al bond by electron donation from the phenyl π-orbitals to the Al atoms.

Tendency for bridging: X > Ph > alkyl

3c,2e bonds formed by a symmetric combination of Al and C orbitals



An additional interaction between the pπ orbital on C and an antisymmetric combination of Al orbitals.



Synthesis

Very useful as alkene polymerization catalysts and chemical intermediates.
Expensive carbanion reagents for the replacement of halogens organic groups by metathesis.

Laboratory scale preparations involves:



Commercial method:



Commercial method for ethylaluminium and higher homologs:



The reaction probably proceeds by the formation of a surface Al—H species that adds across the double bond of the alkene in a hydrometallation reaction.



Reactions:

Alkylaluminum compounds are mild Lewis acids and form complexes with ethers, amines and anions. When heated, often β-hydrogen elimination is responsible for the decomposition of ethyl and higher alkylaluminium compounds. E.g. $Al(^{i}C_4H_9)_3$
Tendency towards bridging structure is: PR_2^- > X^- > H^- > Ph^- > R^-.

The first organoaluminium compound, an alkylaluminium sesqui-halide, $Et_3Al_2I_3$ was reported in 1859 and was formed by reaction of elemental Al and EtI. "Me_3Al" was obtained by George Buckton from aluminium and dimethylmercury as early as 1865. In hydrocarbon solution and in the solid state there is a tendency for R_3Al to dimerise; this is very dependent on the size of the R group, eg a dimer for Me but monomer for tert-butyl. $Me(t\text{-}Bu)_5Al_2$ is found to be a dimer as well with the methyl group and 1 of the t-Bu groups in the bridging positions. The bridging ability is found to be Me > Et > t-Bu and clearly the case above is not what would be predicted on purely statistical terms since there are 5 times as many t-Bu groups as Me groups and there are twice as many terminal positions as bridging positions so the methyl group might have been expected to fill a terminal position.

$Et_3Al_2I_3$

Many organoaluminium compounds are commercially available at quite reasonable prices so that is is rarely necessary to have to prepare them in the laboratory. Reaction of Al turnings with organic halides leads to the alkylaluminium sesqui-halides. The reaction is very exothermic. The sesqui-halides do not have sharp melting or boiling points because they are in fact equilibrium mixtures:

$R_3Al_2X_3$ sesqui halide equilibria

It took almost 100 years before K. Ziegler discovered the synthetic and catalytic potential of organoaluminum compounds. From an industrial viewpoint, the organic compounds of aluminium are probably the most important organometallic compounds.

The reasons for this include:

- inexpensive synthesis from olefin + H_2 + Al (pressure).
- R_3Al can dimerise olefins
- higher alcohols (→ detergents) are made from $R_3Al + CH_2{=}CH_2$.
- In combination with Ti and Zr compounds, R_3Al can polymerise ethylene to give polyethylene
- Reactions with R_3Al proceed in hydrocarbons or even without solvent (unlike RMgX !).
- Useful commercially for polymer synthesis catalysts

Karl Ziegler, who pioneered basic research in the field of organoaluminium compounds developed a strikingly simple yet versatile process for the synthesis of organoaluminium compounds from inexpensive starting materials. The Ziegler Direct Process allows the synthesis of triethylaluminium from aluminum metal, hydrogen and ethylene. The process involves the following:

$$2Al + 3H_2 + 6RHC{=}CH_2 \rightarrow Al_2(CH_2CH_2R)_6 \{R{=}H \text{ for } (Et_3Al)_2\}$$

The Ziegler-Natta polymerisation catalysts were originally formed from Et_3Al with $TiCl_4$ and a schematic representation of the reactions at the heterogeneous surface is given below:

Ziegler Natta polymerisation

Polymerisation of ethene to high-molecular mass polyethylene occurred at relatively low pressures and the polymers were stereoregular. What this means is that isotactic polymers are formed where the R groups are all located on the same side of the carbon backbone. The resulting product gives a crystalline material since packing is more regular. The other varieties of linear polymer are called syndiotactic and atactic and in the first the R groups are on alternate sides of the carbon backbone and in the latter they are randomly distributed.

Isotactic, syndiotactic and atactic linear polymer chains

The importance of his research was soon recognized and he received the 1963 Nobel Prize for Chemistry, together with Giulio Natta who made fundamental contributions to the polymerization field.

Compounds of the type $Me_2Al(\mu\text{-}Ph)_2AlMe_2$ and $Ph_2Al(\mu\text{-}Ph)_2AlPh_2$ show that the bridging phenyl groups are almost vertical compared to the $R_2Al\text{-}AlR_2$ plane and the *ipso*-carbon is a distorted tetrahedral.

A similar case is found with bridging alkynes -C≡C-R where the terminal groups are t-Bu and when the Al is changed to Ga. Although in the latter case the phenyl groups are at right angles to each other.

However a very different arrangement with bridging alkynes has been found where they point towards one of the Al centres. Here the bonding is interpreted as a mixture of σ and π bonds; an Al-C σ bond connects to the first Al but the second Al centre is bound using the C≡C π bond. Examples of this are for $Me_2Al(PhC{\equiv}C)_2AlMe_2$ and for the analogous Gallium compound.

Problems

1. Propose a structure for $Al_2(Me)_4Cl_2$.

   Solution:
   Similar to diborane: 

2. Solution:
   Lower force constant for Si-O-Si bending.

3. Explain how the difference in reactivity between Al-C and Si-C bonds with O-H groups leads to the choice of different strategies for the synthesis of aluminum and silicon alkoxides.

   Solution:

   $Al_2Me_6 + 6\ MeOH \rightarrow 2Al(OMe)_3 + 6\ CH_4$

For reaction of Al_2Me_6 with alcohols, see the text book by Shriver and Atkins.
Tetramethylsilane does not react with methyl alcohol. Therefore, the appropriate reagent is tetrachlorosilane and the reaction is:

$SiCl_4 + 4\ MeOH \rightarrow Si(OMe)_4 + 4HCl.$

Problems: (contd..)

4. Compare formulas of the most stable hydrogen compounds of germanium and arsenic with those of their methyl compounds. Can the differences be explained in terms of the relative electronegativities of C and H?

   Solution:

GeH_4, GeR_4; AsH_3, AsR_3.

The stability of hydrides and alkyls are very similar for each element. This may due to similar H and C electronegativity.

4. To buy from a chemical company, the price of trimethylaluminum is higher than that of triethylaluminum. Is it due to the methods of synthesis? Rationalize the price difference.

   Solution:
   Triethylaluminum can be made in larger quantities by direct reaction of aluminum, hydrogen gas and ethane gas which is a cheaper method.



Preparation of trimethyaluminum involves a more expensive route such as MeCl and aluminum to form $Al_2Me_4Cl_2$ followed by treatment with sodium metal. The sodium metal and MeCl are not cheap as compared to ethane and hydrogen gases.



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23.4C: Gallium, Indium, and Thallium

Learning Objectives

In this lecture you will learn the following

- Chemistry of gallium and indium.
- *How to stabilize M—M multiple bonds*.

Organometallic compounds of gallium and indium



Trialkylgallium compounds are mild Lewis acids, so the corresponding metathesis reaction in ether produces the complex $(C_2H_5)_2OGa(C_2H_5)_3$. Similarly excess use of C_2H_5Li leads to the salt, $Li[Ga(C_2H_5)_4]$.



Alkylindium and alkylthalium compounds may be prepared similar to gallium analogs. $InMe_3$ is monomeric in the gas phase and in the solid the bond lengths indicate that association is very weak. Partial hydrolysis of $TlMe_3$ yields the linear $(MeTiMe]^+$ion, which is isoelectronic and isostructural with $HgMe_2$.

CpIn and CoTl exist as monomers in the gas phase but are associated in solids {Inert-pair effect is displayed for In and Tl}. CpTl is useful as a synthetic reagent in organometallic chemistry because it is not as highly reducing as NaCp.





Species of the type R_4E_2(single E-E bond) and $[R_4E_2]^-$ (with E-E bond order of 1.5) can be prepared for Ga and In with bulky R groups (R = $(Me_3Si)_2CH$, 2,4,6-$^iPr_3C_6H_2$), and reduction of $[(2,4,6\text{-}^iPr_3C_6H_2)_4Ga_2]$ to $[(2,4,6\text{-}^iPr_3C_6H_2)_4Ga_2]^-$ is accompanied by a shortening of the Ga—Ga bond from 252-234 pm.

Using even bulkier substituents, it is possible to prepare gallium(I) compounds, RGa starting from GaI. No structural data are yet available for these monomers
(We are working on it).



Crystallized as dimer but reverts to monomer when dissolved in cyclohexane.





Interest in organometallic comounds of Ga, In and Tl is mainly because of their potential use as precursors to semiconducting materials such as GaAs and InP. Volatile compounds can be used in the growth of thin films by MOCVD (metal organic chemical vapor deposition) or MOVPE (metal organic vapor phase epitaxy) techniques. Precursors include appropriate Lewis base adducts of metal alkyls, e.g. $Me_3Ga.NMe_3$ and $Me_3In.PEt_3$. Thermal decomposition of gaseous precursors result in semiconductors (III-V semiconductors) which can be deposited in thin films.



III-V semiconductors: Derive their name from the old groups 13 and 15, and include AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs and InSb. Off these GaAs is of the greatest commercial interest. Although Si is probably the most important commercial semiconductor, a major advandage of GaAs over Si is that the charge carrier mobility is much greater. This makes GaAs suitable for high-speed electronic devices.

Another important difference is that GaAs exhibits a fuly allowed electronic transition between valence and conduction bands (i.e. it is direct band gap semiconductor) whereas Si is an indirect band gap semiconductor. The consequence of difference is that GaAs (also other III-V types) are more suited than Si for use in optoelectronic devices, since light is emitted more efficiently. The III-Vs have important applications in light-emitting diodes (LEDs).

Problems

1. Predict the structure of monomeric, Cp_3Ga; polymeric Cp_3In and CpIn.

   Solution:
   See the articles Organometallics 1985, 4, 751.
   Inorg. Chem. 1972, 11, 2832.
   Organometallics 1988, 7, 105.

2. The reaction of $[(R_3C)_4Ga_4]$ (R = a bulky substituent) (i) with I_2 in boiling hexane results in the formation of $[(R_3C)GaI]_2$(ii) and $[(R_3C)GaI_2]_2$(iii). Draw the structure and state the oxidation state for (i) - (iii).

   Solution:



3. The I_2 oxidation of $[(^tBu\}_4In_4]$ leads to the formation of the In^{II} compound $[(^tBu\}_4In_4I_4]$ in which each indium atom retains a tetrahedral environment. Draw the correct structure.

   Solution:



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23.5: Group 14

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23.5A: Silicon

Learning Objectives

In this lecture you will learn the following

- Organosilicon and organogermanium compounds.
- Compounds with Si=Si and Ge=Ge bonds.

Organosilicon Compounds

Organosilicon compounds are extensively studied due to the wide range of commercial applications as water repellents, lubricants, and sealants. Many oxo-bridged organosilicon compounds can be synthesized. e.g. $(CH_3)_3Si—O—Si(CH_3)_3$ which is resistant to moisture and air.



The lone pairs on O are partially delocalized into vacant σ*- orbitals of Si, as a result the directionality of the Si-O bond is reduced making the structure more flexible. This flexibility permits silicone elastomers to remain rubber-like down to very low temperature. Delocalization also accounts for low basicity of an O atom attached to silicon as the electrons needed for the O atom to act as a base are partially removed. The planarity of $N(SiH_3)_3$ is also explained by the delocalization of the lone pair on N which makes it very weakly basic.

$$n\,\mathrm{MeCl} + \mathrm{Si/Cu} \xrightarrow{573\,\mathrm{K}} \mathrm{Me}_n\mathrm{SiCl}_{4-n} \tag{23.5A.1}$$

$$\mathrm{SiCl_4} + 4\,\mathrm{RLi} \rightarrow \mathrm{R_4Si} \tag{23.5A.2}$$

$$\mathrm{SiCl_4} + \mathrm{RLi} \rightarrow \mathrm{RSiCl_3} \tag{23.5A.3}$$

$$\mathrm{SiCl_4} + 2\,\mathrm{RMgCl} \rightarrow \mathrm{R_2SiCl_2} + 2\,\mathrm{MgCl_2} \tag{23.5A.4}$$

$$\mathrm{Me_2SiCl} + {}_2{}^t\mathrm{BuLi} \rightarrow {}^t\mathrm{BuMe_2SiCl} + \mathrm{LiCl} \tag{23.5A.5}$$

Si—C bonds are relatively strong (bond enthalpy is 318 kJ mol^{-1}) and R_4Si derivatives possess high thermal stabilities.

Et_4Si on chlorination gives $(ClCH_2CH_2)_4Si$. The hydrolysis of Me_2SiCl_2 produce silicones.

$$\mathrm{Me_3SiCl_2} + \mathrm{NaCp} \rightarrow (\eta^1\text{-Cp})\mathrm{SiHMe_3} \tag{23.5A.6}$$

$(\eta^1\text{-}C_5Me_5)\,2\,SiBr_2$ on treatment with anthracene/potassium gives Cp^*_2Si . The solid state structure of Cp^*_2Si consists of two independent molecules which differ in the relative orientations of the Cp rings. In one molecule, they are parallel and staggered whereas in the other, they are tilted with an angle of 167° at Si.

The reaction between R_2SiCl_2 and alkali metal or alkali naphthalides give cyclo-$(R_2Si)_n$ by loss of Cl^- and Si—Si bond formation.

Bulky R groups favor small rings [e.g. $(2,6\text{-}Me_2C_6H_3)_6Si_3$ and $^tBu_6Si_3$] while smaller R groups encourage the formation of large rings [$Me_{12}Si_6$, $Me_{14}Si_7$ and $Me_{32}Si_{16}$]

$$\mathrm{Ph_2SiCl_2} + \mathrm{Li(SiPh_2)Li} \rightarrow \mathrm{cyclo\text{-}Ph_{12}Si_6} + 2\,\mathrm{LiCl} \tag{23.5A.7}$$

Bulky substituents stabilize $R_2Si{=}SiR_2$ compounds. The sterically demanding 2,4,6-$^iPr_3C_6H_2$ provided first example of compound containing conjugated Si=Si bonds. Has s-cis configuration in both solution and the solid state.



**The spatial arrangement of two conjugated double bonds about the intervening single bond is described as s- cis if synperiplanar and s-trans if antiperiplanar.*

Organogermanium compounds

Et_4Si on chlorination gives ($(ClCH_2CH_2)_4Si$), in contrast to the chlorination of R_4Ge or R_4Sn which yields R_nGeCl_{4-n} or R_nSnCl_{4-n}. Similar germanium compounds wiht conjugated Ge=Ge bonds are also known



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23.5B: Germanium

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23.5C: Tin

Learning Objectives

In this lecture you will learn the following

- *Organotin and organolead compounds and their preparation.*
- *Bonding in tin compounds with Sn=Sn double bonds.*
- *Uses and environmental issues with tin compounds.*
- Reactivity of tetraethyl lead.
- Structural features of organolead compounds.

Preparation of Sn(IV) derivatives



Tin(II) organometallics of the type R_2Sn, containing Sn-C σ-bonds, are stabilized only if R is sterically demanding.



(monomeric in solution and dimeric in solid state). But the dimer does not possess a planar Sn_2R_4framework unlike an analogous alkene, and Sn—Sn bond distance (267 pm) is shorter than a normal Sn—Sn single bond (276 pm).

Sn_2R_4 has a trans bent structure with a weak Sn=Sn double bond



Look into the reactions of R_3SnCl with various reagents to form useful tin containing starting materials
The first organotin(II) hydride was reported only in 2000.



Shows dimeric structure in the solid state containing hydride bridges (Sn-Sn = 312 pm).

Commercial uses and environmental problems

Organotin(II) compounds find wide range of applications due to their catalytic and biocidal properties.

$^{n}Bu_3SnOAc$ is an effective fungicide and bactericide and also a polymerization catalyst.

$^{n}Bu_2Sn(OAc)_2$ is used as a polymerization catalyst and a stabilizer for PVC.

$^{n}Bu_3SnOSn^{n}Bu_3$ is algicide, fungicide and wood-preserving agent.

$^{n}Bu_3SnCl$ is a bactericide and fungicide.

Ph_3SnOH used as an agricultural fungicide for crops such as potato, sugar beet and peanuts.

The cylic compound $(^{n}Bu_2SnS)_3$ is used as a stabilizer for PVC.

Tributyltin derivatives have been used as antifouling agents, applied to the underside of ships' hulls to prevent the build-up of, for example, barnacles.

Global legislation now bans or greatly restricts the use of organotin-based anti-fouling agents on environmental grounds. Environmental risks associated with the uses of organotin compounds as pesticides, fungicides and PVC stabilizers are also a cause for concern.

*A barnacle is a type of arthropod belonging to infraclass Cirripedia in the sub-phylum Crustacea, and is hence related to crabs and lobsters.

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23.5D: Lead

Organolead compounds

Tetraethyllead



Laboratory Scale,



Thermolysis leads to radical reactions.



Tetraalkyl and tetraaryl lead compounds are inert with respect to attack by air and water at room temperature. WHY ????





Me_3PbCl consists of linear chain
Solid state structure of Cp_2Pb shows polymeric nature, but in the gas phase, discrete Cp_2Pb molecules are present which possess the bent structure similar to silicon analogue.
$R_2Pb{=}PbR_2$ are similar to analogues tin compounds

Problems

1. Find out the structures of $(Me_3SiCH_2)_3SnF$ and Me_2SnF_2

   Solution: use VSEPR theory
2.

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23.5E: Coparallel and Tilted C 5 -rings in Group 14 Metallocenes

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SECTION OVERVIEW

23.6: Group 15

Topic hierarchy

23.6A: Bonding Aspects and \(E=E\) Bond Formation

23.6B: Arsenic, Antimony, and Bismuth

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23.6A: Bonding Aspects and $E = E$ Bond Formation

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23.6B: Arsenic, Antimony, and Bismuth

Learning Objectives

In this lecture you will learn the following

- Organoaresnic and organoantimony compounds.
- Preparation and reactivity of pentavlent As and Sb compounds.

Organic chemistry of non-metal phosphorus, metalloids such as arsine and antimony along with metallic element bismuth is termed as organoelement chemistry. The importance given to organoarsenic compounds earlier due to their medicinal values was waded out after antibiotics were discovered and also their carcinogenic and toxic properties were revealed. Also, the synthetically important organometallic compounds of group 13 and 14 masked the growth of group 15 elements. However, the organoelement compounds of phosphorus, arsenic and antimony find usefulness as ligands in transition metal chemistry due to their σ-donor and π-acceptor abilities which can be readily tuned by simply changing the substituents. These donor properties are very useful in tuning them as ligands to make suitable metal complexes for metal mediated homogeneous catalysis. Although organoelement compounds can be formed in both +3 (trivalent and tricoordinated) and +5(pentavalent and tetra or pentacoordinated) oxidation states, trivalent compounds are important in coordination chemistry.

For organoelement compounds of group 15, the energy of E—C bond decreases in the order, E = P > As > Sb > Bi, and in the same sequence E—C bond polarity increases.

Organometallic compounds of As(V) and Sb(V)

Due to the strong oxidizing nature of pentahalides, the direct alkylation or arylation to generate ER_5 is not feasible, but can be prepared in two steps.
A few representative methods of preparation are given below:



Structures and properties

Pentaalkyl or pentaaryl derivatives are moderately thermally stable. On heating above 100°C, they form trivalent compounds as shown below:



Reaction with water,



Pentavalent compounds readily form “tetrahedral onium” cations and “octahedral and hexacoordinatged ate” anions.



In solid state, Ph_5As adopts trigonal bipyramidal geometry, whereas Ph_5Sb prefers square based pyramidal geometry although the energy difference between the two is marginal.

The salts of the type $[R_4E]^+$ adopt tetrahedral geometry, whereas hexacoordinated anions $[R_6E]^-$assume octahedral geometry.

Mixed organo-halo compounds of the type R_nEX_{5-n} adopt often dimeric structures due to the presence of lone pairs of electrons on X which can readily coordinate to the second molecule. The following structural types can be anticipated.



The thermal stability of R_nEX_{5-n} decreases with decreasing ‘n’. Thermal reactions are essentially the reverse reactions of addition reactions used in the preparation of R_5E.



Organometallic compounds of As(III) and Sb(III)

In this lecture you will learn the following

- Preparation of trivalent compounds.
- Mono and bis derivatives.
- Reaction of organo arsenic and antimony compounds.
- Structural features of organolead compounds.

Organometallic compound of As(III) and Sb(III).

Direct synthesis

Mono- derivatives



Direct synthesis (contd..)

Bis derivatives:



Reactions of trialkyl derivatives, R_3E



The transition metal chemistry of R_3E, phosphines, arsines or stibines has been extensively studied because of their distinct donor and acceptor properties. Among them, the phosphines or tertiary phosphines (R_3P) are the most valuable ligands in metal mediated homogeneous catalysis. Interestingly, the steric and electronic properties can be readily tuned by changing the substituents on phosphorus atoms. Chapter 16 is fully dedicated to the chemistry of phosphines.

Properties

Trialkyl derivatives are highly air-sensitive liquids with low boiling points and some of them are even pyrophyric. Triphenyl derivatives are solids at room temperature and are moderately stable and oxidizing agents such as $KMnO_4$, H_2O_2 or TMNO are needed for oxidation to form $Ph_3E{=}O$.

Cyclic and acyclic derivatives containing E—E bonds

E—E single bonds:

The E—E bond energies suggest that they do not have greater stability and the stability decreases down the group.

The simplest molecules include $Ph_2P{—}PPh_2$, $Me_2As{—}AsMe_2$ prepared by coupling reactions:



The weakness of E—E bonds accounts for many interesting reactions and a few of such reactions are listed below:



Cyclic and polycyclic derivatives can be prepared by employing any of the following methods:



Problems

1. Confirm that the octahedral structure of $[Ph_6Bi]^-$ is consistent with VSEPR theory.

   Solution:
   Octahedral similar to PF_6^-
   5 (Bi valence electrons) + 6 (each Ph) + 1 (-ve charge) = 12 electrons

   i.e. six pairs, octahedral geometry

2. Comment on the stability of $BiMe_3$ and $Al_2(^iBu)_6$ with respect to their thermal decomposition and give chemical equations for their decomposition.

   Solution:
   Similar to other heavy p-block elements, Bi—C bonds are weak and readily undergo homolytic cleavage. The resulting methyl radicals will react with other radicals or form ethane

   The $Al_2(^iBu)_6$ dimer readily dissociates. At elevated temperature dissociation is followed by β-hydrogen elimination. This type of elimination is common for organometallic compounds that have alkyl groups with β-hydrogens, can form stable M—H bonds, and can provide a coordination site on the central metal.

   The decomposition reaction is:

Problems: (contd..)

3. Using a suitable Grignard reagent, how would you prepare (i) MeC(Et)(OH)Ph; (ii) $AsPh_3$.

   Solution:

   1. Add a Grignard reagent to a C=O bond, then acidify.

      Several possibilities, e.g.
      Me-C(O)-Et + PhMgBr → Me-C(OMgBr)(Et)(Ph) → MeC(Et)(OH)Ph or Me-C(O)-Ph + EtMgBr →etc
   2. $AsCl_3 + 3PhMgBr \rightarrow AsPh_3 + 3MgBrCl$.

3.

This Module focuses on Main Group Organometallic Chemistry will look at some "simple" methyl and ethyl compounds; $(Me_2As)_2$, Me_3As, Me_2Hg and Et_4Pb.

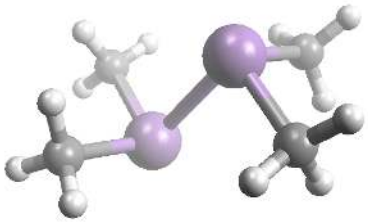
Organoarsenic Chemistry

"Cadet's fuming liquid"

The French pharmacist-chemist, Louis-Claude Cadet de Gassicourt prepared what became known as "Cadet's fuming liquid" in 1757. The reaction involved heating 2 ounces of arsenious oxide with 2 ounces of potassium acetate.

$$As_2O_3 + 4CH_3COOK \rightarrow As_2(CH_3)_4O + 4K_2CO_3 + CO_2 \rightarrow\rightarrow As_2(CH_3)_4 \quad (23.6B.1)$$

gives cacodyl oxide which disproportionates to produce among other things cacodyl, $As_2(CH_3)_4$.



cacodyl

He noted that:

> *"a slightly colored liquid of an extremely penetrating garlic odor distills and then a red-brown liquid which fills the receiver with thick fumes".*

All of the early studies of Cadet's fuming liquid were qualitative in nature, made difficult by the liquid's horrible stench and inflammability, and it was not until the investigations of Robert Wilhelm Bunsen during 1837-1843 that more useful information concerning Cadet's fuming liquid became available. The history of studies on this mixture was reviewed in 2001 [Ref 3.]

Bunsen opted for a large-scale preparation, despite the fact that he was aware of the repulsive and dangerous nature of the expected products. Starting out with **one kilogram** of a 1:1 by weight As_2O_3/$KOOCCH_3$ mixture in a glass retort, he heated it very slowly to red heat in a sand bath. As Cadet had reported, two liquid layers and a solid phase collected in the receiver. Bunsen reported that he obtained ~150 g of the red-brown liquid.

In 1841, Berzelius suggested to Bunsen that the name for the liquid be called "kakodyl" from the Greek meaning "stinking", the English spelling of this was cacodyl.

> *"Accidents with cacodyl compounds could have serious consequences. During his study of cacodyl cyanide, $(CH_3)_2AsCN$, prepared by reaction of 'cacodyl oxide' with a concentrated aqueous solution of mercuric cyanide, an explosion cost Bunsen the partial sight of his right eye and, as Roscoe reports, 'Bunsen was nearly poisoned, lying for days between life and death.' Bunsen recovered and completed his study of cacodyl cyanide, a most unpleasant compound. After distillation of the 'cacodyl oxide'/$Hg(CN)_2$ reaction mixture, the cacodyl cyanide formed beautiful, prismatic crystals underneath the water layer. These were quite volatile (mp 32.5 °C). They were dried by pressing them between sheets of blotting paper. Bunsen noted that it is absolutely necessary to carry out this operation in the open air while breathing through a long glass tube that extends to*

> *fresh air far beyond the volatile crystals. And well might this compound be avoided! Bunsen reported that the vapour from 1 grain (0.0648 g) of cacodyl cyanide in a room produces sudden numbness of the hands and feet, and dizziness and insensibility to the point of unconsciousness. The tongue becomes covered with a black coating. These effects, however, are only temporary, with no lasting problems. (Bunsen, it may be noted, lived to the ripe old age of 88.)" Ref 3.*

Seventy years after its discovery, the question of the composition of Cadet's fuming liquid was addressed by Valeur and Gailliot by means of its fractional distillation under an atmosphere of CO_2. Valeur, A.; Gailliot, P. C. R. *Acad. Sci*. 1927, 185, 956.

Composition of Cadet's fuming liquid (1927)

Compound	% in Cadet's liquid	melting point	boiling point	density
$(CH_3)_3As$	2.6	liquid at -80°C	50°C	1.144
$(CH_3)_2AsOAs(CH_3)_2$ "cacodyl oxide"	40	-57°C	150°C	1.486
$(CH_3)_2As\text{-}As(CH_3)_2$ "cacodyl"	55.9	-5°C	163°C	1.447
Me_7As_3 and Me_5As_3 (mixture)	1.3	very viscous at -80°C	115-120°C /5 mmHg	1.647
$(CH_3As)_5$	0.2	10°C	190°C /5 mmHg	2.15

The use of Cadet's fuming liquid was considered for use in chemical warfare during both WWI and WWII and plants in both Germany and the USA were said to have developed processes for large-scale production. During WWI an organoarsenic compound was used (Lewisite) but not Cadet's liquid.

The exact composition of Cadet's fuming liquid is still unclear but with todays array of sophisticated spectroscopic instruments it should be possible to find a definitive answer. The problems of toxicity etc. are no longer an insurmountable problem given the handling techniques and glassware that were developed beginning with the experimental work of the early synthetic chemists like Bunsen and Schlenk.

"Gosio gas"

Another "simple" methyl derivative, Me_3As, has a long history as well. In 1893 the Italian physician Bartolomeo Gosio published his results on "Gosio gas" that was subsequently shown to contain trimethylarsine. Under wet conditions, the mould *Scopulariopsis brevicaulis* produces significant amounts of methyl arsines via methylation of arsenic-containing inorganic pigments, especially Paris green/Schweinfurt-green("copper arsenite plus copper acetate") and Scheele's Green ("copper arsenite") which were once used in indoor wallpapers. In other cases the arsenic had been added to the wallpaper paste to discourage rodents and insects. Gosio gas was responsible for a number of deaths, and the air in the buildings in which it was being produced had a characteristic garlic-like odour. Gosio established the source of the problem and isolated some of the moulds capable of metabolizing inorganic arsenicals. Pietro Biginelli aspirated the gas from cultures through acidified (HCl) mercuric chloride solution. On the basis of an analysis of the precipitate so obtained, he incorrectly identified the gas as diethylarsine (Et_2AsH). Nonetheless, this was a considerable achievement and established the methodology that Frederick Challenger was to use some 30 years later in his classic studies, beginning with the positive identification of the mould metabolite as trimethylarsine.

Newer studies suggest that trimethylarsine has a lower toxicity than originally thought and may not account for the death and the severe health problems observed in the 19th century which may have arisen due to volatile organics produced from moulds (now linked to what has been called "sick-building syndrome")

Lead arsenate dust from a painted ceiling was the source of the arsenic that caused health problems for Clare Boothe Luce when she was living in Rome as U.S. Ambassador in 1954. No mould action was implicated. One theory was that a washing machine in an upstairs room caused vibrations that dislodged some arsenic containing paint from the stucco decorating her bedroom ceiling!

Me_3As

$AsMe_3$ is a pyramidal molecule as predicted by VSEPR theory. The As-C distances average 151.9 nm, and the C-As-C angles are 91.83°

References

1. Organoarsenic and trimethylarsine on Wikipedia.
2. Scheele's Green killed Napolean?
3. Chem Rev 1989 article on Arsenic in the Environment
4. Toxicity of Me_3As: Urban Myth?

Methylmercury

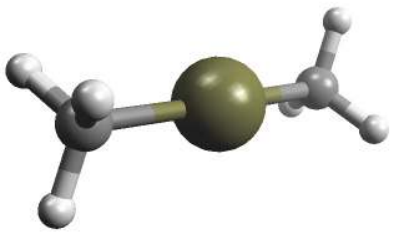
The usual method of ingestion of a metal into the body is:

1. Orally - the Gastrointestinal Tract
2. via the lungs - the Respiratory Tract

a) Orally - (mouth, stomach, small intestine).

Food digestion begins in the mouth where saliva containing the enzyme amylase beaks down starch to lower sugars. Most digestion occurs in the stomach in the presence of HCl (pH ~1.6 ie. 0.17M HCl). In the case of mercury it is quite readily absorbed through the stomach since reaction of mercury salts with HCl produces $HgCl_2$. This neutral covalent molecule (solubility in H_2O 0.5 g/100 mL but 8g/100 mL in ethanol) is absorbed far better than most inorganic ions and this no doubt contributes to its high toxicity.

b) Respiratory tract (nose, lungs).
This is usually unimportant for most metals but in some cases it can be more efficient that via the gastrointestinal tract. For example, lead where 50% of Pb in air can be absorbed but only 5-10% via the gastrointestinal tract. Volatile dimethyl mercury is another case for concern.

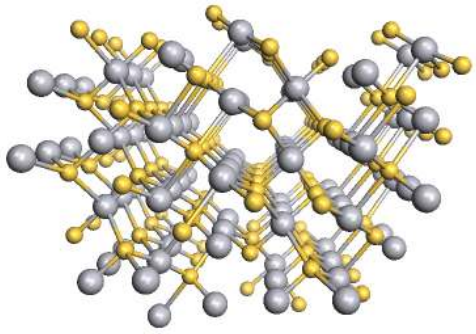


dimethylmercury

The mercury cycle

Mercury is 62nd in terms of natural abundance and is found everywhere, usually as the mineral cinnabar, HgS, although 30 minerals containing Hg are known. The oxidation states are Hg(0), Hg(I) and Hg(II), where Hg(I) has been shown to exist as

Hg_2^{2+}.



HgS - cinnabar

The three Hg species are related by the disproportionation:
$Hg_2^{2+} \rightarrow Hg^0 + Hg^{2+}$ $E° = -0.131$ V
or $K = 6 \times 10^{-3}$

In addition:
Hg_2^{2+}/Hg $E° = 0.789$ V
Hg^{2+}/Hg $E° = 0.854$ V

This means that to oxidise Hg to Hg_2^{2+} an oxidising agent with potential > 0.789V is required, but very importantly < 0.854 V, otherwise oxidation to Hg^{2+} will occur. There are no common oxidants that fit this arrangement so if any reaction occurs the product will be Hg^{2+}. The equilibrium constant of 6×10^{-3} shows that when Hg(I) is formed it is moderately stable, however any agent that reduces the Hg(II) concentration automatically drives the reaction from Left → Right. Given that many Hg(II) derivatives are insoluble then this clearly restricts the range of Hg(I) compounds.

Minamata Disease

There have been several serious outbreaks of mercury poisoning. The most famous was between 1953 and 1965 at Minamata Bay in Japan when 46 people died and 120 suffered severe symptoms. As of March 2001, 2,265 victims had been officially recognised (1,784 of whom had died) and over 10,000 had received financial compensation from Chisso. By 2004, Chisso Corporation had paid $86 million in compensation, and in the same year was ordered to clean up its contamination. On March 29th, 2010, a settlement was reached to compensate as-yet uncertified victims.
The disease was first noticed in cats (who were seen throwing themselves into the sea) and was quickly traced to mercury poisoning acquired as a result of eating contaminated fish (5-10 ppm Hg). The investigations that followed showed that the fish had acquired the high mercury due to the dumping of inorganic mercury salts and methylmercury from the Chisso Co. plastics factory upstream.

Analysis of fish exhibits from museums, some over 90 years old, has shown that mercury levels for ocean fish are similar but that river fish levels have risen as a result of man-made contamination. The forms of mercury occuring in the environment are Hg^{2+} and methylmercury, either $MeHg^+$ or Me_2Hg. Interconversion can be affected by microorganisms.

Aerobes can solubilise Hg^{2+} from cinnabar ($K_{sp} \sim 10^{-53}$) which in sediments was considered safe since the solubility product was so small. The conversion of $S^{2-} \rightarrow SO_3^{2-} \rightarrow SO_4^{2-}$ allows the insoluble sulfide to breakdown and in the process other Hg(II) salts are formed or the mercury may get reduced to Hg(0) enzymatically.
$Hg^{2+} + NADH + H^+ \rightarrow Hg^0 + NAD^+ + 2\ H^+$, where NADH = reduced form of nicotinamideadeninedinucleotide
This conversion can be considered as a detoxification process since Hg^0 is more easily eliminated.

In the environment, sulfate-reducing bacteria take up mercury in its inorganic form and through metabolic processes convert it to methylmercury. Sulfate-reducing bacteria are found in anaerobic conditions, typical of the well-buried muddy sediments of rivers, lakes, and oceans where methylmercury concentrations tend to be highest. Sulfate-reducing bacteria use sulfur rather than oxygen as their cellular energy-driving system. One hypothesis is that the uptake of inorganic mercury by sulfate-reducing bacteria occurs

via passive diffusion of the dissolved complex HgS. Once the bacterium has taken up this complex, it utilizes detoxification enzymes to strip the sulfur group from the complex and replaces it with a methyl group:

$HgS \rightarrow CH_3Hg(II)X + H_2S$

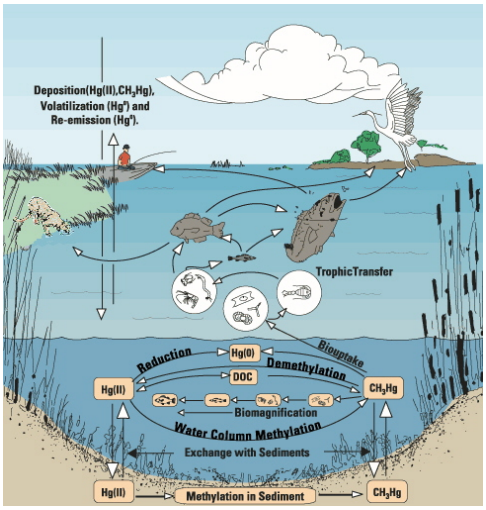
Upon methylation, the sulfate-reducing bacteria transport the new mercury complex back to the aquatic environment, where it is taken up by other microorganisms. Bacteria eliminate Hg by methylating it first to $MeHg^+$ and Me_2Hg. The detoxification process for them is the reverse for us unfortunately! The conversion probably involves vitamin B12 a methyl-cobalt organometallic compound so this is another example of synthesis involving transmetallation.

The major source of methylmercury exposure in humans is consumption of fish, marine mammals, and crustaceans. Once inside the human body, roughly 95% of the fish-derived methylmercury is absorbed from the gastrointestinal tract and distributed throughout the body. Uptake and accumulation of methylmercury is rapid due to the formation of methylmercury-cysteine complexes. Methylmercury is believed to cause toxicity by binding the sulfhydryl groups at the active centers of critical enzymes and structural proteins. Binding of methylmercury to these moieties constitutively alters the structure of the protein, inactivating or significantly lowering its functional capabilities.

Once the Me_2Hg is formed it is volatile and when released into the atmosphere it is readily photolysed by UV light

$Me_2Hg \rightarrow Hg^0 + 2\ CH_3° \rightarrow CH_4$ or C_2H_6

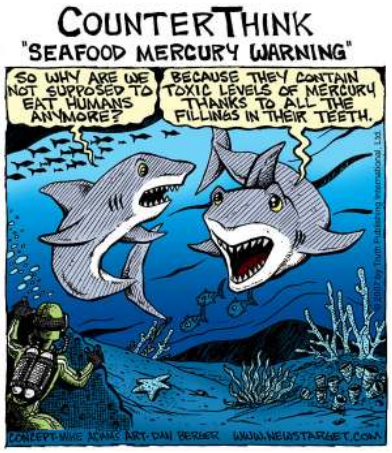
Other microorganisms can convert $MeHg^+$ to $Hg^0 + CH_4$ that is make the mercury considerably less toxic to humans.



The Mercury Cycle

Summary

Organic mercury tends to increase up the food chain, particularly in lakes. The mud at the bottom of a lake may have 100 or 1000 times the amount of mercury than is in the water. Bacteria, worms and insects in the mud extract and concentrate the organic mercury. Small fish that eat them further concentrate the mercury in their bodies. This concentration process, known as "bioaccumulation", continues as larger fish eat smaller fish until the top predator fish in the lake may have methylmercury levels in their tissues that are up to 1,000,000 times the level in the water in which they live. We then eat the fish....



> *To consume a human being would be extremely unhealthy for any animal. Humans carry the highest concentration of toxic chemicals of all creatures on the planet. Their livers, hearts, kidneys and brains are so heavily contaminated with hundreds of different synthetic chemicals that if humans were slaughtered as a meat source, they'd never pass USDA food safety standards.*

from Hg in Humans

Properties of Me_2Hg

Molecular formula	C_2H_6Hg
Molar mass	230.66 g mol^{-1}
Appearance	Colourless liquid
Density	2.96 g/mL
Melting point	-43 °C
Boiling point	87-97 °C
Solubility in water	Insoluble

Laboratory Preparation:
$Hg + 2\ Na + 2\ CH_3I \rightarrow (CH_3)_2Hg + 2\ NaI$

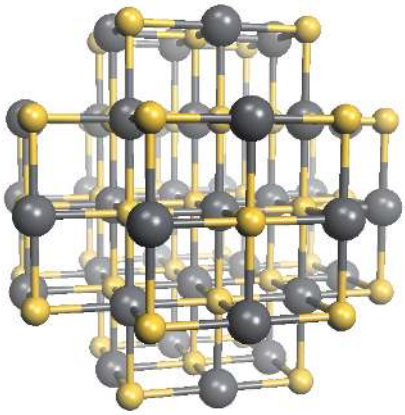
^1H NMR of dimethylmercury showing ^{199}Hg coupling (J ~100.9 Hz)
^{199}Hg has a nuclear spin of ½ and natural abundance of 16.87%. Can you explain the observed splitting pattern?

Methylmercury
Dimethylmercury
Prof Wetterhahn -mercury

Tetraethyllead

Like mercury, lead is primarily obtained from its sulfide ore, in this case Galena, PbS, yet once again there are quite a number of other minerals containing lead. In terms of natural abundance it exists at about 14 ppm in the Earth's crust (37th compared to O),

however it has become well known due to its ease of extraction and the number of uses with technical importance.



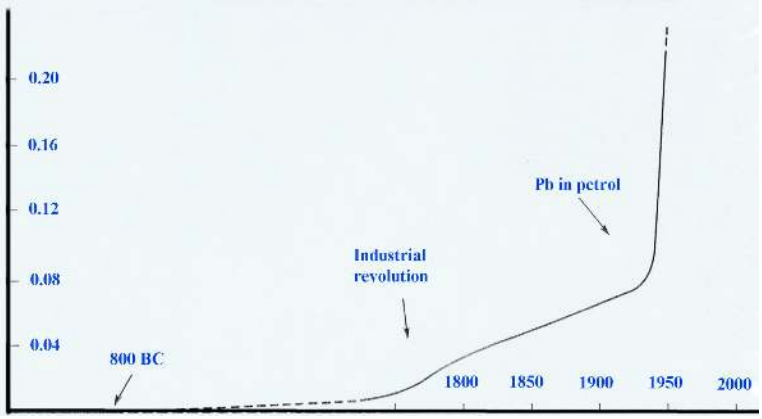
galena, PbS

Lead was probably discovered around 6500 BC in Turkey and by 300 BC the Romans had lead smelters in operation. The toxicity of lead was recorded by the Greeks as early as 100BC. A report from 2BC noted that: *"the drinking of lead causes oppression to the stomach, belly and intestines with wringing pains; it suppresses the urine, while the body swells and acquires and unsightly leaden hue"*.

The possible hazards associated with the use of lead piping in water systems was recognised as long ago as the first century BC and it has even been suggested that the "decline of the Roman Empire" might have been ascribed to the use of lead acetate as an additive to sweeten wine. It is somewhat surprising therefore that the first legislation controlling the industrial hazards of lead industries was not introduced until 1864.

Note that Dr. Wilton Turner (born in Clarendon, Jamaica in the early 1800's) wrote on the inappropriate use of lead in sugar and rum production while running a rum distillery in Guyana. One advocate said he had fed lead to dogs and guinea pigs *for several weeks* and seen no adverse affects in fact the guinea pigs were stolen which he thought was because they looked so fat and healthy!

An examination (in the early 1970's) of the annual snow strata in Northern Greenland and Poland revealled most elegantly that levels in air-borne lead had increased significantly since the Industrial Revolution and very sharply since 1940. Considering that 40-50% can be absorbed by inhalation compared to only 5-10% through ingestion this was cause for concern.



Lead content in North Greenland snow layers (µg per kg)

Leaded gasoline was an economic success from 1926 until 1976, and in fact, its discovery by Thomas Midgley at Charles Kettering's General Motors laboratory was among the most celebrated achievements of automotive engineering. It was often portrayed as the result of genius, luck and a great deal of hard work. It is now considered to be a catastrophic failure and is banned for environmental and public health reasons. {There are still a few countries selling petrol with lead additives.} Even more surprising is that the use of ethanol in fuel was already well established by the time tetraethyllead was introduced as an additive.

Tetraethyllead was supplied for mixing with raw gasoline in the form of "ethyl fluid", which was Et_4Pb blended together with the lead scavengers 1,2-dibromoethane and 1,2-dichloroethane. "Ethyl fluid" also contained a reddish dye to distinguish treated from untreated gasoline and discourage the use of leaded gasoline for other purposes such as cleaning.

Ethyl fluid was added to gasoline in the ratio of 1:1260, usually at the refinery. The purpose was to increase the fuel's octane rating. A high enough octane rating is required to prevent premature detonations known as engine knocking ("knock" or "ping"). Antiknock agents allow the use of higher compression ratios for greater efficiency and peak power. The formulation of "ethyl fluid" was:

- Tetraethyllead 61.45%
- 1,2-Dibromoethane 17.85%
- 1,2-Dichloroethane 18.80%
- Inert materials and dye 1.90%

Effect on Health

Humans have been mining and using this heavy metal for thousands of years, poisoning themselves in the process. Although lead poisoning is one of the oldest known work and environmental hazards, the modern understanding of the small amount of lead necessary to cause harm did not come about until the latter half of the 20th century. No safe threshold for lead exposure has been discovered, that is, there is no known amount of lead that is too small to cause the body harm.

Lead pollution from engine exhaust is dispersed into the air and into the vicinity of roads and easily inhaled. Lead is a toxic metal that accumulates and has subtle and insidious neurotoxic effects especially at low exposure levels, such as low IQ and antisocial behavior. It has particularly harmful effects on children. These concerns eventually led to the ban on Et_4PB in automobile gasoline in many countries. For the entire U.S. population, during and after the Et_4PB phaseout, the mean blood lead level dropped from 13 µg/dL in 1976 to only 3 µg/dL in 1991. The U.S. Centers for Disease Control considered blood lead levels "elevated" when they were above 10 µg/dL. Lead exposure affects the intelligence quotient (IQ) such that a blood lead level of 30 µg/dL is associated with a 6.9-point reduction of IQ, with most reduction (3.9 points) occurring below 10 µg/dL.

Also in the U.S., a statistically significant correlation has been found between the use of Et_4PB and violent crime: taking into account a 22-year time lag, the violent crime curve virtually tracks the lead exposure curve. After the ban on Et_4PB, blood lead levels in U.S. children dramatically decreased.

Even though leaded gasoline is largely gone in North America, it has left high concentrations of lead in the soil adjacent to all roads that were constructed prior to its phaseout. Children are particularly at risk if they consume this, as in cases of pica.

Note as well the work done in 1995 by ICENS on the problem of the old disused lead mine and tailings that affected school children in Kintyre. Over 40 cases were detected with unacceptable levels. ICENS at that time cleaned the community and sought to educate residents about the dangers. A continuation of the research done in Kintyre was to test 628 children at 17 basic schools across the island. Children at a number of basic schools in Kingston and St Catherine were discovered with blood lead levels as low as 45 µg/dL and as high as 60. In two of the cases, children had lead levels of 130 and 202. At this level, they would likely die from the poisoning if untreated.

Properties of Et_4Pb

Molecular formula	$C_8H_{20}Pb$
Molar mass	323.44 g mol^{-1}
Appearance	Colourless, viscous liquid
Density	1.653 g/mL (20 °C)
Melting point	-136 °C
Boiling point	84-85 °C/15 mm Hg
Solubility in water	Insoluble

Laboratory Preparation:
The industrial preparation of tetraethyllead was from the reaction below:
~373K in an autoclave

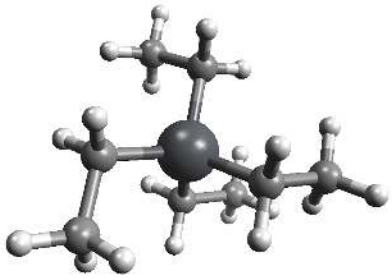
$4\ NaPb + 4\ EtCl \rightarrow Et_4Pb + 3\ Pb + 4\ NaCl$

alloy

or by electrolysis of $NaAlEt_4$ or EtMgCl using a Pb anode.

Laboratory syntheses of R_4Pb compounds in general include the use of Grignard reagents or organolithium compounds.

in ether
$2\ PbCl_2 + 4\ RLi \rightarrow R_4Pb + 4LiCl + Pb$



tetraethyllead

lead timeline
Tetraethyllead
"ethyl" articles

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3. DOI: 10.1021/om0101947

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CHAPTER OVERVIEW

24: Organometallic chemistry- d-block elements

The study of Organometallic chemistry has been important in the growth of chemistry ever since the first compound was synthesized in 1827. Organometallic compounds can be defined as a compound that contains at least one metal-carbon bond, not including cyanide. Organometallic compounds are used in numerous reactions, including but not limited to, the Grignard reaction, and the Simmons-Smith reaction.

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- 24.2: Common Types of Ligand - Bonding and Spectroscopy
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24.1: Introduction

Learning Objectives

In this lecture you will learn the following

- Get a general prospective on the historical background of transition metal organometallic compounds with particular emphasis on metal alkyls.
- Know more about stable metal alkyls.
- Get introduced to transition metal agostic alkyls.
- Develop an understanding of reactions of relevance to metal alkyls like the reductive eliminations, oxidative additions and the halide eliminations.

Transition metal σ−bonded organometallic compounds like the metal alkyls, aryls and the hydrides derivatives are by for the most common organometallic species encountered in the world of chemistry. Yet, these compounds remained elusive till as late as the 1960s and the 1970s.

Historical Background

Metal alkyls of the main group elements namely, Li, Mg, Zn, As and Al, have been known for a long time and which over the years have conveniently found applications in organic synthesis whereas development on similar scale and scope in case of the transition metal counterparts were missing till only recently. The origin of the organometallic compounds traces back to 1757, when Cadet prepared a foul smelling compound called cacodyl oxide from As_2O_3 and CH_3COOK, while working in a military pharmacy in Paris. Years later in 1840, R. W. Bunsen gave the formulation of cacodyl oxide as $Me_2As{-}O{-}AsMe_2$. The next known transition metal organometallic compound happens to be Et_2Zn, which was prepared serendipitously in 1848 from the reaction of ethyl iodide (EtI) and Zn with the objective of generating free ethyl radical. Frankland further synthesized alkyl mercury halides like, CH_3HgI, from the reaction of methyl iodide (CH_3I) and Hg in sunlight. It is important to note that the dialkyl mercury, R_2Hg, and the dialkyl zinc, R_2Zn, have found applications as alkyl transfer reagents in the synthesis of numerous main group organometallic compounds.

Another notable development of the time was of the preparation of Et_4Pb from ethyl iodide (EtI) and Na/Pb alloy by C. J. Lowig and M. E. Schweizer in 1852. They subsequently extended the same method for the preparation of the Et_3Sb and Et_3Bi compounds. In 1859, aluminumalkyliodides, R_2 AlI, were prepared by W. Hallwachs and A Schafarik from alkyl iodide (RI) and Al. The year 1863 saw the preparation of organochlorosilanes, $RmSiCl_{4-m}$, by C. Friedel and J. M. Crafts while the year 1866 saw the synthesis of halide-free alkyl magnesium compound, Et_2Mg, by J. A. Wanklyn from the reaction of Et_2Hg and Mg. In 1868, M. P. Schutzenberger reported the first metal−carbonyl complex in the form of $[Pt(CO)Cl_2]_2$. In 1890, the first binary metal−carbonyl compound, $Ni(CO)_4$ was reported by L. Mond, who later founded the well−known chemical company called ICI (Imperial Chemical Industries). In 1909, W. J. Pope reported the first σ−organotransition metal compound in the form of $(CH_3)_3PtI$. In 1917, the alkyllithium, RLi, compounds were prepared by W. Schlenk by transalkylation reactions. In 1922, T. Midgley and T. A. Boyd reported the utility of Et_4Pb as an antiknock agent in gasoline. A. Job and A. Cassal prepared $Cr(CO)_6$ in 1927. In 1930, K. Ziegler showed the utility of organolithium compounds as alkylating agent while in the following year in 1931, W. Heiber prepared $Fe(CO)_4H_2$ as the first transition metal−hydride complex. O. Roelen discovered the much renowned hydroformylation reaction in 1938, that went on to become a very successful industrial process worldwide.

The large scale production and the use of silicones were triggered by E. G. Rochow, when he reported the ‘direct synthesis’ from methyl chloride (CH_3Cl) and Si using Cu catalyst at 300 °C in 1943. The landmark compound, ferrocene $(C_5H_5)_2Fe$, known as the first sandwich complex was obtained by P. Pauson and S. A. Miller in 1951. H. Gilman introduced the important utility of organocuprates when he prepared $LiCu(CH_3)_2$, in 1952. In the subsequent year 1953, G. Wittig found a new method of synthesizing olefins from phosphonium ylides and carbonyl compounds that fetched him a Nobel prize in 1979. The year 1955 turned out to be a year of path breaking discoveries with E. O. Fischer reporting the rational synthesis of bis(benzene)chromium, $(C_6H_6)_2Cr$ while K. Ziegler and G. Natta announcing the ground breaking polyolefin polymerization process that subsequently gave them the Nobel prizes, E. O. Fischer sharing with G. Wilkinson in 1973 while K. Ziegler and G. Natta shared the same in 1963. In 1956, H. C. Brown reported hydroboration for which he too received the Nobel prize in 1979. In 1963, L. Vaska reported

the famous Vaska's complex, *trans*−$(PPh_3)_2Ir(CO)Cl$, that reversibly binds to molecular oxygen. In 1964, E. O. Fischer reported the first carbene complex, $(CO)_5WC(OMe)Me$. In 1965, G. Wilkinson and R. S. Coffey reported the Wilkinson catalyst, $(PPh_3)_3RhCl$, for the hydrogenation of alkenes. In 1973, E. O. Fischer synthesized the first carbyne complex, $I(CO)_4Cr(CR)$.

After the early 1970s, there were tremendous outburst in activity, in the area of transition metal organometallic chemistry leading to phenomenal developments having far-reaching consequences in various branches of the main stream and interfacial chemistry. Several Nobel prizes that have been awarded to the area in recent times fully recognized the significance of these efforts with Y. Chauvin, R. R. Schrock, and R. H. Grubbs winning it in 2005 for olefin metathesis and Akira Suzuki, Richard F Heck and E. Negishi receiving the same for the Pd catalyzed C−C cross-coupling reactions in organic synthesis in 2010.

Metal alkyls

In day to day organic synthesis, particularly from the application point of view, the metal alkyls are often perceived as a source of stabilized carbanions for reactions with various electrophiles. The extent of stabilization of alkyl carbanions in metal alkyl complexes depend upon the nature of the metal cations. For example, the alkyls of electropositive metals like that of Group 1 and 2, Al and Zn are regarded as polar organometallics as the alkyl carbanions remain weakly stabilized while retaining strong nucleophilic and basic character of a free anion. These polar alkyls are extremely air and moisture sensitive as in their presence they often get hydrolyzed and oxidized readily. Similar high reactivity was also observed in case of the early transition metal organometallic compounds particularly of Ti and Zr. On the contrary the late transition metal organometallic compounds are much less reactive and stable. For example, the Hg−C bond of $(Me{-}Hg)^+$ cation is indefinitely stable in aqueous H_2SO_4 solution in air. Thus, on moving from extremely ionic Na alkyls to highly polar covalent Li and Mg alkyls and to essentially covalent late−transition metal alkyls, a steady decrease in reactivity is observed. This trend can be correlated to the stability of alkyl carbanions that also depended on the nature of hybridization of the carbon center, with sp^3 hybridized carbanions being the least stable and hence most reactive, followed by the sp^2 carbanions being moderately stable while the *sp* carbanions being the least reactive and most stable. The trend also correlates well with the respective p*K*a values observed for CH_4 (p*K*a = ~50), C_6H_6 (p*K*a = ~43) and RC≡CH (p*K*a = ~25).

Stable alkyls

As has been mentioned earlier, that the β−elimination is a crucial destabilizing influence on the transition metal organometallic complexes. Hence, inhibition of this decomposition pathway leads to increased stabilities of organometallic compounds. Thus, many stable alkyl transition metal complexes do not possesses β−hydrogens like, $W(Me)_6$ and $Ti(CH_2Ph)_4$. In some cases despite the presence of the β−hydrogens the organometallic complexes are stable as the β−hydrogens are deposed away from the metal center like in, $Cr(CHMe_2)_4$, and $Cr(CMe_3)_4$. In this category of stable transition metal organometallic compounds also falls the ones that contain β−hydrogens but cannot β−eliminate owing to the formation of a olefinic bond at a bridgehead, which is unfavorable, like in $Ti(6{-}norbornyl)_4$ and $Cr(1{-}adamantyl)_4$. Lastly, some 18 VE metal complexes are stable, again despite having β−hydrogens, for reasons of being electronically as well as coordinatively saturated at the metal center owing to attaining the stable 18 electron configuration.

Agostic alkyls

Agostic alkyls are extremely rare but very interesting species that represents a frozen point in a β−elimination pathway that have fallen short of the completion of the decomposition reaction. Thus, these agostic alkyl complexes can be viewed as snap shots of a β−elimination trajectory thereby providing valuable mechanistic understanding of the decomposition reaction. The agostic interaction has characteristic signatures in various spectroscopic techniques as observed from the decreasing J_{C-H}coupling constant values in the ^1H NMR and the ^{13}C NMR spectra and the lowering of the ν_{C-H}stretching frequencies in the IR spectroscopy. The agostic alkyl complexes can be definitively proven by X−ray diffraction or neutron diffraction studies. The agostic alkyls thus have activated C−H bonds which are of interest for their utility in chemical catalysis. Quite interestingly, many d^0 Ti agostic alkyl complexes do not β−eliminate primarily for the metal center being too electron deficient to donate electron to the σ* C−H orbital as required for the subsequent β−elimination process.

Reductive elimination

Reductive elimination represents a major decomposition pathway of the metal alkyls. Opposite of oxidative addition, the reductive elimination is accompanied by the decrease in the oxidation state and the valence electron count of the metal by two units. The metal alkyl complexes may thus reductively eliminate with an adjacent hydrogen atom to yield an alkane, (R−H) or undergo the same with an adjacent alkyl group to give an even larger alkane (R−R) as shown below.



The reductive elimination is often facilitated by an electron deficient metal center and by sterically demanding ligand systems. Often d^8 metals like Ni(II), Pd(II), and Au(III) and d^6 metals in high oxidation state like, Pt(IV), Pd(IV), Ir(III), and Rh(III) exhibit reductive elimination.

Oxidative addition

Unlike the reductive elimination that represents a decomposition pathway of metal alkyls, the oxidative addition reaction represents a useful method for the formation of the metal alkyl complexes. The oxidative addition thus leads to increase in valence electron count and the oxidation state of the metal center by two units. The oxidative addition reactions are often facilitated by low valent electron rich metal centers and by less sterically demanding ligands.

Halide elimination

β−halide elimination is observed for the early transition metals and the *f*−block elements resulting in the formation of stable alkyl halides. The phenomenon is mostly seen in case of the metal fluorides and arise owing to the very high alkyl−fluoride bond strengths that favor the halide elimination.

Summary

A broader outlook on metal alkyls is obtained from the study of its historical background thus dispelling many myths about these compounds like them being inherently unstable. It also establishes newer founding principles like these compounds indeed being thermodynamically stable under certain experimental conditions and thus facilitating further attempts to take up the synthesis of these compounds. Another important class of transition metal organometallic compounds are the agostic alkyls, which can be viewed as the ones that have proceeded along but have fallen short of the final sequence of the β−elimination step. While oxidative addition reaction remains a key method for synthesizing metal alkyls, the complementary reaction, *i.e*, the reductive elimination, represents a decomposition reaction of these compounds. β−halide elimination reactions are observed for early transition metal elements and *f*−block elements.

Problems

1. Who elucidated the structure of cacodyl oxide?

Ans: R. W. Bunsen in 1840

2. Give the example of the first olefin bound transition metal complex?

Ans: Zeise's salt, $Na[PtCl_3(C_2H_4)]$

3. Who discovered olefin polymerization? Ans: K. Ziegler and G. Natta 4. What kind of metal center promotes oxidative addition reactions? Ans: Electron rich 5. The 18 VE complex would favor/disfavor oxidative addition reactions? Ans: Disfavor

Self Assessment test

1. O. Roelen discovered which famous reaction?

Ans: Hydroformylation

2. What is the first binary metal−carbonyl complex?

Ans: $Ni(CO)_4$

3. Who discovered the hydroboration reaction? Ans: H. C. Brown 4. Reductive elimination reaction is favored by what kind of ligands? Ans: Sterically demanding 5. β−halide elimination is mainly observed for what type of metal halide complexes? Ans: Metal fluorides

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SECTION OVERVIEW

24.2: Common Types of Ligand - Bonding and Spectroscopy

Learning Objectives

In this lecture you will learn the following

- Understand the role lead by ligands in stabilizing organometallic transition metal complexes.
- Know about various synthetic methods available for preparing the organometallic transition metal complexes.
- Understand the various factors like β-elimination and other bimolecular decomposition pathways that contribute to the observed instability of the organometallic transition metal complexes.
- Obtain insight about making stable organometallic transition metal complexes by suppression of the destabilizing factors mentioned.

Ligands play a vital role in stabilizing transition metal complexes. The stability as well as the reactivity of a metal in its complex form thus depend upon the number and the type of ligands it is bound to. In this regard, the organometallic carbon based ligands come in diverse varieties displaying a wide range of binding modes to a metal. In general, the binding modes of the carbon-derived ligands depend upon the hybridization state of the metal bound carbon atom. These ligands can thus bind to a metal in many different ways as depicted below. Lastly, these ligands can either be of *(a)* purely σ−donor type, or depending upon the capability of the ligand to form the multiple bonds may also be of *(b)* a σ−donor/π−acceptor type, in which the σ−interaction is supplemented by a varying degree of π−interaction.



Figure 1.



Figure 2.



Figure 3.

Preparation of transition metal-alkyl and transition metal-aryl complexes

The transition metal−alkyl and transition−metal aryl complexes are usually prepared by the following routes discussed below,

Metathesis

This involves the reactions of metal halides with organolithium, organomagnesium, organoaluminium, organotin and organozinc reagents.



Of the different organoalkyl compounds listed above, the organolithium and organomagnesium compounds are strongly carbanionic while the remaining main group organometallics like the organoalkyl, organozinc and organotin reagents are relatively less carbanionic in nature. Thus, the main group organometallic reagents have attenuated alkylating power, that can be productively used in partial exchange of halide ligands.



Alkene insertion or Hydrometallation

As the name implies, this category of reaction involves an insertion reaction between metal hydride and alkene as shown below. These type reactions are relevant to certain homogeneous catalytic processes in which insertion of an olefin to M−H bond is often observed.



Carbene insertion

This category represents the reaction of metal hydrides with carbenes.



Metallate alkylation reaction

This category represents the reaction of carbonylate anions with alkyl halides as shown below.



Preparation of transition metal-alkyl and transition metal-aryl complexes (contd..)

Metallate acylation reaction

This category involves the reaction of carbonylate anions with acyl halides.



Oxidative addition reaction

Many unsaturated 16 VE transition metal complexes having d^8 or d^{10} configuration undergo oxidative addition reactions with alkyl halides. The oxidative addition reactions proceed with the oxidation state as well as coordination number of the metal increasing by +2.



Addition reaction

This category involves the reaction of an activated metal bound olefin complex with a nucleophile as shown below.



Thermodynamic Stability and Kinetic Lability

The transition metal organometallic compounds are often difficult to synthesize under ordinary laboratory conditions and require stringent experimental protocols involving the exclusion of air and moisture for doing so. As a consequence, many homoleptic binary transition metal−alkyl and transition metal−aryl compounds like, Et_2Fe or Me_2Ni cannot be made under normal laboratory conditions. More interestingly, most of the examples of transition metal−aryl and transition metal−alkyl compounds, known in the literature, invariably contain additional ligands like η^5-C_5H_5, CO, PR_3 or halides.
For example,



Transition metal−carbon (TM−C) bond energy values are important for understanding the instability of transition metal organometallic compounds. In general, the TM−C bonds are weaker than the transition metal−main group element (TM−MGE) bonds (MGE = F, O, Cl, and N) and more interestingly so, unlike the TM−MGE bond energies, the TM−C bond energy values increase with increasing atomic number. The steric effects of the ligands also play a crucial role in influencing the TM−C bond energies and thus have to be given due consideration.

Contrary to the popular belief, the difficulty in obtaining transition metal−aryl and transition metal−alkyl complexes does primarily arise from the thermodynamic reasons but rather the kinetic ones. β−elimination is by far the most general decomposition mechanism that contribute to the instability of transition metal organometallic compounds. β−elimination results in the formation of metal hydrides and olefin as shown below.



β−elimination can also be reversible as shown below.



The instability of transition metal organometallic compounds can arise out of kinetic lability like in the case of the β−elimination reactions that trigger decomposition of these complexes. Thus, the suppression of the decomposition reactions provides a viable option for the stabilization of the transition metal organometallic complexes. The β−elimination reactions in transition metal organometallic complexes may be suppressed under any of the following three conditions.

a. Formation of the leaving olefin becomes sterically or energetically unfavorable
   In the course of β−elimination, this situation arises when the olefinic bond is formed at a bridgehead carbon atom or when a double bond is formed with the elements of higher periods. For instance, the norbornyl group is less prone to decomposition by β−elimination because that would require the formation of olefinic double bond at a bridgehead carbon atom in the subsequent olefin, *i.e*. norbornene, and which is energetically unfavorable.



b. **Absence of β−hydrogen atom in organic ligands**
   Transition metal bound ligands that do not possess β−hydrogen cannot decompose by β−elimination pathway and hence such complexes are generally more stable than the ones containing β−hydrogen atoms. For example, the neopentyl complex, $Ti[CH_2C(CH_3)_3]_4$ (m.p 90 °C), and the benzyl complex, $Zr(CH_2Ph)_4$ (m.p. 132 °C), exhibit higher thermal stability as both of the neopentyl and benzyl ligands lack β−hydrogens.

c. Central metal atom is coordinatively saturated
   Transition metal organometallic complexes in which the central metal atom is coordinatively saturated tend to be more stable due to the lack of coordination space available around the metal center to facilitate β−elimination reaction or other decomposition reactions. Thus, the absence of free coordination sites at the metal is crucial towards enhancing the stability of the transition metal organometallic complexes. For example, $Ti(Me)_4$, which is coordinatively unsaturated can undergo a bimolecular decomposition reaction *via* a binuclear intermediate (**A**), is unstable and exhibits a decomposition temperature of –40 °C. On the contrary, $Pb(Me)_4$, that cannot undergo decomposition by such bimolecular pathway, is more stable and distills at 110 °C at 1 bar atmospheric pressure.



The $Ti(Me)_4$ decomposes by dimerization involving the formation of Ti−C (*3c−2e*) bonds. For $Pb(Me)_4$, such bimolecular decomposition pathway is not feasible, as being a main group element it has higher outer *d* orbital for extending the coordination number. If the free coordination site of $Ti(Me)_4$ is blocked by another ligand, as in $[(bipy)Ti(Me)_4]$, then the thermal stability of the complex, $[(bipy)Ti(Me)_4]$, increased significantly. Other bidentate chelating ligands like *bis*(dimethylphosphano)ethane (dmpe)

also serve the same purpose.

Coordinative saturation thus brings in kinetic stabilization in complexes. For example, $Ti(Me)_4$is extremely reactive as it is coordinatively unsaturated, while $W(Me)_4$ is relatively inert for reasons of being sterically shielded and hence, coordinatively saturated. Thus, if all of the above discussed criteria for the suppression of β-elimination are taken care of, then extremely stable organometallic complexes can be obtained like the one shown below.



Problems

1. Arrange the following compounds in the order of their stability.
(*a*). $Ti(Et)_4$ (*b*). $Ti(Me)_4$ and (*c*). $Ti(6\text{-norbornyl})_4$

Ans: $Ti(Et)_4 < Ti(Me)_4 < Ti(6\text{-norbornyl})_4$ 2. Predict the product of the reaction given below.



Ans: Equi molar amounts of $(Bu_3P)CuD$ and $CH_2{=}CDC_2H_5$ 3. Will the compound β-eliminate,



(a). readily, (b). slowly and (c). not at all.
Explain your answer with proper reasoning.

Ans: Not at all as the ß-hydrogens are pointing away from the metal and cannot participate in ß-elimination recation.

Self Assessment test

1. Write the product(s) of the reactions.



Ans:



Summary

Ligands assume a pivotal role in the stabilization of the organometallic transition metal complexes. There are several methods available for the preparation of the organometallic transition metal complexes. The observed instability of the organometallic transition metal complexes can be attributed to two main phenomena namely β-elimination and bimolecular decomposition reaction that severely undermine the instability of these complexes. The suppression of these decomposition pathway thus pave way for obtaining highly stable organometallic transition metal complexes.

Topic hierarchy

24.2.1: Metal allyl and diene complexes

24.2A: \(\sigma\)-bonded Alkyl, Aryl, and Related Ligands

24.2B: Carbonyl Ligands

24.2C: Hydride Ligands

24.2D: Phosphine and Related Ligands

24.2E: \(\pi\)-bonded Organic Ligands

24.2F: Nitrogen Monoxide

24.2G: Dinitrogen

24.2H: Dihydrogen

24.2: Common Types of Ligand - Bonding and Spectroscopy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

24.2.1: Metal allyl and diene complexes

Learning Objectives

In this lecture you will learn the following

- The metal−allyl complexes.
- The metal−diene complexes.
- The metal−cyclobutadiene complexes.
- The respective metal−ligand interactions.

The allyl ligand is often referred to as an “actor” ligand rather than a “spectator” ligand. It binds to metals in two ways *i.e.* in a η^1 (monohapto) form and a η^3 (trihapto) form (Figure 1). (*i*). In its monohapto (η^1) form, it behaves as an anionic *1e−donor* X type of a ligand analogous to that of a methyl moiety while (*ii*) in a trihapto (η^3) form, it acts as an anionic *3e−donor* LX type of a ligand.



Figure 1.Metal−allyl interaction.

Metal−allyl interaction

Of particular interest are the molecular orbitals namely Ψ_1, Ψ_2 and Ψ_3 of the allyl ligand that interact with the metal in a metal allyl complex. The energy of these molecular orbitals increase with the increase in the number of nodes. Of the three, the Ψ_1 and Ψ_2 orbitals usually engage in ligand to metal σ−donation, with Ψ_1 involving in a dative L−type bonding and Ψ_2 participating in a covalent X−type bonding with the metal *d* orbitals (Figure 2).



Figure 2. Metal−allyl interactions.

Synthesis of the metal allyl complexes

The metal allyl complexes are synthesized by the following methods.

i. From an alkene complex as shown below.



ii. By a nucleophilic attack of an allyl compound as shown below.



iii. By an electrophilic attack of an allyl compound as shown below.



iv. From a diene complex as shown below.



Reactions of metal allyl complexes

The reactivities of the metal allyl complexes toward various species are illustrated below.

i. Reaction with nucleophiles



ii. Reaction with electrophiles



iii. Insertion reaction



iv. Reductive elimination



Diene complexes

1,3−Butadiene is a *4e−donor* ligand that binds to a metal in a *cisoid* conformation. The *Dewar−Chatt* model, when applied to 1,3−butadiene, predicts that the ligand may bind to metal either as a L_2 (π_2) donor type, similar to that of an alkene, or as an LX_2 ($\sigma_2\pi$) donor type, similar to that of a metalacyclopropane form. The L_2 binding of 1,3−butadiene is rare, *e.g.* asin (butadiene)$Fe(CO)_3$, while the LX_2 type binding is more common, *e.g.* as in $Hf(PMe_3)_2Cl_2$. An implication of the LX_2 type binding is in the observed shortening of the C_2-C_3 (1.40 Å) distance alongside the lengthening of the C_1-C_2(1.46 Å) and C_3-C_4 (1.46 Å) distances (Figure 3).



Figure 3. Metal−diene interaction in *cisoid* binding.

The molecular orbitals of the 1,3−butadiene ligand comprises of two filled Ψ_1 (HOMO−1) and Ψ_2(HOMO) orbitals and two empty Ψ_3 (LUMO) and Ψ_4 (LUMO+1) orbitals. In a metal−butadiene interaction the ligand to metal σ−donation occurs from the filled Ψ_2 orbital of the 1,3−butadiene ligand while the metal to ligand π−back donation occurs on to the empty Ψ_3 orbital of the 1,3−butadiene ligand (Figure 4).



Figure 4. Metal−diene interaction.

Though *cisoid* binding is often observed in metal butadiene complexes, a few instances of *transoid* binding is seen in dinuclear, *e.g.* as in $Os_3(CO)_{10}(C_4H_6)$, and in mononuclear complexes *e.g.* as in $Cp_2Zr(C_4H_6)$ (Figure 5).



Figure 5. Metal−diene interaction in *transoid* binding.

Synthesis of metal butadiene complex

Metal butadiene complexes are usually prepared by the same methods used for synthesizing metal alkene complexes. Two noteworthy synthetic routes are shown below.





Metal cyclobutadiene complexes

Cyclobutadiene is an interesting ligand because of the fact that its neutral form, being anti−aromatic (*4π*−electrons), is unstable as a free molecule (Figure 6), but its dianionic form is stable because of being aromatic (*6π*−electrons). Consequently, the cyclobutadiene ligand is stabilized by significant metal to ligand π−back donation to the vacant ligand orbitals.



Figure 6. Electronic structure of cyclobutadiene ligand.

A synthetic route to metal cyclobutadiene complex is shown below.



Problems

1. The hapticities displayed by an allyl moiety in binding to metals are? Ans: 1 and 3. 2. Identify which molecular orbitals of an allyl moiety engage in σ−interaction with a suitable *d* orbital of a metal in a η^3−metal allyl complex? Ans: Ψ_1 and Ψ_2.

3. Predict the product of the reaction.



Ans:



4. Identify which molecular orbitals of a butadiene moiety engage in σ−interaction with a suitable *d*orbital of a metal in a η^4−metal butadiene complex? Ans: Ψ_2.

Self Assessment test

1. Predict the product of the reaction.



Ans:



2. Identify which molecular orbitals of a butadiene moiety engage in π−interaction with a suitable *d*orbital of a metal in a η^4−metal allyl complex? Ans: Ψ_3. 3. Mention the type of orientations displayed by butadiene ligands for binding to metal. Ans: Cisoid (common) and transoid (rare). 4. Comment on the number of π−electrons present in the cyclobutadiene moiety of a metal cyclobutadiene complex. Ans: 6 π−electrons.

Summary

Allyl, 1,3−butadiene and cyclobutadiene together constitute an important class of σ−donor/π−acceptor ligands that occupy a special place in organometallic chemistry. The complexes of these ligands with metals are important intermediates in many catalytic cycles and hence an understanding of their interaction with metal is of significant importance. In this context, the synthesis,

characterization and the reactivities of the organometallic complexes of these ligands are described alongside the respective metal−ligand interactions.

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24.2A: σ -bonded Alkyl, Aryl, and Related Ligands

σ−complexes

σ−complexes are rare compounds, in which the σ bonding electrons of a X−H bond further participate in bonding with a metal center (X = H, Si, Sn, B, and P). The σ complexes thus exhibit an askewed binding to a metal center with the hydrogen atom, containing no lone pair, being more close to the metal center and thereby resulting in a side−on structure. Many times if the metal center is electron rich, then further back donation to the σ* orbital of the metal bound X−H moiety may occur resulting in a complete cleavage of the X−H bond.



24.2A: σ-bonded Alkyl, Aryl, and Related Ligands is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

24.2B: Carbonyl Ligands

Learning Objectives

In this lecture you will learn the following

- The historical background of metal carbonyl complexes.
- The CO ligand and its binding ability to metal.
- Synergism between the ligand to metal forward σ–donation and the metal to ligand backward π–donation observed in a metal-CO interaction.
- The synthesis, characterization and their reactivity of the metal carbonyl compounds.

Metal carbonyls are important class of organometallic compounds that have been studied for a long time. Way back in 1884, Ludwig Mond, upon observing that the nickel valves were being eating away by CO gas in a nickel refining industry, heated nickel powder in a stream of CO gas to synthesize the first known metal carbonyl compound in the form $Ni(CO)_4$. The famous Mond refining process was thus born, grounded on the premise that the volatile $Ni(CO)_4$ compound can be decomposed to pure metal at elevated temperature. Mond subsequently founded the Mond Nickel Company Limited for purifying nickel from its ore using this method.

The carbonyl ligand (CO) distinguishes itself from other ligands in many respects. For example, unlike the alkyl ligands, the carbonyl (CO) ligand is unsaturated thus allowing not only the ligand to σ−donate but also to accept electrons in its π* orbital from d_π metal orbitals and thereby making the CO ligand π−acidic. The other difference lies in the fact that CO is a soft ligand compared to the other common σ−and π−basic ligands like H_2O or the alkoxides (RO−), which are considered as hard ligands.

Being π−acidic in nature, CO is a strong field ligand that achieves greater *d*−orbital splitting through the metal to ligand π−back donation. A metal−CO bonding interaction thus comprises of a CO to metal σ−donation and a metal to CO π−back donation (Figure 1). Interestingly enough, both the spectroscopic measurements and the theoretical studies suggest that the extent of the metal to CO π−back donation is almost equal to or even greater than the extent of the CO to metal σ−donation in metal carbonyl complexes. This observation is in agreement with the fact that low valent−transition metal centers tend to form metal carbonyl complexes.



Figure 1. Orbital diagram showing ligand to metal forward σ-donation and the metal to ligand backward π-donation in metal-CO interaction.

In the metal carbonyl complexes, the direct bearing of the π−back donation is observed on the M−C bond distance that becomes shorter as compared to that of a normal M−C single bond distance. For example, the $CpMo(CO)_3CH_3$ complex, exhibits two kind of M−C bond distances that comprise of a longer Mo−CH_3 distance (2.38 Å) and a much shorter Mo−CO distance (1.99 Å) arising out of a metal to ligand π−back donation. It becomes thus apparent that the metal−CO interaction can be easily characterized using X−ray crystallography. The infrared spectroscopy can also be equally successfully employed in studying the metal−CO interaction. Since the metal to CO π−back bonding involves a π−donation from the metal d_π orbital to a π* orbital of a C−O bond, significant shift of the ν(CO) stretching frequency towards the lower energy is observed in metal carbonyl complexes with respect to that of free CO (2143 cm^{-1}).

Preparation of metal carbonyl complexes

The common methods of the preparation of the metal carbonyl compounds are,

i. *Directly using CO*



The main requirement of this method is that the metal center must be in a reduced low oxidation state in order to facilitate CO binding to the metal center through metal to ligand π−back donation.

ii. Using CO and a reducing agent



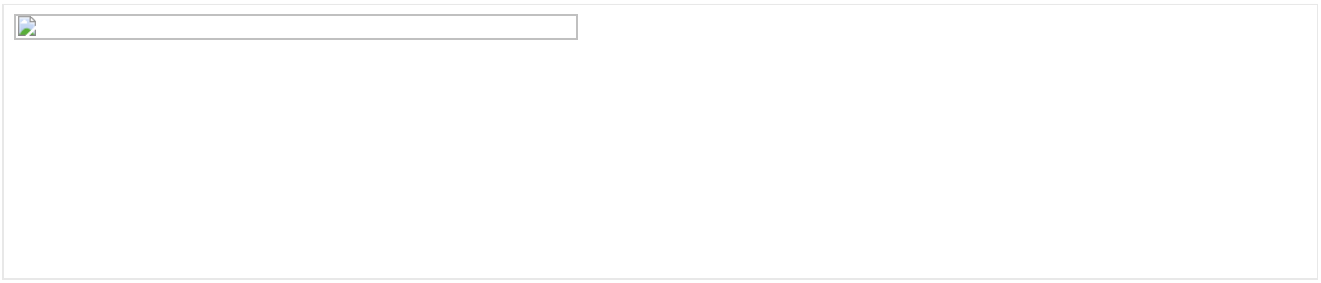
This method is commonly called reductive carbonylation and is mainly used for the compounds having higher oxidation state metal centers. The reducing agent first reduces the metal center to a lower oxidation state prior to the binding of CO to form the metal carbonyl compounds.

iii. From carbonyl compounds

This method involves abstraction of CO from organic compounds like the alcohols, aldehydes and CO_2.

Reactivities of metal carbonyls

i. Nucleophilic attack on carbon



The reaction usually gives rise to carbene moiety.

ii. Electrophilic attack at oxygen



iii. Migratory insertion reaction



The metal carbonyl displays two kinds of bindings in the form of the terminal and the bridging modes. The infrared spectroscopy can easily distinguish between these two binding modes of the metal carbonyl moiety as the terminal ones show ν(CO) stretching band at *ca*. 2100-2000 cm^{-1} while the bridging ones appear in the range 1720−1850 cm^{-1}. The carbonyl moiety can bridge between more than two metal centers (Figure 2).



Figure 2. Different bridging modes of the carbonyl binding to a metal is shown.

Problems

1. How many lone pairs are there in the CO molecule? Ans: Three (one from carbon and two from oxygen). 2. Despite O being more electronegative than C, the dipole moment of CO is almost zero. Explain. Ans: Because of the electron donation from oxygen to carbon. 3. What type of metal centers form metal carbonyl complexes? Ans: Low−valent metal centers. 4. What are the two main modes of binding exhibited by CO ligand? Ans: Terminal and bridging modes of binding.

Self Assessment test

1. Predict the product of the reaction?



Ans: Three (one from carbon and two from oxygen).

2. Upon binding to a metal center the C−O stretching frequency increases/decreases with regard to that of the free CO?

Ans: Decreases. 3. Explain why do low−valent metal centers stabilize CO binding in metal carbonyl complexes? Ans: Because metal to ligand π−back donation. 4. Give an example of a good σ−donor and π−donor ligand? Ans: Alkoxides (RO^-).

Summary

CO is a hallmark ligand of organometallic chemistry. The metal carbonyl complexes have been studied for a long time. The CO ligands bind tightly to metal center using a synergistic mechanism that involves σ−donation of the ligand lone pair to metal and followed by the π−back donation from a filled metal *d* orbital to a vacant σ* orbital of C−O bond of the CO ligand. The metal carbonyl complexes are prepared by several methods. The metal carbonyl complexes are usually stabilized by metal centers in low oxidation states.

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24.2C: Hydride Ligands

Learning Objectives

In this lecture you will learn the following

- Know about metal hydrides, their synthesis, characterization and their reactivity.

Metal hydrides occupy an important place in transition metal organometallic chemistry as the M−H bonds can undergo insertion reactions with a variety of unsaturated organic substrates yielding numerous organometallic compounds with M−C bonds. Not only the metal hydrides are needed as synthetic reagents for preparing the transition metal organometallic compounds but they also are required for important hydride insertion steps in many catalytic processes. The first transition metal hydride compound was reported by W. Heiber in 1931 when he synthesized $Fe(CO)_4H_2$. Though he claimed that the $Fe(CO)_4H_2$ contained Fe−H bond, it was not accepted until 1950s, when the concept of normal covalent M−H bond was widely recognized.

The metal hydride moieties are easily detectable in ^{1}H NMR as they appear high field of TMS in the region between 0 to 60 ppm, where no other resonances appear. The hydride moieties usually couple with metal centers possessing nuclear spins. Similarly, the hydride moieties also couple with the adjacent metal bound phosphine ligands, if at all present in the complex, exhibiting characteristic *cis* (J = 15 − 30 Hz) and *trans* (J = 90 − 150 Hz) coupling constants. In the IR spectroscopy, the M−H frequencies appear between (1500 − 2200) cm^{-1} but their intensities are mostly weak. Crystallographic detection of metal hydride moiety is difficult as hydrogen atoms in general are poor scatterer of X−rays. Located adjacent to a metal atom in a M−H bond, the detection of hydrogen atom thus becomes challenging and as a consequence the X−ray crystallographic method systematically underestimates the M−H internuclear distance by ~ 0.1 Å. However, better data could be obtained by performing the X−ray diffraction studies at a low temperature in which the thermal motion of the atoms are significantly reduced. In light of these facts, the neutron diffraction becomes a powerful method for detection of the metal hydride moieties as hydrogen scatters neutrons more effectively and hence the M−H bond distances can be measured more accurately. A limitation of neutron diffraction method is that large sized crystals are required for the study.

Synthesis

Following reactions are employed for synthesizing metal hydrides.

i. *Protonation reactions*

For this reaction to occur the metal center has to be basic and electron rich.



ii. *From hydride donors*

Generally for this method, a main group hydride is reacted with metal halide.



iii. *Using dihydrogen (H_2) addition*

This method involves oxidative addition of H_2 and thus requires metal centers that are capable of undergoing the oxidative addition step.



iv. *From a ligand*

This method takes into account the β−elimination that occur in a variety of metal bound ligand moieties, thereby yielding a M−H bond.



Reactions of metal hydrides

Metal hydrides are reactive species kinetically and thus participate in a variety of transformations like the ones discussed below.

i. *Deprotonation reactions*

The deprotonation reaction can be achieved by a hydride moiety resulting in the formation of H_2gas as shown below.



ii. *Hydride transfer and insertion*

In this reaction a hydride transfer from a metal center to formaldehyde resulting in the formation of a metal bound methoxy moiety is observed as shown below.



iii. *Hydrogen atom transfer reaction*

An example of hydrogen atom transfer reaction is given below.



It is interesting to note that the nature of hydrogen atom in a M−H bond can vary from being protic in nature, when bound to electron deficient metal centers as in metal carbonyl compounds, to that of being hydridic in nature, when bound to more electropositive early transition metals. In the latter case, the hydride moieties tend to be basic and exhibit hydride transfer reactions with electrophiles like aldehydes or ketones. Furthermore, the protonation of these basic metal hydrides leads to the elimination of dihydrogen (H_2) gas along with the generation of a vacant coordination site at the metal center.

Bridging hydrides

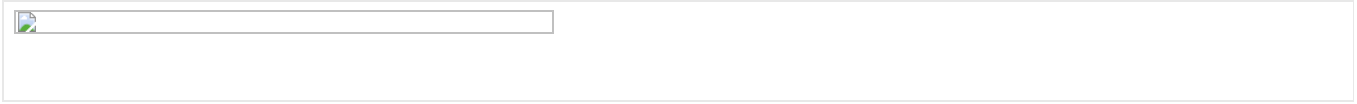
The metal hydrides usually show two modes of binding, namely terminal and bridging. In case of the bridging hydrides, the hydrogen atom can bridge between two or even more metal centers and thus, the bridging hydrides often display bent geometries.

Problems

1. Predict the product of the reaction.



Ans:



2. Give the oxidation state and total valence electron count of the metal center.



Ans: Oxidation state 0 and 18 VE 3. What kind of metal centers would stabilize metal dihydrogen complexes? Ans: Electron deficient and less π basic ligands 4. Specify whether the nature of hydrogen moiety in the complex, $HCo(CO)_4$ is acidic or basic? Ans: Acidic 5. Where do the M−H stretching bands appear in the IR spectrum of metal hydride complexes?

Ans: 1500 to 2200 cm^{-1}

Self Assessment test

1. Predict the product of the reaction.



Ans:



2. Give the oxidation state and total valence electron count of the metal center.



Ans: Oxidation state +2 and 18 VE 3. What kind of metal centers would stabilize classical dihydride complexes? Ans: Electron rich and more p basic ligands 4. Specify whether the nature of hydrogen moiety in the complex, $IrH_5(PCy_3)_2$ is acidic or basic? Ans: Basic

5. Between X−ray diffraction and neutron diffraction, which is a better method for the characterization of the M−H moiety?

Ans: Neutron diffraction

Summary

Metal hydrides are important compounds in the overall scheme of organometallic chemistry as they are involved in many crucial steps of numerous catalytic reactions. Apart from metal hydrides another important class of compounds are transition metal σ−complexes whose simplest variant are the metal dihydrogen complexes. These σ−complexes and the metal dihydrogen complexes are important for the heterolytic activations of the respective metal bound H−heteroatom and the H−H bonds.

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24.2D: Phosphine and Related Ligands

Learning Objectives

In this lecture you will learn the following

- Classification of ligands
- Nature of bonding in phosphines
- Steric and electronic properties of phosphines
- Bonding in phosphines and CO
- Cone angle and its application in catalysis

Classification of Ligands by donor atoms

Ligand is a molecule or an ion that has at least one electron pair that can be donated. Ligands may also be called Lewis bases; in terms of organic chemistry, they are 'nucleophiles'. Metal ions or molecules such as BF_3 (with incomplete valence electron shells (electron deficient) are called Lewis acids or electrophiles).

- Why do molecules like H_2O or NH_3 give complexes with ions of both main group and transition metals. E.g $[Al(OH_2)_6]^{3+}$ or $[Co(NH_3)_6]^{3+}$
- Why other molecules such as PF_3 or CO give complexes only with transition metals.
- Although PF_3 or CO give neutral molecules such as $Ni(PF_3)_4$ or $Ni(CO)_4$ or $Cr(CO)_6$.
- Why do, NH_3, amines, oxygen donors, and so on, not give complexes such as $Ni(NH_3)_4$.

Classical or simple donor ligands

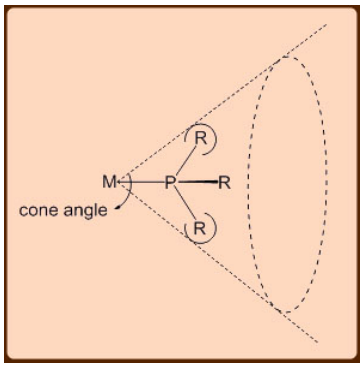
Act as electron pair donors to acceptor ions or molecules, and form complexes of all types of Lewis acids, metal ions or molecules. Non-classical ligands, π-bonding or π-acid ligands: Form largely with transition metal atoms. In this case special interaction occurs between the metals and ligands. These ligands act as both σ-donors and π-acceptors due to the availability of empty orbitals of suitable symmetry, and energies comparable with those of metal t_{2g} (non-bonding) orbitals. e.g. Consider PR_3 and NH_3: Both can act as bases toward H^+, but P atom differs from N in that PR_3 has σ* orbitals of low energy, whereas in N the lowest energy d orbitals or σ* orbitals are far too high on energy to use.

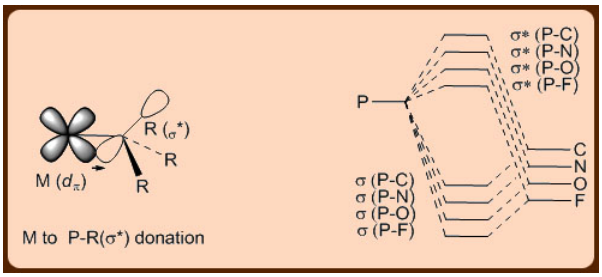
Consider CO that do not have measurable basicity to proton, yet readily reacts with metals like Ni that have high heats of atomization to give compounds like $Ni(CO)_4$.

Ligands may also be classified electronically depending upon how many electrons that they contribute to a central atom. Atoms or groups that can form a single covalent bond are one electron donors. e.g., F, SH, CH_3 etc.,

Compounds with an electron pair are two-electron donors. E.g., NH_3, H_2O, PR_3 etc.,

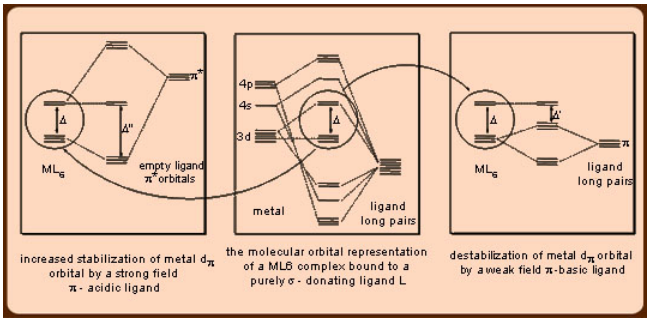
Bonding in Metal –Carbonyl and Metal-Phosphines





Steric factors in phosphines (Tolman's cone angle)

Cone angle is very useful in assessing the steric properties of phosphines and their coordination behavior.



The electronic effect of phosphines can be assessed by IR and NMR spectroscopic data especially when carbonyls are co-ligands. In a metal complex containing both phosphines and carbonyl, the ν(CO) frequencies would reveal the σ-donor or π–acceptor abilities of phosphines. If the phosphines employed are strong σ-donors, then more electron density would move from M (t_{2g} orbitals)- π*(CO) and as a result, a lowering in the ν(CO) is observed. In contrast, if a given phosphine is a poor σ-donor but strong π -acceptor, then phosphine(σ*-orbitals) also compete with CO for back bonding which results in less lowering in ν(CO) frequency.

Another important aspect is the steric size of PR_3 ligands, unlike in the case of carbonyls, which can be readily tuned by changing R group. This is of great advantage in transition metal chemistry, especially in metal mediated catalysis, where stabilizing the metals in low coordination states is very important besides low oxidation states. This condition can promote oxidative addition at the metal centre which is an important step in homogeneous catalysis. The steric effects of phosphines can be quantified with Tolman's cone angle.

Cone angle can be defined as a solid angle at metal at a M—P distance of 228 pm which encloses the van der Waal's surfaces of all ligand atoms or substituents over all rotational orientations. The cone angles for most commonly used phosphines are listed in the following table.

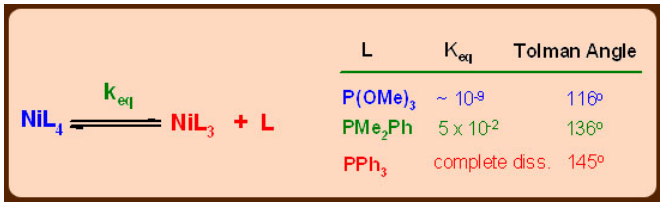
Phosphine	Cone Angle (°)
PH_3	87
PF_3	104
$P(OMe)_3$	107
PMe_3	118
PMe_2Ph	122
PEt_3	132
PPh_3	145
PCy_3	170
$P(Bu^t)_3$	182
P(mesityl)$_3$	212

Phosphines with different cone angles versus coordination number for group 8 metals:

ML_4	ML_3	ML_2
$(Me_3P)_4Ni$		
$(Me_3P)_4Pd$		
$(Me_3P)_4Pt$	$(Ph_3P)_3Pt$	$(tert\text{-}Bu_3P)_2Pt$

Tolman Angle and Catalysis

Sterically demanding phosphine ligands can be used to create an empty coordination site (16 VE complexes) which is an important trick to fine tune the catalytic activity of phosphine complexes.



Contributors and Attributions

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In this lecture you will learn the following

- Know about metal phosphine complexes.
- Have an understanding of the steric and electronic properties of the phosphine ligands.
- Obtain a deeper insight about the metal phosphine interactions.
- Be introduced to other π−basic ligands.

Phosphines are one of the few ligands that have been extensively studied over the last few decades to an extent that the systematic fine tuning of the sterics and electronics can now be achieved with certain degree of predictability. Phosphines are better spectator ligands than actor ligands. Tolman carried out pioneering infrared spectroscopy experiments on the $PR_3Ni(CO)_3$ complexes looking at the $\nu_{(CO)}$stretching frequencies for obtaining an insight on the donor properties of the PR_3 ligands. Thus, a stronger σ−donor phosphine ligand would increase the electron density at the metal center leading to an enhanced metal to ligand π−back bonding and thereby lowering of the $\nu_{(CO)}$ stretching frequencies in these complexes. Another important aspect of the phosphine ligand is its

size that has significant steric impact on its metal complexes. Thus, unlike CO ligand, which is small and hence many may simultaneously be able to bind to a metal center, the same is not true for the phosphine ligands as only a few can bind to a metal center. The number of phosphine ligands that can bind to a metal center also depends on the size of its R substituents. For example, up to two can bind to a metal center in case of the PCy_3 or $P(i\text{−}Pr)_3$ ligands, three or four for PPh_3, four for Me_2PH, and five or six for PMe_3. The steric effect of phosphine was quantified by Tolmann and is given by a parameter called *Cone Angle* that measures the angle at the metal formed by the PR_3 ligand binding to a metal (Figure 1).

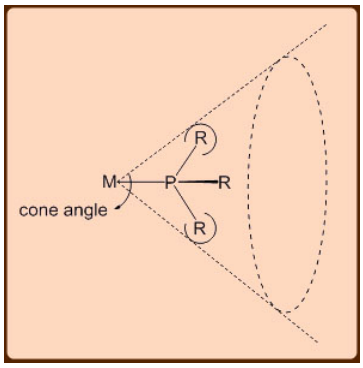


Figure 1. Cone Angle in metal−phosphine complexes.

The *Cone Angle* criteria has been successfully invoked in rationalizing the properties of a wide range of metal phosphine complexes. One unique feature of the phosphine ligand is that it allows convenient change of electronic effect without undergoing much change in its steric effects. For example, PBu_3 and $P(O^iPr)_3$ have similar steric effects but vary in their electronic effects. The converse is also true as the steric effect can be easily changed without undergoing much change in the electronic effect. For example, PMe_3 and $P(o\text{−}tolyl)_3$ have similar electronic effect but differ in their steric effects. Thus, the ability to conveniently modulate the steric and the electronic effects make the phosphine ligands a versatile system for carrying out many organometallic catalysis.

Structure and Bonding

Phosphines are two electron donors that engage a lone pair for binding to metals. These are thus considered as good σ−donors and poor π−acceptors and they belong to the same class with the aryl, dialkylamino and alkoxo ligands. In fact they are more π−acidic than pure σ−donor ligands like $NH_3$and, more interestingly so, their π−acidity can be varied significantly by systematic incorporation of substituents on the P atom. For example, PF_3 is more π−acidic than CO. Analogous to what is observed in case of the benchmark π−acidic CO ligand, in which the metal d_π orbital donates electron to a π* orbital of a C−O bond, in the case of the phosphines ligands, such π−back donation occurs from the metal d_π orbital occurs on to a σ* orbital of a P−R bond (Figure 2). In phosphine ligands, with the increase of the electronegativity of R both of the σ and the σ* orbitals of the P−R bond gets stabilized. Consequently, the contribution of the atomic orbital of the P atom to the σ*−orbital of the P−R bond increases, which eventually increases the size of the σ* orbital of the P−R bond. This in turn facilitates better overlap of the σ* orbital of the P−R bond with the metal d_π orbital during the metal to ligand π−back donation in these metal phosphine complexes.

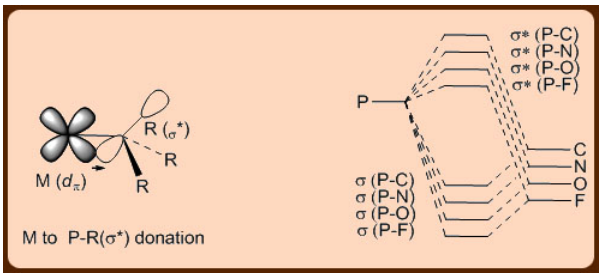


Figure 2. Back donation from the metal d_π orbital to a σ* orbital of a P−R bond.

Starting from CO, which is a strong π−acceptor ligand, to moving to the phosphines, which are good σ−donors and poor π−acceptor ligands, to even going further to other extreme to the ligands, which are both good σ−donors as well as π−donors, a rich variety of phosphine ligands thus are available for stabilizing different types of organometallic complexes. In this context the following ligands are discussed below.

π-basic ligands

Alkoxides (RO^-) and halides like F^-, Cl^- and Br^- belong to a category of π−basic ligands as they engage a second lone pair for π−donation to the metal over and above the first lone pair partaking σ−donation to the metal. Opposite to what is observed in the case of π−acidic ligands, in which the π* ligand orbital stabilizes the d_π metal orbital and thereby affecting a larger ligand field splitting, as consistent with the strong field nature of these ligands (Figure 3), in the case of the π−basic ligands, the second lone pair destabilizes the d_π metal orbitals leading to a smaller ligand field splitting, which is in agreement with the weak field nature of these ligands. The orbitals containing the lone pair of the ligands are usually located on the more electronegative heteroatoms and so they are invariably lower in energy than the metal d_π orbitals. Hence, the destabilization of the metal d_π orbitals occurs due to the repulsion of the filled ligand lone pair orbital with the filled metal d_π orbitals. In case of the situations in which the metal d_π orbitals are vacant, like in d^0 systems of Ti^{4+} ions, the possibility of the destabilization of the metal d_π orbitals do not arise but instead stabilization occurs through the donation of the filled ligand lone pair orbital electrons to the empty metal d_π orbitals as seen in the case of TiF_6 and $W(OMe)_6$. Thus, this scenario in π−basic ligands is opposite to that observed in case of the π−acidic ligands, for which the empty π* ligand orbitals are higher in energy than the filled metal d_π orbitals.

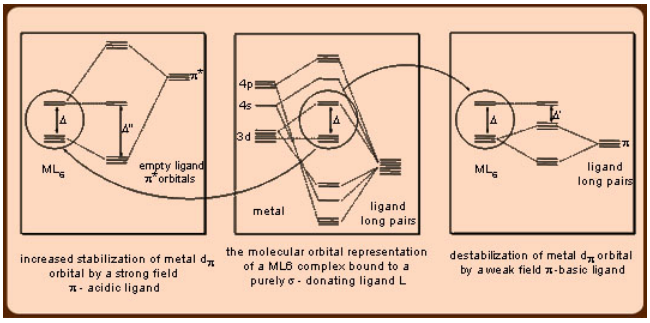


Figure 3. Orbital interactions in the presence of the π−acceptor, (pure) σ−donor and π−basic ligands are shown.

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24.2E: π -bonded Organic Ligands

Learning Objectives

In this lecture you will learn the following

- The metal alkene complexes.
- The metal−olefin bonding interactions.
- The synthesis and reactivities of the metal−olefin complexes.
- The *umpolung* reactivities of olefins in the metal alkene complexes.

Though the first metal olefin complex dates back a long time to the beginning of 19th century, its formulation was established only a century later in the 1950s. While reacting K_2PtCl_4 with EtOH in 1827, the Danish chemist Zeise synthesized the famous Zeise's salt $K[PtCl_3(C_2H_4)]\bullet H_2O$ containing a Pt bound ethylene moiety and which incidentally represented the first metal−olefin complex (Figure 1).



Figure 1. Zeise's salt.

The metal−olefin bonding interaction is best explained by the *Dewar−Chatt* model, that takes into account two mutually opposing electron donation involving σ−donation of the olefinic C=C π−electrons to an empty d_π metal orbital followed by π−back donation from a filled metal d_π orbital into the unoccupied C=C π* orbital. Quite understandably so, for the d^0 systems, the formations of metal−olefin complexes are not observed. The extent of the C=C forward π-donation to the metal and the subsequent π−back donation from the filled d_π orbital to the olefinic C=C π* orbital have a direct bearing on the C=C bond of the metal bound olefinic moiety in form of bringing about a change in hybridization as well as in the C−C bond distance (Figure 2).



Figure 2. Metal olefin bonding interactions.

If the metal to ligand π−back donation component is smaller than the ligand to metal σ−donation, then the lengthening of the C−C bond in the metal bound olefin moiety is observed. This happens primarily because of the fact that the alkene to metal σ−donation removes the C=C π−electrons away from the C−C bond of the olefin moiety and towards the metal center, thus, decreasing its bond order and increasing the C−C bond length. Additionally, as the metal to ligand π−back donation increases, the electron donation of the filled metal d_π orbital on to the π* orbital of the metal bound olefin moiety is enhanced. This results in an increase in the C−C bond length. The lengthening of the C−C bond in metal bound olefin complex can be correlated to the π−basicity of the metal. For example, for a weak π−basic metal, the C−C bond lengthening is anticipated to be small while for a strong π−basic metal, the C−C lengthening would be significant.

Another implication of ligand−metal π−back donation is in the observed change of hybridization at the olefinic C atoms from pure sp^2, in complexes with no metal to ligand π−back donation, to sp^3, in complexes with significant metal to ligand π−back donation, is observed. The change in hybridization from sp^2 to sp^3 centers of the olefinic carbon is accompanied by the substituents being slightly bent away from the metal center in the final metalacyclopropane form (Figure 3). This change in hybridization can be

conveniently detected by ^{1}H and ^{13}C NMR spectroscopy. For example, in case of the metalacyclopropane systems, which have strong metal to ligand π−back donation, the vinyl protons appear 5 ppm (in the ^{1}H NMR) and 100 ppm (in the ^{13}C NMR) high field with respect to the respective position of the free ligands.

An interesting fallout of the metal to ligand π−back bonding is the tighter binding of the strained olefins to the metal center as observed in the case of cyclopropene and norbornene. The strong binding of these cyclopropene and norbornene moieties to the metal center arise out of the relief of ring strain upon binding to the metal. Lastly, in the metal−olefin complexes having very little π−back bonding component, the chemical reactivities of the metal bound olefin appear opposite to that of a free olefin. For example, a free olefin is considered electron rich by virtue of the presence of π−electrons in its outermost valence orbital and hence it undergoes an electrophilic attack. However, the metal bound olefin complexes having predominantly σ−donation of the olefinic π−electrons and negligible metal to ligand π−back donation, the olefinic C becomes positively charged and hence undergoes a nuclophilic attack. This nature of reversal of olefin reactivity is called *umpolung* character.



Figure 3. Metalacyclopropane system and *Dewar−Chatt* model

Synthesis

Metal alkene complexes are synthesized by the following methods.

i. Substitution in low valent metals

$$AgOSO_2CF_3 + C_2H_4 \rightarrow (C_2H_4)AgOSO_2CF_3 \quad (24.2E.1)$$

ii. Reduction of high valent metal in presence of an alkene

$$(cod)PtCl_2 + C_2H_4 \rightarrow [PtCl_3(C_2H_4)]^+ + Cl^- \quad (24.2E.2)$$

iii. From alkyls and related species

$$Cp_2TaCl_3 + n\text{-}BuMgX \rightarrow \{Cp_2TaBu_3\} \quad (24.2E.3)$$



Reaction of alkenes

The metal alkene complexes show the following reactivities.

i. Insertion reaction

These reactions are commonly displayed by alkenes as they insert into metal−X bonds yielding metal alkyls. The reaction occurs readily at room temperature for X = H, whereas for other elements (X = other atoms), such insertions become rare. Also, the strained alkenes and alkynes undergo such insertion readily.



ii. *Umpolung* reactions

Umpolung reactions are observed only for those metal−alkene complexes for which the metal center is a poor π−base and as a result of which the olefin undergoes a nuclophilic attack.

iii. Oxidative addition

Alkenes containing allylic hydrogens undergo oxidative addition to give a allyl hydride complex.

Problems

1. Predict the product of the reaction.



Ans: A = {(CF_2=CF_2)AuMe(PPh_3)} and B = Au(CF_2-CF_2Me)(PPh_3) 2. Specify whether the lengthening/shortening of the C−C bond distance in the metal bound olefin moiety is observed as a result of metal to ligand π−back donation? Ans: Lengthening. 3. Draw the structure of Zeise's salt. Ans:



4. The change in hybridization at the olefinic C from sp^2 to sp^3 primarily arise due to? Ans: Metal-ligand π-back donation.

Self Assessment test

1. Predict the product of the reaction.

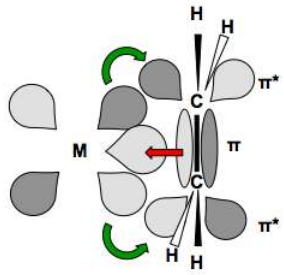


Ans: $[PtCl_3(C_2H_4)]^-$ and Cl^- 2. Specify whether the lengthening/shortening of the C−C bond distance in the metal bound olefin moiety is observed as a result of ligand to metal σ− donation? Ans: Lengthening. 3. Metalacyclopropane intermediate in a metal bound olefin complex is primarily formed due to which kind of interaction? Ans: Metal−ligand π−back donation 4. The oxidation state of Pt in Zeise's salt is? Ans: Pt^{II}

Summary

Alkenes are an important class of unsaturated ligands that bind to a metal by σ−donating its C=C π−electrons and also accepts electrons from the metal in its π* orbital of C=C bond. These symbiotic σ−donation and π−back donation in metal bound olefin complexes have a significant impact on their structure and reactivity properties. Quite importantly, the structural manifestations arising out of these forward σ−donation and π−back donation can be characterized by using ^1H, ^{13}C NMR and IR spectroscopic methods.

Pi-ligands are those that bond to a metal via donating electron density to the metal from their σ-orbitals and their π-orbitals and by the metal center's donation of electron density into the π* orbitals of the ligands. The degree of π* back-donation from the metal depends upon the energy level of the ligand's π* orbitals, the lower the energy, the easier it is for the metal to donate electron density. According to molecular orbital theory, it is the metal's d-electrons that share common symmetry with ligands' p-orbitals that lead to direct bonding with the metal while those that lie in between the axes of the ligands, including d_{xz} and d_{yz} can donate electron density into the empty π* orbitals[1]. The metal orbitals that the ligand participates in backbonding with will help determine the orientation of the ligands in space around the molecule, for example, ethylene blinded to iron will lie in the equatorial plane of the Oh (Octahedral) complex due to the π* orbital being closer in energy to the d_{x2-y2} metal orbital than the dxz orbital[2]. The energy of these orbitals and thus the degree of backbonding that occurs can be changed by altering the substituents of the pi-lignads. substituents. The more electronegative the substituents on an alkene ligand, the lower in energy the π* orbitals and the greater the degree of backbonding. π bonding is not limited to a metal's d-orbitals, but can also occur between f-orbitals and pi-electron density as in more exotic organometallic compounds including uranocene, where δ-bonds play an important role[4]. In addition to alkenes, alkynes can also act as pi-ligands and are more stable than alkenes and thus are better π* acceptors in-part because they have 2 additional π and π* orbitals that can participate in bonding.



Bonding and Pi-Backbonding in a generic metal-ethylene system. Image adapted from Pfenning, Brian W., Principles of Inorganic Chemistry (2015) p. 642. Image used with perimssion (CC BY-SA 4.0; Macbaband).

These type of ligand are anionic and thus act to increase the oxidation state of the metal center. When determining the likely stability of a metal complex using an ionic method of electron counting, each “double-bond” that participates in bonding donates two electrons to the metal center. In an olefin ligand, especially conjugated arenes, not all of the carbons participate directly in bonding[5]. The number of carbon atoms that participate in bonding in an arene ring is referred to as the hapticity symbolized ηn where n is the number of carbon atoms that are directly bonded to the metal center. This allows ligands of this type to play unique roles in organic mechanisms such as what's referred to as "ring slippage" where, in a ligand substitution, the hapticity of a ligand is reduced followed by the addition of a new ligand to the metal center which is then followed by an increase in the hapticity and the rejection of a different ligand.

Hapticity of greater than 1 in a pi-ligand is not limited to cyclic alkenes or aromatic alkenes corresponding to double bonds but whenever the electron density is spread out over multiple carbons. For example, CH2=CH-CH2- (Allyl Anion) can act as a ligand with η3 because its delocalized pi-MO's can share symmetry with the metal center's d-orbitals.

Examples of pi-ligands are cylclopentadiene (as in the famous ferrocene sandwich compound), ethylene, benzene and many other alkenes and alkynes.

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24.2H: Dihydrogen

Metal dihydrogen complexes

The simplest variant of a σ−complex contains a dihydrogen ligand. The first dihydrogen complex was isolated by Kubas, after which many new ones were reported.



Quite expectedly, the dihydrogen moiety bound to a metal in a σ−complex is found to be more acidic (p*K*a = 0 − 20) when compared to the free dihydrogen molecule (p*K*a = 35). It is interesting to note that the p*K*a change associated with the binding of dihydrogen to a metal in a σ−complex relative to that of the free H_2 molecule is significantly larger than the change associated with binding of H_2O to metal. Owing to this inherent acidity, the deprotonation of the metal bound dihydrogen moiety by a base can thus be appropriately employed for heterolytic activation of the dihydrogen moiety as illustrated below.



The dihydrogen complexes of metals are often referred to as nonclassical hydrides. The electron rich π basic metals are anticipated to split the metal bound dihydrogen moieties resulting in classical dihydride complexes. Along the same line of thinking, the electron deficient and less π basic metal would tend to stabilize a dihydrogen complex. The dihydrogen complexes can also be characterized by the X ray diffraction as well as neutron diffraction methods. In IR spectrum, the metal bound H−H stretch appear in the range (2300 − 2900) cm^{-1} while in the ^1H NMR spectrum the same appear between 0 to −10 ppm as a broad peak. The dihydrogen complexes are often characterized by isotopic labeling studies of metal bound H−D moiety that shows a coupling constant of 20 – 34 Hz as supposed to 43 Hz observed in case of the free H−D molecule.

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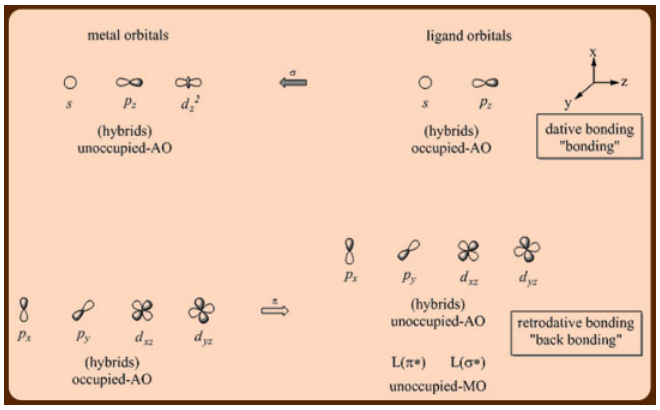
24.3: The 18-electron Rule

Learning Objectives

In this lecture you will learn the following

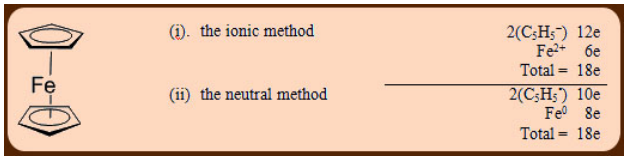
- Have an insight about the stability of the transition metal complexes with respect to their total valence electron count.
- Be aware of the transition metal complexes that obey or do not obey the 18 Valence Electron Rule.
- Have an appreciation of the valence electron count in the transition metal organometallic complexes that arise out of the metal-ligand orbital interactions.

The transition metal organometallic compounds exhibit diverse structural variations that manifest in different chemical properties. Many of these transition metal organometallic compounds are primarily of interest from the prospectives of chemical catalysis. Unlike the main group organometallic compounds, which use mainly *ns* and *np* orbitals in chemical bonding, the transition metal compounds regularly use the $(n-1)d$, *ns* and *np* orbitals for chemical bonding (Figure 1). Partial filling of these orbitals thus render these metal centers both electron donor and electron acceptor abilities, thus allowing them to participate in σ-donor/π-acceptor synergic interactions with donor-acceptor ligands like carbonyls, carbenes, arenes, isonitriles and etc,.

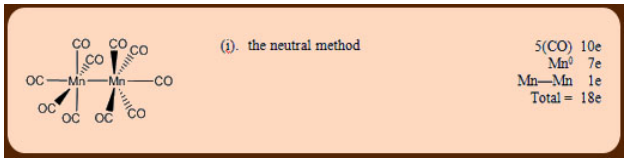


The 18 Valence Electron (18 VE) Rule or The Inert Gas Rule or The Effective Atomic Number (EAN) Rule: The 18-valence electron (VE) rule states that thermodynamically stable transition metal compounds contain 18 valence electrons comprising of the metal *d* electrons plus the electrons supplied by the metal bound ligands. The counting of the 18 valence electrons in transition metal complexes may be obtained by following either of the two methods of electron counting, (*i*). the ionic method and (*ii*). the neutral method. Please note that a metal-metal bond contributes one electron to the total electron count of the metal atom. A bridging ligand donates one electron towards bridging metal atom.

Example 1: Ferrocene $Fe(C_5H_5)_2$



Example 2. $Mn_2(CO)_{10}$



Transition metal organometallic compounds mainly belong to any of the three categories.

a. **Class I** complexes for which the number of valence electrons do not obey the 18 VE rule.

b. **Class II** complexes for which the number of valence electrons do not exceed 18.
c. **Class III** complexes for which the valence electrons exactly obey the 18 VE rule.

The guiding principle which governs the classification of transition metal organometallic compounds is based on the premise that the antibonding orbitals should not be occupied; the nonbonding orbitals may be occupied while the bonding orbitals should be occupied.

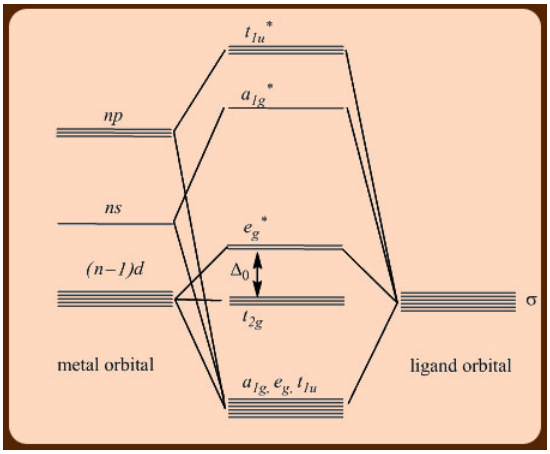


Figure 2. A simplified molecular orbital diagram for an octahedral transition metal complex showing σ−interactions only.

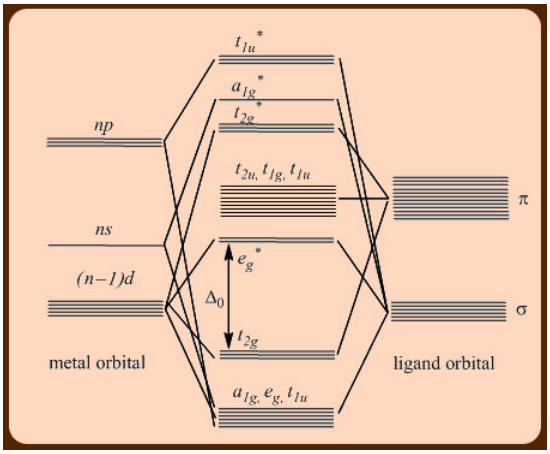


Figure 3. A simplified molecular orbital diagram for an octahedral transition metal complex showing σ−and π−interactions only.

Class I:

In **class I** complexes, the Δ_o splitting is small and often applies to *3d* metals and σ ligands at lower end of the spectrochemical series. In this case the t_{2g} orbital is nonbonding in nature and may be occupied by 0−6 electrons (Figure 2). The e_g* orbital is weakly antibonding and may be occupied by 0−4 electrons. As a consequence, 12−22 valence electron count may be obtained for this class of compounds. Owing to small Δ_{tetr} splitting energy, the tetrahedral transition metal complexes also belongs to this class.

Class II:

In **class II** complexes, the Δ_o splitting is relatively large and is applicable to *4d* and *5d* transition metals having high oxidation state and for σ ligands in the intermediate and upper range of the spectrochemical series. In this case, the t_{2g} orbital is essentially nonbonding in nature and can be filled by 0−6 electrons (Figure 3). The e_g* orbital is strongly antibonding and is not occupied at all. Consequently, the valence shell electron count of these type of complexes would thus be 18 electrons or less.

Class III:

In **class III** complexes, the Δ_o splitting is the largest and is applicable to good σ donor and π acceptor ligands like CO, PF_3, olefins and arenes located at the upper end of the spectrochemical series. The t_{2g}orbital becomes bonding owing to interactions with ligand orbitals and should be occupied by 6 electrons. The e_g* orbital is strongly antibonding and therefore remains unoccupied.

Problems

State the oxidation state of the metal and the total valence electron count of the following species.

1. $V(C_2O_4)_3^{3-}$

Ans: +3 and 14 2. $Mn(acac)_3$ Ans: +3 and 16 3. $W(CN)_8^{3-}$ Ans: +5 and 17 4. $CpMn(CO)_3$ Ans: 0 and 18 5. $Fe_2(CO)_9$ Ans: 0 and 18 Self Assessment test

State the oxidation state of the metal and the total valence electron count of the following species.

1. TiF_6^{2-}

Ans: +4 and 12 2. $Ni(en)_3^{2+}$ Ans: +2 and 20 3. $Cu(NH_3)_6^{2+}$ Ans: +2 and 21 4. $W(CN)_8^{4-}$ Ans: +4 and 18 5. $CH_3Co(CO)_4$ Ans: 0 and 18

Summary

The transition metal complexes may be classified into the following three types. (i). The ones that do not obey the 18 valence electron rule are of class I type (ii). the ones that do not exceed the 18 valence electron rule are of class II and (iii). the ones that strictly follow the 18 valence electron rule. Depending upon the interaction of the metal orbitals with the ligand orbitals and also upon the nature of the ligand position in spectrochemical series, the transition metal organometallic compounds can form into any of the three categories.

The 18-electron rule is used primarily for predicting and rationalizing formulae for stable metal complexes, especially organometallic compounds. The rule is based on the fact that the valence shells of transition metals consist of nine valence orbitals (one s orbital, three p orbitals and five d orbitals), which collectively can accommodate 18 electrons as either bonding or nonbonding electron pairs. This means that, the combination of these nine atomic orbitals with ligand orbitals creates nine molecular orbitals that are either metal-ligand bonding or non-bonding. When a metal complex has 18 valence electrons, it has achieved the same electron configuration as the noble gas in the period. The rule and its exceptions are similar to the application of the octet rule to main group elements.

This rule applies primarily to organometallic compounds, and the 18 electrons come from the 9 available orbitals in d orbital elements (1 s orbital, 3 p orbitals, and 5 d orbitals). The rule is not helpful for complexes of metals that are not transition metals, and interesting or useful transition metal complexes will violate the rule because of the consequences deviating from the rule bears on reactivity. If the molecular transition metal complex has an 18 electron count, it is called **saturated**. This means that additional ligands cannot bind to the transition metal because there are no empty low-energy orbitals for incoming ligands to coordinate. If the molecule has less than 18 electrons, then it is called **unsaturated** and can bind additional ligands.

Electron counting

Two methods are commonly employed for electron counting:

1. Neutral atom method: Metal is taken as in zero oxidation state for counting purpose
2. Oxidation state method: We first arrive at the oxidation state of the metal by considering the number of anionic ligands present and overall charge of the complex

To count electrons in a transition metal compound:

1. Determine the oxidation state of the transition metal and the resulting d-electron count.
   - Identify if there are any overall charges on the molecular complex.
   - Identify the charge of each ligand.
2. Determine the number of electrons from each ligand that are donated to the metal center.
3. Add up the electron counts for the metal and for each ligand.

Typically for most compounds, the electron count should add up to 18 electrons. However, there are many exceptions to the 18 electron rule, just like there are exceptions to the octet rule.

Reactivity

The 18 electron rule allows one to predict the reactivity of a certain compound. The associative mechanism means that there is an addition of a ligand while a dissociative mechanism means that there is a loss of a ligand. When the electron count is less than 18, a molecule will most likely undergo an associative reaction. For example: $(C_2H_4)PdCl_2$

- 16 electron count
- Would it more likely lose a C_2H_4 or gain a CO? Losing a C_2H_4 results in a 14 electron complex while gaining a CO gives an 18 electron complex. From the 18 electron rule, we will expect that the compound will more likely undergo an associative addition of CO.

Example 24.3.1:

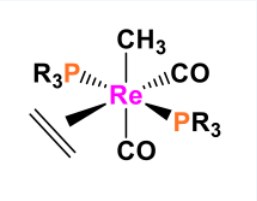


Figure 24.3.1: Saturated Re metal complex with 18 electron count. (CC SA-BY 4.0; Derrekli)

1. There is no overall charge on the molecule and there is one anionic ligand (CH_3^-)
   - The Re metal must have a positive charge that balances out the anionic ligand charge to equal the 0 overall molecular charge. Since there is a -1 charge contribution from the methyl ligand, the Re metal has a +1 charge.
   - Because the Re metal is in the +1 oxidation state, it is a d^6 electron count. It would have been its regular d^7 electron count if it had a neutral (0) oxidation state.
2. The CH_3^- ligand contributes 2 electrons. Each CO ligand contributes 2 electrons. Each PR_3 ligand contributes 2 electrons. The H2C=CH2 ligand contributes 2 electrons.
3. Adding up the electrons:
   - Re(1): 6 electrons
   - CH_3^-: 2 electrons
   - 2 x CO: 2 x 2 electrons = 4 electrons
   - 2 x PR_3: 2 x 2 electrons = 4 electrons
   - $H_2C=CH_2$: 2 electrons
   - Total: 18 electrons

In this example, the molecular compound has an 18 electron count, which means that all of its orbitals are filled and the compound is stable.

Example 24.3.2: $[M(CO)_7]^+$

The 18 electron rule can also be used to help identify an unknown transition metal in a compound. Take for example $[M(CO)_7]^+$. To find what the unknown transition metal M is, simply work backwards:

1. 18 electrons
2. Each (CO) ligand contributes 2 electrons
   - 7 x 2 electrons = 14 electrons
3. 18 - 14 = 4 electrons
4. d^4
5. M(I) oxidation state
6. The unknown metal M must be V, Vanadium

Example 24.3.3: $[Co(CO)_5]^z$

Similarly to Example 2, the 18 electron rule can also be applied to determine the overall expected charge of an molecule. Take for example $[Co(CO)_5]^z$. To find the unknown charge z:

1. 18 electrons
2. Each CO ligand contributes 2 electrons
    1. 5 x 2 electrons = 10 electrons
3. Co is typically d^9
4. 9 + 10 = 19 electrons
5. To satisfy the 18 electron rule, the $[Co(CO)_5]^z$ compound must have a charge of z = +1.

Ligand Contributions

Below is a list of common organometallic ligands and their respective electron contributions.

Neutral 2e donors	Anionic 2e donors	Anionic 4e donors	Anionic 6e donors
PR_3 (phosphines)	X^- (halide)	$C_3H_5^-$ (allyl)	Cp^- (cyclopentadienyl)
CO (carbonyl)	CH_3^- (methyl)	O^{2-} (oxide)	O^{2-} (oxide)
alkenes	CR_3^- (alkyl)	S^{2-} (sulfide)	
alkynes	Ph^- (phenyl)	NR^{2-} (imide)	
nitriles	H^- (hydride)	CR_2^{2-} (alkylidene)	
	R_nE^- (silyl, germyl, alkoxo, amido etc.)	OR^- (alkoxide, bridging ligand)	
		SR^- (thiolate, bridging ligand)	
		NR_2^- (inorganic amide, bridging ligand)	
		PR_2^- (phosphide, bridging ligand)	

Exceptions

Generally, the early transition metals (group 3 to 5) could have an electron count of 16 or less. Middle transition metals (group 6 to group 8) commonly have 18 electron count while late transition metals (group 9 to group 11) generally have 16 or lower electron count. When a structure has less than an 18 electron count, it is considered electron-deficient or coordinately unsaturated. This means that the compound has empty valence orbitals, making it electrophilic and extremely reactive. If a structure has "too many electrons," that means that not all of the bonds are covalent bonds, and thus some has to be ionic bonds. These bonds are weaker compared to covalent bonds. However, these organometallic compounds that have an electron count greater than 18 are fairly rare.

Summary

The 18-electron rule is similar to the octet rule for main group elements, something you might be more familiar with, and thus it may be useful to bear that in mind. So in a sense, there's not much more to it than "electron bookkeeping".

References

1. Pfenning, Brian (2015). *Principles of Inorganic Chemistry*. Hoboken, New Jersey: John Wiley & Sons, Inc. pp. 629–631. ISBN 9781118973868.

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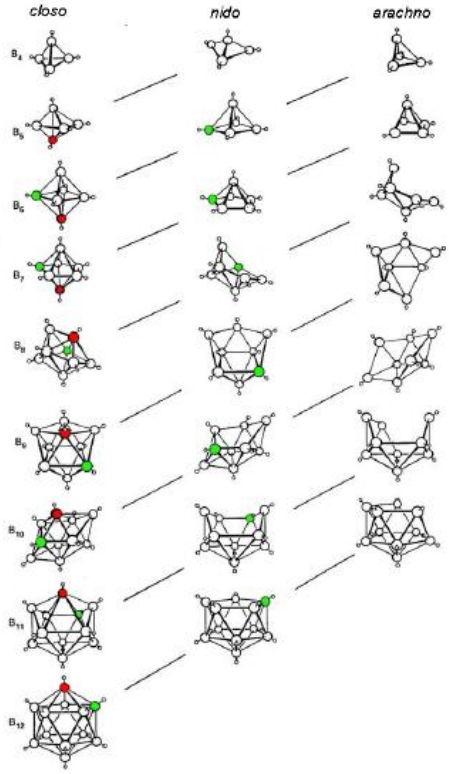
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24.5: The Isolobal Principle and Application of Wade's Rules

Ken Wade developed a method for the prediction of shapes of borane clusters; however, it may be used for a wide range of substituted boranes (such as carboranes) as well as other classes of cluster compounds. Wade's rules are used to rationalize the shape of borane clusters by calculating the total number of skeletal electron pairs (SEP) available for cluster bonding. In using Wade's rules it is key to understand structural relationship of various boranes.



*Structural relationship between closo, nido, and arachno boranes (and hetero-substituted boranes). The diagonal lines connect species that have the same number of skeletal electron pairs (SEP). Hydrogen atoms except those of the B-H framework are omitted. The red atom is omitted first, the green atom removed second. Adapted from R. W. Rudolph, Acc. Chem. Res., 1976, **9**, 446.*

Wade's rules:

The general methodology to be followed when applying Wade's rules is as follows:

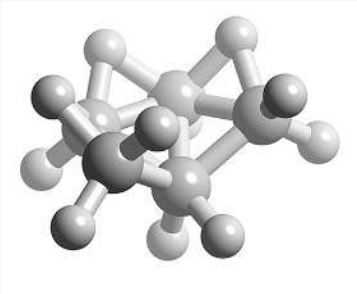
1. Determine the total number of valence electrons from the chemical formula, i.e., 3 electrons per B, and 1 electron per H.
2. Subtract 2 electrons for each B-H unit (or C-H in a carborane).
3. Divide the number of remaining electrons by 2 to get the number of skeletal electron pairs (SEP).
4. A cluster with *n* vertices (i.e., *n* boron atoms) and *n*+1 SEP for bonding has a *closo* structure.
5. A cluster with *n*-1 vertices (i.e., *n*-1 boron atoms) and *n*+1 SEP for bonding has a *nido* structure.
6. A cluster with *n*-2 vertices (i.e., *n*-2 boron atoms) and *n*+1 SEP for bonding has an *arachno* structure.
7. A cluster with *n*-3 vertices (i.e., *n*-3 boron atoms) and *n*+1 SEP for bonding has an *hypho* structure.
8. If the number of boron atoms (i.e., *n*) is larger than *n*+1 SEP then the extra boron occupies a capping position on a triangular phase.

Example 24.5.1: B_5H_{11}

What is the structure of B_5H_{11}?

Solution

1. Total number of valence electrons = (5 x B) + (11 x H) = (5 x 3) + (11 x 1) = 26
2. Number of electrons for each B-H unit = (5 x 2) = 10
3. Number of skeletal electrons = 26 – 10 = 16
4. Number SEP = 16/2 = 8
5. If n+1 = 8 and n-2 = 5 boron atoms, then n = 7
6. Structure of n = 7 is pentagonal bipyramid, therefore B_5H_{11} is an *arachno* based upon a pentagonal bipyramid with two apexes missing.



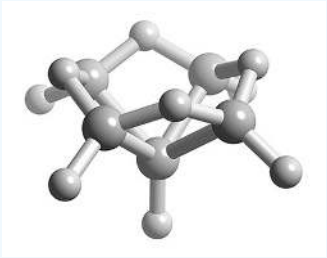
Ball and stick representation of the structure of B_5H_{11}.

Example 24.5.2: B_5H_9?

What is the structure of B_5H_9?

Solution

1. Total number of valence electrons = (5 x B) + (9 x H) = (5 x 3) + (9 x 1) = 24
2. Number of electrons for each B-H unit = (5 x 2) = 10
3. Number of skeletal electrons = 24 – 10 = 14
4. Number SEP = 14/2 = 7
5. If n+1 = 7 and n-1 = 5 boron atoms, then n = 6
6. Structure of n = 6 is octahedral, therefore B_5H_9 is a *nido* structure based upon an octahedral structure with one apex missing.



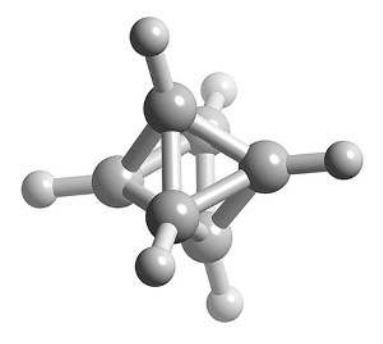
Ball and stick representation of the structure of B_5H_9.

Example 24.5.3: $B_6H_6^{2-}$

What is the structure of $B_6H_6^{2-}$?

1. Total number of valence electrons = (6 x B) + (3 x H) = (6 x 3) + (6 x 1) + 2 = 26
2. Number of electrons for each B-H unit = (6 x 2) = 12
3. Number of skeletal electrons = 26 – 12 = 14

4. Number SEP = 14/2 = 7
5. If n+1 = 7 and n boron atoms, then n = 6
6. Structure of n = 6 is octahedral, therefore $B_6H_6^{2-}$ is a *closo* structure based upon an octahedral structure.



Ball and stick representation of the structure of $B_6H_6^{2-}$.

Table 24.5.1 provides a summary of borane cluster with the general formula $B_nH_n^{x-}$ and their structures as defined by Wade's rules.

Table 24.5.1: Wade's rules for boranes.

Type	Basic formula	Example	# of verticies	# of vacancies	# of e- in B + charge	# of bonding MOs
Closo	$B_nH_n^{2-}$	$B_6H_6^{2-}$	n	0	3n + 2	n + 1
Nido	$B_nH_n^{4-}$	B_5H_9	n + 1	1	3n + 4	n + 2
Arachno	$B_nH_n^{6-}$	B_4H_{10}	n + 2	2	3n + 6	n + 3
Hypho	$B_nH_n^{8-}$	$B_5H_{11}^{2-}$	n + 3	3	3n + 8	n + 4

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- R. W. Rudolph, *Acc. Chem. Res.*, 1976, **9**, 446.
- K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.

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24.6: Total Valence Electron Counts in d-block Organometallic Clusters

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24.6A: Single Cage Structures

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SECTION OVERVIEW

24.7: Types of Organometallic Reactions

Organometallic reactions can usually be classified as one of the following classes:

- ligand dissociation/ligand association
- reductive elimination/oxidative addition
- σ bond metathesis/4-centered reaction
- insertion/de-insertion
- Lewis acid activation of electrophile

Topic hierarchy

24.7A: Substitution of CO Ligands

24.7B: Oxidative Addition

24.7C: Alkyl and Hydrogen Migrations

24.7D: \(\beta\)-Hydrogen Elimination

24.7E: \(\alpha\)-Hydrogen Abstraction

24.7F: Summary

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24.7A: Substitution of CO Ligands

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24.7B: Oxidative Addition

Learning Objectives

In this lecture you will learn the following

- The oxidative addition reactions.
- The reductive elimination reactions.
- Various mechanistic pathways prevalent for these reactions.

Oxidative addition (OA) is a process that adds two anionic ligands *e. g*. A and B, that originally are a part of a A-B molecule, like in H_2 or Me−I, on to a metal center and is of significant importance from the perspective of both synthesis and catalysis. The exact reverse of the same process, in which the two ligands, A and B, are eliminated from the metal center forming back the A−B molecule, is called the reductive elimination (RA). As A and B are anionic X type ligands, the oxidative addition is accompanied by an increase in the coordination number, valence electron count as well as in the formal oxidation state of the metal center by two units. The oxidative addition step may proceed by a variety of pathways. It requires the metal center to be both coordinatively unsaturated and electron deficient.



Oxidative addition transfers a single mononuclear metal center having 16 VE to a 18 VE species upon oxidative addition. Another frequently observed pathway is that a 18 VE complex looses a ligand to become a 16 VE species which then undergoes an oxidative addition. Apart from above two types, another possible pathway for oxidative addition proceeds as a binuclear oxidative addition in which each of the two metal centers undergo change in oxidation state, electron count and coordination number by one unit instead of two. This type of a binuclear oxidative addition is observed for a 17 VE metal complex or for a binuclear 18 VE metal complex having a metal−metal bond and, for which the metal has a stable oxidation state at a higher positive oxidation state by one unit.



It is interesting to note that in the oxidative addition the breakage of A−B σ−bond occurs as a result of a net transfer of electrons from the metal center to a σ*−orbital of the A−B bond, thus resulting in the formation of the two new M−A and M−B bonds. The oxidative addition is facilitated by electron rich metal centers having low oxidation state whereas the reductive elimination is facilitated by metal centers in higher oxidation state. Table 1. Common types of oxidative addition reactions.



Abbreviations: Lin. = linear, Tet. = tetrahedral, Oct. = octahedral, Sq. Pl. = square planar, TBP = trigonal bipyramidal, Sq. Pyr. = square pyramidal: 7-c, 8-c = 7- and 8-coordinate.

In principle, the oxidative addition is the reverse of reductive elimination, but in practice one may dominate over the other. Thus, the favorability of one over the other is depends on the position of equilibrium, which is further dependent on the stability of the two oxidation states of the metal and on the difference of bond strengths of A−B versus that of the M−A and M−B bonds. For example, metal hydride complexes frequently undergo reductive elimination to give alkanes but rarely an alkane undergoes oxidative addition to give an alkyl hydride complex. Along the same line, alkyl halides frequently undergo oxidative addition to a metal giving metal−alkyl halide complexes but these complexes rarely reductively eliminate to give back alkyl halides. Usually the oxidative addition is more common for 3rd row transition metals because they tend to possess stronger metal ligand bond strengths. The oxidative addition is also favored by strong donor ligands, as they stabilize the higher oxidation state of the metal. The

oxidative addition reaction can expand beyond transition metals as observed in the case of the Grignard reagents as well as for some main group elements.

Oxidative addition may proceed by several pathways as discussed below.

Concerted oxidative addition pathway

Oxidative addition may proceed by a concerted 3−centered associative mechanism involving the incoming ligand with the metal center. Specifically, the addition proceeds by the formation of a σ−complex upon binding of an incoming ligand say, H_2, followed by the cleavage of the H−H bond as a result of the back donation of electrons from the metal to the σ*−orbital of the H−H bond. Such type of addition is common for the H−H, C−H and Si−H bonds. As expected these proceed by two steps (*i*) the formation of a σ−complex and (*ii*) the oxidation step. For example, the oxidative addition of H_2 to Vaska's complex $(PMe_3)_2Ir(CO)Cl$ proceeds by this pathways.



S_N2 pathway

This pathway of oxidative addition is operational for the polarized AB type of ligand substrates like the alkyl, acyl, allyl and benzyl halides. In this mechanism, the L_nM fragment directly donates electrons to the σ*−orbital of the A−B bond by attacking the least electronegative atom, say A, of the AB molecule and concurrently initiating the elimination of the most electronegative atom of the AB molecule in its anionic form, B^-. These reactions proceed *via* a polar transition state that is accompanied by an inversion of the stereochemistry at the atom of attack by the metal center and are usually accelerated in polar solvents.



Radical pathway

This type of oxidative addition proceeds *via* a by radical pathway that generally are vulnerable to the presence of impurities. The radical processes can be of non−chain and chain types. In a non−chain type of mechanism, the metal (M) transfer one electron to the σ*−orbital of the RX bond resulting in the formation of a radical cation $M^{+\bullet}$ and a radical anion $RX^{-\bullet}$. The generation of the two radical fragments occurs by the way of the elimination of the anion X^- from the radical anion $RX^{-\bullet}$ leaving behind the radical $R^\bullet$ while the subsequent reaction of X^- anion with the radical cation $M^{+\bullet}$ generates the other radical $MX^\bullet$ in the course of the reaction. Such type of non−chain type of oxidative addition is observed for the addition of the alkyl halide to $Pt(PPh_3)_3$ complexes.



The other type in this category is the chain radical type reaction that is usually observed for the oxidative addition of EtBr and $PhCH_2Br$ to the $(PMe_3)_2Ir(CO)Cl$ complex. For this process a radical initiator is required and the reaction proceeds along a series of known steps common to a radical process.



Ionic pathway

This is kind of pathway for the oxidative addition reaction is common to the addition of hydrogen halides (HX) in its dissociated H^+ and X^- forms. The ionic pathways are usually of the following two types (*i*) the ones in which the starting metal complex adds to H^+ prior to the addition of the halide $X^-$and (*ii*) the other type, in which the halide anion X^- adds to the starting metal complex first, and then the addition of proton H^+ occurs on the metal complex.





Reductive Elimination

The reductive eliminations are reverse of the oxidative addition reactions and are accompanied by the reduction of the formal oxidation state of the metal and the coordination numbers by two units. The reductive eliminations are commonly observed for d^8 systems, like the Ni(II), Pd(II) and Au(III) ions and the d^6 systems, like the Pt(IV), Pd(IV), Ir(III) and Rh(III) ions. The reaction may proceed by the elimination of several groups. 

Binuclear Reductive Elimination

Similar to what has been observed in the case of binuclear oxidative addition, the binuclear reductive elimination is also observed in some instances. As expected, the oxidation state and the coordination number decrease by one unit in the binuclear reductive elimination pathway. alt

Problems

1. What kind of metal centers favor oxidative addition? Ans: Electron rich low valent metal centers. 2. Complete the sentence correctly.

(*a*) Reductive elimination is frequently observed in coordinatively saturated/unsaturated metal complexes.
(*b*) Reductive elimination is accompanied by increase/decrease in the oxidation state of the metal.
(*c*) Oxidative addition is accompanied by increase/decrease in the coordination number of the metal.

Ans:
(a) Saturated.
(b) Decrease in the oxidation state by two units.
(c) Increase in the coordination number by two units. 3. State the various mechanistic pathways involved in oxidative addition reactions. Ans: Concerted oxidative addition, S_N2 mechanism, radical and ionic mechanism. 4. Complete the reaction.

alt

Ans:



Self Assessment test

1. What kind of metal centers favor reductive elimination? Ans: Electron deficient high valent metal centers.

2. Complete the sentence correctly.

(*a*) Oxidative addition is frequently observed in coordinatively saturated/unsaturated metal complexes.
(*b*) Oxidative addition is accompanied by increase/decrease in the oxidation state of the metal.
(*c*) Reductive elimination is accompanied by increase/decrease in the coordination number of the metal.

Ans:
(a) Unsaturated.
(b) Increase in the oxidation state by two units.
(c) Decrease in the coordination numbers by two units. 3. How does the geometry of the square planar complexes change upon oxidative addition reactions? Ans: Square planar to octahedral. 4. Complete the reaction.



Ans:



Summary

The oxidative addition and the reductive elimination reactions are like the observe and reverse of the same coin. The oxidative addition is generally observed for metal centers with low oxidation state and is usually accompanied by the increase in the oxidation state, the valence electron count and the coordination number of the metal by two units. Being opposite, the reductive elimination is seen in the case of the metal centers with higher oxidation state and is accompanied by the decrease in the oxidation state, the valence electron count and the coordination number of the metal by two units. The oxidative addition may proceed by a variety of pathways that involve concerted, ionic and the radical based mechanisms. More interestingly, the oxidative addition and reductive elimination reactions are not solely restricted to the mononuclear metal complexes but can also be observed for the binuclear complexes.

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24.7C: Alkyl and Hydrogen Migrations

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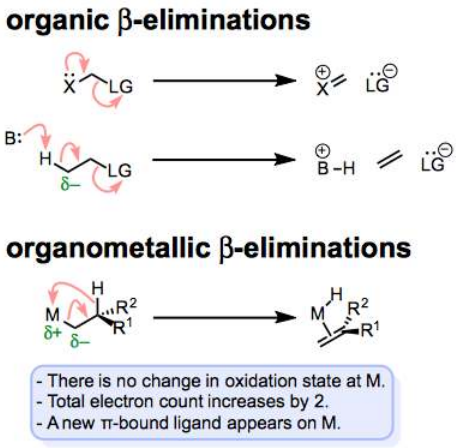
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24.7D: β -Hydrogen Elimination

In organic chemistry class, one learns that elimination reactions involve the cleavage of a σ bond and formation of a π bond. A nucleophilic pair of electrons (either from another bond or a lone pair) heads into a new π bond as a leaving group departs. This process is called β-elimination because the bond β to the nucleophilic pair of electrons breaks. Transition metal complexes can participate in their own version of β-elimination, and metal alkyl complexes famously do so. Almost by definition, metal alkyls contain a nucleophilic bond—the M–C bond! This bond can be so polarized toward carbon, in fact, that it can promote the elimination of some of the world's worst leaving groups, like –H and –CH3. Unlike the organic case, however, the leaving group is not lost completely in organometallic β-eliminations. As the metal donates electrons, it receives electrons from the departing leaving group. When the reaction is complete, the metal has picked up a new π-bound ligand and exchanged one X-type ligand for another.



Comparing organic and organometallic β-eliminations. A nucleophilic bond or lone pair promotes loss or migration of a leaving group.

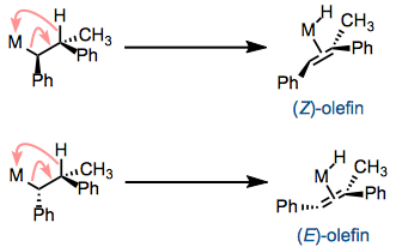
In this post, we'll flesh out the mechanism of β-elimination reactions by looking at the conditions required for their occurrence and their reactivity trends. Many of the trends associated with β-eliminations are the opposite of analogous trends in 1,2-insertion reactions. A future post will address other types of elimination reactions.

β-Hydride Elimination

The most famous and ubiquitous type of β-elimination is **β-hydride elimination**, which involves the formation of a π bond and an M–H bond. Metal alkyls that contain β-hydrogens experience rapid elimination of these hydrogens, provided a few other conditions are met.

The complex must have an open coordination site and an accessible, empty orbital on the metal center. The leaving group (–H) needs a place to land. Notice that after β-elimination, the metal has picked up one more ligand—it needs an empty spot for that ligand for elimination to occur. We can envision hydride "attacking" the empty orbital on the metal center as an important orbital interaction in this process.

The M–C_α and C_β–H bonds must have the ability to align in a syn coplanar arrangement. By "syn coplanar" we mean that all four atoms are in a plane and that the M–C_α and C_β–H bonds are on the same side of the C_α–C_β bond (a dihedral angle of 0°). You can see that conformation in the figure above. In the syn coplanar arrangement, the C–H bond departing from the ligand is optimally lined up with the empty orbital on the metal center. Hindered or cyclic complexes that cannot achieve this conformation do not undergo β-hydride elimination. The need for a syn coplanar conformation has important implications for eliminations that may establish diastereomeric olefins: β-elimination is stereospecific. One diastereomer leads to the (E)-olefin, and the other leads to the (Z)-olefin.



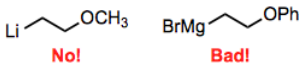
β-elimination is stereospecific. One diastereomer of reactant leads to the (Z)-olefin and the other to the (E)-olefin.

The complex must possess 16 or fewer total electrons. Examine the first figure one more time—notice that the total electron count of the complex increases by 2 during β-hydride elimination. Complexes with 18 total electrons don't undergo β-elimination because the product would end up with 20 total electrons. Of course, dissociation of a loose ligand can produce a 16-electron complex pretty easily, so watch out for ligand dissociation when considering the possibility of β-elimination in a complex. Ligand dissociation may be reversible, but β-Hydride elimination is almost always irreversible.

The metal must bear at least 2 d electrons. Now this seems a bit strange, as the metal has served as nothing but an empty bin for electrons in our discussion so far. Why would the metal center need electrons for β-hydride elimination to occur? The answer lies in an old friend: backbonding. The $\sigma_{C-H} \rightarrow M$ orbital interaction mentioned above is not enough to promote elimination on its own; an $M \rightarrow \sigma^*_{C-H}$ interaction is also required! I've said it before, and I'll say it again: backbonding is everywhere in organometallic chemistry. If you can understand and articulate it, you'll blow your instructor's mind.

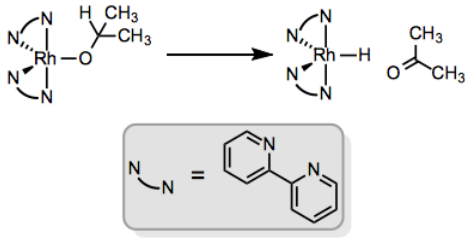
Other β-Elimination Reactions

The leaving group does not need to be hydrogen, of course, and a number of more electronegative groups come to mind as better candidates for leaving groups. β-Alkoxy and β-amino eliminations are usually thermodynamically favored thanks to the formation of strong M–O and M–N bonds, respectively. These reactions are so favored in β-alkoxyalkyl "complexes" of alkali and alkaline earth metals (R–Li, R–MgBr, etc.) that using these as σ-nucleophiles at carbon is untenable. Such compounds eliminate immediately upon their formation. I had an organic synthesis professor in undergrad who was obsessed with this—using a β-alkoxyalkyl lithium or β-alkoxyalkyl Grignard reagent in a synthesis was a recipe for red ink. β-Haloalkyls were naturally off limits too.



Watch out…these are not stable compounds!

The atom bound to the metal doesn't have to be carbon. β-Elimination of alkoxy ligands affords ketones or aldehydes bound at oxygen or through the C=O π bond (this step is important in many transfer hydrogenations, and an analogous process occurs in the Oppenauer oxidation). Amido ligands can undergo β-elimination to afford complexes of imines; however, this process tends to be slower than β-alkoxy elimination.



β-Elimination helps transfer the elements of dihydrogen from one organic compound to another.

Incidentally, I haven't seen any examples in which the β atom is not carbon, but would be interested if anyone knows of an example!

Applications of β-Eliminations

As with many concepts in organometallic chemistry, there are two ways to think about applications of β-elimination. One can take either the “inorganic” perspective, which focuses on the metal center, or the “organic” perspective, which focuses on the ligands.

With the metal center in focus, we can recognize that β-hydride elimination has the wonderful side effect of establishing an M–H bond—a feat generally difficult to achieve in a selective manner via oxidative addition of X–H. If the ligand from which the hydrogen came displaced something more electronegative, the whole process represents reduction at the metal center. For example, imagine rhodium(III) chloride is mixed with sodium isopropoxide, $NaOCH(CH_3)_2$. The isopropoxide easily displaces chloride, and subsequent β-hydride elimination affords a rhodium hydride, formally reduced with respect to the chloride starting material. See p. 236 of this review for more.

With the ligand in focus, we see that the organic ligand is oxidized in the course of β-hydride elimination. Notice that the metal is reduced and the ligand oxidized! A π bond replaces a σ bond in the ligand, and if the conditions are right, this represents a bona fide oxidation (as opposed to a mere elimination). For example, oxidative addition into a C–H bond followed by β-hydride elimination at a C–H bond next door sets up an alkene where two adjacent C–H bonds existed before, an oxidation process. These dehydrogenation reactions are incredibly appealing in a theoretical sense, but still at an early stage when it comes to scope and practicality.

Summary

We already encountered β-hydride elimination in an earlier series of posts on metal alkyl complexes, where we noted that it’s a very common decomposition pathway for metal alkyls. β-Hydride elimination isn’t all bad, however, as it can be an important step in catalytic reactions that result in the oxidation of organic substrates (dehydrogenations and transfer hydrogenations) and in reactions that reduce metal halides to metal hydrides. The general idea of β-elimination involves the transfer of a leaving group from a ligand to the metal center with simultaneous formation of a π bond in the ligand. β-Elimination requires an open coordination site and at least two d electrons on the metal center, and eliminations of chiral complexes are stereospecific. The leaving group is commonly hydrogen, but need not be—the more electronegative the leaving group, the more favorable the elimination. Stronger π bonds in the product also encourage β-elimination, so eliminations that form carbonyl compounds or imines are common.

In the next post, we’ll explore other types of organometallic elimination reactions, which establish π bonds at different positions in metal alkyl or other complexes. α-Eliminations, for example, establish metal-carbon, -oxygen, or -nitrogen multiple bonds, which are generally difficult to forge through other means

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24.7E: \(\alpha\)-Hydrogen Abstraction

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24.8: Metal Carbonyls - Selected Reactions

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24.9: Metal Carbonyl Hydrides and Halides

7.2: Metal Hydrides

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24.10: Alkyl, Aryl, Alkene, and Alkyne Complexes

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24.10A: σ -Bonded Alkyl and Aryl Ligands

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24.10B: Alkene Ligands

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24.10C: Alkyne Ligands

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24.11: Allyl and Buta-1,3-diene Complexes

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24.11A: Allyl and Related Ligands

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24.11B: Buta-1,3-diene and Related Ligands

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24.12: Carbene and Carbyne Complexes

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Learning Objectives

In this lecture you will learn the following

- The metal−ligand multiple bonding and their relevance in.
- The Fischer type carbene complexes.
- The Schrock type carbene complexes.

The organometallic compounds containing metal−ligand multiple bonds of the types, M=X and M≡X (X = C, N, O) are of current interest as they are valuable intermediates in many important catalytic cycles. In this regard, considerable attention has been paid towards developing an understanding of the metal−ligand multiply bonded systems like that of the metal carbene LnM=CR2 type complexes and of the metal carbyne LnM≡CR type complexes. A detailed account of the metal−carbene complexes is presented in this chapter.

Metal-carbene Complexes

Carbenes are highly reactive hexavalent species that exist in two spin states, i.e. (i) in a singlet form (), in which two electrons are paired up and (ii) in a triplet form (), in which the two electrons remain unpaired. Of the two, the singlet form is the more reactive one. The instability of carbene accounts for its unique reactivity like that of the insertion reaction, which has aroused significant interest in recent years. The singlet carbene and the triplet carbene bind differently to metals, with the singlet one yielding Fischer type carbene complexes while the triplet one yielding Schrock type carbene complexes (Figure 1).

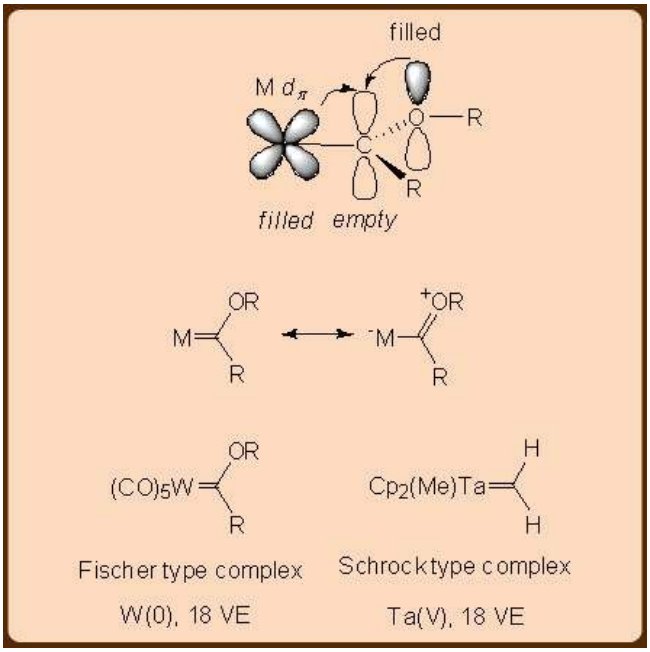


Figure 1. Metal−ligand multiple bonding in the Fischer and Schrock carbene system.

The LnM=CR2 type Fischer carbene complexes comprise of two dative covalent interactions that include (i) a LnM←CR2 type ligand to metal σ−donation and (ii) a LnM→CR2 type metal to ligand π−back donation. The Fischer type carbene complexes are usually formed with metal centers at a low oxidation state. These are also commonly observed for the more electron rich late−transition metals that participate in the LnM→CR2 type metal to ligand π−back donation. Another characteristic of the Fischer type carbene complex is the presence of the heteroatom substituents like R = OMe or NMe2 on the carbene CR2 moiety which makes the carbene carbon significantly cationic (δ+) to facilitate the LnM→CR2 type metal to ligand π−back donation.



Figure 2. Fischer and Schrock type complexes.

Similarly, the LnM=CR2 type Schrock carbene complexes comprise of two covalent interactions that involve one electron donation towards the σ−bond from each of the metal LnM and the carbene CR2 fragments. Schrock carbene complexes are thus formed with the metal centers having high oxidation state and are usually observed for electron deficient early−transition metals (Figure 2).

Carbene complexes can be prepared by the following methods.

i. by the reaction with electrophiles



ii. by H^-/H^+ abstraction reactions as shown below



iii. from low−valent metal complexes



Because of the electronically different metal−ligand interaction that exist between the LnM and the carbene CR2 moiety, the reactivity of Fischer and Schrock carbene complexes are completely different. For example, the Fischer type carbene complexes undergo attack by nucleophiles at its carbene−C center.



The Schrock type carbene complexes on the other hand undergo attack by electrophiles at its carbene−C center.

Summary

The metal−ligand multiple bonding is of significant interest as many of the compounds containing such bonds are important intermediates in various catalytic cycles. The metal−ligand doubly bonded carbene systems can exist in two varieties like the Fischer type and the Schrock type carbene complexes. Due to their different electronic structures, the reactivities of these Fischer type and the Schrock type carbene complexes differ significantly, with the former undergoing nucleophilic attack while the later undergo electrophilic attack at their respective carbene−C centers.

Metal-carbyne complexes

The metal−ligand multiply bonded systems even extended beyond the doubly bonded Fischer and the Schrock carbenes to the triply bonded $L_nM{\equiv}CR$ type Fischer carbyne and the Schrock carbyne complexes. Similar to carbene that exists in a singlet and a triplet spin state, the carbyne also exists in two other spin states *i.e* in a doublet and a quartet form.

Upon binding to the metal in its doublet spin state as in the Fischer carbene system, the carbyne moiety donates two electrons *via* its *sp* hybridized lone pair containing orbital to an empty metal *d* orbital to yield a $L_nM \leftarrow CR$ type ligand to metal dative bond. It also makes a covalent π−bond through one of its singly occupied p_z orbital with one of the metal *d* orbitals. The carbyne−metal interaction consist of two ligand to metal interactions namely a dative one and a covalent one that together makes the carbyne moiety a LX type of a ligand. In addition to these two types of ligand to metal bonding interactions, there remains an empty p_y orbital on the carbyne−C atom that can accommodate electron donation from a filled metal *d* orbital to give a metal to ligand π−back bonding interaction (Figure 1).



Figure 1. Metal−ligand multiple bonding in the Fischer and Schrock carbyne system.

Analogously, in the quartet carbyne spin state in the Schrock carbyne systems three covalent bonds occur between the singly occupied *sp*, $p_y$and p_z orbitals of carbyne−C moiety with the respective singly occupied metal *d* orbitals (Figure 1).

Similar to what has been observed earlier in the case of the Fischer carbenes and Schrock carbenes, the Fischer carbyne complexes are formed with metal centers in lower oxidation states for *e.g.* as in $Br(CO)_4W{\equiv}CMe$, while the Schrock carbyne complexes are formed with metals in higher oxidation state, *e.g.* as in $(t{-}BuO)_3W{\equiv}Ct{-}Bu$.

Carbyne complexes can be prepared by the following methods.

i. The Fischer carbyne complexes can be prepared by the electrophilic abstraction of a methoxy group from a methoxy methyl substituted Fischer carbene complex.



ii. Schrock carbynes can be prepared by the deprotonation of a α−CH bond of a metal−carbene complex.



iii. by an α−elimination reaction on a metal−carbene complex



iv. by metathesis reaction



The reactivities of Fischer and the Schrock carbynes mirror that of the Fischer and Schrock carbenes. For example, the Fischer carbyne undergo nucleophilic attack at the carbyne−C atom while the Schrock carbyne undergo electrophilic attack at the carbyne−C atom.

Summary

The theme of metal−ligand multiple bonding extends beyond the doubly bonded Fischer and the Schrock carbene systems to even triply bonded Fischer and the Schrock carbyne systems. The carbyne moieties in these Fischer and the Schrock carbyne systems respectively exist in a doublet and a quartet spin state. The carbyne complexes are generally prepared from the respective carbene analogues by the abstraction of alkoxy (OR), proton (H^+), hydride (H^-) moieties, the α−elimination reactions and the metathesis reactions. The reactivity of the Fischer and the Schrock carbyne complexes parallel the corresponding Fischer and the Schrock carbene counterparts with regard to their reactivities toward electrophiles and nucleophiles.

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24.13: Complexes Containing η 5 -cyclopentadienyl Ligands

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24.13A: Ferrocene and other Metallocenes

Learning Objectives

In this lecture you will learn the following

- The cyclopentadienyl ligands.
- The synthesis and reactivity of metal−cyclopentadienyl complexes.
- The metal−cyclopentadienyl interaction.

Cyclopentadienyl moiety acts as an important “spectator” ligand and is quite ubiquitous in organometallic chemistry. It remains inert to most nucleophiles and electrophiles and solely engages in stabilizing organometallic complexes. The cyclopentadienyl ligands form a wide array of organometallic compounds exhibiting different formulations that begin with the so-called “piano stool” $CpML_n$ (n = 2,3 or 4) type ones and extends to the most commonly observed “metallocene” Cp_2M type ones to even go beyond further to the “bent metallocene” Cp_2MX_n (n = 1,2 or 3) type ones. In the “piano stool” $CpML_n$ structure, the cyclopentadienyl (Cp) ligand is regarded as the “seat” of the piano stool while the remaining L ligands are referred to as the “legs” of the piano stool. Though the cyclopentadienyl ligand often binds to metal in a η^5 (pentahapto) fashion, *e. g.* as in ferrocene, the other form of binding to metal at lower hapticities, like that of the η^3 (trihapto) binding *e. g.* as in $(\eta^5\text{−Cp})(\eta^3\text{−Cp})W(CO)_2$ and that of the η^1 (monohapto) binding *e. g.* as in $(\eta^5\text{−Cp})(\eta^1\text{−Cp})Fe(CO)_2$, are also seen on certain rare occasions.

The binding modes of the cyclopentadienyl ligand in metal complexes can be ascertained to a certain degree by ^1H NMR in the diamagnetic metal complexes, in which the Cp−protons appear as a singlet between 5.5−3.5 ppm while the β and γ hydrogens come at 7−5 ppm.

Cyclopentadienyl−metal interaction

The frontier molecular orbital of the cyclopentadienyl ligand contains 5 orbitals (Ψ_1−Ψ_5) residing in three energy levels (Figure 1). The lowest energy orbital Ψ_1 does not contain any node and is represented by an a_1 state, followed by a doubly degenerate e_1 states that comprise of the Ψ_2 and $\Psi_3$orbitals, which precede another doubly degenerate e_2 states consisting of Ψ_4 and Ψ_5 orbitals.



Figure 1.Molecular orbital diagram of cyclopentadienyl ligand.

The above frontier molecular orbital diagram becomes more intriguing on moving over to the metallocenes that contain two such cyclopentadienyl ligands. Specifically, in the Cp_2M system, (*e. g.* ferrocene) each of these above five molecular orbital of the two cyclopentadienyl ligands combines to give ten ligand molecular orbitals in three energy levels (Figure 2). Of these, the orbitals that subsequently interact with the metal orbitals to generate the overall molecular orbital correlation diagram for the Cp_2M type of complexes are shown below (Figure 3).



Figure 2. Metal−cyclopentadienyl Bonding interactions.



Figure 3. MO diagram of ferrocene.

Generic metallocene Cp_2M type complexes are formed for many from across the 1st row transition metal series along Sc to Zn. The number of unpaired electrons thus correlates with the number unpaired electrons present in the valence orbital of the metal (Figure 4). Of the complexes of the 1st row transition metal series, the manganocene exists in two distinct forms, one in a high-spin form with five unpaired electrons, *e.g.* as in Cp_2Mn and the other in a low-spin form with one unpaired electron, *e.g.* as in Cp^*_2Mn owing to the higher ligand field strength of the Cp* ligand. Cobaltocene, Cp_2Co, has 19 valence electrons (VE) and thus gets easily oxidized to the diamagnetic 18 VE valence electron species, Cp_2Co^+. Of these metallocenes, the much-renowned ferrocene, Cp_2Fe is a diamagnetic 18 VE complex, whose molecular orbital diagram is shown above (Figure 3).



Bent metallocenes

Bent metallocenes are Cp_2MX_n type complexes formed of group 4 and the heavier elements of groups 5−7. In these complexes the frontier doubly degenerate e_2g orbitals of Cp_2M fragment interacts with the filled lone pair orbitals of the ligand (Figure 5).



Figure 5. Bent metallocene.

Synthesis of cyclopentadienyl-metal complexes

The metal−cyclopentadienyl complexes are synthesized by the following methods.

i. from Cp−



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ii. from Cp+



iii. from hydrocarbon



Reactivity of cyclopentadienyl-metal complexes

The reactivity of cyclopentadienyl−metal complexes of the type Cp_2M is shown for a representative nickellocene complex.

i. reaction with NO



ii. reaction with PR_3



iii. reaction with CO



iv. reaction with H^+



Summary

Cyclopentadienyl moiety is almost synonymous with the transition metal organometallic complexes as the ligand played a pivotal role at the early developmental stages of the field of organometallic chemistry in the 1960s and 1970s. An important quality of the cyclopentadienyl ligand is that it behaves as an extremely good “spectator” ligand being inert to nucleophiles and electrophiles and displays uncanny ability towards stabilizing metal complexes of elements from across the different parts of the periodic table. Cyclopentadienyl moiety thus forms several types of complexes of different formulations like that of the “piano stool” $CpML_n$ (n =

2,3 or 4) types, the metallocene Cp_2M types and the bent metallocene Cp_2MX_n (n = 1,2 or 3) types. Cyclopentadienyl metal complexes make valuable catalysts for many chemical transformations of interest to academia and industries alike. The cyclopentadienyl moiety participates in a complex interaction with the metal involving ligand frontier molecular orbitals and the metal valence orbitals. Cyclopentadienyl metal complexes can be accessed by many methods.

Problems

1. Comment on the p−acceptor property of the cyclopentadienyl ligand. Ans: The ligand being anionic shows very little π-acceptor properties. 2. Give the total valence electron count at the metal in a nickellocene complex. Ans: 20 electrons. 3. Explain why the metal center in cobalticene gets easily oxidized. Ans: 19 electrons cobalticene gets easily oxidized to 18 electron Cp_2Co^+. 4. Specify the number unpaired electrons present in chromocene. Ans: 2

Self Assessment test

1. Specify the number of unpaired electron present in vanadocene. Ans: The ligand being anionic shows very little π-acceptor properties. 2. What different hapticities are exhibited by cyclopentadienyl ligand? Ans: 1, 3, and 5. 3. Specify the hapticities of the cyclopentadienyl ligands in $Cp_2W(CO)_2$. Ans: 5 and 3. 4. Specify the hapticity of the cyclopentadienyl ligands in $CpRh(CO)_2(PMe_3)$. Ans: 3.

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24.13B: (η 5 − C p) 2 F e 2 (C O) 4 and Derivatives

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24.14: Complexes Containing η 6 - and η 7 -ligands

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24.14A: η 6 -Arene Ligands

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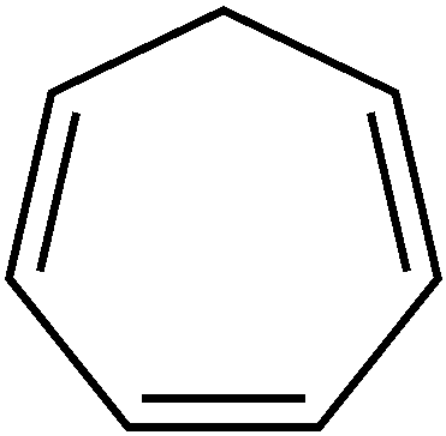
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24.14B: Cycloheptatriene and Derived Ligands



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24.15: Complexes Containing the η 4 -cyclobutadiene Ligand

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SECTION OVERVIEW

24.16: Transition Metal Complexes

Topic hierarchy

24.16.1: Organolead Chemistry

24.16.2: Organomercury Chemistry

24.16.3: Organozinc Chemistry

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24.16.1: Organolead Chemistry

Tetraethyllead

Like mercury, lead is primarily obtained from its sulfide ore, in this case Galena, PbS, yet once again there are quite a number of other minerals containing lead. In terms of natural abundance it exists at about 14 ppm in the Earth's crust (37th compared to O), however it has become well known due to its ease of extraction and the number of uses with technical importance.



galena, PbS

Lead was probably discovered around 6500 BC in Turkey and by 300 BC the Romans had lead smelters in operation. The toxicity of lead was recorded by the Greeks as early as 100BC. A report from 2BC noted that:

> *"the drinking of lead causes oppression to the stomach, belly and intestines with wringing pains; it suppresses the urine, while the body swells and acquires and unsightly leaden hue".*

The possible hazards associated with the use of lead piping in water systems was recognized as long ago as the first century BC and it has even been suggested that the "decline of the Roman Empire" might have been ascribed to the use of lead acetate as an additive to sweeten wine. It is somewhat surprising therefore that the first legislation controlling the industrial hazards of lead industries was not introduced until 1864.

Note that Dr. Wilton Turner (born in Clarendon, Jamaica in the early 1800's) wrote on the inappropriate use of lead in sugar and rum production while running a rum distillery in Guyana. One advocate said he had fed lead to dogs and guinea pigs *for several weeks* and seen no adverse affects in fact the guinea pigs were stolen which he thought was because they looked so fat and healthy!

An examination (in the early 1970's) of the annual snow strata in Northern Greenland and Poland revealed most elegantly that levels in air-borne lead had increased significantly since the Industrial Revolution and very sharply since 1940. Considering that 40-50% can be absorbed by inhalation compared to only 5-10% through ingestion this was cause for concern.

Lead content in North Greenland snow layers (µg per kg)

Leaded gasoline was an economic success from 1926 until 1976, and in fact, its discovery by Thomas Midgley at Charles Kettering's General Motors laboratory was among the most celebrated achievements of automotive engineering. It was often portrayed as the result of genius, luck and a great deal of hard work. It is now considered to be a catastrophic failure and is banned for environmental and public health reasons. {There are still a few countries selling petrol with lead additives.} Even more surprising is that the use of ethanol in fuel was already well established by the time tetraethyllead was introduced as an additive.

Tetraethyllead was supplied for mixing with raw gasoline in the form of "ethyl fluid", which was Et_4Pb blended together with the lead scavengers 1,2-dibromoethane and 1,2-dichloroethane. "Ethyl fluid" also contained a reddish dye to distinguish treated from untreated gasoline and discourage the use of leaded gasoline for other purposes such as cleaning.

Ethyl fluid was added to gasoline in the ratio of 1:1260, usually at the refinery. The purpose was to increase the fuel's octane rating. A high enough octane rating is required to prevent premature detonations known as engine knocking ("knock" or "ping"). Antiknock agents allow the use of higher compression ratios for greater efficiency and peak power. The formulation of "ethyl fluid" was:

- Tetraethyllead 61.45%
- 1,2-Dibromoethane 17.85%
- 1,2-Dichloroethane 18.80%
- Inert materials and dye 1.90%

Effect on Health

Humans have been mining and using this heavy metal for thousands of years, poisoning themselves in the process. Although lead poisoning is one of the oldest known work and environmental hazards, the modern understanding of the small amount of lead

necessary to cause harm did not come about until the latter half of the 20th century. No safe threshold for lead exposure has been discovered, that is, there is no known amount of lead that is too small to cause the body harm.

Lead pollution from engine exhaust is dispersed into the air and into the vicinity of roads and easily inhaled. Lead is a toxic metal that accumulates and has subtle and insidious neurotoxic effects especially at low exposure levels, such as low IQ and antisocial behavior. It has particularly harmful effects on children. These concerns eventually led to the ban on Et_4PB in automobile gasoline in many countries. For the entire U.S. population, during and after the Et_4PB phaseout, the mean blood lead level dropped from 13 µg/dL in 1976 to only 3 µg/dL in 1991. The U.S. Centers for Disease Control considered blood lead levels "elevated" when they were above 10 µg/dL. Lead exposure affects the intelligence quotient (IQ) such that a blood lead level of 30 µg/dL is associated with a 6.9-point reduction of IQ, with most reduction (3.9 points) occurring below 10 µg/dL.

Also in the U.S., a statistically significant correlation has been found between the use of Et_4PB and violent crime: taking into account a 22-year time lag, the violent crime curve virtually tracks the lead exposure curve. After the ban on Et_4PB, blood lead levels in U.S. children dramatically decreased.

Even though leaded gasoline is largely gone in North America, it has left high concentrations of lead in the soil adjacent to all roads that were constructed prior to its phaseout. Children are particularly at risk if they consume this, as in cases of pica.

Note as well the work done in 1995 by ICENS on the problem of the old disused lead mine and tailings that affected school children in Kintyre. Over 40 cases were detected with unacceptable levels. ICENS at that time cleaned the community and sought to educate residents about the dangers. A continuation of the research done in Kintyre was to test 628 children at 17 basic schools across the island. Children at a number of basic schools in Kingston and St Catherine were discovered with blood lead levels as low as 45 µg/dL and as high as 60. In two of the cases, children had lead levels of 130 and 202. At this level, they would likely die from the poisoning if untreated.

Properties of Et4Pb

Molecular formula	$C_8H_{20}Pb$
Molar mass	323.44 g mol^{-1}
Appearance	Colourless, viscous liquid
Density	1.653 g/mL (20 °C)
Melting point	-136 °C
Boiling point	84-85 °C/15 mm Hg
Solubility in water	Insoluble

Laboratory Preparation:
The industrial preparation of tetraethyllead was from the reaction below:
~373K in an autoclave

$$4\,NaPb + 4\,EtCl \longrightarrow Et_4Pb + 3\,Pb + 4\,NaCl \qquad (24.16.1.1)$$

alloy or by electrolysis of $NaAlEt_4$ or EtMgCl using a Pb anode. Laboratory syntheses of R_4Pb compounds in general include the use of Grignard reagents or organolithium compounds.

$$2\,PbCl_2 + 4\,RLi \longrightarrow R_4Pb + 4\,LiCl + Pb \qquad (24.16.1.2)$$

in ether

tetraethyllead

lead timeline
Tetraethyllead
"ethyl" articles

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24.16.2: Organomercury Chemistry

Learning Objectives

In this lecture you will learn the following

- Dialkymercury preparation.
- Mercury toxicity.
- Mercury poisoning.

Organometallic compounds of mercury:

$$2RMgX + HgX_2 \longrightarrow HgR_2 + MgX_2 \qquad (24.16.2.1)$$

Reaction proceeds due to both electronegativity and hardness considerations.

Dialkylmercury compounds are very versatile starting materials for the synthesis of many organometallic compounds of more elctropositive metals by transmetallation. However, owing to high toxicity of alkylmercury compounds, other synthons are preferred. In striking contrast to the high sensitivity of dimethylzinc to oxygen, dimethylmercury survives exposure to air.

Mercury Toxicity

The toxicity of mercury arises from the very high affinity of the soft Hg atom for sulfhydryl (—SH) groups in enzymes. Simple mercury-sulfur compounds have been studied as potential analogs of natural systems. The Hg atoms are most commonly four-coordinated, as in $[Hg_2(SMe)_6]^{2-}$.

Mercury poisoning was a serious concern even from early days. Issac Newton, Alfred Stock worked in the early 20th century. Later in 60s awareness came following the incidence of brain damage and death it caused among the inhabitants in Minamata, Japan. Mercury from a plastic company was allowed to escape into a bay where it found its way into fish that were later eaten. Research has shown that bacteria found in sediments are capable of methylating mercury, and that species such $HgMe_2$ and $[HgCH_3]^+$ enter the food chain because they readily penetrate cell walls. The bacteria appear to produce $HgMe_2$ as a means of eliminating toxic mercury ions through their cell walls and into the environment.

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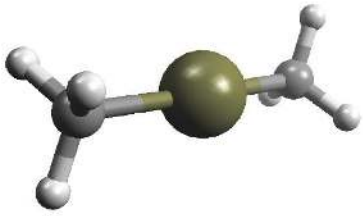
Methylmercury

The usual method of ingestion of a metal into the body is:
a) Orally - the Gastrointestinal Tract
b) via the lungs - the Respiratory Tract

a) Orally - (mouth, stomach, small intestine): Food digestion begins in the mouth where saliva containing the enzyme amylase beaks down starch to lower sugars. Most digestion occurs in the stomach in the presence of HCl (pH ~1.6 ie. 0.17M HCl). In the case of mercury it is quite readily absorbed through the stomach since reaction of mercury salts with HCl produces $HgCl_2$. This neutral covalent molecule (solubility in H_2O 0.5 g/100 mL but 8g/100 mL in ethanol) is absorbed far better than most inorganic ions and this no doubt contributes to its high toxicity.

b) Respiratory tract (nose, lungs): This is usually unimportant for most metals but in some cases it can be more efficient that via the

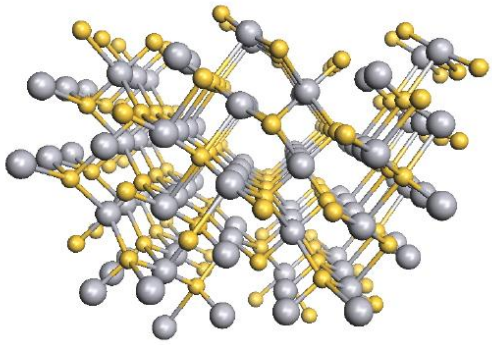
gastrointestinal tract. For example, lead where 50% of Pb in air can be absorbed but only 5-10% via the gastrointestinal tract. Volatile dimethyl mercury is another case for concern.



dimethylmercury

The Mercury Cycle

Mercury is 62nd in terms of natural abundance and is found everywhere, usually as the mineral cinnabar, HgS, although 30 minerals containing Hg are known. The oxidation states are Hg(0), Hg(I) and Hg(II), where Hg(I) has been shown to exist as Hg_2^{2+}.



HgS - cinnabar

The three Hg species are related by the disproportionation:

$Hg_2^{2+} \rightarrow Hg^0 + Hg^{2+}$ $E° = -0.131$ V or $K = 6 \times 10^{-3}$

In addition:

Hg_2^{2+}/Hg $E° = 0.789$ V
Hg^{2+}/Hg $E° = 0.854$ V

This means that to oxidise Hg to Hg_2^{2+} an oxidising agent with potential > 0.789V is required, but very importantly < 0.854 V, otherwise oxidation to Hg^{2+} will occur. There are no common oxidants that fit this arrangement so if any reaction occurs the product will be Hg^{2+}. The equilibrium constant of 6×10^{-3} shows that when Hg(I) is formed it is moderately stable, however any agent that reduces the Hg(II) concentration automatically drives the reaction from Left → Right. Given that many Hg(II) derivatives are insoluble then this clearly restricts the range of Hg(I) compounds.

Minamata Disease

There have been several serious outbreaks of mercury poisoning. The most famous was between 1953 and 1965 at Minamata Bay in Japan when 46 people died and 120 suffered severe symptoms. As of March 2001, 2,265 victims had been officially recognised (1,784 of whom had died) and over 10,000 had received financial compensation from Chisso. By 2004, Chisso Corporation had paid $86 million in compensation, and in the same year was ordered to clean up its contamination. On March 29th, 2010, a settlement was reached to compensate as-yet uncertified victims.

The disease was first noticed in cats (who were seen throwing themselves into the sea) and was quickly traced to mercury poisoning acquired as a result of eating contaminated fish (5-10 ppm Hg). The investigations that followed showed that the fish had

acquired the high mercury due to the dumping of inorganic mercury salts and methylmercury from the Chisso Co. plastics factory upstream.

Analysis of fish exhibits from museums, some over 90 years old, has shown that mercury levels for ocean fish are similar but that river fish levels have risen as a result of man-made contamination. The forms of mercury occuring in the environment are Hg^{2+} and methylmercury, either $MeHg^{+}$ or Me_2Hg. Interconversion can be affected by microorganisms.

Aerobes can solubilize Hg^{2+} from cinnabar (K_{sp} ~10^{-53}) which in sediments was considered safe since the solubility product was so small. The conversion of $S^{2-} \rightarrow SO_3^{2-} \rightarrow SO_4^{2-}$ allows the insoluble sulfide to breakdown and in the process other Hg(II) salts are formed or the mercury may get reduced to Hg(0) enzymatically.

$$Hg^{2+} + NADH + H^{+} \longrightarrow Hg^{0} + NAD^{+} + 2\,H^{+} \tag{24.16.2.2}$$

where NADH = reduced form of nicotinamideadeninedinucleotide. This conversion can be considered as a detoxification process since Hg^0 is more easily eliminated.

In the environment, sulfate-reducing bacteria take up mercury in its inorganic form and through metabolic processes convert it to methylmercury. Sulfate-reducing bacteria are found in anaerobic conditions, typical of the well-buried muddy sediments of rivers, lakes, and oceans where methylmercury concentrations tend to be highest. Sulfate-reducing bacteria use sulfur rather than oxygen as their cellular energy-driving system. One hypothesis is that the uptake of inorganic mercury by sulfate-reducing bacteria occurs via passive diffusion of the dissolved complex HgS. Once the bacterium has taken up this complex, it utilizes detoxification enzymes to strip the sulfur group from the complex and replaces it with a methyl group:

$$HgS \longrightarrow CH_3Hg(II)X + H_2S \tag{24.16.2.3}$$

Upon methylation, the sulfate-reducing bacteria transport the new mercury complex back to the aquatic environment, where it is taken up by other microorganisms. Bacteria eliminate Hg by methylating it first to $MeHg^{+}$ and Me_2Hg. The detoxification process for them is the reverse for us unfortunately! The conversion probably involves vitamin B12 a methyl-cobalt organometallic compound so this is another example of synthesis involving transmetallation.

The major source of methylmercury exposure in humans is consumption of fish, marine mammals, and crustaceans. Once inside the human body, roughly 95% of the fish-derived methylmercury is absorbed from the gastrointestinal tract and distributed throughout the body. Uptake and accumulation of methylmercury is rapid due to the formation of methylmercury-cysteine complexes. Methylmercury is believed to cause toxicity by binding the sulfhydryl groups at the active centers of critical enzymes and structural proteins. Binding of methylmercury to these moieties constitutively alters the structure of the protein, inactivating or significantly lowering its functional capabilities.

Once the Me_2Hg is formed it is volatile and when released into the atmosphere it is readily photolysed by UV light

$$Me_2Hg \longrightarrow Hg^{0} + 2\,CH_3^{\cdot} \longrightarrow CH_4 \;\; \text{text or} \;\; C_2H_6 \tag{24.16.2.4}$$

Other microorganisms can convert $MeHg^{+}$ to Hg^0 + CH_4 that is make the mercury considerably less toxic to humans.

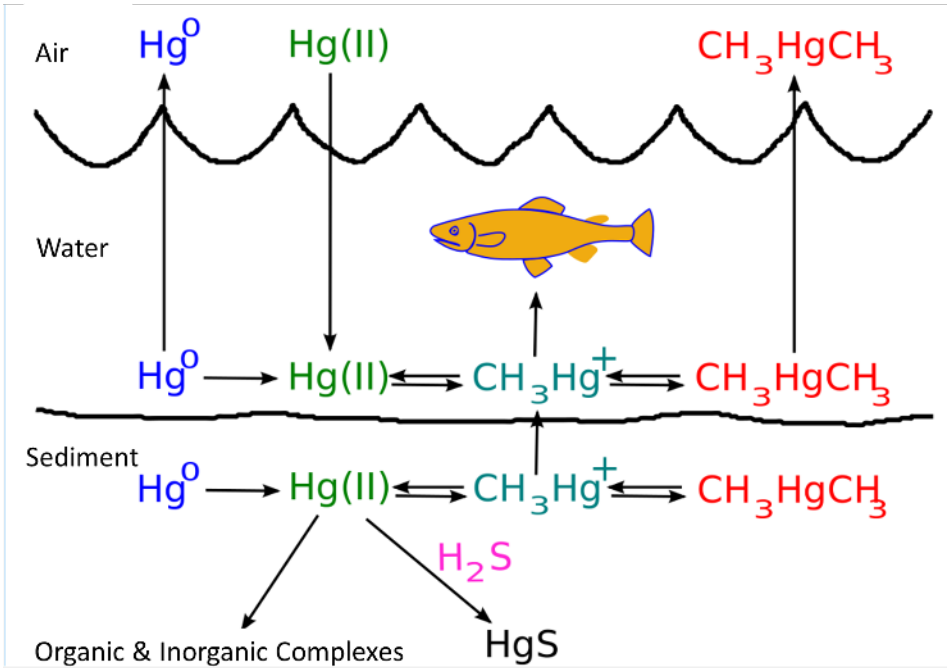


Figure 24.16.2.1: Chemistry of the mercury cycle. (GNU FDL; after Xhmikos Wkimedia Commons)

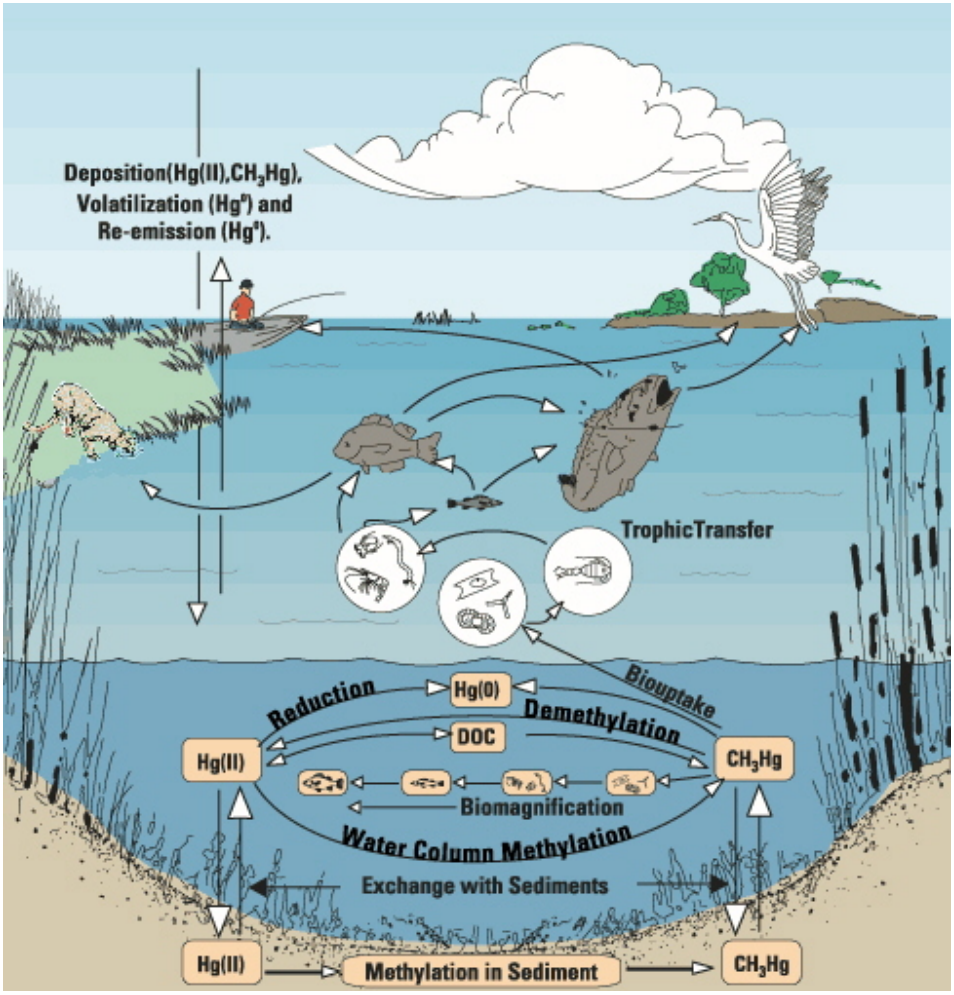


Figure 24.16.2.2: The mercury cycle showing biogeochemical interactions. (Copyright; author via source)

Summary

Organic mercury tends to increase up the food chain, particularly in lakes. The mud at the bottom of a lake may have 100 or 1000 times the amount of mercury than is in the water. Bacteria, worms and insects in the mud extract and concentrate the organic mercury. Small fish that eat them further concentrate the mercury in their bodies. This concentration process, known as "bioaccumulation", continues as larger fish eat smaller fish until the top predator fish in the lake may have methylmercury levels in their tissues that are up to 1,000,000 times the level in the water in which they live. We then eat the fish....

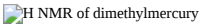
> *To consume a human being would be extremely unhealthy for any animal. Humans carry the highest concentration of toxic chemicals of all creatures on the planet. Their livers, hearts, kidneys and brains are so heavily contaminated with hundreds of different synthetic chemicals that if humans were slaughtered as a meat source, they'd never pass USDA food safety standards.*

Table 24.16.2.1: Properties of Me_2Hg

Molecular formula	C_2H_6Hg
Molar mass	230.66 g mol^{-1}
Appearance	Colourless liquid
Density	2.96 g/mL
Melting point	-43 °C
Boiling point	87-97 °C
Solubility in water	Insoluble

Laboratory Preparation:

$Hg + 2\ Na + 2\ CH_3I \rightarrow (CH_3)_2Hg + 2\ NaI$



^1H NMR of dimethylmercury showing ^{199}Hg coupling (J ~100.9 Hz)

^{199}Hg has a nuclear spin of ½ and natural abundance of 16.87%. Can you explain the observed splitting pattern?

Methylmercury
Dimethylmercury
Prof Wetterhahn -mercury

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24.16.3: Organozinc Chemistry

Learning Objectives

In this lecture you will learn the following

- Organometallic compounds of zinc and cadmium.
- Structural features of organozinc compounds.

Organometallic compounds of zinc and cadmium

Dialkyl compounds of Zn, Cd and Hg do not associate through alkyl bridges. Dialkylzinc compounds are only weak Lewis acids, organocadmium compounds are even weaker, and organomercury compounds do not act as Lewis acids except under special circumstances.

The Group 12 metals form linear molecular compounds, such as $ZnMe_2$, $CdMe_2$ and $HgMe_2$, that are not associated in solid, liquid or gaseous state or in hydrocarbon solution.

They form 2c, 2e bonds. Unlike Be and Mg analogs, they do not complete their valence shells by association through alkyl bridges. The bonding in these molecules are similar to d^{10} metals such as Cu^I, Ag^I and Au^I with linear geometry ($[N{\equiv}C\text{-}M\text{-}C{\equiv}N]^-$, M = Ag or Au). This tendency is sometimes rationalized by invoking *pd* hybridization in the M^+ ion, which leads to orbitals that favor linear attachment of ligands (similar to *spd* hybridization).



The preference for the linear coordination may be due to the similarity in energy of the outer ns, n*p* and (n-1)*d* orbitals, which permits the formation of collinear *spd* hybrids.

The hybridization of *s*, p_z and d_z2 with the choice of phases shown here produces a pair of collinear orbitals that can be used to form strong σ-bonds.

Organozinc and organocadmium compounds

Convenient route is metathesis with alkylaluminium or alkyllithium compounds.
With alkyllithium compounds it is the electronegativity which is decisive, whereas between Al and Zn it is hardness considerations correctly predict the formation of softer $ZnCH_3$ and harder AlCl pairs.



Alkylzinc compounds are pyrophoric and readily hydrolyzed, whereas alkylcadmium compounds react more slowly with air. Due to mild Lewis acidity, dialkylzinc and dialkylcadimum compounds form stable complexes with amines, especially with chelating amines.
The Zn—C has greater carbanionic character than the Cd—C bond.

For example, addition of alkylzinc compounds across the carbonyl group of a ketone:



This reaction do not proceed with the less polar alkylcadmium or alkylmercury compounds, but organolithium, organomagnesium and organoaluminium compounds can promote this reaction readily since all of which contain metals with lower electronegativity

than zinc.

Interestingly, the cyclodipentadienyl compounds are structurally unusual. CpZnMe is monomeric in the gas phase with a pentahapto Cp group.

In the solid state it is associated in a zig-zag chain, each Cp group being pentahapto with respect to two Zn atoms. 

Problems:

1. Do you think that the following reaction proceeds? If so, why and how?



Solution:

Al_2Me_6 being an electron deficient molecule readily exchanges two methyl groups with zinc for two chloride ions. Since chloride ions have sufficient electron in their valence shell act as four electron donor through bridging coordination mode. $Al_2Cl_2Me_4$ is no longer an electron deficient molecule.

Diethyzinc is the cheapest available organozinc compound and accounts for 60% of all references to diorganozinc reagents. The remainder coming from dimethyl (21%), dibutyl (4%), diisopropyl (4%), diphenyl (5%) and others (6%).

The different methods for preparing diorganozinc compounds can be grouped into four general approaches:

(a) the oxidative addition between zinc metal and an alkyl halide followed by Schlenk equilibration,

$$2\,\mathrm{RX} + 2\,\mathrm{Zn} \longrightarrow \mathrm{R_2Zn} + \mathrm{ZnX_2} \tag{24.16.3.1}$$

(b) the transmetallation of a zinc halide with an organometallic reagent,

$$2\,\mathrm{RM} + 2\,\mathrm{ZnX_2} \longrightarrow \mathrm{R_2Zn} + 2\,\mathrm{MX} \tag{24.16.3.2}$$

(c) the transmetallation of a diorganozinc starting material with an organometallic reagent, and

$$2\,\mathrm{RM} + \mathrm{R'_2Zn} \longrightarrow \mathrm{R_2Zn} + 2\,\mathrm{R'M} \tag{24.16.3.3}$$

(d) the zinc-halogen exchange between an alkyl halide and a diorganozinc

$$2\,\mathrm{RX} + \mathrm{R'_2Zn} \longrightarrow \mathrm{R_2Zn} + 2\,\mathrm{R'X} \tag{24.16.3.4}$$

Frankland prepared Et_2Zn from EtI and Zn metal via EtZnI by distilling the more volatile Et_2Zn which shifted the Schlenk equilibrium towards further product. No reaction occurred until 150 °C, but at 200 °C the Zn/EtI reaction proceeded with "tolerable rapidity", giving white crystals and leaving a colourless, mobile liquid. The sealed tube containing this reaction mixture remained sealed for some months because the only eudiometer required for the combustion of the product gases for their analysis was destroyed. In October 1848, Frankland returned to the University of Marburg to the laboratory of Robert Bunsen in order to obtain his Ph.D. under Bunsen's guidance. He took along with him the sealed tube from his EtI/Zn experiment at Queenwood College, Hampshire, England. He prepared the methyl derivative at about the same time and the apparatus shown in the paper reporting their preparation shows just how imaginative Frankland had become to cope with the air and moisture sensitivity of the products.

Apparatus for the preparation of diorganozinc compounds. Section A was where MeI was heated, B is the receiver containing the sample tubes d and e, C was a $CaCl_2$ drying tube to prevent moisture and D was for generation of gaseous H_2 to flush out and rid the system of air.

Frankland described these procedures in such detail to illustrate the painstaking, time-consuming care required in those days when working with extremely air and moisture-sensitive liquids. In 1877 Frankland noted in a 1000 page English translation of his

papers that when

> *"I cut off the upper part of the tube in order to try the action of water upon the solid residue. On pouring a few drops of water upon the residue, a green-blue flame, several feet long, shot out of the tube, causing great excitement among those present. Professor Bunsen, who had suffered from arsenical poisoning during his research on cacodyl, suggested that the spontaneously inflammable body, which diffused an abominable odour through the laboratory, was that terrible compound, which might have been formed by arsenic present as an impurity in the zinc used in the reaction, and that I might be already irrecoverably poisoned. These forebodings were, however, quelled in a few minutes by an examination of the black stain [which was zinc] left upon porcelain by the flame; nevertheless, I did afterward experience some symptoms of zinc poisoning."*

Dimethyl- and diethylzinc were the first available sources of nucleophilic alkyl groups, useful for the alkylation of inorganic and organometallic halides and of organic C=O and C=N-containing electrophiles. Early examples of the alkylation of metal-halogen functions were described by Frankland and others, and the dialkylzincs have been useful in this application ever since. Since they are less reactive than the comparable Grignard and organolithium reagents, they are particularly useful in the partial alkylation of element polyhalides, e.g., $\mathrm{PCl_3} \longrightarrow \mathrm{RPCl_2}$.

The first use of a dialkylzinc in organic synthesis appears to have been reported by Freund of the University of Lemberg in 1861. In his search for a synthesis of ketones, he added acetyl chloride to diethylzinc. He had a difficult time obtaining a pure product but finally identified it as $CH_3C(O)Et$.

$$2\,\mathrm{CH_3C(O)Cl} + \mathrm{Et_2Zn} \longrightarrow 2\,\mathrm{CH_3C(O)Et} + \mathrm{ZnCl_2} \qquad (24.16.3.5)$$

In 1867 Butlerow, in Russia, prepared tertbutyl alcohol by reaction of 2 equiv of dimethylzinc with acetyl chloride on a large scale, using 250 g of dimethylzinc. In this paper, Butlerow disputes Frankland's report of the toxic effects of dimethylzinc, saying that he and co-workers had worked with this compound for 5 years without taking any special precautions and never had a problem. He noted that smoking in the presence of dimethylzinc vapors (or, more correctly, vapors of the oxidation and hydrolysis products of dimethylzinc) changes the taste of the tobacco; it becomes unpleasantly sweetish!!

Following the discovery of the usefulness of Grignards in organic synthesis there was a decrease in the studies on Zn compounds until about 1984 when it was noted that enantioselective reactions could be performed using diorganoZn compounds.

Addition reaction of organozinc compounds to carbonyl compounds

The Barbier reaction (1899) is an organic reaction between an alkyl halide and a carbonyl group as an electrophilic substrate in the presence of magnesium, aluminium, zinc, indium, tin or its salts. The reaction product is a primary, secondary or tertiary alcohol. The reaction is similar to the Grignard reaction but the crucial difference is that the Barbier reaction is a one-pot synthesis whereas a Grignard reagent is prepared separately before addition of the carbonyl compound. Barbier reactions are nucleophilic addition reactions that usually take place with relatively inexpensive and water insensitive metals or metal compounds in contrast to Grignard reagents or organolithium reagents. For this reason it is possible in many cases to run the reaction in water which makes the procedure part of green chemistry. On the downside organozincs are much less nucleophilic than Grignards. The Barbier reaction is named after Victor Grignard's teacher Philippe Barbier.

An example of the Barbier reaction is the reaction of allyl bromide with benzaldehyde and zinc powder in water:

Barbier Reaction: The observed diastereoselectivity for this reaction is erythro : threo = 83 : 17

The catalytic enantioselective alkylation of aldehydes to afford enantioenriched secondary alcohols has been extensively studied since the 1980s. Diorganozinc reagents were the most widely used nucleophiles in this reaction, due to their low propensity to add

to carbonyl derivatives without the presence of a suitable catalyst. A wide range of catalysts were investigated to optimise the conditions and conversion and to obtain the secondary alcohols in high enantiomeric excess.

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CHAPTER OVERVIEW

25: Catalysis and some industrial processes

Topic hierarchy

25.1: Introduction and Definitions
25.2: Catalysis - Introductory Concepts
25.2A: Energy Profiles for a Reaction - Catalysed Versus Non-Catalysed
25.2B: Catalytic Cycles
25.2C: Choosing a Catalyst
25.3: Homogeneous Catalysis - Alkene (Olefin) and Alkyne Metathesis
25.4: Homogeneous Catalytic Reduction of N_2 to NH_3
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25.7: Heterogeneous Catalysis - Surfaces and Interactions with Adsorbates
25.8: Heterogeneous Catalysis - Commercial Applications
25.8A: Alkene Polymerization - Ziegler-Natta Catalysis and Metallocene Catalysts
25.8B: Fischer-Tropsch Carbon Chain Growth
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25.8D: Production of SO_3 in the Contact Process
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25.8F: Zeolites as Catalysts for Organic Transformations - Uses of ZSM-5
25.9: Heterogeneous Catalysis - Organometallic Cluster Models

Thumbanil: Wilkinson's Catalyst.

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SECTION OVERVIEW

25.2: Catalysis - Introductory Concepts

Topic hierarchy

25.2A: Energy Profiles for a Reaction - Catalysed Versus Non-Catalysed

25.2B: Catalytic Cycles

25.2C: Choosing a Catalyst

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25.2A: Energy Profiles for a Reaction - Catalysed Versus Non-Catalysed

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25.2B: Catalytic Cycles

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25.2C: Choosing a Catalyst

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25.3: Homogeneous Catalysis - Alkene (Olefin) and Alkyne Metathesis

Learning Objectives

In this lecture you will learn the following

- The application of organometallic complexes in homogeneous catalysis.
- Alkene isomerization.
- Alkene and the arene hydrogenations.
- Transfer hydrogenation.

One of the most important exploits of the organometallic chemistry is its application in the area of homogeneous catalysis. The field has now expanded its territory to accommodate in equal measures many large-scale industrial processes as well as numerous small scale reactions of the day-to-day organic synthesis. A few representative examples of organometallic catalysis are outlined below.

Alkene Isomerization

Alkene isomerization is a transformation that involve a shift of a double bond to an adjacent position followed by 1,3−migration of a H atom. The isomerization reaction is transition metal catalyzed.



The alkene isomerization reaction may proceed by two pathways, (*i*) one through a η^1−alkyl intermediate and (*ii*) the other through η^3−allyl intermediate. In the η^1−alkyl pathway, an alkene first binds to a metal at a vacant site next to M−H bond and then subsequently undergoing an insertion into the M−H bond thus creating back the vacant site. The resultant species then undergoes a H atom transfer from the alkyl moiety to give the isomerized olefin along with the regeneration of the M−H species.



The η^3−allyl mechanism requires the presence of two vacant sites. This mechanism goes through a η^3−allyl intermediate formed by a C−H activation at the allylic position of the olefin formed after binding to the metal and alongside leads to the formation of a M−H bond. Subsequent H transfer from the metal back to the η^3−allyl moiety leads to the alkene isomerized product.



Alkene Hydrogenation

The transition metal catalyzed alkene hydrogenation reactions are of significant industrial and academic interest. These reactions involve the H_2 addition on a C=C bond of olefins to give alkenes. The alkene hydrogenation may proceed by three different pathways namely the (*i*) oxidative addition (*ii*) heterolytic activation and (*iii*) the homolytic activation of the H_2 molecule.

The oxidative addition pathway is commonly observed for the Wilkinson's catalyst $(PPh_3)_3RhCl$ and is the most studied among all of the three pathways that exist. The catalytic cycle initiates with the oxidative addition of H_2 followed by alkene coordination. The resultant species subsequently get converted to the hydrogenated product.



The second pathway proceeds by the heterolytic activation of the H_2 molecule and requires the presence of a base like NEt_3, which facilitates the heterolytic cleavage by abstracting a proton from the H_2 molecule and leaving behind a hydride H^- ion that participates in the hydrogenation reaction. This type of mechanism is usually followed by the $(PPh_3)_3RuCl_2$ type of complexes.



Homolytic cleavage of H_2 is the third pathway for the alkene hydrogenation. It is the rarest of all the three methods and proceeds mainly in a binuclear pathway. Paramagnetic cobalt based $Co(CN)_5^{3-}$ type catalysts carries out alkene hydrogenation by this pathway *via* the formation of the $HCo(CN)_5^{3-}$species.



Arene hydrogenations

Examples of homogeneous catalysts for arene hydrogenation are rare though it is routinely achieved using catalysts like Rh/C under the heterogeneous conditions. A representative example of a homogeneous catalyst of this class is $(\eta^3-\text{allyl})Co[P(OMe)_3]_3$ that carry out the deuteration of benzene to give the all-*cis*-$C_6H_6D_6$ compound.



Transfer hydrogenation

This is a new kind of a hydrogenation reaction in which the source of the hydrogen is not the H_2molecule but an easily oxidizable substrate like isopropyl alcohol. The method is particularly useful for the reduction of ketones and imines but not very effective for the olefins.



Summary

The applications of organometallic compounds in homogeneous catalysis have transcend the boundaries of industry to meet the day-to-day synthesis in laboratory scale reactions. The alkene isomerization is one such application of homogeneous catalysis by the transition metal organometallic complexes. The hydrogenation reactions of alkene, arene, ketone and imine substrates are achieved by several types of the transition metal organometallic catalysts. They also proceed by different mechanisms involving oxidative addition, heterolytic and homolytic cleavages of the H−H bond. The transfer hydrogenation reaction uses easily oxidizable substrates like *i*−PrOH instead of H_2 as the hydrogenation source.

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25.4: Homogeneous Catalytic Reduction of N 2 to N H 3

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SECTION OVERVIEW

25.5: Homogeneous Catalysis - Industrial Applications

Topic hierarchy

25.5A: Alkene Hydrogenation

25.5B: Monsanto and Cativa Acetic Acid Synthesis

25.5C: Tennessee-Eastman Acetic Anhydride Process

25.5D: Hydroformylation (Oxo-process)

25.5E: Alkene Oligomerization

25.5F: C−C cross-coupling reactions

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25.5A: Alkene Hydrogenation

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25.5C: Tennessee-Eastman Acetic Anhydride Process

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25.5D: Hydroformylation (Oxo-process)

Learning Objectives

In this lecture you will learn the following

- The hydroformylation reaction and its mechanism.
- The C−C cross-coupling reactions and their mechanisms.

It is truly an exciting time for the field of organometallic chemistry as its potentials in homogeneous catalysis are being realized in an unprecedented manner. The growth in the field organometallic chemistry has been rightly acknowledged by the award of three Nobel prizes in over a decade in the areas of asymmetric hydrogenation (Nyori and Knowles in 2001), olefin metathesis (Grubbs, Schrock and Chauvin in 2006) and palladium mediated C−C cross coupling reactions (Suzuki, Negishi and Heck, 2010). A few representative examples of such landmark discoveries of homogeneous catalysis by organometallic compounds are discussed below.

Hydroformylation reaction

Hydroformylation, popularly known as the "oxo" process, is a Co or Rh catalyzed reaction of olefins with CO and H_2 to produce the value-added aldehydes.



The reaction, discovered by Otto Roelen in 1938, soon assumed an enormous proportion both in terms of the scope and scale of its application in the global production of aldehydes. The metal hydride complexes namely, the rhodium based $HRh(CO)(PPh_3)_3$ and the cobalt based $HCo(CO)_4$ complexes, catalyzed the hydroformylation reaction as shown below.



Hydroformylation, also known as oxo synthesis or oxo process, is an important homogeneously catalyzed industrial process for the production of aldehydes from alkenes.[1] This chemical reaction entails the addition of a formyl group (CHO) and a hydrogen atom to a carbon-carbon double bond. This process has undergone continuous growth since its invention in 1938: Production capacity reached 6.6×106 tons in 1995. It is important because the resulting aldehydes are easily converted into many secondary products. For example, the resulting aldehydes are hydrogenated to alcohols that are converted to plasticizers or detergents.

Hydroformylation is also used in specialty chemicals, relevant to the organic synthesis of fragrances and natural products. The development of hydroformylation, which originated within the German coal-based industry, is considered one of the premier achievements of 20th-century industrial chemistry.

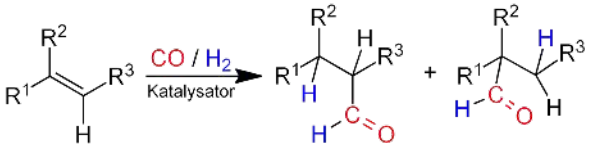


Figure 25.5D.1: Hydroformylation of an Alkene (R^1 to R^3 organyl groups (i. e. Alkyl- or Aryl group) or hydrogen).

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25.5E: Alkene Oligomerization

Learning Objectives

In this lecture you will learn the following

- The alkene metathesis reactions and their different variants.
- The application of metal carbenes in alkene metathesis reactions.
- The functional group tolerance, air and moisture sensitivity and high efficiency as important catalyst attributes for the alkene metathesis reactions.

The application of organometallic chemistry in homogenous catalysis is progressively increasing with the fast pace of discovery of new catalysts in the area. The benefits of organometallic catalysis have now percolated to all facets of the chemical world that span from the confines of the industry to the day-to-day small scale use in organic synthesis in academic laboratories. Quite a few of these applications of organometallic complexes in homogeneous catalysis have made a permanent imprint on the ever going developmental process that is constantly transforming our day-to-day life. An example of such a success story is of alkene metathesis, which is described in this chapter.

Alkene metathesis

Alkene metathesis reactions are gaining wide popularity in synthesizing unsaturated olefinic compounds as well as the unsaturated polymeric counterparts. Central to this catalysis is a metal carbene intermediate that reacts with olefins to give different olefinic compounds or even the unsaturated olefinic polymers depending upon the reaction conditions of the metathesis reaction. Metathesis is an unusual transformation in which a C=C is broken and also formed during catalysis to generate new unsaturated olefins.



Though a large variety of metal−carbene catalysts have been developed for the metathesis reaction, only a few have been found to be functional group tolerant. Thus a critical step in broadening the utility of metathesis reaction has been in developing catalysts that are functional group tolerant. In this regard, the early-transition metal based carbene catalysts like that of the Ti based ones are highly oxophilic and hence are intolerant to the functional groups. On the other hand, the more electron-rich Mo and W based catalysts are of intermediate character. Finally, the late-transition metal based Ru catalysts are found to be exceptionally tolerant toward functional groups but all the while exhibiting high reactivity toward olefinic bonds. In this context notable are the Grubb's Ru catalyst, which is easy to handle, and the Schrock's Mo catalyst, which display high activity.



Figure 1. The Grubb's and the Schrock's catalyst.

The metathesis reaction as such stands for a family of related reactions all of which involve a "cutting and stitching" of olefinic bonds leading to different unsaturated products. When two different olefin substrates are used, the reaction is called the "cross metathesis" owing to the fact that the olefinic ends are exchanged.



The metathesis reactions can even extend further to the conjugated dienes that can undergo Ring Closing Metathesis (RCM) in systems where the ring strain is not too high in the final product. The reverse of Ring Closing Metathesis (RCM) is called the Ring Opening Metathesis (ROM), and which is usually favored in the presence of large excess of C_2H_4.



The variants of metathesis often used in producing polymers are, (*i*) the Acyclic Diene Metathesis (ADMET) and (*ii*) the Ring Opening Metathesis Polymerization (ROMP), in which the relief of ring-strain of cycloalkenes drives the polymerization reaction forward. Both of these reactions, produce long chain polymers in a living fashion and as a result of which these reactions are useful for producing block copolymers $-(AAABBBB)_n-$.



Though several possibilities have been debated for the mechanism of the metathesis reaction, the one proceeding *via* a metalacyclobutane intermediate has gained credence.



Several important industrial applications have emerged out of the metathesis reaction like that of the commercial synthesis of the housefly pheromone.



Similarly, the polycyclopentadiene polymer, which is formed from the Ring Opening Metathesis Polymerization (ROMP) of dicyclopentadiene substrate, is used for bullet proof related applications because of its exceptional strength owing to its cross-linked nature.



Summary

Alkene metathesis represents a distinct class of related chemical reactions that involve the “cutting and stitching” of olefinic bonds to give unsaturated organic products. Depending upon the nature of the product formed, different type of alkene metathesis reactions exist like the alkene metathesis, cross-metathesis, Ring Closing Metathesis (RCM), Ring Opening Metathesis (ROM), Acyclic Diene Metathesis (ADMET), and the Ring Opening Metathesis Polymerization (ROMP). A commonality that runs through all of these different varieties of the metathesis reaction is its mechanism that involves a catalytically active metal−carbene species. The mechanism is said to be proceed *via* a 4−membered metalacyclobutane intermediate. The alkene metathesis has found important applications in organic synthesis as well as in the chemical industry.

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25.5F: C−C cross-coupling reactions

Learning Objectives

In this lecture you will learn the following

- The C−C cross-coupling reactions and their mechanisms.

The palladium catalyzed cross-coupling reactions are a class of highly successful reactions with applications in the organic synthesis to have emerged recently. The reactions carry out a coupling of the aryl, vinyl or alkyl halide substrates with different organometallic nucleophiles and as such encompasses a family of C−C cross-coupling reactions that are dependent on the nature of nucleophiles like that of the B based ones in the Suzuki-Miyuara coupling, the Sn based ones in the Stille coupling, the Si based ones in the Hiyama coupling, the Zn based ones in the Negishi coupling and the Mg based ones in the Kumada coupling reactions (Figure 1).

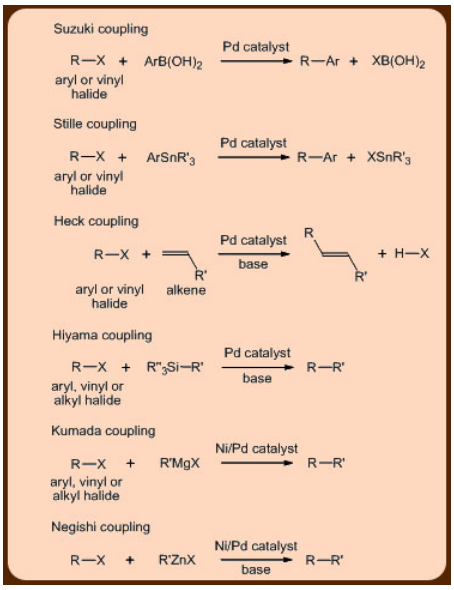


Figure 1. Various types of the palladium mediated C−C cross-coupling reactions.

An unique feature of these reactions is the exclusive formation of the cross-coupled product without the accompaniment of any homo-coupled product. Another interesting feature of these coupling reactions is that they proceed *via* a common mechanism involving three steps that include the oxidative addition, the transmetallation and the reductive elimination reactions (Figures 2 and 3).

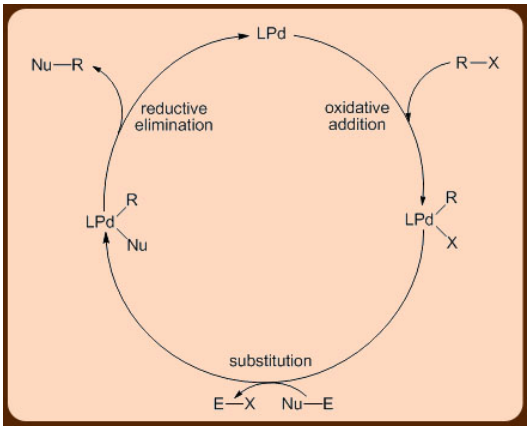


Figure 2. A general catalytic cycle for the palladium mediated C−C cross-coupling reactions.

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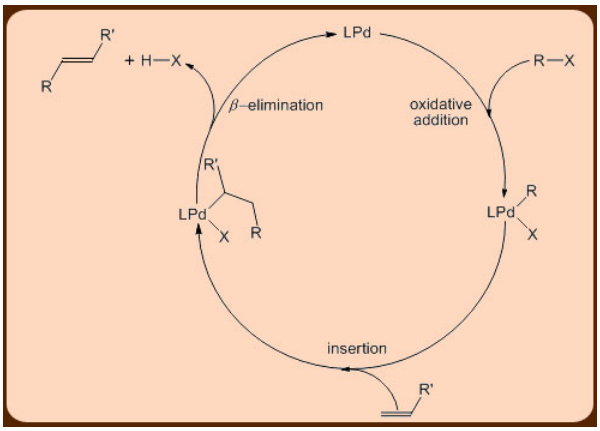


Figure 3. A catalytic cycle for the palladium mediated Heck coupling reaction.

Summary

Organometallic complexes play a pivotal role in several successful homogeneous catalysis reactions like that of the hydroformylation and the C−C cross-coupling reactions. These reactions are important because of the fact that both of the hydroformylation and the C−C cross-coupling reactions give more value added products compared to the starting reactants. The palladium catalyzed C−C cross-coupling reactions are a class of highly successful reactions that have permanently impacted the area of organic synthesis in a profound way to an extent that the 2010 Nobel prize has been conferred on one of these reactions thereby recognizing the importance of the C−C cross-coupling recations.

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25.6: Homogeneous Catalyst Development

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25.6A: Polymer-Supported Catalysts

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25.6C: d-Block Organometallic Clusters as Homogeneous Catalysts

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25.7: Heterogeneous Catalysis - Surfaces and Interactions with Adsorbates

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25.8: Heterogeneous Catalysis - Commercial Applications

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25.8A: Alkene Polymerization - Ziegler-Natta Catalysis and Metallocene Catalysts

Learning Objectives

In this lecture you will learn the following

- Olefin polymerization.
- Mechanism involved in polymerization process.

Ziegler Natta Polymerization Catalysts





Insertion of aluminum alkyls into olefins was studied by Ziegler. During the systematic investigation of olefin polymerization, Ziegler realized that the most effective catalyst is the combination of $TiCl_4/AlEt_3$which can polymerize ethylene at pressure as low as 1 bar. The application of Ziegler method to the polymerization of propylene and its establishment and the investigation of bulk properties was carried out by Natta and hence the methodology is called Ziegler-Natta process.



Important discovery: R_3Al + Lewis acids.



In the absence of reaction mechanism with solid proof, it is presumed that the reaction is due to the heterogeneous catalysis in which fibrous $TiCl_3$, alkylated on its surface is considered to be the active catalyst species.



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25.8B: Fischer-Tropsch Carbon Chain Growth

The Fischer-Tropsch process is a catalytic chemical reaction in which carbon monoxide (CO) and hydrogen (H_2) molecules (i.e., "syngas") are converted into hydrocarbons of various molecular weights according to the following equation:

$$(2\,n+1)\ H_2 + n\,CO \longrightarrow C_nH_{2n+2} + n\,H_2O$$

where n is an integer. Thus, for $n = 1$, the reaction represents the formation of methane.

$$3\,H_2 + CO \longrightarrow CH_4 + H_2O \tag{25.8B.1}$$

The Fischer-Tropsch synthesis reaction, in theory, is a condensation polymerization reaction of CO. The Fischer-Tropsch process conditions are usually chosen to maximize the formation of higher molecular weight hydrocarbon liquid fuels which are higher value products.

There are other side reactions taking place in the process, among which the **water-gas-shift reaction.**

$$CO + H_2O \longrightarrow H_2 + CO_2$$

is predominant. Depending on the catalyst, temperature, and type of process employed, hydrocarbons ranging from methane to higher molecular paraffins and olefins can be obtained. Small amounts of low molecular weight oxygenates (e.g., alcohol and organic acids) are also formed.

Mechanism

The Fischer-Tropsch process produces a wide range of hydrocarbon products with different chain lengths. The process involves several steps including:

- Initiation: Adsorption of CO onto the catalyst surface and its dissociation into carbon and oxygen atoms.
- Propagation: Repeated addition of methylene units ($-CH_2-$) to the growing carbon chain.
- Termination: The chain growth stops when a hydrogen atom is added to the end of the chain, forming a final hydrocarbon product.
- Chain growth probability (α):

This parameter describes the likelihood of a growing chain adding another carbon atom in each propagation step. A higher α value indicates a greater tendency to form longer hydrocarbon chains.

Catalysts

The type of catalyst used significantly affects the chain growth probability and product distribution. For example, cobalt catalysts tend to produce shorter chains compared to iron catalysts. Factors like temperature, pressure, and hydrogen-to-carbon monoxide ratio can also influence chain growth by impacting the rate of various reaction steps. Catalysts considered for Fischer-Tropsch synthesis are based on transition metals of iron, cobalt, nickel and ruthenium. FT catalyst development has largely been focused on the preference for high molecular weight linear alkanes and diesel fuels production. Among these catalysts, it is generally known that:

- Nickel tends to promote methane formation as in a methanation process in Equation 25.8B.1.
- Iron is relatively low cost and has a higher water-gas-shift activity, and is therefore more suitable for a lower hydrogen/carbon monoxide ratio (H_2/CO) syngas such as those derived from coal gasification
- Cobalt is more active, and generally preferred over ruthenium (Ru) because of the prohibitively high cost of Ru. In comparison to iron, Co has much less water-gas-shift activity, and is much more costly.

Given these constraints, commercially available Fischer-Tropsch catalysts are either cobalt or iron based. In addition to the active metal, the Fe catalysts at least typically contain a number of promoters, including potassium and copper, as well as high surface area binders/supports such as silica and/or alumina. Only iron-based FT catalysts are currently used commercially for converting coal-derived syngas into FT liquids, given Fe catalyst's inherent water gas shift capability to increase the H_2/CO ratio of coal-derived syngas, thereby improving hydrocarbon product yields in the FT synthesis. Fe catalysts may be operated in both high-temperature regime (300-350°C) and low-temperature regime (220-270°C), whereas Co catalysts are only used in the low-

temperature range. This is a consequence of higher temperatures causing more methane formation, which is worse for Co compared to Fe.

References

- https://www.netl.doe.gov/research/ca...ia/ftsynthesis

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25.8C: Haber Process

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25.8D: Production of $S\ \ O\ 3$ in the Contact Process

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25.8E: Catalytic Converters

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25.8F: Zeolites as Catalysts for Organic Transformations - Uses of ZSM-5

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25.9: Heterogeneous Catalysis - Organometallic Cluster Models

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CHAPTER OVERVIEW

26: d-Block Metal Complexes- Reaction Mechanisms

Mechanisms of ligand substitution and electron-transfer reactions in coordination complexes. While, a proposed mechanism must be consistent with all experimental facts. it **cannot** be proven, since another mechanism may also be consistent with the experimental data.

Topic hierarchy

- 26.1: Introduction
- 26.2: Ligand Substitutions - Some General Points
  - 26.2A: Kinetically Inert and Labile Complexes
  - 26.2B: Stoichiometric Equations Say Nothing About Mechanism
  - 26.2C: Types of Substitution Mechanism
  - 26.2D: Activation Parameters
- 26.3: Substitution in Square Planar Complexes
  - 26.3A: Rate Equations, Mechanism, and the Trans-effect
  - 26.3B: Ligand Nucleophilicity
- 26.4: Substitution and Racemization in Octahedral Complexes
  - 26.4A: Water Exchange
  - 26.4B: The Eigen-Wilkins Mechanism
  - 26.4C: Stereochemistry of Substitution
  - 26.4D: Base-Catalysed Hydrolysis
  - 26.4E: Isomerization and Racemization of Octahedral Compleces
- 26.5: Electron-transfer Processes
  - 26.5A: Inner-sphere Mechanism
  - 26.5B: Outer-sphere Mechanism

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SECTION OVERVIEW

26.2: Ligand Substitutions - Some General Points

Topic hierarchy

26.2A: Kinetically Inert and Labile Complexes

26.2B: Stoichiometric Equations Say Nothing About Mechanism

26.2C: Types of Substitution Mechanism

26.2D: Activation Parameters

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26.2A: Kinetically Inert and Labile Complexes

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26.3A: Rate Equations, Mechanism, and the Trans-effect

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26.3B: Ligand Nucleophilicity

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26.4A: Water Exchange

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26.4E: Isomerization and Racemization of Octahedral Compleces

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26.5A: Inner-sphere Mechanism

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26.5B: Outer-sphere Mechanism

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CHAPTER OVERVIEW

27: f-Block Metals- Lanthanides and Actinides

Topic hierarchy

27.1: Introduction
27.2: f-Orbitals and Oxidation States
27.3: Atoms and Ion Sizes
27.3A: The Lanthanoid Contraction
27.3B: Coordination Numbers
27.4: Spectroscopic and Magnetic Properties
27.4A: Electronic Spectra and Magnetic Moments - Lanthanoids
27.4B: Luminescence of Lanthanoid Complexes
27.4C: Electronic Spectra and Magnetic Moments - Actinoids
27.5: Sources of the Lanthanoids and Actinoids
27.5A: Occurrence and Separation of the Lanthanoids
27.5B: The Actinoids
27.6: Lanthanoid Metals
27.7: Inorganic Compounds and Coordination Complexes of the Lanthanoids
27.7A: Halides
27.7B: Hydroxides and Oxides
27.7C: Complexes of Ln(III)
27.8: Organometallic Complexes of the Lanthanoids
27.8A: \(\sigma\)-Bonded Complexes
27.8B: Cyclopentadienyl Complexes
27.8C: Bis(arene) Derivatives
27.8D: Complexes Containing the \(\eta^8\)-cyclooctatetraenyl Ligand
27.9: The Actinoid Metals
27.10: Inorganic Compounds and Coordination Complexes of Thorium, Uranium, and Plutonium
27.10A: Thorium
27.10B: Uranium
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27.11: Organometallic Complexes of Thorium and Uranium
27.11A: (\sigma\)-Bonded Complexes
27.11B: Cyclopentadienyl Derivatives
27.11C: Complexes Containing the \(\eta^8\)-cyclooctatetraenyl Ligand

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27.3A: The Lanthanoid Contraction

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