UNIVERSITY OF ARKANSAS AT LITTLE ROCK: CHEM 1403 GENERAL CHEMISTRY II



Robert Belford
University of Arkansas at Little Rock

LibreTexts™

University of Arkansas at Little Rock

University of Arkansas at Little Rock: Chem 1403 General Chemistry II

Robert Belford

This text is disseminated via the Open Education Resource (OER) LibreTexts Project (https://LibreTexts.org) and like the thousands of other texts available within this powerful platform, it is freely available for reading, printing, and "consuming."

The LibreTexts mission is to bring together students, faculty, and scholars in a collaborative effort to provide and accessible, and comprehensive platform that empowers our community to develop, curate, adapt, and adopt openly licensed resources and technologies; through these efforts we can reduce the financial burden born from traditional educational resource costs, ensuring education is more accessible for students and communities worldwide.

Most, but not all, pages in the library have licenses that may allow individuals to make changes, save, and print this book. Carefully consult the applicable license(s) before pursuing such effects. Instructors can adopt existing LibreTexts texts or Remix them to quickly build course-specific resources to meet the needs of their students. Unlike traditional textbooks, LibreTexts' web based origins allow powerful integration of advanced features and new technologies to support learning.



LibreTexts is the adaptable, user-friendly non-profit open education resource platform that educators trust for creating, customizing, and sharing accessible, interactive textbooks, adaptive homework, and ancillary materials. We collaborate with individuals and organizations to champion open education initiatives, support institutional publishing programs, drive curriculum development projects, and more.

The LibreTexts libraries are Powered by NICE CXone Expert and was supported by the Department of Education Open Textbook Pilot Project, the California Education Learning Lab, the UC Davis Office of the Provost, the UC Davis Library, the California State University Affordable Learning Solutions Program, and Merlot. This material is based upon work supported by the National Science Foundation under Grant No. 1246120, 1525057, and 1413739.

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation nor the US Department of Education.

Have questions or comments? For information about adoptions or adaptions contact info@LibreTexts.org or visit our main website at https://LibreTexts.org.

This text was compiled on 08/25/2025

TABLE OF CONTENTS

Licensing

1: General Information

- 1: Hypothes.is

10: Review

- 10.1: Lewis Dot Structures
- 10.2: VSEPR
- 10.3: Molecular Polarity

11: Intermolecular Forces and Liquids

- 11.0: Prelude
- 11.1: States of Matter and Intermolecular Forces
- 11.2: Ion-Dipole Forces
- 11.3: Dipole-Dipole Forces
- 11.4: NonPolar Molecules and IMF
- 11.5: Hydrogen Bonds
- 11.6: Properties of Liquids

12: Solids

- 12.0: Prelude
- 12.1: Crystal Lattices and Unit Cells
- 12.2: Ionic Solids
- 12.3: Bonding in Metals and Semiconductors
- 12.4: Network and Amorphous Solids
- 12.5: Phase Diagrams

13: Solutions

- 13.1: Prelude
- 13.2: Units of Concentration
- 13.3: Solvation Processes
- 13.4: Pressure and Temperature Effects on Solubility
- 13.5: Colligative Properties
- 13.6: Colloidal Mixtures

14: Rates of Chemical Reactions

- 14.1: Prelude
- 14.2: Rates of Chemical Reactions
- 14.3: Reaction Conditions and Rate
- 14.4: Effect of Concentration on Reaction Rate
- 14.5: Integrated Rate Law
- 14.6: Energetics and Reaction Rates
- 14.7: Reaction Mechanisms

15: Equilibria

- 15.1: Chemical Equilibrium
- 15.2: Equilibrium Constant and Reaction Quotient
  - Clicker1
- 15.3: Determining an Equilibrium Constant
- 15.4: Using Equilibrium Constants in Calculations
- 15.5: Equilibrium Constants and Coupled Reactions
- 15.6: Disturbing a Chemical Equilibrium

16: Acids and Bases

- 16.1: Brønsted-Lowry Concept of Acids and Bases
- 16.2: Water and the pH Scale
- 16.3: Equilibrium Constants for Acids and Bases
- 16.4: Acid-Base Properties of Salts
- 16.5: Acid-Base Equilibrium Calculations
- 16.6: Molecular Structure, Bonding, and Acid-Base Behavior
- 16.7: Lewis Concept of Acids and Bases

17: Aqueous Equilibria

- 17.1: Common Ion Effect
- 17.2: Controlling pH- Buffer Solutions
- 17.3: Acid-Base Titrations
- 17.4: Solubility of Salts
- 17.5: Precipitation Reactions
- 17.6: Equilibria Involving Complex Ions
- 17.7: Solubility and Complex Ions

18: Entropy and Free Energy

- 18.1: Spontaneity and Energy Transfer
- 18.2: Dispersal of Energy- Entropy
- 18.3: Entropy - A Microscopic Understanding
- 18.4: Entropy Measurements and Values
- 18.5: Second Law and Gibbs Free Energy
- 18.6: Gibbs Free Energy

19: Electron Transfer Reactions

- 19.1: Electrical Fundamentals
- 19.2: Oxidation-Reduction Reactions
- 19.3: Electrochemical Cells
- 19.4: Electrochemical Cell Fundamentals
- 19.5: Standard Electrochemical Potentials
- 19.6: Electrochemistry and Thermodynamics
- 19.7: Electrochemical Cells under Nonstandard Conditions
- 19.8: Corrosion
- 19.9: Electrolysis
- 19.10: Counting Electrons

20: Coordination Chemistry

- 20.1: Werner's Theory of Coordination Compounds
- 20.2: Ligands
- 20.3: Nomenclature
- 20.4: Isomerism
- 20.5: Optical Isomerism in Metal Complexes
- 20.6: Stability Aspects of Complex-Ion Equilibria
- 20.7: Chelation
- 20.8: Bonding in Octahedral Complex Ions- Crystal Field Theory
- 20.9: Bonding in Non-Octahedral Complex Ions- Crystal Field Theory
- 20.10: Magnetic Behavior of Atoms, Molecules, and Materials
- 20.11: Magnetic Behavior of Complex Ions
- 20.12: Optical Properties of Coordination Compounds (Color)

21: Nuclear Chemistry

- 21.1: Components of the Nucleus
- 21.2: Nuclear Reactions
- 21.3: Nuclear Radiation
- 21.4: Rates of Radioactive Decay
- 21.5: Stability of the Atomic Nucleus
- 21.6: The Origin of the Elements
- 21.7: Transmutation of the Elements
- 21.8: Nuclear Fission
- 21.9: Nuclear Fusion
- 21.E: Nuclear Chemistry (Exercises)

Appendix 1: Google Sheets

- 1: Google Sheets Basics

Index

Glossary

Detailed Licensing

Licensing

*A detailed breakdown of this resource's licensing can be found in **Back Matter/Detailed Licensing**.*

CHAPTER OVERVIEW

1: General Information

Topic hierarchy

1: Hypothes.is

1: General Information is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

1: Hypothes.is

Hypothes.is Web Annotations

This class will use the Hypothes.is web annotation service that is integrated into LibreText. You need to go to https://web.hypothes.is/ and create an account. If possible, please start your username with the first four letters of your last name followed by the first three letters of your first name, followed by anything you want, so you can easily be identified for grading purposes. So my user name could be belfrob99. You will then need to join the class group, which is a private group. You will be sent an email invitation or contact your instructor, and you should only make annotations in the group.

The following YouTube gives a quick demonstration on the use of the Hypothes.is Web Annotation service.



Video 1.1: 4:10 min Youtube showing how to use tags to organize hypothes.is annotations.

Making Annotations

To make an annotation you simply highlight the text you want to annotate, choose "Annotate" and write in the overlay. Note, the first time you open up a page it will post to "Public" and you need to change that to your class group. Once you have started posting to the class group that will be the default option, but initially the default is public.

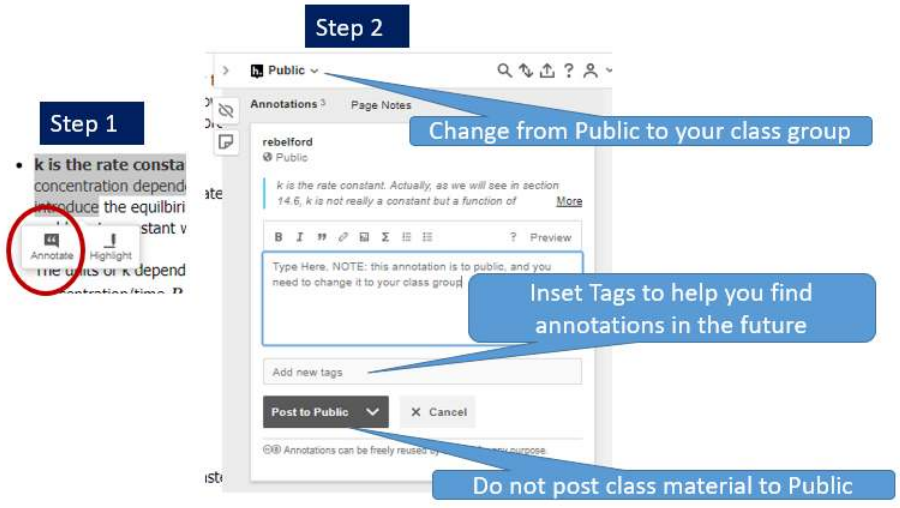


Figure 1.1: To annotate you simply highlight text and write in the overlay. (Copyright; Belford, cc.0)

If you tag your annotation you can easily find it by going to your homepage in hypothes.is and then filtering by tags. So you may want to make tags like "exam 1", or "nomenclature". If you then filter with your hypothes.is user name and exam 1, you see those items you tagged. If you just do exam 1, you filter for everything the class tagged exam 1. You can then click the contextual link

by the annotation, and hypothes.is will open that page, navigate to the highlighted text and display the annotation. (Note: In LibreText the highlights are hidden by default, and you need to click the "eye" with the slash over it (figure 1.2)).

Using the Hypothes.is Overlay to read discussions

By default the hypothes.is overlay is closed and you do not see the annotations.

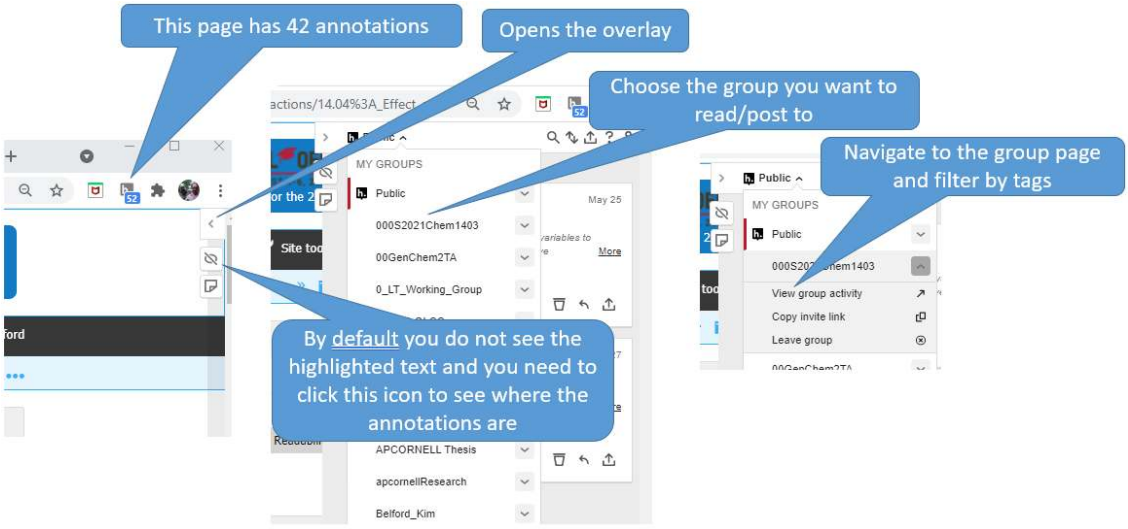


Figure 1.2: By default the overlay is closed and annotations are hidden. This image shows how to pick a group and view group activity (Copyright; Belford CC0)

Figure 1.2 shows how to pick a group and view group activity.

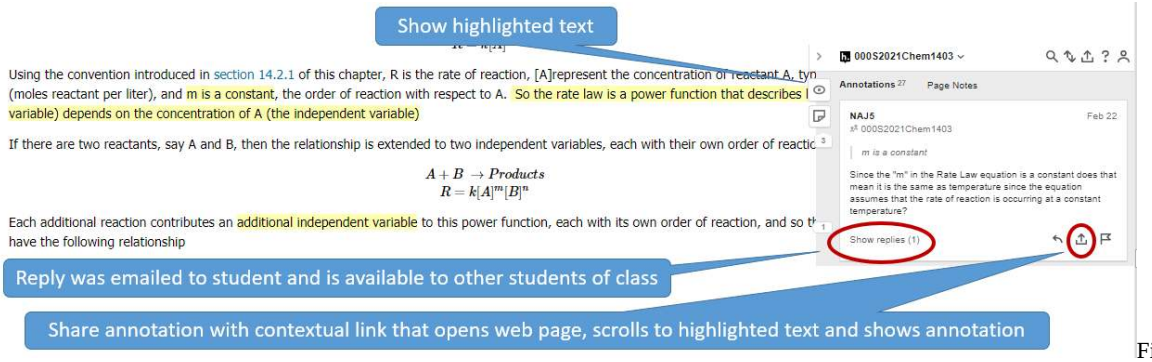


Figure 1.3: Annotation and highlights text being displayed. (Copyright; Belford CC0)

Using tags

There are two fundamental ways to use tags, (1) to communicate with your instructor or other students, and (2), to take and organize notes by setting up a tag taxonomy for categorizing your annotations.

Communicating with Annotations

If you highlight text within Libretexts and tag an annotation "**question",** the instructor will know you want the annotation to be reviewed**.** You should do this even if there is a typo or spelling error you wish to bring to the instructor's attention. That is, **question** means you want the instructor to review the annotation. At least twice a week the instructor will filter the class for annotations tagged **question**, and respond to the questions.

Tag Taxonomic Categorization

You can use a tag taxonomy to organize your notes and then use the filter function to search your notes. In figure 1.4 you can link to 573 annotations by opening the S2021Chem1403 group in hypothes.is. When you did this you were actually using a group tag ["group: S2021Chem1403"] which shows in the search window. If you scroll down the page you see all the tags and members, and if you click on a member, you find the annotations that member made. Here, member "[user:rebelford'] had made 40 annotations to this group. Now this user was an instructor and he had reviewed student annotations before lecture of 2/21/2021 and made a tag ["tag:2_22_21"] to link to material students were having trouble with, so he could quickly navigate to that material during lecture.

Figure 1.4: Hypothes.is search filtered by the group tag 0UALR-OLCC (which was a class group) and a student's tag "Ch.3-ToDo". (Copyright; Belford CC0)

Tips on using tags

- Use Autocomplete: don't make redundant tags (HELP, Help and help all mean the same thing).
- Do not worry if others use the same tag, but adding your user tag, you will only see things you tag.
- Create assessment tags (exam 1, quiz 1,....)
- Create topic tags (VSEPR, Lewis Dot, electronegativty...)
- Be creative and create tags that make sense to you.

Warning: You can not tag someone else's tag. If you tag a reply it currently will not work. That is, the tag shows in the reply, but does not get processed, and so does not show on the group landing page. We are trying to add that feature, but it is not available now.

If the student clicks the contextual link hypothes.is will open the webpage that was highlighted, scroll down to the highlighted section and show the annotation in the overlay. This allows students to organize their notes on LibreText and quickly find content. If you get the chrome plugin you can even annotate material outside of LibreText and connect it to your material and notes within LibreText, as long as the material does not require a login to access. It should also be noted that you can not highlight hidden text within LibreText (like the answers to exercises), and if you have a question on the answer to an exercise, you should highlight the question, not the answer.

Commentary on Tagging

The following are some comments that might assist you in productively using hypothes.is as you study.

1. The tag filter is a Boolean AND function. So, if you have a set of tags on several items, they will all show up in a filter using those tags.

2. Both tags and annotations can be "living", that is you can add/remove tags and you can edit your comments after you fist post them (you can only tag and edit your own comments, you can respond to other people's comments). For example, you may tag something with an action like "memorize", and once you have memorized it, you can remove the tag.

3. The annotations supplement your notes. So if I say something in lecture about a topic, and you put it in the annotation, than you can access it in the context of my textbook (I will be doing a lot of lecturing from the textbook content). Therefor, your tag schema (conceptual framework) is not just about the narrative of my text, but also of your notes. That is, as you read and think, you can preserve your thought in the annotation, and tag it in the context of the thought (associating your annotation with the highlighted text). So you can use the tags to structure a navigational pathway through both my text and your notes, while also connecting them.

Finally, this is really a high level metacognitive activity. If you tag everything "exam1" or "remember", it essentially becomes a useless tag. You need to think about how a topic is important and how it fits in the framework of the other topics of the class, and it will take some practice to come up with tags that work for you. But one of the challenges of today's information landscape is the huge amount of information that is instantly available at your fingertips, and developing these skills will give you a tool that can assist you in other classes beyond chemistry.

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has

both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

1: Hypothes.is is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

10: Review

Topic hierarchy

10.1: Lewis Dot Structures
10.2: VSEPR
10.3: Molecular Polarity

Introduction

In the first part of Gen Chem 2 we will predict physical properties of matter like boiling/melting points, and physical behavior like predicting if two substances will mix with each other. The class will start by quickly reviewing intermolecular forces, which require knowing if a substance is polar or not. This review section contains material from General Chemistry 1 that you need to know for General Chemistry 2, but which General Chemistry 2 will not cover. Specifically, you need to review Lewis Dot Structures, Molecular Geometries and predicting if a molecule is polar. Here is an outline to give you a big picture perspective on why we need to review this.

- Physical properties and behavior are influenced by the types of intermolecular forces matter has.
- Determining intermolecular forces requires identifying if a molecule is polar or not.
- Determining polarity requires knowing the geometry of the molecule.
- Determining the geometry requires knowing the Lewis dot structure.

So the workflow for predicting a molecules properties and behavior sort of follow the above in reverse order.

Step 1: Determine Lewis Dot Structure (where are the bonds and where are the lone pairs of electrons)
Step 2: Determine the Molecular Geometry (using VSEPR)
Step 3: Determine molecular polarity from bond polarities and molecular symmetry

This review will have 3 sections that relate to this workflow (10.1, 10.2 & 10.3). Each section is a very brief summary of key concepts with links to the relevant General Chemistry 1 chapters. This material will not be covered in lecture, but you are expected to know it, and it is fair material for exams and quizzes..

Contributors and Attributions

- Bob Belford

This page titled 10: Review is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

10.1: Lewis Dot Structures

Introduction: Lewis Dot Structure Review

In order to predict molecular properties you need to be able to draw a Lewis Dot Structure. There are multiple techniques for doing this, and if you have your general chemistry 1 notes and feel confident, review those. Chapter 8 of the UALR Gen Chem 1 LibreTexts covers this material.

Specifically:
8.2: Covalent Bonding and Lewis Structures
8.3 Resonance
8.5 Drawing Lewis Dot Structures (note: This is Handout 1.1 below, which is just 2 pages, and I suggest you print it, and follow it while working out Lewis dot structures)

Worksheets

Handout 10.1.1: Lewis Dot Structure Procedures
http://chemwiki.ucdavis.edu/@api/deki/files/60817/vsepr-1-Review.pdf

The above handout is what I give my students in General Chemistry 1, and is covered in section 8.5. By following this handout you will identify resonance structures, and exceptions to the octet rule. The two videos below show how you use this handout. If you are good with Lewis dot structures and have learned another technique, that is fine, and you do not need to use this technique. (There are many paths to the top of the mountain, and once there, the view is the same.) Simply speaking, this is the path I teach. You should print this and use it while working out the problems in the following worksheet (Handout **10.1.2**)

Handout 10.1.2: Lewis Dot Structure Worksheet
http://chemwiki.ucdavis.edu/@api/deki/files/61154/vsepr1_WorkSheet.pdf

The above worksheet is designed to be used with handout **10.1.1**. Once completed, the same set of molecules will be used in the VESPR worksheet R.2.2 (next section).

Video Tutorials on Lewis Dot Structures

Example 10.1.1:

1. Draw Lewis dot structure for Sulfur Trioxide (SO_3). (You should look at Handout **10.1.1** while watching.)



Video 1.1*: Please look at Handout 1: Lewis dot structure technique while watching this video. Note steps 1 and 2 are switched between the video and the handout, but all the rest are the same.*

Question: Why does sulfur trioxide require resonance structures? In your answer, think about how a Lewis dot structure represents a bond, and the nature of PI bonds.

Answer

Lewis dot structures treat a bond as an electron pair shared between 2 nuclei, which is drawn as a line between two atoms. In sulfur trioxide, there is a pi bond between 4 atoms, not 3. Thus you can not draw a Lewis dot structure of sulfur trioxide, but need to draw three resonance structures, with the average of them being a representation of the molecule. Note, the sulfur is sp^2 hybridized giving it a trigonal planar geometry, and the unhybridized p orbital forms the pi bond with with overlap of the p orbitals of each oxygen, with electron density above and below the plan of the molecule.

Example 10.1.2:

Lewis dot structure for Sulfite (SO_3^{-2}). You should look at Handout **10.1.1** while watching.



***Video 8.5.2**: Please look at Handout 1: Lewis dot structure technique while watching this video. Note steps 1 and 2 are switched but all the rest are the same.*

Question: What is the formal charge of each atom in the Lewis dot structure of sulfite?

Answer

The sulfur has a [+1] formal charge as it donates 6 electrons to the structure, but has 5 around it. Each of the oxygens has a [-1] as they also donate 6 electrons to the molecule, but have 7 around them. Note the sum of the formal charges over all atoms is the charge of the ion. See section 8.4 Formal Charges if you need to review these.

Class Activity

This page titled 10.1: Lewis Dot Structures is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

10.2: VSEPR

Introduction:

This part of the review goes over the use of Valence Shell Electron Repulsion Theory (VSEPR) to determine molecular geometries. You should review your general chemistry 1 notes. If they are not available, go to
section 8.6: Molecular Geometries

Worksheets

Handout 10.2.1 : Overview of Structures:
 http://chemwiki.ucdavis.edu/@api/deki/files/60818/VESPR_Geometry_Handout.pdf T
The above 3 page handout gives the basic VESPR geometries of table 2.1 (below), along with the hybrid orbitals (review section

Handout **10.2.2** : VSEPR Worksheet
 http://chemwiki.ucdavis.edu/@api/deki/files/61155/vsepr2_Worksheet.pdf
The above handout is a continuation of the exercise in section 10.1 Lewis Dot Structures. You should fill out that handout first, and then use it while filling out this handout.

Molecular Geometries

Table 1 shows some examples of geometries with a central atom A is bonded to two or more X atoms. As indicated in several of the geometries below, non-bonding electrons can strongly influence the molecular geometry of the molecule. Note: "E" represent lone pairs of electrons

Table **10.2.1** :

6	5	4	3	2
AX_6  octahedral	AX_5  trigonal bipyramidal	AX_4  tetrahedral	AX_3  trigonal planar	AX_2 linear
1 lone pair of electrons				
AX_5E  square pyramidal	AX_4E  distorted tetrahedron	AX_3E  pyramidal	AX_2E  nonlinear	AXE linear
2 lone pairs of electrons				
AX_4E_2  square planar	AX_3E_2  T-shaped	AX_2E_2  bent		

These structures can generally be predicted, when A is a nonmetal, using the "valence-shell electron-pair repulsion model (VSEPR) discussed in the next section. This image table was borrowed from Paul Groves LibreText, and the rotating molecules were created by Robyn Rindge.

Exercise 10.2.1

What is the molecular geometry of triiodide (I_3^-), which has two bonding and 3 lone pairs? (It is not in the above table)

Answer

Linear

10.2: VSEPR is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

10.3: Molecular Polarity

Introduction

Review sections:
8.7 Bond Polarity and Electronegativity
8.8 Bond and Molecular Polarity:

Key Concepts

You should know the following terms and concepts from general chemistry 1. Please review that material

- electronegativity (χ)
  - periodic trends
  - possible values
  - Use in predicting bond types
- Dipole Moment (μ)
  - Debye (concept)
- 3 Fundamental VSEPR Geometries
  - linear
  - trigonal planar
  - tetrahedral
- 2 Secondary VSEPR Geometries
  - Trigonal Bipyrimidal (linear along axis,trigonal planar along equatorial plan)
  - Octahedral (linear along three Cartesian axes)
- Ability to identify if a molecule is polar and predict direction (not magnitude) of dipole
  - Rudimentary Vector Addition

Electronegativity

The electronegativity of an atom is used to indicate if bonding electrons are equally, or uneqully shared, when that atom is bonded to another atom. The atom with the higher electronegativity pulls the electron cloud more than the atom with the lower electronegativity. The values of electronegativity range from 0.7 to 4.0, it is unitless, and although it is assigned to an atom, it is not a property of an atom like ionization potential or electron affinity. The following YouTube gives a good description of electronegativity, and please review section 8.7: Bond Polarity and Electronegativity. You need to know the periodic trends of increasing (or decreasing) electronegativity.



3:32 min YouTube by professor Dave going over the basics of electronegativity (https://youtu.be/PoQjsnQmxok).

Dipole Moment

A dipole moment (μ) occurs when the center of positive charge on a molecule does not align with the center of negative charge, and this results in a region of partial positive and partial negative charge, ie., a dipole. HCl has a dipole moment.

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl} \tag{10.3.1}$$

Molecules with a dipole moment not only align with external electric fields, but interact with each other through dipole-dipole interactions (where the opposite charged dipoles attract and the like charged ones repel).

Molecular Shape and Polarity

A polar bond in a diatomic molecule results in a polar molecule. If there are more than one bond in a molecule, all the bonds contribute to the molecules dipole moment, and if they are symmetrically oriented, they cancel out. So a symmetric molecule like carbon dioxide, which has polar bonds, is nonpolar. Review section 8.8: Bond and Molecular Polarity. The following YouTube gives a quick and decent coverage of symmetry and molecular polarity.



Professionally developed YouTube video uploaded by Wendell Thomas.

Note, at the end of the above youtube they use polarity to predict which of two isomers (molecules with the same formula) has the higher boiling point, which is the kind of problem you will have on your first exam.

Summary of Symmetric Structures

A=central atom, B,C,D = atoms of type B,C or D, E=Lone pair electrons

1. sp hybrid
   - Linear
     - AB_2
2. sp^2 hybrid
   - Trigonal planar
     - AB_3
3. sp^3 hybrid
   - tetrahedral
     - AB_4
4. sp^3d hybrid
   - trigonal bipyramidal
     - AB_5
     - AB_2C_3 (B in axial positions, C in equatorial plane)
   - linear

- AB_2E_3 (B in axial positions, E - lone pairs in equatorial plane)

5. sp^3d^2 hybrid
   - Octahedral
     - AB_6
     - AB_4C_2 (B along X & Y axes, C along Z axis)
     - $AB_2C_2D_2$ (B along X, C along Y and D along Z axes)
   - Square Planar
     - AB_4E_2 (B along X & Y axes, E - lone pairs along Z axis)

10.3: Molecular Polarity is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

11: Intermolecular Forces and Liquids

11.0: Prelude
11.1: States of Matter and Intermolecular Forces
11.2: Ion-Dipole Forces
11.3: Dipole-Dipole Forces
11.4: NonPolar Molecules and IMF
11.5: Hydrogen Bonds
11.6: Properties of Liquids

The following box will aggregate annotations with the public hypothes.is tag of f21c1403c11:

This page titled 11: Intermolecular Forces and Liquids is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

11.0: Prelude

Introduction:

In this chapter we are going to look at intermolecular forces, the forces "between molecules", and the liquid state (phase) of matter. Before this we should review some of the fundamentals of so called "Intramolecular forces", those within a molecule. So far we have looked at 4 basic types of chemical bonds:

1. **Ionic Bonds** (resulting from coulombic interactions of positive cations with negative anions)
2. **Covalent Bonds** (resulting by the sharing of valence electrons in orbitals that involve two or more nuclei)
3. **Polar Covalent Bonds** (covalent bonds involving non-equal sharing of electrons by multiple nuclei)
4. **Metallic Bonds** (these have only been mentioned, and will be covered in chapter 12, but they are different than the above)

In section 8.1 Chemical Bond Formation, we introduced the Arkel-Ketelaar diagram to identify which type of bond occurs as a result of :

1. The average electronegativity (χ)of the bonding atoms (x-axis).
   - metals have low values (0.7-2.0ish), alloys are metallic compounds
   - Nonmetals have high values (2.5-4), molecules are compounds of nonmetals
2. The difference ($\Delta\chi$) in electronegativities (y-axis).
   - $\Delta\chi$<0.5, covalent or metallic compound (covalent if high χ, and metallic if low χ\)
   - 0.5<$\Delta\chi$<2.0, polar covalent
   - $\Delta\chi$>2.0, ionic (between metal (low χ) and nonmetal (high χ)

(Note: these values are "Rule of Thumb" values)

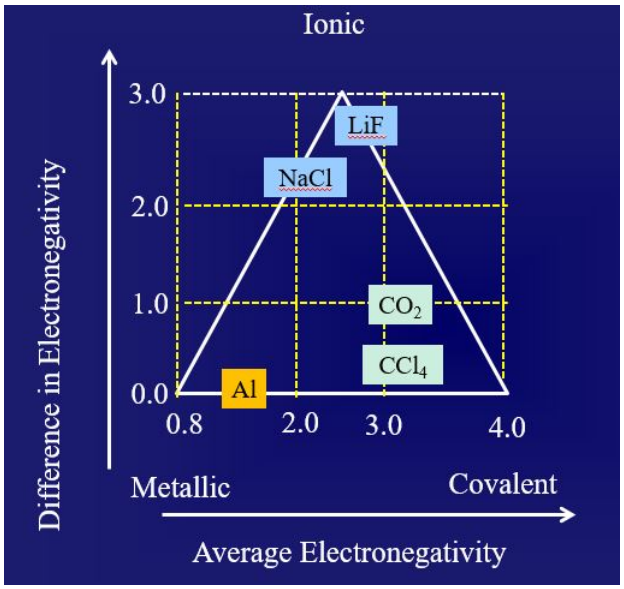


Figure 11.0.1: Van Arkel-Ketelaar diagram showing what type of bond will occur between two atoms. (Remember, due to symmetry polar bonds can result in nonpolar molecules and here we are just talking about bonds).

Chemical bonds are the result of coulombic interactions between charged particles, where like charges repel and opposite charges attract. In the case of covalent bonds, these are between electrons and the nuclei of one atom with the electrons and nuclei of another. In the case of ionic bonds, these are between cations and anions. Coulombic interactions can be described by Coulomb's Law:

$$E = k\frac{q_1 q_2}{r} \qquad F = k\frac{q_1 q_2}{r^2} \tag{11.0.1}$$

- **E is the potential energy**
- **F is the force**

- **k is a proportionality constant**
  - in a vacuum $k = \frac{1}{4\pi\epsilon_o}$
- **r is the distance** of separation (note that the potential goes to zero when they are separated by infinity)
- **q is the charge** of the ions

It is important to note that a negative potential correlates to a bond. This is a consequence of the First Law of Thermodynamics and can be understood by looking at the Quick Review on the Covalent Bond and the Potential Well. What you realize is that zero potential correlates to r approaching infinity (the ions are too far away to interact), and that from the first law of thermodynamics, positive energy correlates to adding energy to the system. To break a bond you must add energy, and if the broken bond equates to zero energy, the bond energy must be negative. This makes complete sense when you look at the potential well diagram.

Quick Review: Covalent Bond and Potential Well

Covalent bonds were introduced in sections 2.5 (Chemical Compounds) and 9.2 (Valence Bond Theory) of the first semester class, where a bond occurs when electrons on one atom become attracted to the nucleus of the other atom and these interactions can be described by the potential well. Figure 11.0.2is the potential well for diatomic hydrogen, and it should be noted that there are both are both attractive and repulsive Coulombic interactions, which result in a dynamic oscillation type of bond (see Video 2.5.1).

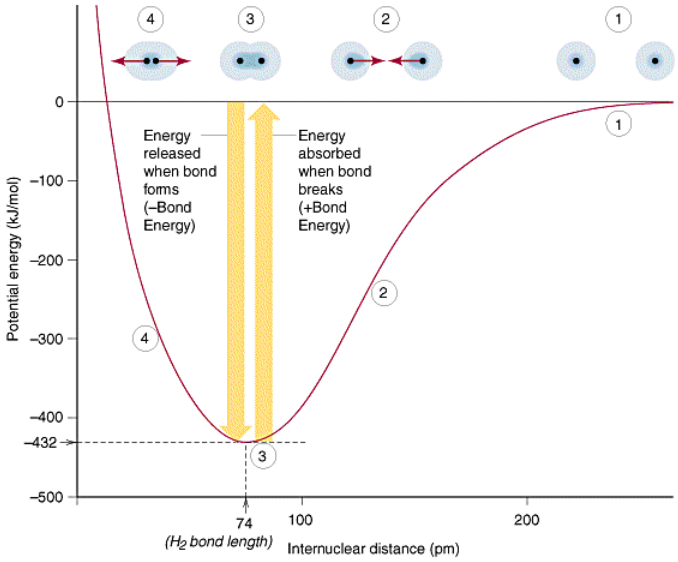


Figure 11.0.2: The potential well diagram for the formation of a sigma bond in diatomic hydrogen.When the atoms are too close nuclear/nuclear repulsion dominates, forcing them apart, when they are a bit past the "optimal distance" the nuclear/electron repulsions dominate bringing them together. They thus oscillate around an equilibrium position (the bond length). If they move too far apart the bond is broken and the atoms separate.

In this diagram there are 4 regions of the potential well.

Region 1 - Zero Interactions: When the two H atoms are separated by great distance the bond interaction is zero (the denominator of Coulomb's law is so large the value approaches zero).

Region 2 - Net Attractive Interactions: As the atoms come closer together the valence electrons of one atom are attracted to the nucleus of the other, with a net attractive force, that overcomes the nuclear-nuclear and electron-electron repulsion.

Region 3 - Oscillating Bond: The "bond length" and bond energy are described by the bottom of the curve (see Video 2.5.1) as the bond oscillates between the net attractive forces of region 2 with the net repulsive forces of region 4.

Region 4 - Net Repulsive Interactions: As the atoms get closer to each other nuclear-nuclear and electron-electron repulsions start to dominate.

Key Points

1. Bond energies of Coulombic in nature.
   - This is important as "intermolecular" forces are also Coulombic in nature.

2. Bonds are at a lower energy than the separated atoms
3. Bond energies can be described as either:
    - Formation Energies (exothermic processes)
        - Energy is released to form a bond
    - Dissociation Energies (endothermic processes
        - Energy is consumed to break a bond

Test Yourself

Homework

11.0: Prelude is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.1: States of Matter and Intermolecular Forces

Learning Goals

- Identify States of Matter
- Introduce concept of IMF (InterMolecular Forces) or van der Waals forces
- Introduce properties of matter that can depend on IMFs

We have learned how chemistry is the study of matter and how matter transforms from one type of "stuff" into another. We have been introduced to 4 states of matter and the next two chapters will look at the condensed phases of matter, the solid and liquid states. We are going to start with a quick review, and then move into the cohesive forces that hold matter together.

States of Matter:

1. Gas State (Chapter 10)
    - Compressible, variable density
    - Fluid with negligible resistance to flow
    - Dispersed state where matter fills entire volume of container
    - negligible IMFs (InterMolecular Forces)
2. Liquid State (Chapter 11)
    - Incompressible, essentially constant density
    - Fluid of measurable viscosity (resistance to flow)
    - essentially constant density (varies slightly with temperatue)
    - cohesive IMFs hold it together
3. Solid State (Chapter 12)
    - Incompressible, essentially constant density
    - Non-Fluid, maintains own shape
4. Plasma State (Chapter 1A.3.2.4, not thoroughly covered in this class)
    - High Energy State (stellar matter)
    - Has free electrons and charged particles

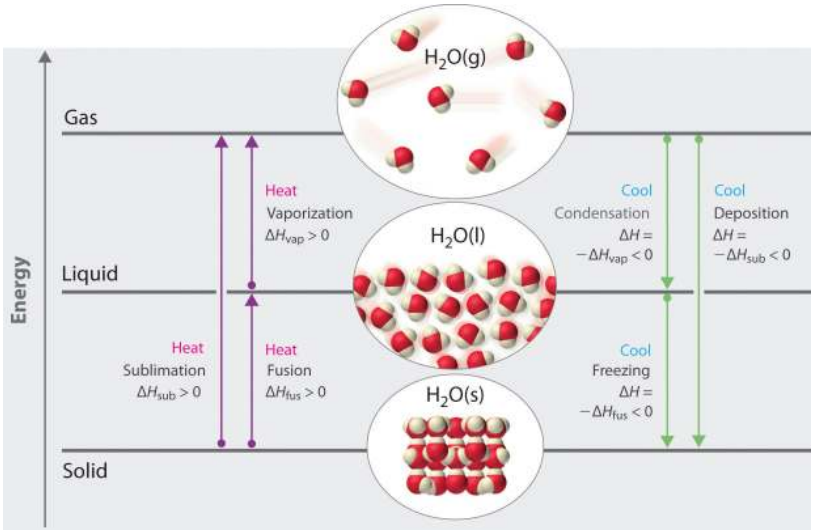


Fig. 11.1a: Energy diagram showing states of water and the phase transitions between these states.

You should already be familiar with the 6 phase transitions described in figure 11.1a

- Melting: The transition from the solid to the liquid phase
- Freezing: The transition from the liquid phase to the solid phase
- Evaporating: The transition from the liquid phase to the gas phase
- Condensing:The transition from the gas phase to the liquid phase
- Sublimation: The transition from the solid phase to the gas phase
- Deposition: The transition from the gas phase to the solid phase

It should be mentioned that the majority of matter in the universe is in a fourth state, the plasma state, which we will not be considering in this chapter. A plasma is a high energy gas with free moving positive ions and electrons flowing around. Stars are in the plasma state and it is actually the most common state in the universe. Figure 11.1b shows the transitions between all 4 states of matter.

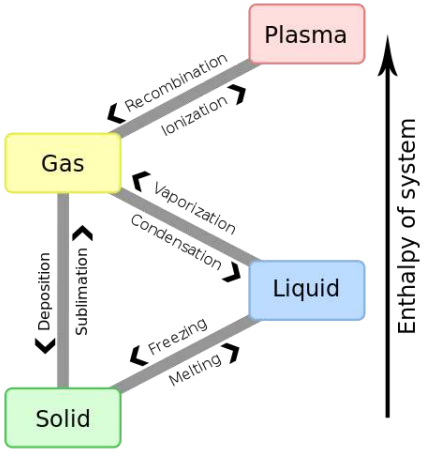


Fig. 11.1b: Four states of matter with transitions between them.

Intermolecular Forces (IMF)

The the term InterMolecular Force (IMF) literally means the forces between molecules, and as such, is often a misnomer, as simply speaking, not all matter is composed of molecules. Yet this term is used pervasively, and so we will use it, but first lets compare it to the so called "intramolecular forces", the forces within the proverbial "molecule." We typically consider two types of bonds, ionic (which are not molecular) and covalent (which are molecular). So if I have liquid water, where the discrete entity of matter is the H_2O molecule, there are two type of bonds, those between H and O of a water molecule (covalent intramolecular) and those between the H of one molecule and the O of another (intermolecular).

Shortcomings of the term Intermolecular

1. We classify bonds between an ion and polar molecule as intermolecular, when in reality, the ion need not be a molecule (polyatomic ions are molecules, monatomic ions are not).
2. Not all covalently bonded compounds are molecules with discrete formula, like diamond, which is a covalent network, and so even though it is a covalently bonded entity, it does not fit the paradigm of a molecule with a unique molecular formula.

With these shortcomings in mind we are going to look at the following types of Intermolecular Forces. It should also be noted that the later types of forces are also called van der Waals forces, which are the short range forces of attraction between atoms or molecules that do not fit into the model of a covalent or ionic bond.

Types of Intermolecular Forces

1. Ion-Dipole Forces (these may not be true IMF, but we will call them IMFs)
   - Solutions
2. Dipole-Dipole Forces (between two polar molecules)
   - Pure substance or solutions
3. Hydrogen Bonding (special type of dipole-dipole)
   - Pure substance or solutions
4. Dipole-Induced Dipole (between polar and nonpolar molecules)
   - Solutions
5. Instantaneous Dipole-Induced Dipole (between two nonpolar molecules, often called London Dispersion Forces)
   - Solutions or Pure Substances

Please note that in recognizing what type of intermolecular forces are involved we need to know if a molecule is polar or non-polar. This requires a review of Lewis Dot Structures, VSEPR Theory, Electronegativety, and Bond Polarity.

Properties of Matter that Depend on IMFs

- boiling point, melting point, stable phases
- enthalpies of phase transitions
- vapor pressure
- solubility and miscibility of different substances
- viscosity

There are many physical properties of matter that are strongly influenced by IMFs, and over the next few chapters we will look at many of these. Lets ask a simple question;

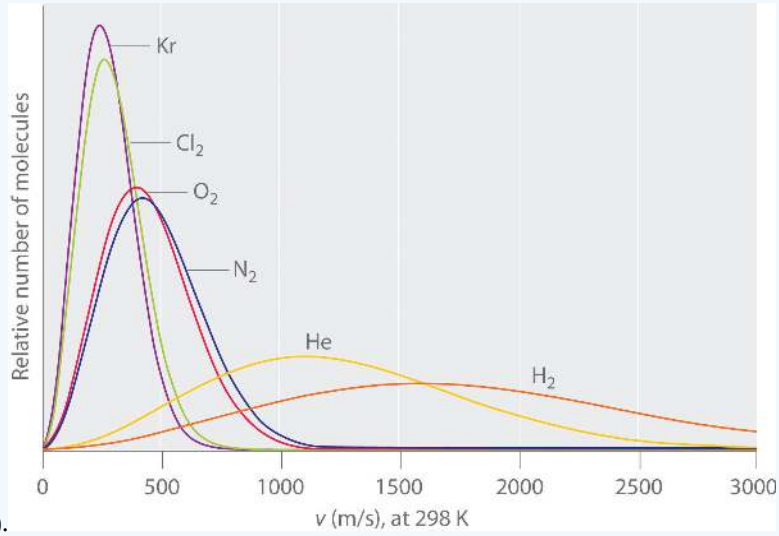
Exercise 11.1.1

At a given temperature, would it be easier to vaporize a light molecule or a heavy molecule?

Answer

You need more information. From our study of gases and the Kinetic Molecular Theory we learned that the average kinetic energy of a molecular system is proportional to the absolute temperature, and both molecules have the same average kinetic energy, and so at first thought, we would predict that the lighter molecule would tend to have the higher velocity (review Graham's Law of Effusion) and be easier to vaporize (see image below).

The problem is we need to identify the intermolecular forces that attract the molecules to each other, and if the lighter molecule had stronger intermolecular forces, this would be wrong. Look at the case of carbon dioxide and water (the next question deals with this).



Note: This image is for the velocity distribution of a gas at a given temperature, and not a liquid, but the concept is valid, in that if all other things are equal, lighter molecules tend to move faster, and gas phase systems move faster than liquid. The problem is, there are often other factors, as indicated in the next question, on why is carbon dioxide a gas at ambient questions while water is a liquid?

Exercise 11.1.2

So why at ambient conditions is Carbon Dioxide (the heavier molecule at 44 amu) a gas, but water (the lighter molecule at 18 amu) is a liquid?

Answer

That is, shouldn't it be easier to vaporize the lighter molecule than the heavier one? The answer lies within the Intermolecular Forces, and if you review molecular shapes and polarity you will see that water is a polar molecule while carbon dioxide is non-polar, and this leads to different physical properties like the boiling and melting points. That is, in this chapter you will learn that water has stronger intermolecular forces than carbon dioxide, and that is why it is a liquid, while carbon dioxide is a gas. But to answer that question you first had to determine the Lewis Dot Structure, then determine the geometry, and then determine the polarity of the molecule, and so you should have a basic understanding of that pre-requisite material before proceeding.

Another interesting things to note about molecular properties that result from IMFs is that they are not really properties of a single molecule, but the result of an ensemble or large system of many molecules, which must be viewed as a whole, and not as individual molecules. Simple speaking, an individual molecule can not have a boiling point, which is really a function of the interaction between a large number of molecules. So the boiling point of water is not a property of a water molecule, but a bunch of water molecules. So, if you have a liquid at a given temperature there is a distribution of velocities, some of the molecules have enough kinetic energy to escape the attractive cohesive forces on the surface and enter the vapor phase, while others do not. So the vapor pressure above a liquid is also influenced by intermolecular forces. The point is some properties of a substance, like it's atomic mass or its polarity, are the property of a single molecule, while others, like the melting point or vapor pressure, are the properties of a huge number (ensemble) of molecules

Test Yourself

Homework

This page titled 11.1: States of Matter and Intermolecular Forces is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

11.2: Ion-Dipole Forces

Ion-Dipole Interactions

Ion-Dipole Forces are involved in solutions where an ionic compound is dissolved into a polar solvent, like that of a solution of table salt (NaCl) in water. Note, these must be for solutions (and not pure substances) as they involve two different species (an ion and a polar molecule).

$$Na^+ \leftrightarrow (H_2O)_n$$

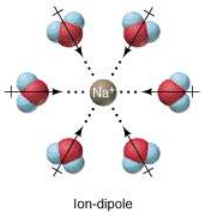


Figure 11.2.1: Ion-Dipole interaction. Note the oxygen end of the dipole is closer to the sodium than the hydrogen end, and so the net interaction is attractive (see figure 11.2.2).

The name "Ion dipole forces" describes what they are, which simply speaking, are the result of the Coulombic electrostatic interactions between an ion and the charged ends of a dipole. Note that here, the term **"Intermolecular Force" is a misnomer**, even though it is commonly used, as these are the forces between ions with molecules possessing a dipole moment, and ions do not have to be molecular. To gain an understanding of the nature of these forces we can start by looking at the Coulombic potential between two ions (Equation 11.2.1) and ask the following question.

Exercise 11.2.1

What is the difference between Coulombic Ion-Ion and Ion-Dipole interactions in terms of the distance between the particles?

Answer

One is an inverse distance relationship, the other is an inverse distance square relationship. The following material explains this.

In the introduction to this chapter we saw that two charged particles q_1 and q_2 had a potential energy related to Equation 11.2.1, and this describes the potential energy interaction between two ions.

$$\underbrace{E = k\frac{q_1 q_2}{r}}_{\text{ion-ion potential}} \tag{11.2.1}$$

For ion-dipole interactions the interaction is between a dipole moment (μ), which is really a vector with a magnitude of $\delta \cdot r$, where δ is the value of the partial charge in the dipole moment (δ^+ or δ^-, noting they are of the same magnitude, just opposite in sign), with an ion of charge q. (We are using δ to indicate the partial charge in the dipole just to prevent it from being confused with q, the charge of the ion).

So there are two ion-dipole interactions, with one being attractive and the other repulsive, as shown in figure 11.2.2

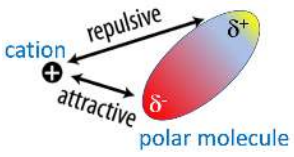


Figure 11.2.2: *Interactions between a positive cation and a polar molecule.*

Now if you think about it, the cation repels the positive end of the dipole and attracts the negative end, so the negative end is closer to the cation than the positive end. This means the attractive energies are greater than the repulsive (as they are closer together, the r of coulombs law is in the denominator of eq. So the net force is attractive since the radius (in the denominator of Coulombs Law, Equation 11.2.1) for the +/- attraction is smaller than the radius for the +/+ repulsion. This difference is greatest when the polar molecule is "touching" the cation, and as they become further separated the relative differences in the radii between the two interactions become less, and at great distances they become equal, making these short range forces. This can be understood by looking at Figure 11.2.3

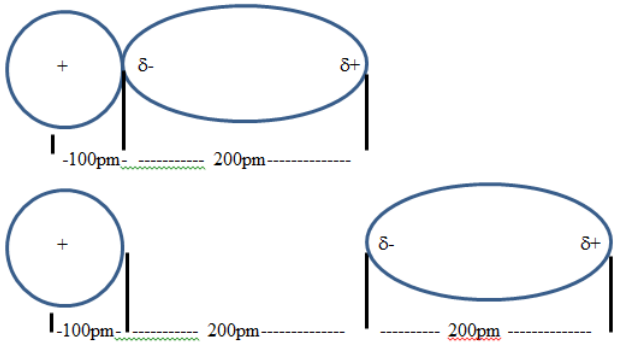


Figure 11.2.3: *Showing how the relative distance between the ion-dipole interaction falls off as they become separated. In the top interaction the +/+ radius is 3 times as far as the +/- (300 pm to 100 pm), but in the bottom it is 5/3rds as far (500 pm to 300 pm) and so the difference between the repulsive and attractive forces is less. That is, at large distances the distances between the ion and the two partial charges narrow with a consequent cancelation of the effect.*

The result in an inverse square of the distance function ($1/r^2$) for the decrease for ion-dipole interactions as compared to a 1/r effect for ion-ion interactions, as shown in Equation 11.2.2.

$$\underbrace{E \propto \frac{-|q_1|\mu_2}{r^2}}_{\text{ion-dipole potential}} \tag{11.2.2}$$

or

$$\underbrace{E = -k\frac{|q_1|\mu_2}{r^2}}_{\text{ion-dipole potential}} \tag{11.2.3}$$

(ion-dipole potential)

- α means "proportional to" (the proportionality constant depends on the medium)
- r is the distance of separation.
- q is the charge of the ion (only the magnitude of the charge is shown here.)
- k is the proportionality constant (Coulomb's constant).
- μ is the permanent dipole moment of the polar molecule (sections 8.7.4.2 and 8.8).
  From section 8.7 and 8.8 we treat define the dipole moment by the following equation

$$\vec{\mu} = q\,\vec{r} \tag{11.2.4}$$

where q is the partial charge of each end of the dipole (δ^+ *or* δ^-) and r is the separation between the charges within the dipole, but these symbols are being used to describe the ion interactions in equations 11.2.1-11.2.3, and so we will rewrite eq. 11.2.4 with δ instead of q representing the magnitude of the partial charge of the dipole (δ^+ *or* δ^-) and $\vec{d}$ representing the distance between the center of positive and negative charge in the polar molecule $\vec{r}$.

$$\vec{\mu} = \delta\,\vec{d} \tag{11.2.5}$$

Realize eq. 11.2.4 is the most common way to describe the dipole moment, but when looking at ion-dipole interactions there are two types of charges (those of the ion, and the partial charge separations of the dipoles), and two types of distance, the distance between the ion and dipole, and the distances between the dipoles. So for this section we will rewrite eq. 11.2.4 in terms of 11.2.5.

> **Note**
>
> Equations 11.2.1 and 11.2.3 are dimensionally equivalent. This is because μ has the units charge times distance (Equation 11.2.4), and if you substitute eq. 11.2.5 into eq. 11.2.3, you will see it is dimensionally equivalent to 11.2.1

Key differences between ion/ion and ion/dipole interactions

1. Ions have integer charges (1,2,3.. for cations and -1,-2,-3... for anions), while dipole's have partial charges ($\delta^{+ \, or \, -}$) and the partial charges can be very small fractions.
2. Ion-ion interactions fall off slower than ion-dipole. Tripling the distance between two ions reduces the energy by 1/3, while tripling the distance between the ion and a dipole reduces it by 1/9. That is, one is inversly proportional to the distance between them (1/r) and one is proportional to the inverse square of the distance ($1/r^2$).

Exercise 11.2.2

Why does the Coulombic ion-dipole equation (11.2.2) have a negative sign and the absolute value on the charge, while the ion-ion equation (11.2.1) does not?

Answer

- The ion dipole interactions are always attractive resulting in a lowering of the potential energy. Since μ is always positive, but q can be positive (cation) or negative (anion), so we use it's absolute value and add the negative sign to ensure there is a lowering of energy. For ion-ion, they can be attractive (+/-) which results in a negative E, or repulsive (+/+ or -/-), both of which result in a positive E.

Exercise 11.2.3

How does the ion-dipole equation show that ion dipole interactions are shorter range than ion-ion interactions?

Answer

- The ion-ion interaction energy is inversely proportional to the distance between the ions (1/r), while the ion-dipole energy is inversely proportional to the square ($1/r^2$). So doubling the distance decreases the first by a factor of 2, and the later by a factor of 4 (and tripling the distance decreases the first by a factor of 3, and the later by a factor of 9). So ion dipole interactions are much shorter ranged.

It also needs to be understood that these equations are based on electrostatic interactions and molecules in a solution are rotating and vibrating and actual systems are quite complicated, with the medium (molecular environment) influencing the actual behavior. Coulombs constant is based on the permittivity of an electric field in a vacuum, and actual chemical systems are not in a vacuum, and so the permittivity will be different. The important thing to realize is that these interactions are Coulombic in nature, and these equations show this in terms of the magnitude of the charges and their distances from each other, which are the two major factors influencing the strength of intermolecular forces. In this class we will not be calculating dipole moments or the magnitudes of them, but understanding how to read the equations, and developing qualitative understandings that allow us to predict trends.

It should also be understood that not all ion-dipole interactions are in solutions. For example, hydrated salts where the water is "captured" in a crystal's interstitial regions (holes in the lattice) are ion-dipole in nature. In fact these can be necessary to form certain crystalline geometries as the polar water molecule can reduce the repulsion of like charges within a lattice. We will look at crystals in the next chapter.

Periodic Trends and Hydration Energy

The enthalpy of hydration is often defined as the energy released when a mole of a gaseous cation is dissolved in water, and is related to ion-dipole forces.

$$M^+_{(g)} + water \rightarrow M^+_{(aq)} \tag{11.2.6}$$

The smaller the cation, the closer the particles, and for a given charge the stronger the ion-dipole forces and the greater the enthalpy of hydration (more exothermic). This is exemplified by the enthalpies of hydration in Table 11.2.1. It needs to be noted that the above definition aligns with thermodynamic principles, where greater means more exothermic (negative). That is, from the first law of thermodynamics a positive energy change occurs when is energy added to the system (endothermic) and a negative energy change occurs when is is released (exothermic). The small Lithium ion has a lower value (-515 kJ/mol) than the larger Cesium (-263 kJ/mol), meaning it is more exothermic, and more energy is released. This may be easier to see by looking at the back reaction, where you need to add energy to remove the hydrated ion and place it in the gas phase, since adding energy is endothermic, the reaction as drawn must be exothermic.

Table **11.2.1***: Enthalpies of hydration for alkali metals show the smaller the radi the larger the energy, and this is related to the ion-dipole forces of the solvated ions.*

Cation	Ionic Radius (pm)	Enthalpy of Hydration (kJ)
Li^+	90	-515
Na^+	116	-405
K^+	152	-312
Rb^+	166	-296
Cs^+	181	-263

From general chemistry 1 students should know the trends in the sizes of ions, and based on these, they should be able to predict the relative rankings of the ions in table 11.2.1. Since lithium is smaller, it would take more energy to remove it, so the formation of the hydrated ion is more exothermic (negative) than the large Cesium. You must always correlate the sign of an energy to its process, and recognize that you can "form" or "break" any bond or intermolecular force. As written, this is the formation, which is the exothermic process. If you had written the reverse reaction, all the values would be positive.

Hydrated Salts: Ion-dipole forces also explain why many salts will trap water when they crystallize and form hydrated salts. This is common for small cations like sodium and lithium, which form hydrates like sodium carbonate decahydrate Na_2CO_3-$10H_2O$, while larger salts like rubidium and cesium do not tend to form hydrates, as they have weaker ion-dipole interactions.

Test Yourself

Homework

References

1. Chemical Principles: Atkins and Jones

Contributors and Attributions

- Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:
- Anonymous

This page titled 11.2: Ion-Dipole Forces is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

11.3: Dipole-Dipole Forces

Dipole–Dipole Interactions

Dipole-Dipole interactions occur between **polar molecules.** In section 8.8 we learned that polar covalent bonds occur between atoms of different **electronegativity** (section 8.7), where the more electronegative atom attracts the electrons more than the electropositive atom, and based on the geometry, this may or may not result in a polar molecule. If the center of positive charge (defined by the nuclei) does not coincide with the center of negative charge (defined by the electron orbitals), the molecule is polar, which is easiest to visualize for nonsymmetric orientations of bonds between atoms of different electronegativities. That is, a polar molecule with a permanent dipole results if all the bond dipole vectors add to a net dipole. In this case the molecule's center of positive charge (denoted by δ^+) does not coincide with the center of negative charge (denoted by δ^-) and the molecular dipole moment (μ) is this partial charge times the distance between them. Please review sections 8.7 and 8.8 if needed, and remember that if bond dipoles are of symmetric orientation, like in the linear carbon dioxide, they cancel each other and the molecule is non-polar. So polar bonds can result in non-polar molecules! You should also note that the center of positive charge need not be where there is a nucleus. For example, in water, the center of positive charge is half way between the two hydrogens.

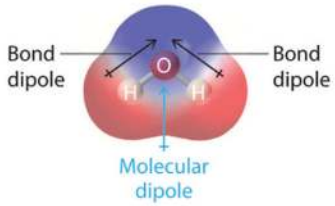


Figure 11.3.1: Water's dipole moment has a positive center between the two nuclei of the hydrogens.

Although molecules in a liquid are in constant motion, they tend to align in the lowest energy orientation, which would be to maximize attractions (parts a & b of fig. 11.3.1) and minimize repulsion (parts c & d of fig. 11.3.1). This follows the same logic we used for ion-dipole interactions, in that the attractive interactions cause dipoles of opposite charge to be closer, resulting in stronger interactions, while dipoles of like charge tend to be farther apart, resulting in reduced interactions. Therefore, unlike ion-ion interactions, but like ion-dipole interactions, dipole-dipole are always attractive.

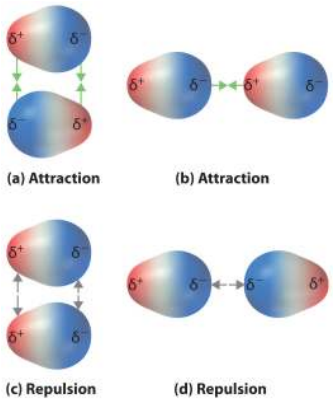


Figure 11.3.2: *Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.*

Exercise **11.3.1**

Why are the attractive forces greater than the repulsive?

Answer

Molecules in a liquid are in constant motion and experience both attractive and repulsive dipole–dipole interactions, as shown in Figure 11.3.2. For reasons similar to those outlined in the section on ion-dipole forces (11.2), the attractive interactions dominate the repulsive because the attraction causes them to be closer together, which increases the Coulombic interactions. Likewise, the repulsions mean they move farther away, which reduces the Coulombic interactions.

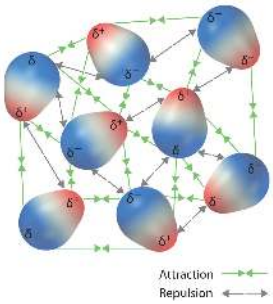


Figure 11.2.2: Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules

The equation for dipole-dipole potential energy is

$$E\,\alpha\,\frac{-\mu_1\mu_2}{r^3} \qquad (11.3.1)$$

$$or$$

$$\underbrace{E=-k\frac{\mu_1\mu_2}{r^3}}_{\text{dipole-dipole potential}}$$

This can be compared to eq. 11.2.1 (ion/ion) and 11.2.2 (ion-dipole), and it becomes clear that the dipole-dipole forces are even shorter range. (remember μ =qd, where q is the *|($\delta^{+/-}$)| of the dipole, and d is the distance between δ^+ and δ^-*. This is further weaker because the magnitude in the charge is a partial charge and less than 1, while the charge in an ion is +/- 1, 2,3...(an integer multiple of 1).

Note that R is an inverse cube power, and so doubling the distance reduces the energy by a factor of 8. Also note that this is consistent with eq.'s 11.2.2 and 11.2.4 because the term mu has distance built into it.

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge.

Exercise 11.3.2

Show how $\frac{-\mu_1\mu_2}{r^3}$, $\frac{-|q_1|\mu_2}{r^2}$ and $\frac{q_1q_2}{r}$ are dimensionally equivalent?

Answer

$\frac{-\mu_1\mu_2}{r^3}=\frac{(dq_1)(dq_2)}{r^3}$, which has units of $\frac{charge^2}{length}$

$\frac{-\mu_1|q_2|}{r^2}=\frac{(dq_1)(q_2)}{r^2}$, which has units of $\frac{charge^2}{length)}$

$\frac{q_1q_2}{r}$, has units of $\frac{charge^2}{length)}$

In summary, the above relationships show that the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–dipole interactions, which in turn fall off quicker than ion-ion interactions. Doubling the

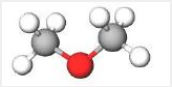
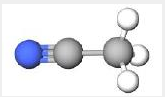
distance ($r \rightarrow 2r$) decreases the attractive energy between ions (which is proportional to 1/r) by one-half, which increases ion-dipole by 1/4, that is ($1/2^2$), while dipole-dipole interactions decrease to 1/8 ($1/2^3$).

Boiling Point Trends

Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases. Using what we learned about predicting relative bond polarities from the electronegativities of the bonded atoms, we can make educated guesses about physical properties that depend on intermolecular forces, like the relative boiling points of similar molecules.

Exercise 11.3.3

Given the following information:

Compound	C_3H_6 (cyclopropane)	CH_3OCH_3 (dimethyl ether)	CH_3CN (acetonitrile)
Structure			
Molar Mass (g/mol)	42	46	41

(a) Associate the following Dipole Moments with the above compounds: Zero D, 1.30 D and 3.9 D. (Hint: rank in order of increasing polarity)

Answer

Cyclopropane is nonpolar and is zero, dimethyl either is 1.30 and acetonitrile is 3.9. The cyclopropane was a gift, but differentiating the second two is tougher, as oxygen is more electronegative (χ = 3.5) then nitrogen (χ=3.0), but acetonitrile is linear while dimethyle ether is bent, and part of the two bond dipoles cancel, and the later has a far greater effect (both oxygen and nitrogen are highly electronegative). That is, the dipole for dimethyl ether goes straight up from the oxygen to in between the two carbons, and the horizontal components cancel out. In acetonitrile there is no such cancellation.

(b) Associate the following boiling points with the above compounds: Rank in order of increasing boiling point. 240K, 248K & 355K

Answer

The boiling points follow the trends in the strength of the intermolecular forces, so cyclopropane is 240K, dimethyl ether is 248 and acetonitrile is 355.

Test Yourself

Homework

This page titled 11.3: Dipole-Dipole Forces is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

11.4: NonPolar Molecules and IMF

Introduction

Van der Waals interactions are very weak short range interactions involving non-polar molecules and are inversely proportional to the 6th power of the distance of separation. There are two types of IMF involving non-polar molecules.

1. **Dipole-Induced Dipole:** The Intermolecular forces between a polar and non-polar molecule.

$$E = -k\frac{\mu_1^2\alpha_2}{r^6} \tag{11.4.1}$$

2. **Instantaneous Dipole-Induced Dipole**: (London Dispersive Forces) The intermolecular forces between two nonpolar molecules.

$$E = -k\frac{\alpha_1\alpha_2}{r^6} \tag{11.4.2}$$

- k is the proportionality constant (this is not Coulomb's constant, it has different units)
- r is the distance of separation between the molecules.
- α is the polarizability of the non-polar molecule (see below), it has units of C m^2V^{-1}.
- μ is the permanent dipole moment of the polar molecule.

$$\vec{\mu} = q'\,\vec{d} \tag{11.2.3}$$

where q' is the partial charge of each end of the dipole ($\delta^+ or\ \delta^-$) and d is the separation between the charges within the dipole

Polarizability (α)

The ease with which an electron cloud can be distorted by an electric field is its polarizability.

$$\mu_{ind} = \alpha E \tag{11.4.3}$$

Where

- E denotes the strength of the electric field and
- α is the polarizability constant with units of C m^2V^{-1}.

All molecules are polarizable, but this is important in nonpolar symmetric molecules as it relates to how easy an external field can induce a dipole in the otherwise nonpolar molecule, and give it polar character. When an external electric field is applied it can attract electrons towards its positive pole and repulse them from its negative pole, which induces ("brings about or gives rise to") a dipole. The "tighter" the electrons are held by the molecule's nuclei the harder it is to induce a dipole, the "looser" the electrons are held, the easier it is to induce a dipole. The Polarizability (α) of a molecule is a measure of the ease with which a dipole can be induced. Molecules with a large $alpha$ are easy to induce a dipole.

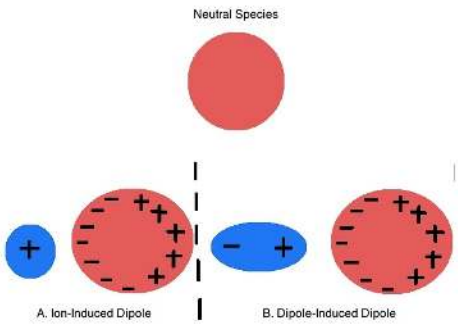


Figure 11.4.1: *A neutral nonpolar species's electron cloud is distorted by (A.) an Ion and (B.) a polar molecule, to induce a dipole moment.*

Note, α has distance square in the denominator

In general, polarizability inversely correlates with the strength of the interaction between electrons and the nucleus. The tighter the valence electrons are held by the nuclei the less polarizable the molecule or atom. Conversely, well shielded valence electrons that are far from the nuclei in diffuse orbitals are highly polarizable, and easily distorted by external electric fields. In figure 11.4.1, the Electric field is coming from the (A.) positive charged ion, and (B.) the positive end of the dipole. Note, if a negative ion (or negative end of a dipole) approached a neutral molecule, the opposite would occur, as it would repel electrons, inducing a positive dipole in the neutral molecule that is near it, and a negative one that is far away.

Factors that Influence Polarizability

The relationship between polarizability and the factors of electron density and atomic radii, and molecular orientation are as follows:

1. The greater the number of electrons, the greater the polarizability.
2. The greater the distance of electrons from nuclear charge, the greater the polarizability of the atom.

Exercise 11.4.1

Rank the noble gasses in order of increasing polarizability (least to most)

Answer

He<Ne<Ar<Kr<Xe<Rn

Dipole-Induced Dipole Forces

These occur between a polar molecule and a nonpolar molecule, and thus must describe solutions. The polar molecule with a permanent dipole induces a dipole moment in the non-polar molecule. The more polarizable the nonpolar molecule, the easier it is to induce a dipole, and so the greater the interaction. .

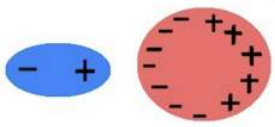


Figure 11.4.d: Dipole (blue) inducing a dipole in an otherwise non-polar (red) molecule

$$E = -k\frac{\mu_1^2\alpha_2}{r^6} \tag{11.4.4}$$

These are the intermolecular forces for the dissolution of many types of gases in a solvent like water. The most common gases in the atmosphere are small nonpolar compounds like nitrogen, oxygen and carbon dioxide. A saturated solution of oxygen is 256 \mu M, or 2.56x10^{-4} moles/l, which is an indication of how weak these intermolecular forces are. Larger and more polarizable nonpolar molecule tend to have higher solubility in polar solvents than smaller molecules of lower polarizability. We need to be careful in extrapolating trends here though, especially if the solute is not a gas, and will take a more detailed look at solutions in chapter 13, where in addition to the solute/solvent interactions described by dipole-induced dipole interactions of polar/nonpolar intermolecular interactions, we will also take into account solute/solute and solvent/solvent interactions.

Instantaneous Dipole-Induced Dipole Forces (London Dispersion Forces)

Instantaneous Dipole: A non-polar molecule like H_2, O_2 ,He or Ne are symmetric with their center of electron density over all time coinciding with their center of positive charge, resulting in a symmetric non-polar molecule. This symmetry is actually the time average of the molecular wavefunction, and at any instant in time the electron distribution may be asymmetric, resulting in short lived transient dipole moment. This is called an instantaneous dipole.

Induced Dipole: Just as ions and polar molecules can induce a dipole moment in an adjacent nonpolar molecule, so can an instantaneous dipole. The polarizability is a measure of how easy it is to induce a dipole. For symmetric nonpolar molecules these

can form waves as successive instantaneously induced dipoles that in turn induce dipoles on their neighbors, and thus are often called dispersion forces.

London Dispersion Forces and Polarizability

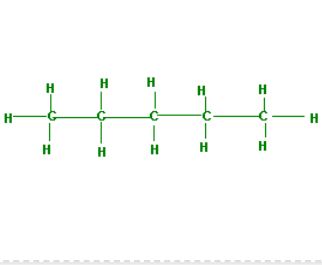
The dispersion force is the weakest intermolecular force. It is an attractive force that arises from an instantaneous dipole inducing a transient dipole in an otherwise non-polar molecule. Surrounding molecules are influenced by these temporary dipole moments and a sort of chain reaction results in which subsequent weak, dipole-induced dipole interactions are created. These cumulative dipole-induced dipole interactions create the attractive dispersion forces. Dispersion forces are the forces that make nonpolar substances condense to liquids and freeze into solids when the temperature is low enough. These occur with polar molecules too, but since they are weaker, they are normally negligible.

Polarizability affects dispersion forces in the following ways:

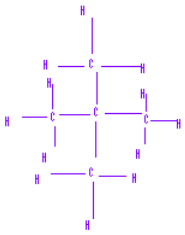
- As polarizability *increases*, the dispersion forces also become *stronger*. Thus, molecules attract one another more *vigorously* and melting and boiling points of covalent substances *increase* with *larger* molecular mass and volume.
- Polarazibility also affects dispersion forces through the molecular shape of the affected molecules. Elongated molecules have electrons that are less tightly held, increasing their polarizability and thus strengthening the dispersion forces.

Exercise 11.4.2

Consider two isomers of C_5H_{10}, n-pentane and neopentane (2,2-dimethylepropane). Note, isomers are different molecules with the same molecular formula (C_5H_{10}, these are called "structural isomers" because the atom connectivity is different).



n-pentane



neopentane (2,2-dimethylepropane)

(a) What are the dominant intermolecular forces for these isomers

Answer

Since these are both nonpolar, they have London Dispersion or Instantaneous-Induced Dipole interactions

(b) Which has the stronger intermolecular forces and why?

Answer

n-pentane is more elongated and so has a larger polarizability, and thus has stronger dispersion forces than the tighter neopentane

(c) n-pentane bp=36^{o}C, while, neopentante bp=10^{o}C, why are they different?

Answer

n-pentane has the stronger dispersion forces, and thus requires more energy to vaporize, with the result of a higher boiling point.

Van der Waals Forces

It should be noted that short range molecular interactions with a $1/r^6$ distance dependency are collectively referred to as Van der Waals interactions, being named of Johannes van der Waals. These include dipole-dipole forces in the gas phase, London

dispersion forces and dipole-induced dipole forces. It should also be noted that London dispersion forces occur all the time, but are often negligible compared to other forces.

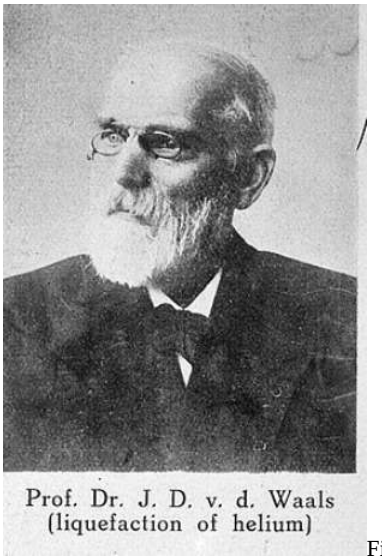


Figure 11.4.5: Johannes Diderik van der Waals (1837-1923), Dutch physicist and thermodynamicist who studied gasses and their condensation to liquids. (CC0: WikiMedia Commons)

In van der Waals thesis he not only postulated the existence of molecules (atoms were actually still being disputed at the time), but was one of the first to postulate intermolecular forces between them, which have often been collectively lumped into "van der Waals forces". The van der Waals equation of state for gases took into account deviations from ideality due to the volume of gases and their intermolecular attractions. The size of molecules are often identified by their van der Waals radii.

Test Yourself

Homework

Sources: Chemical Principles: The Quest for Insight, 4th Ed., Atkins & Jones

This page titled 11.4: NonPolar Molecules and IMF is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

11.5: Hydrogen Bonds

Introduction

Figure 11.5.1: In this rotating model oxygen are red, carbon grey and hydrogen white.

Hydrogen bonds are a strong type of dipole-dipole interaction. As a Rule of Thumb, they are weaker than covalent and ionic ("intramolecular") bonds", but stronger than most dipole-dipole interactions. There are two requirements for hydrogen bonding.

Two Requirements for Hydrogen Bonding:

1. **First molecule has hydrogen attached to a highly electronegative atom (N,O,F).**
   - (hydrogen bond donor)
2. **Second molecule has a lone pair of electrons on a small highly electronegative atom (N,O,F).**
   - (hydrogen bond acceptor)

Highly electronegative atoms like N, O, and F can not completely remove the valence electron from hydrogen and form an ion because there are no core electrons in hydrogen. Removing the hydrogen's 1s electron would produce a subatomic particle, the proton, whose small size results in a high charge density that would pull back the electron. So it will not happen. The result is that hydrogen forms polar covalent bonds when attached to an electronegative atom and does not form ions. The electronegative atoms pull on the valence electron "deshields" the hydrogen's proton resulting in a large $\delta+$ charge over a small area. A highly electronegative atom has a large $\delta-$ charge and if it has a lone pair of electrons, they are strongly attracted to the "deshielded proton" of another hydrogen and create a hydrogen bond. It should also be noted that the small size of the hydrogen allows it to move in real close, resulting is a strong bonding interaction.

? Exercise 11.5.1

How many hydrogens in figure 11.5.1 can form hydrogen bonds?

Answer

Only one, the one at the very top which is attached to the highly electrongative oxygen atom (red), all the others are attached to carbon and can not hydrogen bond.

Does Chlorine form Hydrogen Bonds?

Even though chlorine is highly electronegative, the best answer is no, and in this class we will consider chlorine not to form hydrogen bonds (even though it has the similar electronegativity as oxygen - 3.16 vs. 3.44). This is because chlorine is large and its lone electron is in a diffuse orbital, covering a large area, and thus do not have the high charge density to act as a strong hydrogen bond acceptor. But it does form weak hydrogen bonds in solid crystalline hydrogen chloride at very low temperatures.

H-Bonds and Water

H-bonding occurs in water. In the liquid state they are rapidly being formed and broken as the mobile particles move over each other. Note in figure 11.5.2 that there are two types of O-H bonds, the intramolecular O-H bond within a molecule (bond length = 1.01Å) and the intermolecular bond between atoms (bond length = 1.75Å). The closeness of the bond length indicates that the intramolecular bond is very strong, and of comparable magnitude to the intramolecular one. On a macroscopic scale this is obvious to anyone who falls on ice (frozen water) and quickly realizes how hard it is, and how strong the bonds are that hold the water molecules to each other.

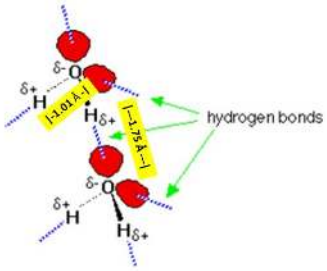


Figure 11.5.2: Hydrogen bonding interactions within water. Note the similarity in length between the intermolecular O---H bond, and the intramolecular O-H bond.

Water also has two lone pairs and two H atoms attached to the highly electronegative oxygen. This means each water molecule can participate in up to 4 bonds (two where it is the h-bond acceptor, and two where it is the h-bond donor). One interesting consequence of this is that water forms a 3D crystalline structure that is sort of based on a distorted tetrahedron. That is, the oxygen is sp^3 hybridized with a tetrahedral electronic geometry, having two bonding orbitals and two lone pairs. All of these are involved with hydrogen bonds. The lone pairs are functioning as H-bond acceptors, and the hydrogen on the bonding orbitals are functioning as h-bond donors. So each oxygen is attached to 4 hydrogens, two are 1.01Å covalent bonds and two are 1.75 Å hydrogen bonds, and this results in a structure like figure 11.5.3, which has lots of void space, and the consequence that ice is less dense than liquid water and floats.

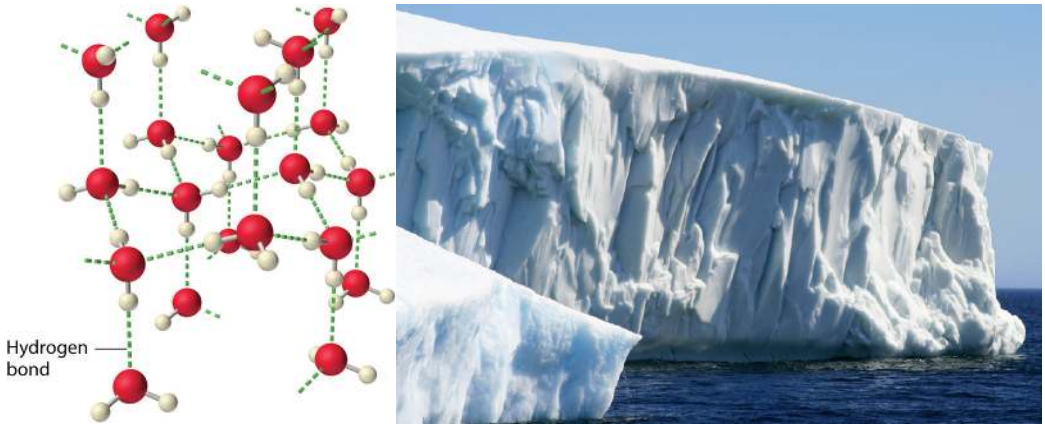


Figure 11.5.3: Hydrogen bonding and the crystal structure of ice (left), which floats on liquid water (cc0.0, negative space)

The fact that ice floats has great ramifications for life. The ice, with it's void space, acts as an insulator. If the ice sunk to the bottom, lakes would completely freeze and aquatic life like fish would not be able to survive the winters.

Hydrogen Bonding and Biology

We have all heard of DNA, which consists of nucleotide strands that join together to form the infamous double helix. DNA helix showing the base pairs adenine/thymine (A-T) an Guanine/Cytosine. (G-C), which form the double helix through the base pair interactions that are made through hydrogen bonding (11.5.4).

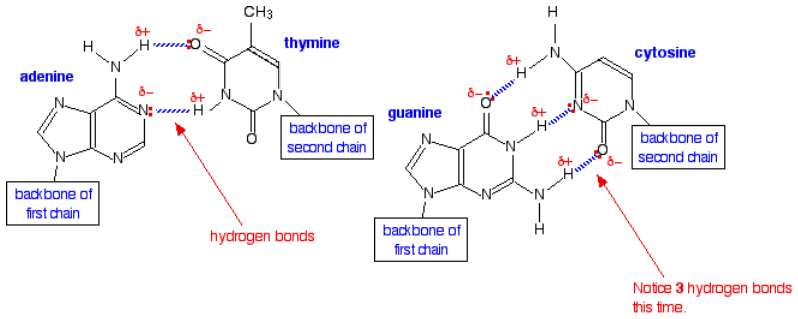


Figure 11.5.5: The adenine-thymine base pair held together by two hydrogen bonds(left) and the guanine-cytosine base pair held together by three hydrogen bonds (right). These are the

Proteins are based on amino acids and have four structural levels (Figure 11.5.5): Primary, Secondary, Tertiary, and Quaternary.

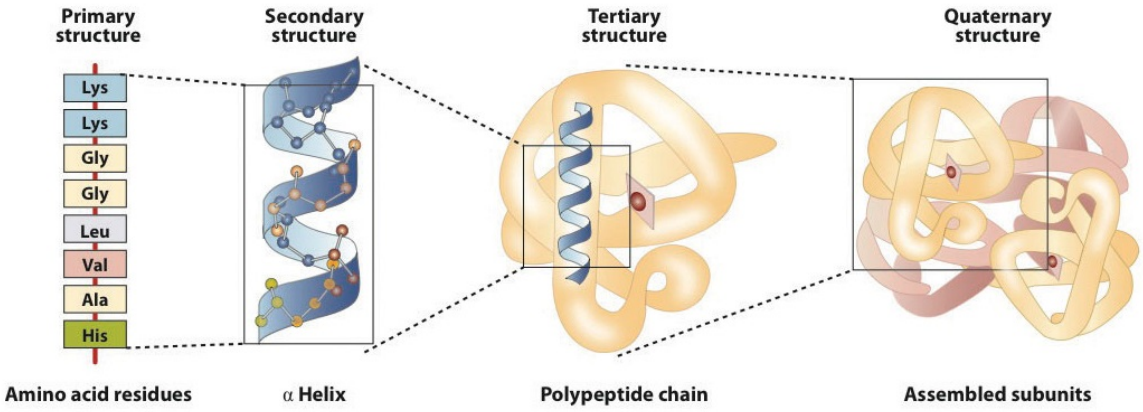


Figure 11.5.6: The 4 structural levels of proteins

The secondary level structure of proteins form alpha helixes and beta-pleated sheets, which are held together by hydrogen bonds.

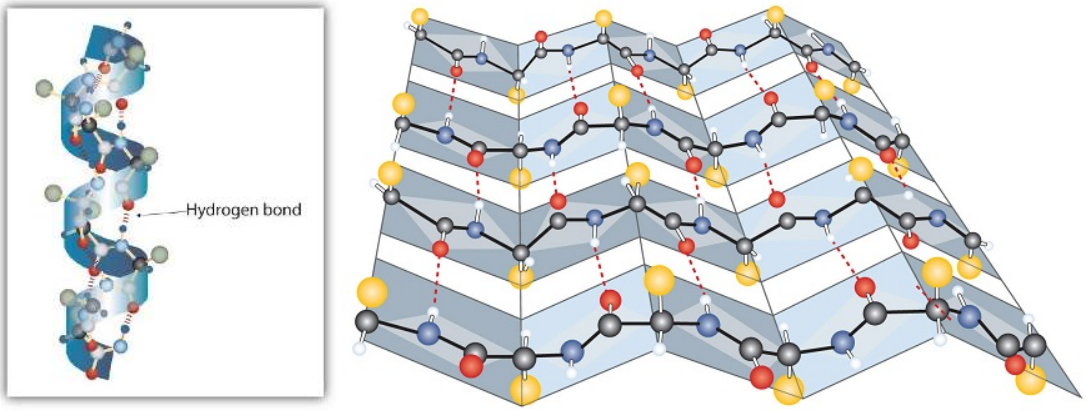


Figure 11.5.7: Protein alpha helixes (left) and beta pleated sheets (right) maintain their secondary structure through hydrogen bonding interactions (dotted red lines in the beta pleated sheet).

Test Yourself

Homework

Contributors and Attributions

- Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Jose Pietri (UCD)
- Jim Clark (Chemguide.co.uk)

This page titled 11.5: Hydrogen Bonds is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

11.6: Properties of Liquids

Introduction

Now that we have covered the basic Intermolecular Forces, we will cover some of the properties of liquids. These will include:

1. Vaporization and Condensation
2. Vapor Pressure
   - Enthalpy of Vaporization
   - Clausius-Claperyon Equation
3. Boiling Point
4. Critical Temperature and Pressure
5. Surface Temperature and Pressure

Vaporization and Condensation

A molecule in a liquid which is moving towards the surface of the liquid may have enough kinetic energy to overcome the cohesive forces that hold the molecules in the liquid together and escape into the vapor (gas) phase. Likewise a molecule in the gas (vapor) phase that collides with molecules on the surface of the liquid can transfer energy to the liquid molecules and enter the liquid phase. This results in two phase transitions.

1. **Vaporization** - the physical change of state where a chemical entity transforms from a liquid to a vapor.
2. **Condensation** - the physical change of state where a chemical entity transforms from a gas (vapor) to a liquid.

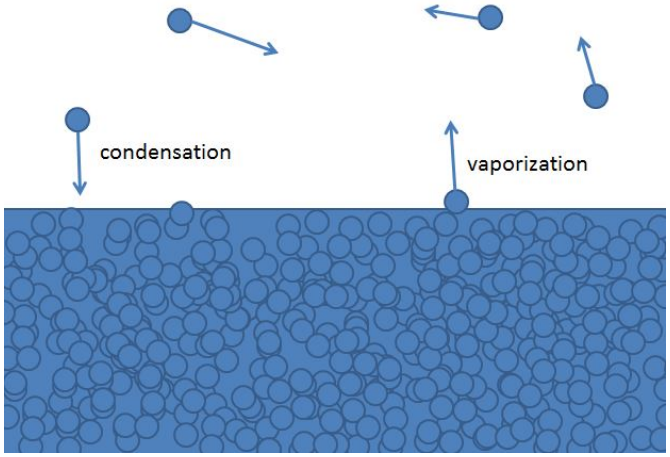


Figure 11.6.1: Two phase diagram showing molecules in the liquid phase entering the gas phase (vaporization) and those in the gas phase entering the liquid phase (condensation).

This concept can also be extended to solids which undergo sublimation and deposition, and we can define two types of substances:

1. **Volatile Substance** - a substance that can vaporize or sublime.
2. **Nonvolatile Substance** - a substance that does not vaporize or sublime.

A volatile substance has a measurable vapor pressure, which is the partial pressure due to the molecules that have entered the gas phase. A nonvolatile substance does not have a measurable vapor pressure. It should also be noted that the terms "vapor" and "gas" are often used synonymously, although there is an implicit difference. A vapor phase molecule is a gas phase molecule, but it is implied that there can be particles in a solid or liquid phase too. That is, the system is, or was, heterogeneous. So if a sample of water entirely vaporizes (so there is no liquid left), it is a pure gas, but it is often referred to as a vapor, even though it was a pure gas.

In this chapter we will look at liquids and in the next chapter we will look at solids.

Vapor Pressure

The vapor pressure of liquid substance is the partial pressure due to the particles of that substance which have enough kinetic energy to overcome the cohesive forces near the surface of the liquid and enter the gas phase and form a vapor. The moment a chemical entity enters the gas phase it can hit the surface and condense back into the liquid phase (Figure 11.6.1). If we ignore intermolecular interactions for the molecules that enter the vapor phase we can use the ideal gas law (PV=nRT) to correlate the vapor pressure to the number of particles in that phase, where the vapor pressure becomes the partial pressure due to the gas.

$$P_A = \frac{n_A RT}{V} \tag{11.6.1}$$

Vapor Pressure as an Equilibrium Pressure

Although Equation 11.6.1 describes the pressure due to a liquid (A) whose molecules have entered the vapor phase, this is not always what chemists refer to as the vapor pressure. Chemists consider the **Vapor Pressure to be the Equilibrium Pressure when the Rate at which Chemical Entities Vaporize Equals the Rate at which they Condense**. If these rates are not equal the total number of molecules in the vapor phase changes, and so the vapor pressure changes. When they are equal you have a dynamic equilibrium, where individual particles are continually vaporizing and condensing, but the number of particles in the gas phase is constant and this results in a constant valued equilibrium pressure, which is what is referred to as the Vapor Pressure of that substance (above its liquid surface). These values do depend on the temperature (see below) and are often tabulated in thermodynamic tables as a function of the temperature.

Figure 11.6.2 illustrate this concept. Imagine you had a volatile liquid (a liquid which can vaporize) that completely filled a container so there was no space above the liquid, (so there could be no vapor). If you then instantly removed some of the liquid (say with a syringe), there would be a void above the liquid, but no molecules. They would start to evaporate, and the rate at which they evaporate would be related to the surface (the greater the surface area the faster the rate) and the temperature (which describes the average kinetic energy of the system. If the temperature and surface area are constant, then the rate of evaporation is constant (green line, Figure 11.6.2). Initially there were no liquid particles in the gas phase, and so both the partial pressure (Figure 11.6.3) and the initial rate of condensation (Figure 11.6.2) are zero. As soon as some molecules enter the gas phase the partial pressure starts to rise (eq. 11.6.1 & Figure 11.6.3), and some of these molecules can now collide with the surface and condense. As the number of particles in the gas phase increases the rate at which they collide with the surface increases and so the rate of condensation increases (Figure 11.6.2). The number of particles in the gas phase keeps rising until the rate at which they evaporate (a constant value) equals the rate at which they condense, and a **dynamic equilibrium pressure is achieved** (the flat region of the curves in figures 11.6.2 & 3).

You need to be alert, that **the constant valued equilibrium pressure is what chemists refer to as the vapor pressure**, although if a system was not at equilibrium (left of the dotted line indicating the rates of condensation and vaporization are equal), we would still call that a vapor pressure. Figure 11.6.4 shows an apparatus for measuring the vapor pressure of a liquid. This is often a challenge for students, as the meaning of a word is often dependent on the context, (like is oxygen a monatomic atom "O" or a diatomic molecule "O_2"?) Unless we are specifically describing a system that is not in equilibrium, the vapor pressure is the equilibrium pressure when the rates of evaporation equal condensation, and that has a specific value (which is a function of the temperature).

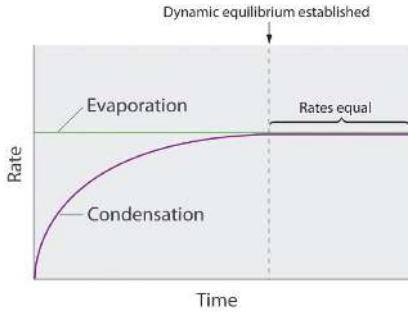


Figure 11.6.2: The rates of evaporation and condensation for a volatile liquid substance that at time zero, can enter a gas phase at constant temperature. The rate of evaporation is related to the surface area and thus constant, while the rate of condensation depends on the number of particles in the gas phase, and increases over time, until it reaches the rate of evaporation, at which time a dynamic equilibrium is achieved.

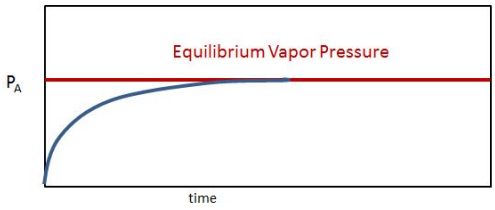


Figure 11.6.3: This figure correlates with figure 11.6.c, but shows how the partial pressure of the volatile liquid (A) increases with time. What chemists refer to as the vapor pressure of a substance is the equilibrium vapor pressure.

It needs to be emphasized that the vapor pressure is an equilibrium phenomena, and thus requires the gas to be in a closed container. If a container of water is closed, some will evaporate until it reaches its equilibrium vapor pressure. If the container is open to the atmosphere, all the water will eventually evaporate and you will have a gas, not a gas in equilibrium with its liquid.

Temperature Dependence of Vapor Pressure

We need to realize that concepts like liquid, gas, vaporization and condensation are not properties of individual chemical entities like a molecule or atom, but of a huge number of them, and need to be viewed as properties of an ensemble of particles, and not of individual atoms or molecules. A group of molecules has its energies distributed over a range of values resulting in velocity profiles like those in figure 11.6.5. The area under the curves are equal and represent the total number of molecules in a sample. As the temperature increases the curve flattens out and stretches to the

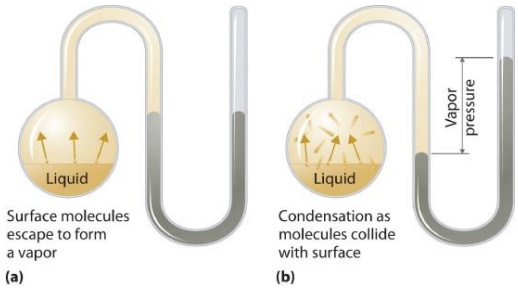


Figure 11.6.4: A closed end manometer (the right side is not exposed to the atmosphere) is at equilibrium (the liquid in the tube, lets say mercury, is at the same height) and there is initially no liquid. At time (a), a volatile liquid is injected into the bulb on the left which starts to evaporate displacing the mercury, and the mercury rises to a max value (when the rate of evaporation equals condensation), and that equilibrium pressure is the vapor pressure of the volatile compound (in units of mm Hg, or Torr, if the liquid is Hg).

right as more molecules move faster. If V_{escape} is the minimum velocity required to escape the surface of the liquid, only those molecules with a velocity equal or greater to this can escape (shaded part of the curve). It is clear from figure 11.6.5 that the fraction of molecules that can enter the gas phase (ratio of the shaded area to the total area under the curve) increases as the temperature rises, and so the number of molecules in the vapor phase increases as the temperature increases. This results in an increase in the vapor pressure as a function of temperature, which is plotted in figure 11.6.6 for a variety of substances.

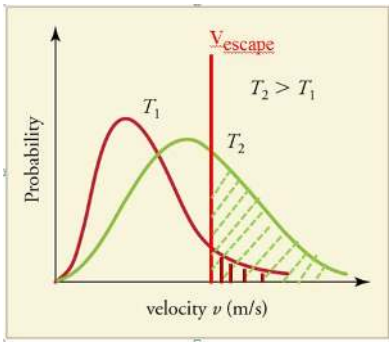


Figure 11.6.5: Velocity profile showing how the individual molecules in a substance have varying kinetic energies. If V_{escape} represents the the minimum velocity that a molecule near the surface needs to escape the liquid phase, then only those molecules with a velocity greater than it can enter the gas phase. As the temperature increases, the number of molecules with a velocity greater than V_{escape} increases, and more of the molecules enter the vapor phase.

It should be noted that just because a particle is moving fast enough to escape the surface does not mean it will, as it must also be moving in the correct direction.

In the next figure (11.6.6) we are looking at the vapor pressure as a function of temperature. This is an important diagram to understand as it relates molecular structure to the vapor pressure of a substance. That is, for molecules of similar mass, the stronger the intermolecular forces the lower the vapor pressure. We can sort of visualize an interplay between two different and opposing energies; increasing kinetic energy which favors the vapor phase, while increasing intermolecular forces favors the liquid phase. In the next section we will look into this in more detail, and you should reference back to this diagram.

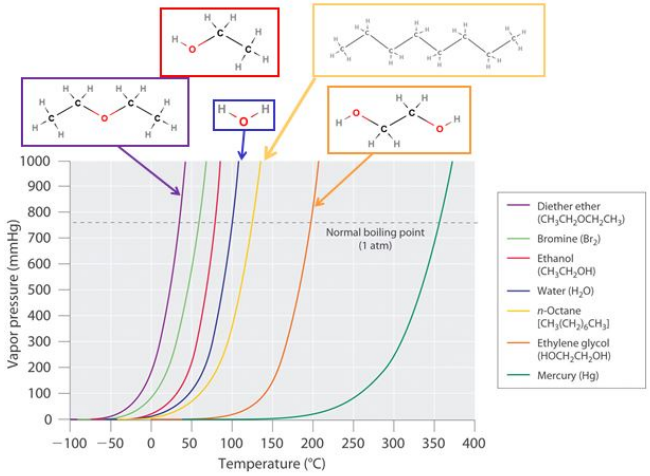


Figure 11.6.6: Plot of vapor pressure as a function of temperature for a variety of substances. It should be noted that this is a "bounded function", with the lower end being the melting point, and the upper end being the boiling point of a substance. That is, the concept of vapor pressure requires the existence of a liquid phase. So for water at 1 atm pressure, the lower end is 0°C (as below that you have ice) and the upper end is 100°C, as above that you have a pure gas.

Vapor Pressure: Intermolecular Forces, Particle Masses and the Enthalpy of Vaporization

From the Kinetic Molecular Theory of Gases and our studies of Grahm's Law of Effusion we know that the kinetic energy is proportional to the absolute temperature, and as we raise the temperature we raise the kinetic energy, $1/2mv^2$ (where m=mass and v=velocity), and thus a light molecule would move faster than a heavy one. Of course for a gas or a liquid you have an ensemble of particles and there is a velocity distribution function as in figure 11.6.7, with lighter particles tending to move faster than heavier ones (if they have similar intermolecular forces).

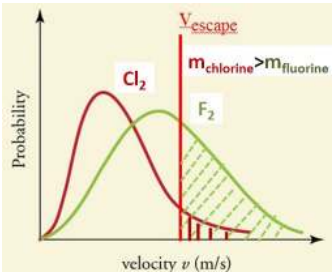


Figure 11.6.7: Constant temperature velocity profile of two similar non polar molecules, chlorine and fluorine. Note that the lighter molecules tend to move faster than the heavier ones, and if there was a temperature where they both exist as a liquid, the vapor pressure of the fluorine would be higher than the chlorine.

In Summary:

- Lighter molecules tend to move faster than heavier ones at a given temperature, and so increasing mass leads to a lowering of the vapor pressure.
- Stronger intermolecular forces suppresses the vapor pressure

These effects are evident in 11.6.6, where we can observe several trends at a given pressure and you should be able to explain these

- At a given temperature $\mathbf{P_{diethyl\ ether}>P_{ethanol}>P_{water}>P_{ethylene\ glycol}}$. Diethyl ether is nonpolar and so even though it is the heaviest, has the weakest intermolecular forces and is easiest to vaporize. The other three compounds are not only polar, but have hydrogen bonds. Ethanol has one OH group while both water and ethylene glycol both have two, so even though it is heavier than water, is has a lower vapor pressure. Water and ethylene glycol both have two OH groups, but water is lighter, and so has a higher vapor pressure.
- At a given temperature $\mathbf{P_{water}>P_{n\text{-}octane}}$ as even though the water has hydrogen bonds, the n-octane a 114 amu, weighting 6.3 times as much as the water, and being a large highly polarizable molecule with a lot of surface areas has strong London dispersion forces.
- Mercury has a very low vapor pressure and it needs to be realized that being a metal has metallic bonds, which we will cover in the next chapter. Although mercury is a liquid at standard conditions with a small vapor pressure, its vapor represents a serious health problem as it bioaccumulates.

The **enthalpy of vaporization** is the enthalpy required transform one mole of a substance from a liquid to a vapor, and is influenced by both the particles mass and its intermolecular forces. The higher the enthalpy of vaporization the more energy required to vaporize a substance and the lower the vapor pressure. Higher mass and stronger intermolecular forces result in a higher enthalpy of vaporization, and a lower vapor pressure.

Clausius-Clapeyron Equation: Mathematical derivation of the vapor pressure

In essence the vapor pressure above a liquid represents the partitioning of the particles between two phases, the liquid and the gas, that is, there is a fraction of the particles in each phase. There is an interplay between the enthalpy of vaporization (the higher it is, the more they want to be in the

liquid phase) and the kinetic energy. The equation that describes this is the Clausius-Clapeyron, which is an exponential function. Like any exponential function, there are two forms, the exponential form, and the natural log form

$$\underbrace{P_A = ke^{-\frac{\Delta H_{vap,A}}{RT}}}_{\text{exponential form}} \tag{11.6.2}$$

$$\underbrace{\ln P_A = -\frac{\Delta H_{vap,A}}{RT} + C}_{\text{logarithmic form}} \tag{11.6.3}$$

where:

- P_A=Vapor Pressure above volatile liquid "A"
- $\Delta H_{vap,A}$ = Enthalpy of Vaporization for "A", always positive because it is endothermic
- R = 8.314J/mol-K (Ideal gas constant)
- T = Absolute Temperature in Kelvin (always positive
- k=a positive constant in units of Pressure, we will treat it as an "unknown constant", but it is related to the highest possible pressure, and will not be used in our calculations.
- C=lnk another constant we will not use

Lets take a closer look at the term

$$e^{-\frac{\Delta H_{vap,A}}{RT}} = \frac{1}{e^{\frac{\Delta H_{vap,A}}{RT}}} \tag{11.6.4}$$

- The term in eq. 11.6.4 itself is a fraction because the enthalpy of vaporization is endothermic (positive), and R and T are positive, so it is of the form $\frac{1}{e^{positive\ number}} = \frac{1}{number>1}$=a fraction
  - $\Delta H_{vap,A}$
    - As $\Delta H_{vap,A}$ gets small and approaches zero, the fraction approaches 1 as e^0=1
    - As $\Delta H_{vap,A}$ gets large and $e^{\text{large number}}$ gets very large, and the reciprocal of a large number approaches zero.
  - RT This is the molar kinetic energy term associated with three dimensional translational motion (Through the ideal gas law it is related to PV work, from section 5.1). Remember one of the postulates of the Kinetic Molecular Theory was that the Kinetic Energy of a gas is proportional to the absolute temperature, R is the molar proportionality constant (PV/n=RT).
    - As T gets small, the fraction approaches zero
      - 1/T gets large, so $e^{\frac{1}{RT}}$ gets large and $\frac{1}{e^{\frac{1}{RT}}}$ approaches zero
    - As T gets large, the fraction approaches one
      - 1/T gets small and approaches zero, so $e^{\frac{1}{RT}}$ approaches e^0, which is 1, and $\frac{1}{e^{\frac{1}{RT}}}$ approaches one

In Summary:

Small $\Delta H_{vap,A}$ and high T favor large Vapor Pressures because the fraction $e^{-\frac{\Delta H_{vap,A}}{RT}}$ approaches 1.

Large $\Delta H_{vap,A}$ and low T favor low Vapor Pressures because the fraction $e^{-\frac{\Delta H_{vap,A}}{RT}}$ approaches 0.

Remember, at constant pressure, the smallest T is defined by the freezing point, and the highest T is defined by the boiling point, and only in this range do you a system where a vapor can be in equilibrium with it liquid. Below this temperature the liquid freezes, and above it have a gas (once they system has reached equilibrium).

From eq. 11.6.3, the slope of the linear plot of the $\ln P_v$ as a function of the reciprocal temperature (1/T) is equal to $-\Delta H_{vap,A}/R$ and can be used to measure the enthalpy of vaporization.

Two State Form of the Clausius-Claperyron Equation:

The two state approach will be used over and over this semester, and was introduced in gen chem 1 in the gas laws (section 10.2.4) when it was applied to the ideal gas equation, and here is is applied to the Clausius-Claperyon Equation, which is an exponential equation. Note, there are two forms, the exponential and the logarithmic.

Exponential form:

Knowing P_{vap} at one T and $\Delta H_{vap,A}$ you can calculate it at another temperature. You start by dividing eq 11.6.2 at one state (state 1: $P_{vap,1}$,T_1) by the same equation at another state (state 2 :$P_{vap,2}$,T_2.)

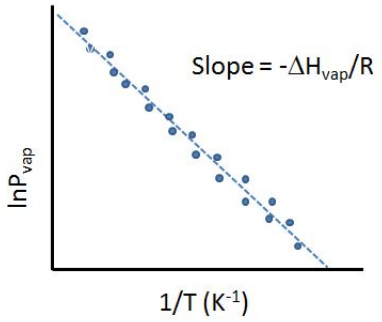


Figure 11.6.8: A plot of the natural log of the vapor pressure versus reciprocal temperature can be used to measure the enthalpy of vaporization. $\Delta H_{vap,A}$ =-R(Slope).

$$\frac{P_{v,1}}{P_{v,2}} = \frac{ke^{-\frac{\Delta H_v}{RT_1}}}{ke^{-\frac{\Delta H_v}{RT_2}}} = \frac{e^{-\frac{\Delta H_v}{RT_1}}}{e^{-\frac{\Delta H_v}{RT_2}}} = e^{-\frac{\Delta H_v}{R}(\frac{1}{T_1}-\frac{1}{T_2})} \tag{11.6.5}$$

If you know the vapor pressure at one Temperature, (T_2), you can rearrange the above equation to determine it at another temperature (T_1)

$$P_{v,1} = P_{v,2}\, e^{\frac{\Delta H_v}{R}(\frac{T_1-T_2}{T_2T_1})} \tag{11.6.6}$$

Logarithmic Form:

You can take the natural log of eq. 11.6.5 and solve for the enthalpy of vaporization

$$ln(\frac{P_1}{P_2}) = -\frac{\Delta H_V}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \tag{11.6.7}$$

This can be rearranged to

$$\Delta H_V = \frac{R}{\frac{1}{T_2}-\frac{1}{T_1}} ln(\frac{P_1}{P_2}) \tag{11.6.8}$$

or

$$\Delta H_V = \frac{RT_1T_2}{T_1-T_2} ln\frac{P_1}{P_2} \tag{11.6.9}$$

There are advantages to the forms represented in equations 11.6.6 and 11.6.9 in that they are easier to "read". You know that as T goes up, the vapor pressure goes up, and you know that the enthalpy of vaporization must be positive.

Lets look at 11.6.6:

- If T_1<T_2, then the exponent on the right side is negative, and a fraction, meaning P_2>P_1, which makes sense.
- If T_1>T_2, then the exponent on the right side is positive, the number is greater than 1, meaning P_2<P_1, which makes sense.

Lets look at 11.6.9

- If T_1<T_2, then P_1<P_2 ,
  - The 1/(T_1.T_2) term is negative
  - P_1/P_2 ,is a fraction and ln of a fraction is a negative number

This means the enthalpy of vaporization is a positive number as dividing a negative number into a positive number gives a negative number, and it makes sense.

- If T_1>T_2, then P_1>P_2 ,
  - The 1/(T_1.T_2) term is positive
  - P_1/P_2 ,is greater than 1 and the ln is a positive number

Once again, the enthalpy of vaporization is positive.

The Clausius-Claperyon equation is the first equation we cover this semester that is of this form. As the semester progresses we will have other similar equations, like the Arrhenius equation (exam 2) and Gibbs Free Energy Equation (exam 4). These may be a bit intimidating now, but by the end of the semester you will be able to manipulate these equations.

Exercise 11.6.1

Calculate the vapor pressure of water at 45^o C if it is 12.79 torr at 15^o C, given:

Substance	ΔH_f^o
$H_2O(l)$	-285.8
$H_2O(g)$	-241.8



Answer

72.27 Torr, which is not far off from the published value of 71.93 Torr. Note, we first solved the equation and then assigned the states. There are many correct forms this equation can take. At the end of the problem you should always ask, does my answer make sense? In this case we raised the temperature, which caused the vapor pressure to go up, and that makes sense. If in a problem you raise the temperature, and the pressure goes down, you need to take a closer look at your work to see if you can find your mistake. Usually it is either a math mistake, or not properly assigning your data to the algebraic variables. That is why I create a table with a column for each state, as it reduces the chance of switching the values.

Boiling Point

The definition of the boiling point is when the vapor pressure equals ambient (surrounding) pressure. At this pressure molecules within the bulk of the liquid turn to a vapor and bubble up through the liquid. This is the difference between boiling and evaporation.

What is the difference between boiling and evaporation?

- **Evaporation** - surface phenomena where liquid molecules at the surface vaporize and escape the cohesive (attractive) forces and enter the gas phase
- **Boiling** - a bulk fluid phenomena where the liquid state becomes unstable and spontaneously forms a vapor, even if it is not near the surface. This occurs when the vapor pressure equals ambient pressure. When you see water boil, those bubbles are not air bubbles, but water vapor.

What are the two ways to boil a substance

1. At constant pressure (isobar), raise the Temperature until the vapor pressure equals the ambient pressure
2. At constant temperature (isotherm) lower the ambient pressure until it equals the vapor pressure.

This explains how a pressure cooker or autoclave works to cook food or sterilize equipment because you can raise the temperature above 100ºC. It also explains why you have to boil an egg longer in the mountains, because the ambient pressure is lower. Table 11.6.1 shows how the boiling pt. a different locations on the earth changes as the elevation changes (remember, the pressure is due to the "column of air" on top of you, and the higher up you are, the less air their is above you.

What is meant by NORMAL BOILING POINT?

The normal boiling point is the temperature a substance boils at 1 atmosphere pressure

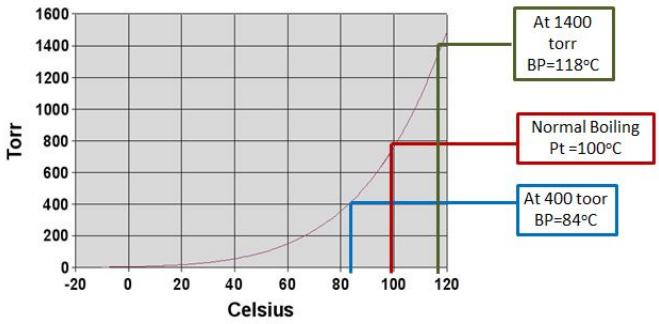


Figure 11.6.9*: Vapor pressure curve for water, showing how the temperature at which water boils depends on the pressure.*

Table 11.6.1 Boiling points at different locations on the earth.

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water (°C)
Mt. Everest, Nepal/Tibet	29,028	240	70
Bogota, Colombia	11,490	495	88
Denver, Colorado	5280	633	95
Washington, DC	25	759	100
Dead Sea, Israel/Jordan	−1312	799	101.4

Exercise 11.6.1

Given the following melting and boiling points, give two reasons why Iodine is a solid and fluorine is a gas at STP?

Halogen	mp(K)	bp(K)
F_2	53.5	85.0
Cl_2	172.2	238.6
Br_2	265.9	331.9
I_2	386.7	457.5

Answer

All of the above molecules are nonpolar and have London Dispersion forces interacting between them (Instantaneous dipole-induced dipole).

- Reason 1: The fluorine molecules are lighter and thus tend to move faster at a given temperature than the heavier iodine molecules (look at velocity profiles).
- Reason 2: Iodine is more polarizable and thus has stronger intermolecular forces. It is more polarizable because it has (a) more electrons and (b) a larger volume, that results in its electrons being less tightly held (and thus more polarizable).

Boiling points are an indicator of intermolecular forces, and we will look at the phenomena of boiling in more detail in a later section of this chapter. From the kinetic molecular theory of gases we learned that the kinetic energy of a molecule is proportional to its absolute temperature, where $KE_{Translation} = 1/2mv^2$, (m is the mass, and v is the velocity). We also learned that there is a velocity profile with different molecules moving at different speeds, but that heavier molecules tend to move slower than lighter ones (remember macroscopic observables like liquids and boiling are the result of the interactions of a huge number of molecules which possess a distribution of energies). So all things equal, we would anticipate that it is easier to boil a lighter molecule than a heavier one, and we would predict the heavier one to have a higher boiling point.

Class Activity

Figure 11.6.4 shows the trend for various hydrides of different families of the periodic table. Our predictions based on molar mass work for group IV (CH_4 through SnH_4), but does not work for groups VII, VI and V, where the hydrides of the second period (N,O,F) have higher boiling points than would be predicted from their mass trends.

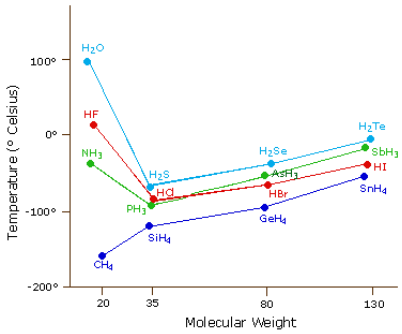


Figure 11.6.10: Periodic trends in boiling point for various hydrides.

There are a multitude of questions that can come out of figure 11.6.4, and you should familiarize yourself with this figure. You should also revisit this figure after we have covered the section on boiling. Right now let it suffice that to boil a substance you need to overcome the intermolecular forces that hold the liquid together (the cohesive forces), and that as you increase the temperature you increase the kinetic energy of the molecules (so they can escape the liquid and become a vapor).

First, lets look at the group 4 hydrides (CH_4, SiH_4, GeH_4& SnH_4),. As we go down the table from carbon to silicon to germanium to Tin we see an increase in the boiling points. These are symmetric nonpolar molecules and there are two reasons why going down this family shows an increase in the boiling point.

1. Going down group 4 the mass increases, requiring a higher temperature for molecules to gain enough kinetic energy to vaporize.
2. Going down the table the valence electrons occupy more diffuse orbitals, resulting in a higher polarizability, which in turn results in larger London dispersion forces.

So both of these trends would indicate an increase in the boiling point as we go down the family.

Second, ammonia, hydrofluoric acid and water show a deviation in this trend. That is, they are lighter, but there is an increase in their boiling points. This is due to hydrogen bonding. That is, although these molecules are lighter, they have very strong intermolecular forces, which must be overcome for them to boil.

Third, water has a higher boiling point than HF, yet fluorine is more electronegative than oxygen, it is also smaller, and so you would expect the HF hydrogen bond to be stronger than the OH hydrogen bond. In fact, this is all true, and what this argument does not take into account is the number of hydrogen bonds. That is, the cohesive forces that hold the liquid together are not just the strength of the bonds, but also the number of bonds. Each HF molecule has one H, and 3 lone pairs on the fluorine. So in a macroscopic system like a mole of HF (remember that to be a liquid, you need a lot of molecules), each HF would on average be involved with 2 bonds, one involving the hydrogen (hydrogen donor), and one involving a fluorine lone pair (hydrogen acceptor), and simple speaking, there are not enough hydrogens to use up all the lone pairs, (two of the fluorine's lone pairs are not involved in H bonds.) In the case of water, the number of lone pairs equals the number of hydrogens, and so each water molecule can on the average, be involved with 4 hydrogen bonds. So even though the individual hydrogen bonds in water may be weaker than in HF, there are more of them, making the boiling point of water higher than HF.

Exercise 11.5.2: Look at Real Molecules (Exam Material)

Before reading on, look at the following three molecules and their boiling points, and try and answer the following 2 questions.

pentane	$CH_3CH_2CH_2CH_2CH_3$	B.Pt: 36.3°C
butan-1-ol	$CH_3CH_2CH_2CH_2OH$	B.Pt: 117°C
2-methylpropan-1-ol	CH_3CHCH_2OH (with CH_3 branch)	B.Pt: 108°C

1. Why is pentane's boiling point so much lower than the other two?

Answer

Pentane is non polar and the other two have hydrogen bonds through the OH group.

2. Why does butan-1-ol have a higher boiling point than 2-methylpropan-1-ol?

Answer

Both of these molecules are isomers with the same chemical constituents ($C_4H_{10}O$) and both have an OH group than can be involved with hydrogen bonds. But butan-1-ol is more diffuse, thus more polarizable and has stronger van der Waals (London dispersion) interactions

Exercise 11.6.2

Predict the trend in boiling points for the following linear hydrocarbons: CH_4, C_2H_6, C_3H_8, C_4H_{10} and C_5H_{12}:

Answer

$CH_4 < C_2H_6 < C_3H_8 < C_4H_{10} < C_5H_{12}$. because that is the direction of (a) increasing mass and (b) increasing polarizability and thus increasing Lodon Dispersion forces.

Exercise 11.6.3

Rank the following in order of increasing boiling point.

1. HF, HCl, HBr and HI

Answer

HCl < HBr < HI < HF. HI is greater than HBr because of its mass, which in turn is greater than HCl, but the lighter HF breaks this trend because it has strong hydrogen bonds, and thus even though it is the lightest, if has the strongest intermolecular forces and thus has the highest boiling point. Note here the trends of mass and of polarity go in opposite directions, in that HCl is more polar the HBr, which is turn is more polar than HI.

Surface Tension, Capillary Action and Viscosity

Introduction

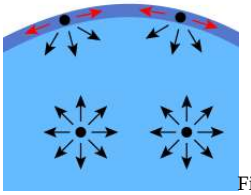
Cohesive forces are the forces of attraction between particles within a substance (or phase), and adhesive are between two different substances (or phases). These can explain properties like surface tension and viscosity, and phenomena like capillary action and why meniscus sometimes are concave and other times are convex.

- **Cohesive Forces** - the intermolecular forces of attraction holding the particles of a liquid together.
- **Adhesive Forces** - the intermolecular forces between a liquid's molecules and another substance, like a glass surface.

You should be able to predict trends based on intermolecular forces for these.

Surface Tension

On the surface of a liquid, there are negligible adhesive forces attracting the liquid to the gas phase, but substantial cohesive forces attracting the liquid to itself. The result is that particles near the surface of the liquid feel a net force pulling them into the liquid, with a resulting contraction in volume, which is why liquids form drops. The surface tension is related to the force required to increase the surface area, and can explain why objects like a paper clip can float if they are on the surface, but sink if they are placed below the surface. The stronger the intermolecular forces, the greater the surface tension.


Figure 11.6.10: Image showing how surface area contracts due to cohesive forces (public domain Wikipedia)



1:24 youtubeYoutube on Surface Tension by Berkeley Lab's Molecular Foundry, https://youtu.be/ciqNNRlS2yA .

Capillary Action

Through capillary action polar liquids like water can rise up narrow diameter tubes against the force of gravity.

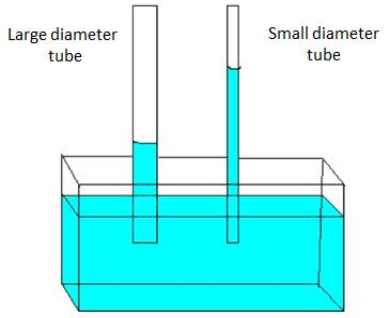


Figure 11.6.11: Ccapillary actions showing how the thinner the tube, the higher the water rises.

In reality, not all substances rise up, some even fall down. This is the result of the interaction of a liquid with a solid, and there are two types of forces at play, cohesive and adhesive.

Glass is based on silicon dioxide (like sand) and the surface has a lot of hydroxy groups (OH) that can participate in hydrogen bonds. This results in strong adhesive forces with polar solvents like water, and if the adhesive forces are greater than the cohesive forces, the water will crawl up the small capillary tube as illustrated in figure 11.6.m.

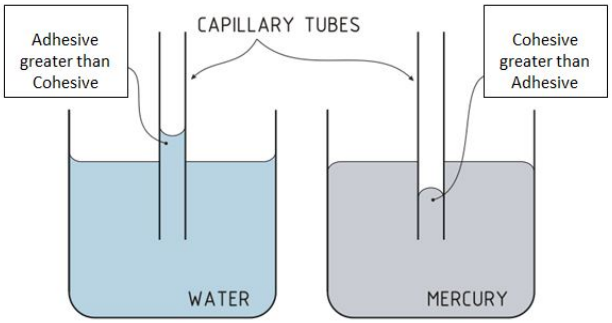


Figure 11.6.12: *Two glass capillary tubes placed in a polar and nonpolar liquids. In the case of the glass in water, the adhesive forces are greater than the cohesive and the water is attracted up the tube. In the case of mercury, which is not attracted to the glass, the cohesive forces are greater than the adhesive, and there is an actual depression as the mercury is repulsed from the tube.*

Meniscus: The meniscus curves up when the adhesive forces > cohesive and down when the cohesive forces > adhesive. In the case of water and glass, a slight film of water creeps up the surface of large diameter devices like burettes and graduated cylinders, and you read from the bottom of the meniscus. In the case of instruments like mercury thermometers and barometers, you read from the top of the meniscus.

- Adhesive > Cohesive - meniscus goes up
- Cohesive > Adhesive - meniscus goes down

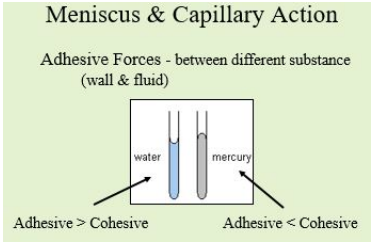


Figure 11.6.13: *Diagram showing different types of meniscus.*

Viscosity - Resistance to Flow

The viscosity of a fluid is a measurement of its resistance to flow. A high viscous fluid is like molasses and has a large resistance to flow, while a low viscous fluid would be like water and have a low resistance to flow. The following 2 You Tubes demonstrate high and low viscous fluids.



0.33 min Youtube showing a high and low viscous fluids being poured, https://youtu.be/vNzTYzjLgKE .



0.33 min YouTube animation showing lead ball being dropped into two cylinders, one with a high viscous fluid and one with a low viscous fluid.

The units of viscosity are the poise (P) or centipoise (cP

$1P = 0.1N\ s\ m^{-2} = 0.1$ Pascal-second
$1cP = 0.001N\ s\ m^{-2}$

Table 11.6.2: Viscosity and surface tension for a variety of substances. Not how non-polar molecules like diethyl ether have a low viscosity while molecules with heavy hydrogen bonding like glycerol have a large viscosity.

Common liquid	Viscosity /cP	Surface tension /N m-1
Diethyl ether	0.233	0.0728
Chloroform	0.58	0.0271
Benzene	0.652	0.0289
Carbon tetrachloride	0.969	0.0270
Water	1.002	0.0728
Ethanol	1.200	0.0228
Mercury	1.554	0.436
Olive oil	84	-
Castor oil	986	-
Glycerol	1490	0.0634
Glasses	very large	-

Viscosity is a strong function of temperature as indicated in table 11.6.3

Table 11.6.3: Viscosity of water as a function of temperature.

Temperature /°C	Viscosity /cP
20	1.002
40	0.653
60	0.467
80	0.355

Temperature /°C	Viscosity /cP
100	0.282

Automobile oil lubricates you car's engine and are rated by their viscosity with an SAE (Society of Automotive Engineers) number with SAE 5 being low viscosity oil (appropriate for winter conditions) and SAE 40 or 50 being more viscous and appropriate for summer conditions.

Supercritical Fluids

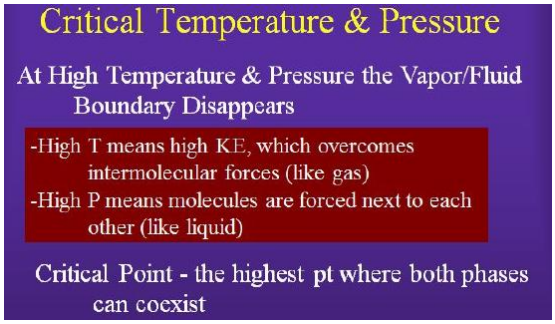
At very high pressure and temperatures the boundary between the a gas and its liquid disappears. That is, at high temperature there is a lot of kinetic energy, which dominates the intermolecular forces and the system behaves like a gas with very low viscosity (like a gas), but at high pressure the particles are pushed close to each other and the density rises to that of a liquid.

d

At the Critical point the two fluid phases become one, and there is not boundary between them. At pressures and temperatures above the critical point you have a supercritical fluid.

There are two fluid phases, the gas and the liquid.

- Gas Phase,
  - favored at low pressure (particles are far apart)
  - Favored at high temperature (particles have high kinetic energy make attractive forces negligible)
- Liquid Phase
  - Favored at high pressure (molecules are close to each other)
  - Favored at low temperature (attractive forces are able to compete with motion and keep molecules together



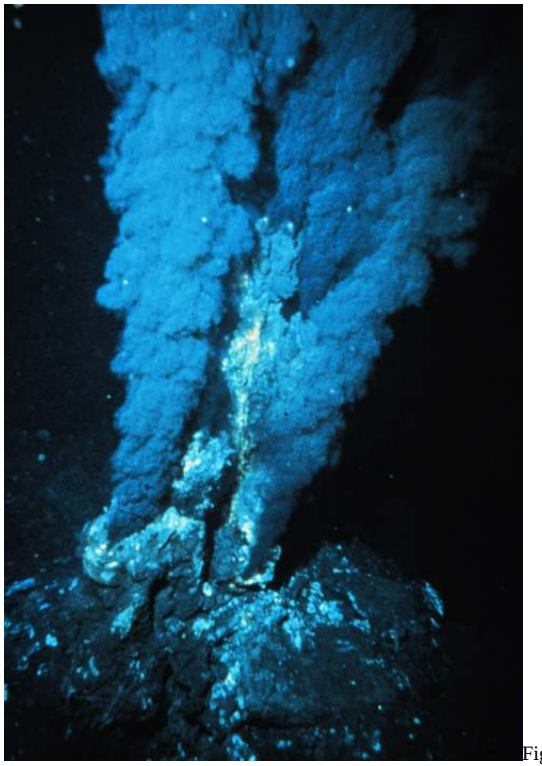
The following video was created at ETH Zurich as part of a Carbon Capture and Storage Exhibit. In this video they have two substances of different densities that "float" on liquid carbon dioxide at 28°C and 69 bar, but one is more dense than supercritical carbon dioxide. They then raise it to the critical point 31.1°C and 73.9 bar and the phases merge, with the one float sinking, and the other moving around. They then return to the initial condition, and the boundary reforms with both floats returning to the surface.



YouTube developed by ETH Zurich describing supercritical fluids https://youtu.be/P9EftqFYaHg

We will return to supercritical fluids and the critical point in the next chapter when we cover phase diagrams.

Supercritical fluids can occur in underwater volcanoes deep below the surface where the pressure is high and the

Figure 11.6.1: Black smokers, it is likely the volcanic fluids are at supercritical conditions although they cool when they reach the surface, but on occasions these can be supercritical. (Public Domain, P. Rona, NOAA Photolibrary)

In Class Activities

Test Yourself

homework

This page titled 11.6: Properties of Liquids is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

CHAPTER OVERVIEW

12: Solids

Topic hierarchy

12.0: Prelude
12.1: Crystal Lattices and Unit Cells
12.2: Ionic Solids
12.3: Bonding in Metals and Semiconductors
12.4: Network and Amorphous Solids
12.5: Phase Diagrams

This page titled 12: Solids is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

12.0: Prelude

Types of Solids

Solids are incompressible nonfluid substances that retain their shape. Being incompressible, solids have an essentially constant density. In this chapter we will look at crystaline and amorphous structures. We will not look a polymer based compounds, which are huge macromolecules comprised of repeating units of linked smaller monomers. Plastics are synthetic polymers and biological material like the lignin in plant cells, or proteins (chains of linked amino acids) are also polymeric in nature. In this class we will focus on inorganic structures like crystaline solids. At the simplest level you can break solids into crystalline and amorphous structures

- Crystalline Solids - have ordered atomic & molecular structure. Structures like table salt (NaCl), metals, diamonds and quartz form crystals. Table salt is an ionic crystal where the cation and anion form a lattice. Believe it or not, metals form simple crystal structures that we may not see on the macroscopic level. Diamonds and quartz are covalent crystals. In the case of diamond it is atomic carbon atoms that are linked in a tetrahedtral arrangement. In the case of quartz it is silicon dioxide units covalently bonded in repeating arrays.

- Amorphous Solids - have randomly arranged atomic and molecular structure, sort of like a fluid frozen in time. Glass and many stones are amorphous in nature.



Figure 12.0.1: left, amorphous apache tears in perlite. The apache tear is composed of black obsidian, a volcanic glass. The white perlite is also an amorphous volcanic glass that traps water (CC3.0, Lech Darski, WikiMedia Commons). Right, purple amethyst crystals, which are quartz. The violet color comes from various transition metal ions trapped in the crystal arrays, like Fe^{+3}. (CC0, Bob Belford)

Types of Crystalline Solids

- Ionic Solid - cations and anions held together by coulombic forces (salts, section 12.2)
- Metallic solids - held together by metallic bonds (section 12.3).
- Amorphous Solids
- Covalent Network Solids (networks of covalent bonds, section 12.4)
  - Molecular covalent network - held together by strong intermolecular forces or repeating covalent bonds between molecules (ice water, quartz, polymers)
  - Atomic covalent network - held together by covalent bonds between atoms (diamond)



Figure 12.0.2: Left, Ice Crystal (CC0, Roert Kraft, publicdomainpictures.net. Right, NaCl Halite crystals (CC0 Bob Belford)



Figure 12.0.3: Left, Copper Ore (GNU 1.2, Jon Zander, wikimedia commons), right, 2 caret diamond on engagement ring (CC3.0, קוליברי טבעות אירוסין, wikimedia commons)

Phase Diagrams

The final part of this chapter deals with Phase diagrams (section 12.5). These tell us which phases are stable at different Temperatures and Pressures. For example, the phase diagram below tells you the stable states of carbon at various temperatures and pressures.

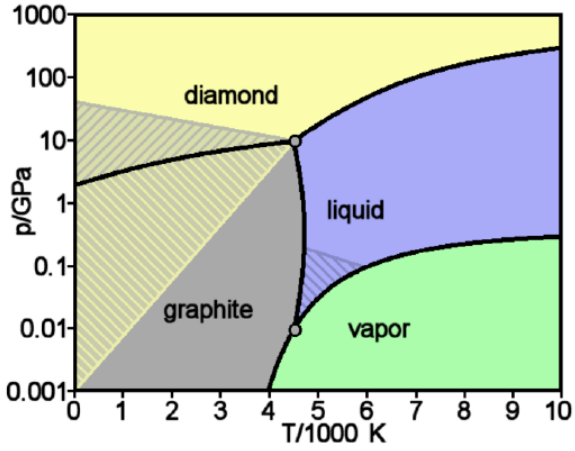


Figure 12.0.4:Phase diagram for carbon. (Public Domain, Wikimedia Commons)

Test Yourself

12.0: Prelude is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

12.1: Crystal Lattices and Unit Cells

The Unit Cell

This section deals with the geometry of crystaline systems. These could describe how metal atoms pack when they form metallic solids, or how ions pack when they form ionic crystals. We will look at the ionic structures in the next section, and here focus on the generic unit cell and it's application to metallic structures.

There are 7 types of unit cells (figure 12.1.a), defined by edge lengths (a,b,c) respectively along the x,y,z axis and angles α, β, and γ. In this class we will only focus on the **cubic unit cell**, and there are three types of cubic cells that you need to be familiar with, and these are represented in figure 12.1.b.

- α = angle in the yz plane
- β = angle in the xz plane
- γ = angle in the xy plane

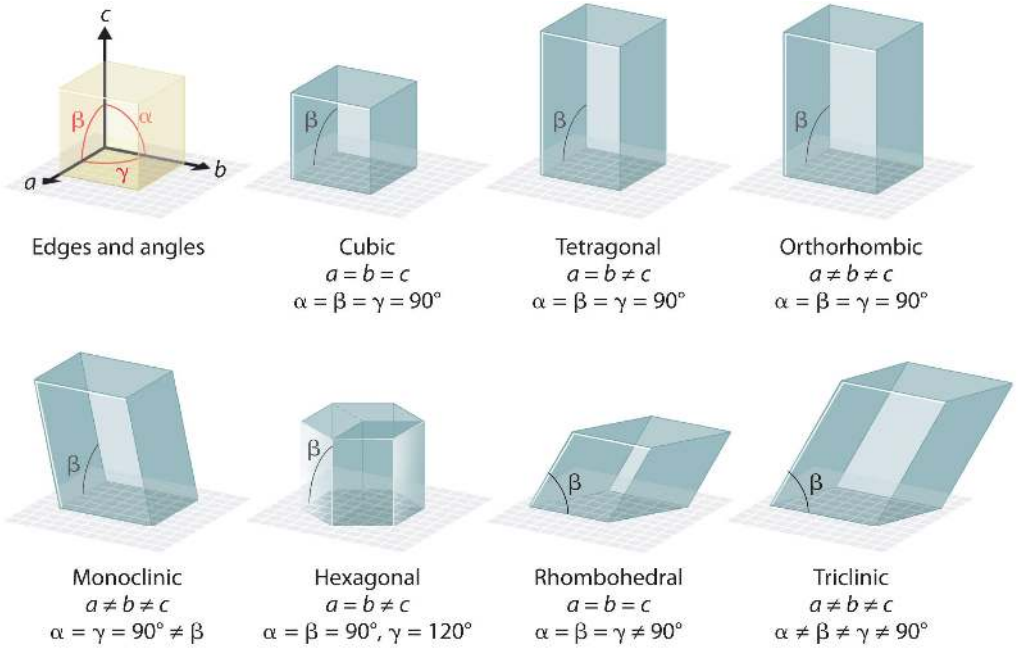


Figure12.1.1: The 7 types of unit cells. In this class we will only look at cubic systems, and will identify 3 types of cubic unit cells (figure. 12.b)

Cubic Unit Cell

The cubic unit cell is the smallest repeating unit when all angles are 90^o and all lengths are equal (figure 12.1.b) with each axis being defined by a Cartesian coordinate (x,y,z). Each cubic cell has 8 atoms in each corner of the cube, and that atom is shared with 8 neighboring cells. In the Body Centered Cubic Cell (BCC) there is an additional atom in the center of the cube, and in the face centered cubic cell, an atom is shared between two unit cells along the face. Please watch the YouTube video as this can help a lot.

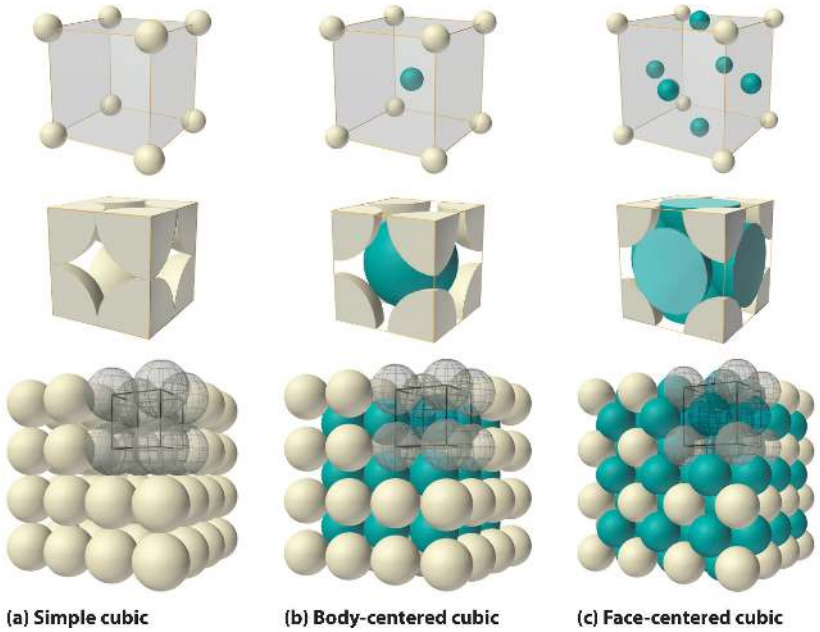
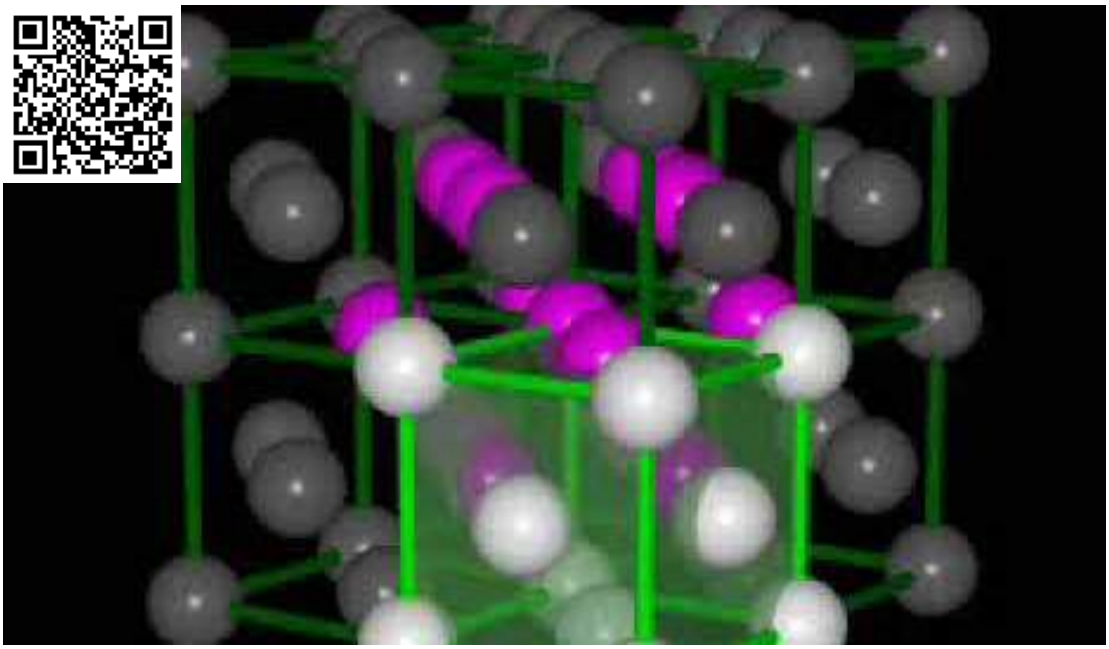


Figure12.1.2: Three type of cubic unit cells, each is described in detail below.



***Video*12.1.1** : *"Lattice Structure Part 1", created by Mark McClure, narrated by Sally Vallabha of UN-Pembroke, https://youtu.be/Rm-i1c7zr6Q*

Simple (Primative) Cubic Unit Cell

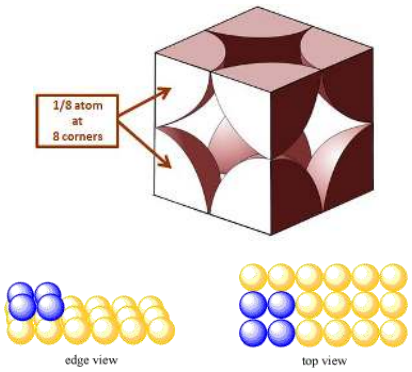


Figure12.1.3: Unit cell for primitive cubic cell and stacking diagram for Simple Cubic Stacking which this results in.

- 1 particle per unit cell
- coordination number = 6
- 52% of space occupied by particles
- Simple Cubic Stacking
  - along Cartesian coordinates
  - very inefficient and rarely seen in nature (radioactive α Polonium is the only known example at STP, Wikipedia)

Body centered cubic unit cell

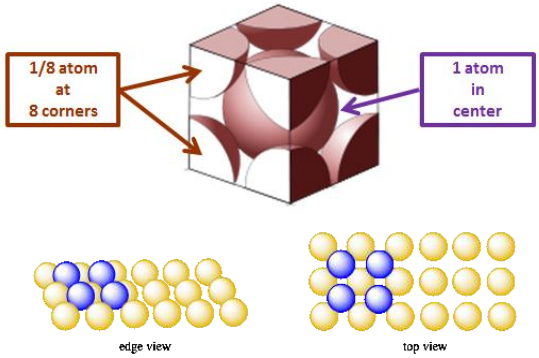


Figure12.1.4: Unit cell for body centered cubic cell and stacking hexagonal close packed structure it results in. This has a repeating alignment of ABABABAB where every other layer lines up.

- 2 particles per unit cell
- coordination number = 8
- 68% of space occupied by particles
- Hexagonal Close Packing (HCP)
  - second layer sits in grove of first with third in grove of second and in line with first (ABA structure)
  - Common with metals, including all alkali, Cr, V, Ba and Fe

Face Centered Cubic

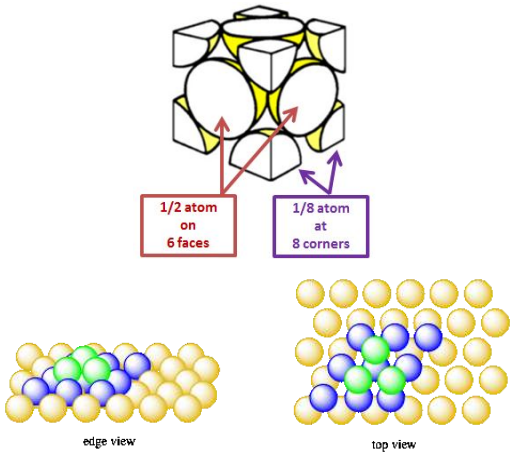


Figure12.1.5: Unit Cell for face centered unit cell, and diagram of Cubic Close Packed structure that it results in. Note each row has neighbors shifted from the Cartesian coordinate of their plan, and as you move up the lattice there is an ABCABCABC stacking , where every third layer is aligns. This is the form oranges would stack in a grocery store.

- 4 particles per unit cell
- coordination number = 12
- 74% of space occupied by particles
- Cubic Closest Packing Structure
  - explained in video 12.1.a at 5' 26".
  - along Cartesian coordinates
  - very inefficient and rarely seen in nature

Determining Atomic Radius from Density, Molar Mass and Crystal Structure

The strategy is to use the following to calculate the volume of the unit cell, and then the length of each side. Once this is done, you can use the packing and the geometry of the structure to calculate the radii. The information you need is:

- density
- Molar Mass
- Avogadro's number
- Number atoms per unit cell (1 for simple, 2 for body centered and 4 for face centered)
- Pythagorean theorem ($a^2 + b^2 = c^2$)
- Volume of a cube ($V=l^3$)

You may also want to review SI prefixes (section 1B.1.3.3 of General Chemistry 1) and not that 1 Å is 10^{-10}m

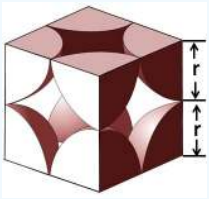
So these all have a similar strategy

1. Calculate Volume of Unit Cell (number of atoms in unit cell depends on type of cell)
2. Calculate length of the sides of the unit cell (same for all)
3. Use packing to figure radii (different for each type)

A. Simple Cubic Cell

Exercise 12.1.1

A. Given the density of Polonium = 9.32g/ml, calculate radii of a Polonium atom if it forms a Simple Cubic Cell.



Problem: Polonium is the only element that is simple cubic (has 1 atom/unit cell). Note the length of unit cell is 2 radii, and thus if we can calculate the length of the unit cell, we can calculate the radius. When we say there is one atom per unit cell, we are not saying the volume of the atom is the volume of the unit cell. It is 52% the volume (see above).



Video12.1.2 Solution to the radii of Po from its density.

Answer

1. Find the volume of the unit cell

$$\frac{1 atom Po}{unit cell}(\frac{1 mol Po}{6.02x10^{23} atoms})(\frac{208.9 g Po}{mol})(\frac{1 ml}{9.32 g}) = 3.72x10^{-23}\frac{ml}{unit\ cell}$$

2. Find the length of the unit cell

$$l = \sqrt[3]{V}] = \sqrt[3]{3.72x10^{-23} cm^3} = 3.34x10^{-8} cm = 334 pm$$

3. Find radii

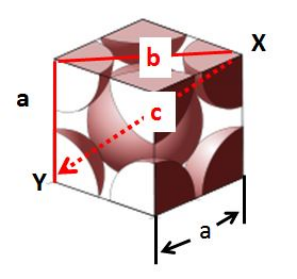
Since each side is 2r, r is 1/2 half the length, or 167pm

.

https://chem.libretexts.org/@go/page/43268

Exercise 12.1.2

Problem: Molybdenum forms body centered cubic cells, if the density of Mo is 10.28 g/ml, what would its radius be?.



This is the toughest, as the diagonal through the cell from vertices X to Y with length "c" equals 4 radii. It makes a right triangle with side a and b, the diagonal of a face, we note that $a^2+a^2=b^2$ and $a^2+b^2=c^2$



Answer

1. Find Volume of unit cell:

$$\frac{2 atom Mo}{unit cell}\left(\frac{1 mol Mo}{6.02x10^{23} atoms}\right)\left(\frac{95.95 g\ Mo}{mol}\right)\left(\frac{1 ml\ Mo}{10.26 g}\right) = 3.11x10^{-23}\frac{ml}{unit\ cell} \tag{12.1.1}$$

2. Find length of unit cell

$$[a = \sqrt[3]{V}] = \sqrt[3]{3.11x10^{-23} cm^3} = 3.15x10^{-8} cm = 314 pm \tag{12.1.2}$$

3. Find radii

   a. Find diagonal of face "b"

$$b = \sqrt[2]{2a^2} = \sqrt[2]{2(314)^2} = 444 pm \tag{12.1.3}$$

   b. Find diagonal through cube "c"

$$c = \sqrt[2]{a^2+b^2} = \sqrt[2]{314^2+444^2} = 544 pm \tag{12.1.4}$$

   c. "c" = 4r, so r=136pm

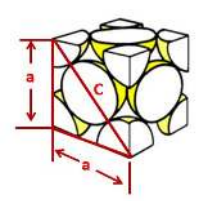
Note, in the video I used Å (Angstroms) while in the answer I used picometers. You should be able to convert between these, and review the "advanced technique" of section 1B.3.5.1 if needed, but we now that 1M = 10^{10} Å =10^{12}pm, so the conversion factor from picometers to Angstroms is

$$\frac{10^{12} pm}{10^{10} Å} \text{ or } \frac{10^{2} pm}{Å} \tag{12.1.5}$$

C. Face Centered Cubic

Exercise 12.1.3

Problem: Calcium forms a face centered cubic cell with a density of 1.54 g/ml, what would its radius be?





Answer

1. Find Volume of unit cell:

$$\frac{4 atom Ca}{unit cell}\left(\frac{1 mol CA}{6.02x10^{23} atoms}\right)\left(\frac{40.08 g\, Ca}{mol}\right)\left(\frac{1 ml\, Mo}{1.54 g}\right) = 1.73x10^{-22}\frac{ml}{unit\ cell} \tag{12.1.6}$$

2. Find length of unit cell

$$a = \sqrt[3]{V}] = \sqrt[3]{1.72x10^{-22} cm^3} = 5.57x10^{-8} cm = 557 pm \tag{12.1.7}$$

3. Find radii

   a. Find diagonal of face "c"

$$c = \sqrt[2]{2a^2} = \sqrt[2]{2(557)^2} = 787 pm \tag{12.1.8}$$

   b. since the diagonal of the surface is 4r, r=197pm

Crystal Defects

Defects in a crystal can give it unique properties. Defects occur when another entity becomes part of the crystal, and there are many types of defects, two that are worth noting are substitutional and interstitial. A dopant is a compound that is added to a crystal and can alter its properties.

Substitutional Defects

These occur when a different substance substitutes for one of the components of the crystal. For example Ruby is Al_2O_3 with a few Cr^{+3} replacing Al^{+3} ions . Alloys involve one metal substituting for another. Bronze is a substitutional alloy of copper with about 12%, and Brass is an alloy of copper with zin, The properties of the alloy can be varied by changing the % composition.

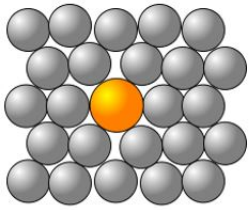


Figure 12.1.6: Substitutional defect

Interstitial Defects

These occur when a substance which is not part of the crystal fits into the interstitial regions, and does not displace a component of the crystal. Carbide steel is a form of interstitial defect where carbon enters the holes of the iron structure, and this affects its properties like hardness and ductility.

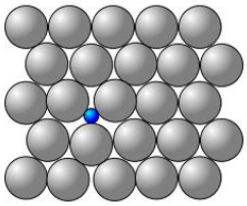


Figure 12.1.7: Example of an interstitial defect,

In Class Activities

Test Yourself

Homework

- Contributors and Attributions
  - Bob Belford
  - some images from anonymous
  - some images from anonymous were modified
  - some images from Chris P Schaller

This page titled 12.1: Crystal Lattices and Unit Cells is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

12.2: Ionic Solids

Introduction

Ionic compounds form many types of crystal structures, and they tend to be more complicated than those of the closest packing schemes introduced in the last section. There are several reasons for this. First, the charge of the ions may not be the same, but they must be in a ratio that is neutral, and form a lattice that minimizes repulsion between like charges while maximizing the attraction between opposite charges. Second, the anion and cation are different entities, and may have completely different volumes. In this case the structure is often based on the larger ion (usually the anion) and the smaller ion fits in the "holes or void space. Finally, many ionic compounds form hydrated salts, where water is trapped within the holes or voids of the crystal lattice.

Lets look at the difference between Cesium Chloride and sodium chloride, both of which are alkyl chlorides.

Cesium chloride

In the cesium chloride both the cation and the anion of similar volumes and if you imagine a primitive cubic structure of one, with the central hole being occupied by the other (as in body centered cubic). Sort of like a primitive anionic structure offset by a primitive cationic structure.

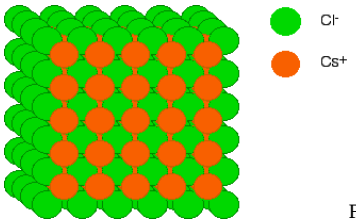


Figure 12.2.1:Structure of Cesium chloride showing how each ion forms a primitive cubic structure with respect to itself.

When the size of the ions are substantially different, more complicated geometries form.

Sodium chloride

Sodium chloride forms the halide structure, with the chloride ions forming a face centered packing, and the sodium entering the octahedral holes.

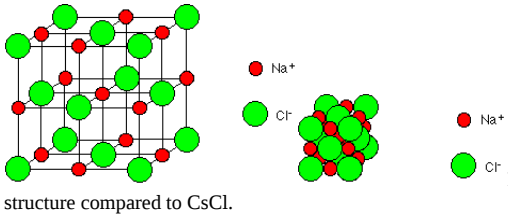
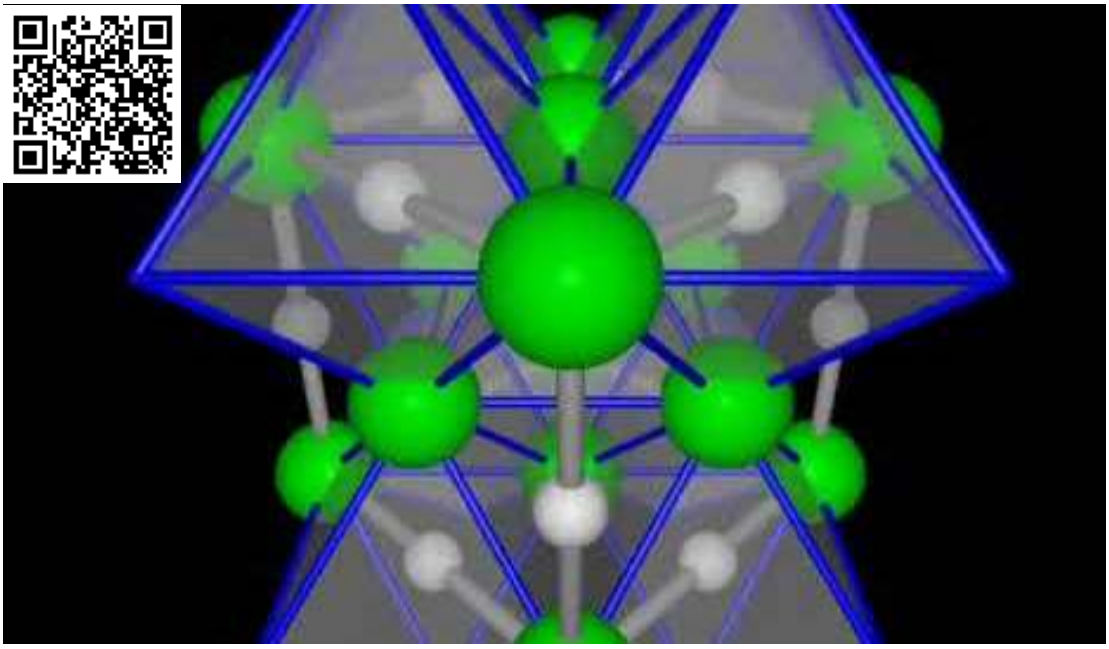


Figure 12.2.2: Sodium chloride structure, note how the difference in size changes the structure compared to CsCl.

The following YouTube video explains how face centered cubic cells in a close packed structure have both octahedral and tetrahedral holes. In the case of octahedral holes, there is a 1:1 ration of hole to particles, but in the case of tetrahedral holes, there is a 2:1 ratio.



***Video*12.2.1** : YouTube Video: Ionic Lattices by Mark McClure and Sally Vallabha at UNC-Pembroke, https://youtu.be/F4Du4zI4GJ0

Calcium fluoride (CaF_2)

Calcium fluoride forms the fluorite structure, where the Calcium forms a face centered cubic structure with the fluoride entering the tetrahedral holes.

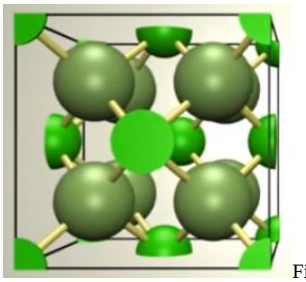
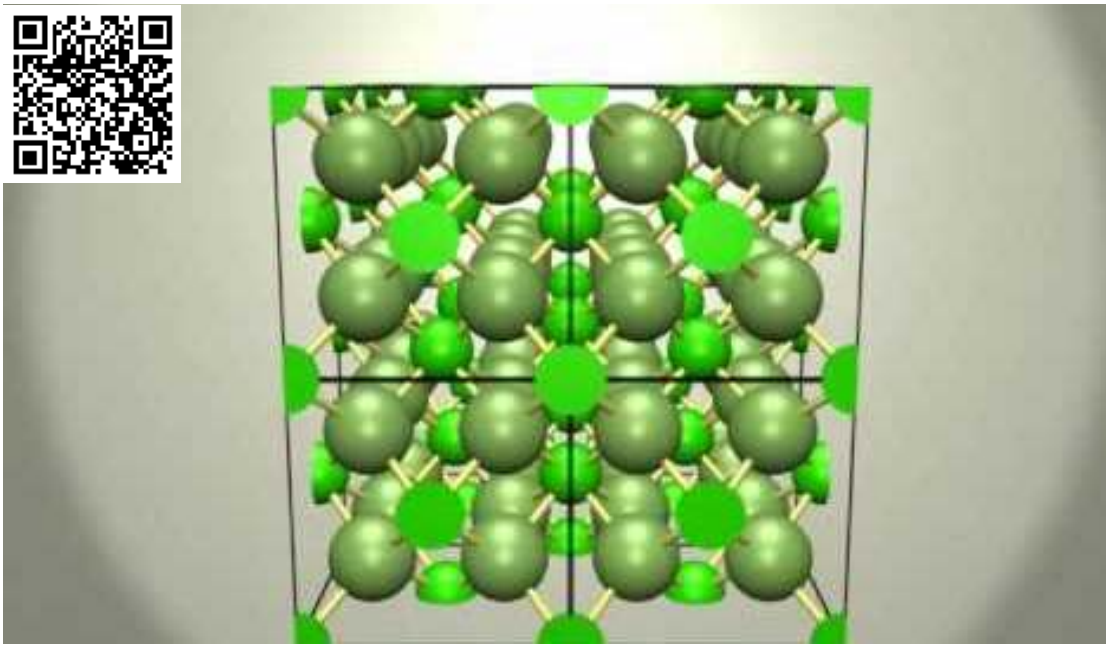


Figure 12.2.3: Fluorite structure of Calcium fluoride. Note how the Ca has a face centered structure with 4 atoms to the unit cell, and there are 8 fluorides inside the 8 tetrahedral holes. Please watch both videos.

***Figure*12.2.3** : .

This Youtube does a good job of showing the face centered structure of the calcium in calcium fluoride



***Video*12.2.2** :This Youtube: Fluorite, Calcium Fluoride, Calcium Difluorite crystal was posted by Manuel Moreira Baptista and is directly available at https://youtu.be/xyeHDoOxyXU .

Lattice Energy

We have looked at coulombs law and see that the energy of interaction between two charged particles separated in space can be described by the following equation,

$$E = \frac{q_1 q_2}{(4\pi\epsilon_0)r} \tag{12.2.1}$$

A closer look shows that this does not account for the high bond strength of a crystal lattice, which is because a crystal is not two isolated ions, but the result of multiple charges at multiple distances interacting at the same time. None the less, we can see some initial trends come out of understanding coulombs law, and these are observable in Table 12.3.1. The first is that the smaller the ion, the greater the lattice energy. The second is the greater the charge, the greater the lattice energy. So from that level, Coulomb's law is very useful in predicting trends.

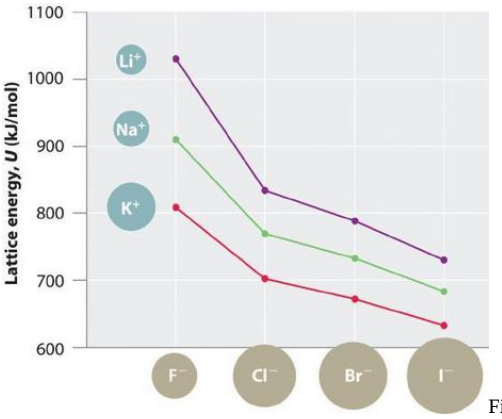


Figure 12.2.4: Trends of lattice energies as function of ion charges. In this chart the energy is being shown as a dissociation energy, the energy required to break a mol of the crystal lattice into its separated ions.

> **Note**
>
> General trends in Lattice Energy can be predicted by Coulombs Law for the attractive forces between the cation and anion, but the actual energy is much more complicated as each ion interacts with multiple neigboring ions, with some of those being the repulsive forces between like charges. As we will see below, we can calculate the Lattice Energy through an energy cycle (Born Haber cycle). So the actual Lattice energy is not predicted by Coulombs law, although general trends can be predicted by coulombs law.

What is the Definition of Lattice Enthalpy

- Some textbooks state it is the energy change when a mole of an ionic compound is dissociated into its gaseous ions (an endothermic process with a positive value).

$$M_m X_{n(s)} \rightarrow M^{n+}_{(g)} + X^{m-}_{(g)} \tag{12.3.2}$$

  Within this definition, the lattice enthalpy will always correspond to an Endothermic Process, i.e., $\Delta H > 0$
- Other textbooks state it is the energy change when a mole of an ionic compound is formed from its gaseous ions (an exothermic process with a negative value)

$$M^{n+}_{(g)} + X^{m-}_{(g)} \rightarrow M_m X_{n(s)} \tag{12.3.3}$$

  Within this definition, the lattice enthalpy will always correspond to an Exothermic Process, i.e., $\Delta H < 0$

Do not be fooled, the |value| is the same, and you may need to interpret whether it is a formation or dissociation energy. Familiarize yourself with Table 12.3.1 and be able to predict the periodic trends represented in the table.

Representative Calculated Lattice Energies as Dissociation Energies	
Substance	E (kJ/mol)
NaF	910
NaCl	788
NaBr	732
NaI	682
$MgCl_2$	2326
$SrCl_2$	2127
AlF_3	5,492
Al_2O_3	15,300

Representative Calculated Lattice Energies as Formation Energies	
Substance	E (kJ/mol)
NaF	-910
NaCl	-788
NaBr	-732
NaI	-682
$MgCl_2$	-2326
$SrCl_2$	-2127
AlF_3	-5,492
Al_2O_3	-15,300

***Table* 12.2.1** *: Lattice Energies expresses as dissociation energies (right) and formation energies (left).*

Note: You should not be confused by the difference in signs. If a crystal forms, it is more stable than the isolated ions, otherwise it will not form. So a negative value implies a formation enthalpy, and a positive value implies a dissociation enthalpy. Since energy is conserved, they are of equal magnitude, it is just that one direction is endothermic (breaking the bonds), and the other is exothermic (making the bonds).

Exercise 12.2.1

Rank the following in order of increasing lattice energy (stronger energies, so more negative for formation, and more positive for dissociation). Justify your answers

LiF, LiCl, LiBr, LiI, MgF_2, $MgBr_2$, CdS, Al_2O_3:

Answer

LiI < LiBr < LiCl < LiF because they are all +1/-1 and so size of ions matter, with the smaller ions resulting in stronger forces.

LiF < $MgBr_2$ because the charges increase (+2/-1) interaction, and that effect is typically more important than radii

$MgBr_2$ < MgF_2 because fluoride is smaller than bromide (they have the same charges)

MgF_2 < CdS because CdS has higher charges (+2/-2) vs (+2/-1)

Al_2O_3 has the largest crystal lattice energy because it has huges charges (+2/-3) and the ions are very small.

So the trend is

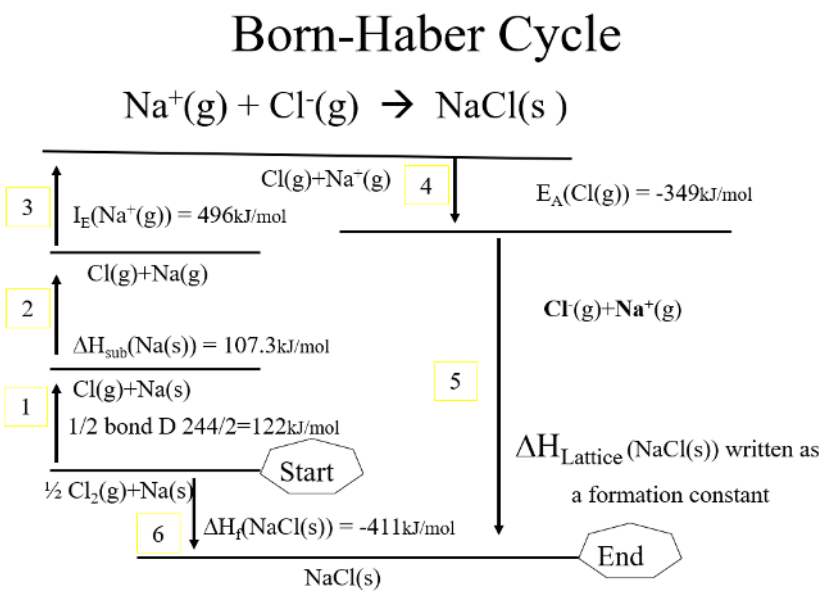
LiI < LiBr < LiCl < LiF < $MgBr_2$ < MgF_2 < CdS < Al_2O_3

Energy Cycles and the Born Haber Equation

The first law states that energy is conserved, and internal energy and enthalpy are state functions, which means their value is path independent. That is, the energy difference between two states is independent of the energy used to transition between the states. (You could pick a pencil off the floor and put in on your desk, or pick it up, run around the building, and put in on the desk. At the end, the energy difference of the pencil on the desk and the floor is the same, but the work done depends on the path you took).

This principle allows you to calculate the energy of a path you can not directly measure, and this is effectively an application of Hess's Law, although to more complex processes. In the figure below, you can calculate the lattice energy for the formation of Sodium chloride from the following known values

- Bond dissociation energy of chlorine (section. 8.9)
- Enthalpy of sublimation of sodium (section 5.7.4-calculate from enthalpies of formation)
- ionization energy of sodium (section 7.3.3)
- electron affinity of chlorine (section 7.3.4)
- enthalpy of formation of sodium chloride (s) (section 5.7.3)



$\Delta H_f(NaCl(s)) = 1/2 bond\ D + \Delta H_{sub}(Na) + I_P(Na(g) + E_A(Cl(g) + \Delta H_{Lattice}(NaCl(s))$ Figure 12.2.5: Born Haber cycle showing two paths for making NaCl(s) from its elements in their standard states, with one path involving the lattice energy. Since all the other steps (CC0 Bob Belford)

The molar enthalpy of formation of table salt [NaCl(s)] is the energy change associated with making one mole of the crystal sodium chloride from its elements in their standard state (1/2 mole of $Cl_2(g)$ and 1 mole Na(s)).

As energy is conserved, the energy change from the **Start** to the **End** is the same no matter the path. So

step 6 = step1 + step2 + step3 + step4 + step 5

so

Step5 = step6 - step1 - step2 - step3 - step4

If you know 5 of the steps, you can calculate the 6th. In this case, you are calculating step 5. Note: steps going up are endothermic (+ values) and those going down are exothermic (-) values. If two paths go to the same state, the final difference in energy must be the same, or energy is not conserved.

Step 1: 1/2 bond dissociation energy of $Cl_2(g)$ -Known (122 kJ/mol)
Step 2: Enthalpy of sublimation of Na(s) - Known (107.3 kJ/mol)
Step 3: Ionization energy of Na(g) - Known (496 kJ/mol)
Step 4: Electron affinity of Cl(g) - Known (-349 kJ/mol)
Step 5: Lattice formation energy of NaCl - Unkown
Step 6: Enthalpy of formation of NaCl - Known (-411 kJ/mol)

Step5 = step6 - step1 - step2 - step3 - step4
Step 5 = (-411 -122 -107.3 - 496 -(-349) kJ/mol = -7,873 kJ/mol (as a formation energy)

Exercise 12.2.2

Calculate the Lattice Energy (Enthalpy of formation) for Rubidium Chloride, given:

- $\Delta H_f^\circ[Rb(g)] = 80.9 kJ/mol$
- $\Delta H_f^\circ[RbCl(s)] = -435.4 kJ/mol$

- I_E(Rb)=403kJ/mol
- E_A(Cl) = -349kJ/mol
- Bond Dissociation Energy (Cl-Cl) = 244kJ/mol



Video12.2.1: Description of Born Harbor energy cycle and its use to calculate the lattice enthalpy of formation for RbCl.



Video12.2.2: Using Hess's Law to solve for an unknown enthalpy, the lattice enthalpy of formation for barium chloride

Answer

-692.3 kJ/mol (as an formation energy).

In Class Activities

Test Yourself

Homework

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 12.2: Ionic Solids is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

12.3: Bonding in Metals and Semiconductors

To date we have avoided metallic bonds, and due to time, this course will be very weak on them, and semiconductors.

Characteristics of Metals

- low ionization energies (can easily lose electrons and form cations)
- low electronegativities (tend to have partial positive charge in polar bonds - are electropositive)
- lustrous (shiny)
- malleable - can be beat into thin sheets (their bonds are flexible and not rigid with a fixed geometry)
- ductile - can be drawn into wires.
- thermal and electrical conductors

Electron Sea Model

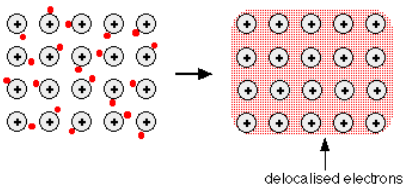


Figure 11.4.a. Pictorial representation of electron sea model.

Atomic cores (nuclei and core electrons) form the "spheres" while valence electrons become attracted to multiple nuclei, and are free to move about the bulk of the electron. This is a qualitative description but there is value to it.



Video 12.3.1: 0:26 Minute animation on electron sea model uploaded by Chemsurvival (https://youtu.be/V5tj-xADB1c)

Molecular Orbital (MO) and Band Theory

In general chemistry 1 we covered molecular orbital theory and saw how two orbitals could overlap to form a bonding orbital and an antibonding orbital. This was for simple diatomic molecules, isolated in space and Band Theory expands this to systems where many orbitals and electrons from multiple atoms mix. If you think about it, this is the fundamental premise of the Electron Sea Model, in that there is a mixing of the valence orbitals of multiple orbitals. And when we say multiple, we mean huge numbers (10^{23}).

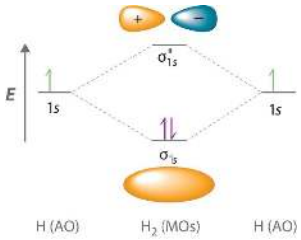


Figure 11.4.b. MO electron configuration for hydrogen showing bonding and antibonding orbitals

We then expanded this concept to the second period of the period table, and were able to explain phenomena like the diamagnetic properties of oxygen.

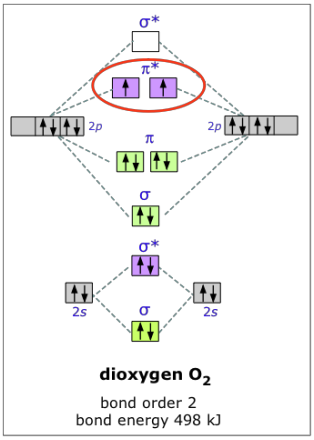
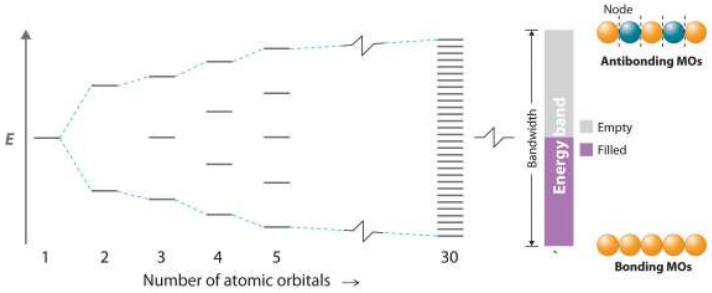


Figure 11.4.c. MO diagram for oxygen, showing how the 2s and three 2p atomic orbitals of 2 oxygen atoms create 8 molecular orbitals.

There are several postulate of MO theory that we should review

1. The number of Molecular Orbitals equals the number of Atomic Orbitals mixed.
2. Each orbital has a discrete energy
3. Orbitals need to be of similar energy to mix,
4. Bonding Orbital result when orbital wave functions complement each other
5. Antibonding orbitals repulse when orbital wave functions cancel each other

When the number of orbitals becomes huge, the energies of the mixed orbitals merge and you effectively a blurring of the energy levels, and a band of available energy states.



Metallic bonds involve electrons delocalized over multiple nuclei and so the number of atomic orbitals that combine to form molecular orbitals is so huge that the energy gap between them becomes negligible, and they in effect form bands. But there are two types of molecular orbirtals, bonding and antibonding. Electrons in the bonding orbitals form the valence band, and electrons in the antibonding are not localized on a specific nuclei and form the conductance band.

Conductors, Insulators and Semiconductors

We live in a world full of electronics and many of the students of this class are engineering students who need to know the basics behind the devices they will work with. Although during our exams this class will not go into band gap theory, it is worth mentioning.

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 and the conduction band is so large that electrons cannot make the energy jump from the valence band to the conduction band, and thus they stay localized to the nuclei they are associated with.

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.



Video12.3.2 6:31 min Youtube introducing introducing band theory as applied to conductivity and semiconductors (https://youtu.be/5zz6LlDVRl0)

This page titled 12.3: Bonding in Metals and Semiconductors is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

12.4: Network and Amorphous Solids

Introduction

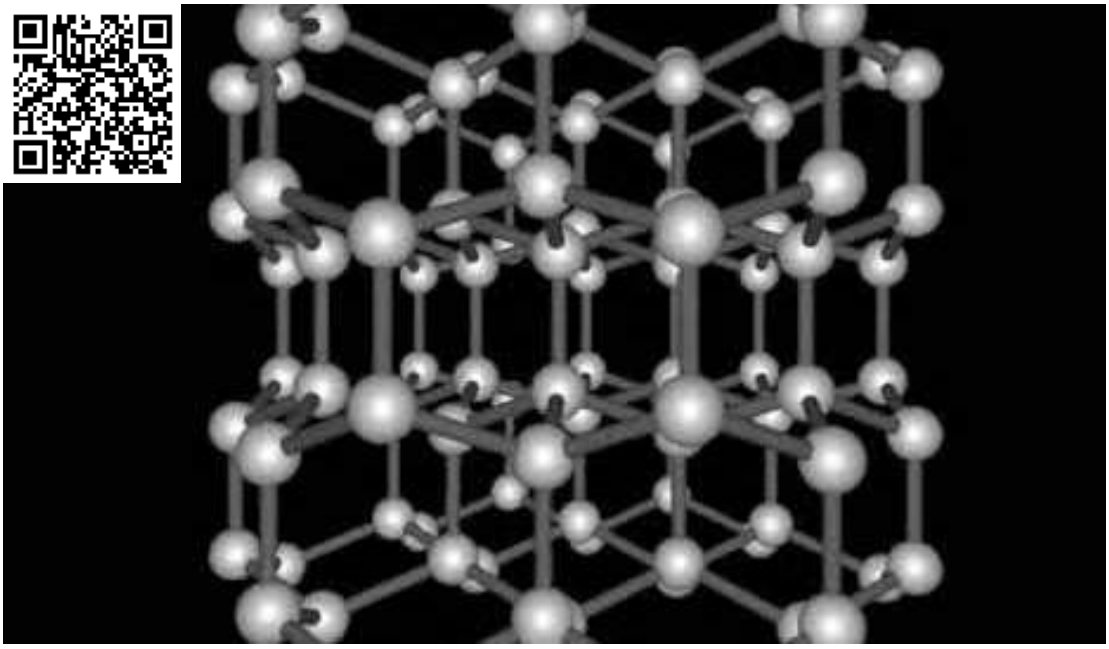
We have described solids in terms of metals and ionic compounds with crystalline structures. Atoms and molecules can also form extended networks of covalent bonds. There are two basic types of covalent network solids, either atomic networks or molecular networks.

1. Covalent Network Solids
    1. Atomic Network Solids
    2. Molecular Network Solids
2. Amorphous Solids

In the above

Atomic Network Solids

A molecule represents an specific chemical species of nuclei connected together with covalent bonds and a defined chemical formula. In contrast, the chemical formula of an ionic compound, which does not describe the smallest entity, but the ratio of cations and anions that results in a neutral structure. Yet there is another type of covalent compound which extends like the lattice of an ionic lattice, and that is the covalent network solid.



***Video*12.4.1** *:* Youtube

Diamond -

Diamond is made of covalent carbon-carbon bonds extending in three dimensions. The geometry is tetrahedral resulting from sp^3 hybrid carbons and there is no molecular formula, as this results in a 3D extended network based on the hybridization.

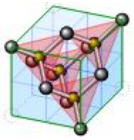


Figure12.4.1: Figure showing sp^3 hybridized carbon in diamond atomic network

Graphite

Graphite is sp^2 hybridized carbon forming planar sheets

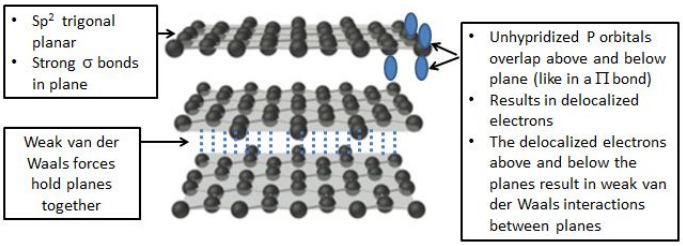


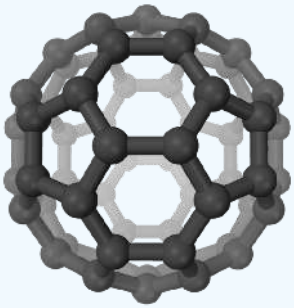
Figure12.4.2: Atomic network of carbon in graphite.

Exercise 12.4.1

Allotropes are different forms of the same element. Diamonds and graphite are allotropes of carbon. Do you know another allotrope of carbon? The later of a specific molecular formula (C_{60}) while diamond and graphite form extended networks of covalent bonds.

Answer

Buckminsterfullerene is an allotrope of carbon. It is not a network solid as it has a formula, (C_{60}).



Molecular Network Solids

The difference between an atomic network and a molecular network is the molecular network consists of extended molecular units. Sand and ice are examples of molecular network solids

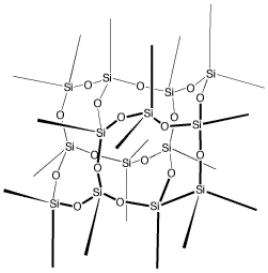


Figure12.4.3: A major component of sand is silica, which has the approximate formula of SiO_2, with this basic unit stretching in 3 dimensions as a molecular extended network. In reality the structure is variable, with hydrogen also being involved. (Image borrowed from Chris Schaller)

Amorphous Solid

Amorphous solids are non-crystalline and do not have repeating structural order. The word comes from greek "a" without and "morphe" (form). Glass is a type of amorphous solid, in fact there are arguments as to if glass is a solid or a liquid.



Figure12.4.4: Desert glass, uploaded from wikicommons

Test Yourself

Contributors

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

Images credits

- Chris Schaller, WIkipedia,
- H. Raab, Wikicommons
- modified anonymous

This page titled 12.4: Network and Amorphous Solids is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

12.5: Phase Diagrams

Introduction

So far we have covered 6 phase transitions, 4 involving solids.

Sublimation (solid --> gas)
Deposition (gas--> solid)

Fusion (solid --> liquid)
Freezing (liquid --> solid)

evaporation (liquid --> gas)
condensation (gas --> liquid)

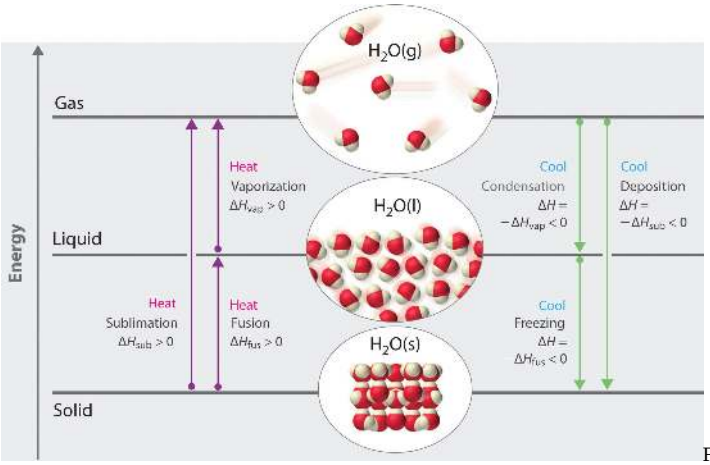


Figure 12.5.1: 6 phase transitions

Sublimation

Iodine is a substance that sublimes, as can be seen in the following YouTube.



Video 12.5.1: 1:39 min YouTube demonstrating the sublimation and deposition of iodine (https://youtu.be/jX9pskbKSw0)

This Youtube shows Iodine subliming at room temperature (an endothermic process absorbing energy), and then they place a cold surface above it, and demonstrate deposition as the vapor converts directly to a solid (an exothermic process).

Carbon dioxide (dry ice) is a common substance that sublimes, and liquid carbon dioxide can not exist at atmospheric pressure. A phase diagram can help you predict the stable phase of matter as a function of Pressure and temperature.

Phase Diagrams

Phase diagrams describe the stable state (or states) of matter as a function of pressure and temperature, so if you know the pressure and temperature of a system, you can determine the stable state. Figure 12.5.2 shows a generic state diagram. We note there are four regions in this diagram (solid, liquid, gas and supercritical fluid). We also see boundary lines between the solid, liquid and gaseous phases, which describe the pressure and temperature at which the two phases can exist in equilibrium. For example, if you took a piece of solid and placed it at a P&T where that substance is stable as a liquid, the solid will melt.

At high temperature and pressure there is a fourth phase where the boundary between the two fluid phases disappears, that is represented by B, the critical point. If you increase the temperature or pressure above this point you have a supercritical fluid. That is, at high temperature the system has so much kinetic energy that it wants to act as a gas, while at high pressure the molecules are so close together that it acts as a liquid, and the boundary between the gas and liquid phase disappears, resulting in a. Supercritical fluids were introduced in chapter 11 (sec 11.6.5). You will also note a point where the three phase boundaries converge, this is the triple point (point c on the diagram.)

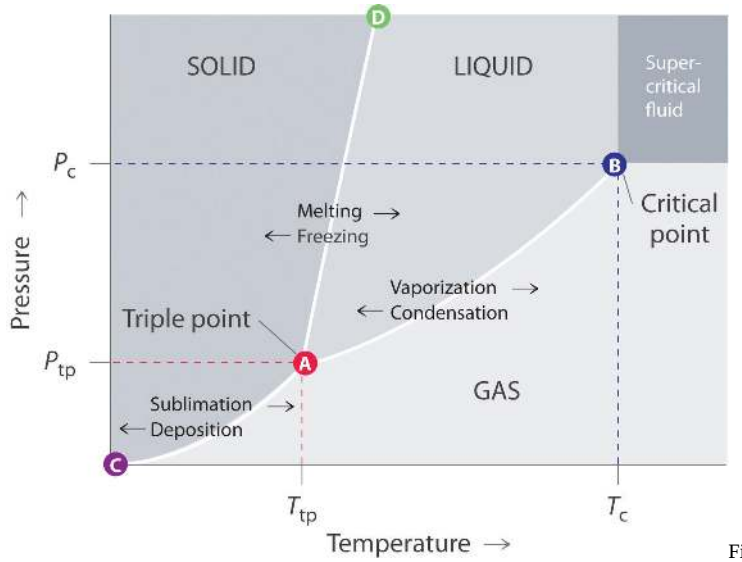


Figure 12.5.2: Copy and Paste Caption here. (Copyright; author via source)

Figure 12.7.a: Typical phase diagram of a substance showing solid, liquid and gaseous phases.

Features of the Phase Diagram

There are several things you need to know in a phase diagram

Regions: (phase regions)

- **Solid Region** - only a solid is stable in this range of P&T, (a liquid or gas would spontaneously convert to a solid).
- **Liquid Region** - only a liquid is stable in this range of P&T, (a solid would spontaneously melt and a gas condense).
- **Gaseous Region** - only a vapor is stable in this range of P&T, (solids and liquids would spontaneously convert to a vapor).

Boundaries Lines (two phase equilibrium boundaries)

- **Solid/Gas Two Phase Line** (pts. A to C) - both a solid and gas can coexist in equilibrium at these T&P, adding heat causes sublimation, removing it causes deposition.
- **Solid/Liquid Two Phase Line** (pts. A to D) - both solid and liquid can coexist in equilibrium at these T&P, adding heat causes melting, removing it causes freezing.
- **Liquid/Gas Two Phase Line** (pts. A to C) - both liquid and gas can coexist in equilibrium at these T&P, adding heat causes vaporization, removing it causes condensation.

Points

- **Triple Point** (point A) - the pressure and temperature at which all three phases can coexist. Note, up until May 20, 2019 the definition of the Kelvin (and degree Celsius) is **1/273.16 the triple point of water**. Today the Kelvin is based on 4 fundamental constants (Boltzmann's, Planck's, speed of light and Cs frequency, see section 1B.3.3.1.2)

- **Critical Point** (point B) - the highest temperature and pressure at which there is a phase boundary between a gas and a liquid (see section 4 of 11.6)

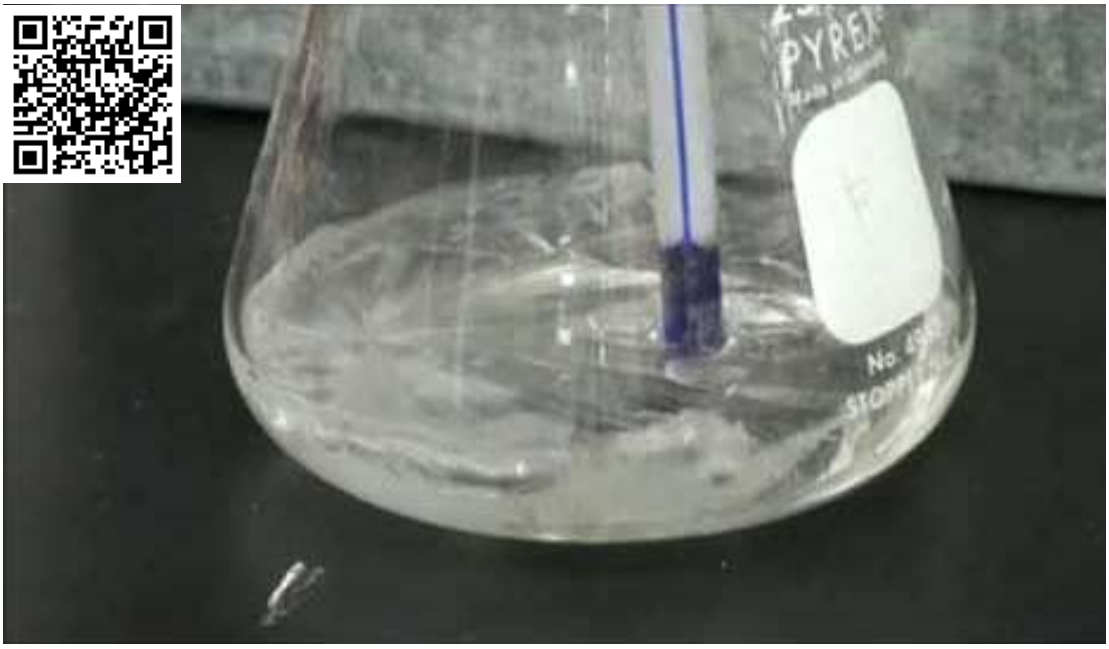
Note most systems are not energetically isolated. A substance on the solid/liquid equilibrium line would maintain a constant ratio of the solid to liquid as long as no energy was entering or leaving the system. So we say two phases can coexist and be stable in a two phase region, you could have a stable system as 25% water and 75% ice and it would not change over time, but if heat entered, ice would melt, and if heat left, water would freeze. At the triple point three regions can coexist in equilibrium.



Video 12.5.2 10:52 min Youtube uploaded by Georgianna Allen that describes the regions of a phase diagram and phase changes involved with isothermal and isobaric paths. (https://youtu.be/ejg27ozbPA8)

Triple Point

The triple point is the temperature and pressure where all three phases are stable and can coexist in an isolated system where no energy is being added or lost. As there is only one temperature and pressure where all three phases can coexist, the triple point is an exact point that can be reproduced in the laboratory. Because of this, it is used to define the SI unit of temperature, the Kelvin, which is defined as 1/273.16 the triple temperature of water (P,T = 0.0060373 atm, 273.16K). This is also the definition of the Celsius degree, which is much better than the centigrade scale, which is 1/00 the difference between the boiling and freezing point of water at 1 atm (which is harder to reproduce in the lab). It should also be noted that the slope of the solid/liquid equilibrium line of water of figure 12.7.d is exaggerated to show that it is negative, and the normal freezing point of water is 273.15K .



YoutubePageIndex{3}\): 2:05 min Youtube video of Triple Point demonstration of Tert-Butyl, (is https://youtu.be/BLRqpJN9zeA).

Critical Point

At pressures and temperatures above the critical point the boundary between the two fluid phases (gas and liquid) disappear and you have a supercritical fluid (section 11.6.6). One of the goals of green chemistry (sec 1A.2) is to reduce waste streams, which often are the results of solvents used in synthesis processes. In the next section (sec. 13.0) we will learn that "like dissolves in like", that is, polar solvents dissolve polar compounds and nonpolar solvents dissolve nonpolar compounds. Supercritical carbon dioxide are green alternatives to common organic solvents like benzene and carbon tetrachloride, both of which are toxic and dangerous to the environment. The following YouTube uses a phase diagram to show how supercritical carbon dioxide is used to extract an organic compound from plant matter, the pressure is then lowered below the critical point and the CO_2 turns to a gas and is separated from the solute, and then recompressed back to a supercritical fluid and recycled, removing the solvent from the waste stream.



Video 12.5.4: 1:56 min Youtube on "The Science Behind Supercritical CO_2 Extraction". (https://youtu.be/AipBc6yBOF4)

Isobaric and Isothermal Transitions

- Isobar - Horizontal path along phase diagram (at constant pressure).
- Isotherm - Vertical path along phase diagram (at constant temperature).

Isobaric Transitions

(Isos = Greek for "equal", Barps = Greek for weight, although isobar actually means constant pressure, as in barometric pressure and not weight).

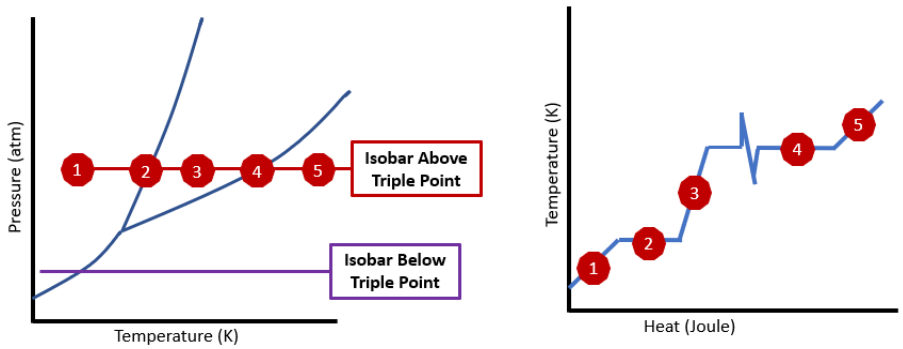


Figure 12.5.3: *Phase diagram for water showing two isobaric transitions (left) above the triple point (red) and below the triple point (purple), and heating curve for water (right) correlated to the isobaric transition above the triple point (red). (CC.0 Bob Belford)*

The left part of 12.5.3shows two isobaric transitions for converting a solid to a gas. The top transition is above the triple point and so liquid water is stable, while the lower transition is below the triple point and the solid sublimes to a gas without ever forming a liquid phase. The graph on the right represents a heating curve as covered in gen chem 1 (sec 5.3.3).

1. Represents a region on both diagrams related to heating ice from -10 to the freezing point and the heat $Q_1=mc_{solid}\Delta T$
2. Is a point on the phase diagram and the region on the heating curve related to melting the ice, $Q_2 = n\Delta H_{fus}$.
3. Represents a region on both diagrams related to heating ice from -10 to the freezing point and the heat $Q_3=m_{liquid}\Delta T$
4. Is a point on the phase diagram and the region on the heating curve related to melting the ice, $Q_4 = n\Delta H_{vap}$.
5. Represents a region on both diagrams related to heating ice from -10 to the freezing point and the heat $Q_5=mc_{vap}\Delta T$

It is important to understand the relationship of these graphs and the differences. The phase diagram represents the phase that would exist for a system at equilibrium as a function of the pressure and temperature. The right diagram shows how the temperature changes as heat is added (or lost), which if done at constant pressure, moves a substance along an isobar on the phase diagram. The numbers in red of the two diagrams correlate to each other.

Isothermal Transition

(Isos = Greek for "equal", Therme = Greek for heat, although isotherm actually means constant temperature, not heat)

An isothermal is a vertical line, as in figure

Figure 12.7.c.

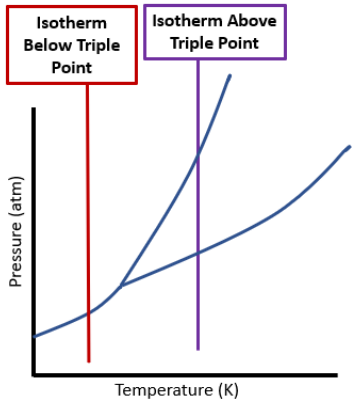


Figure 12.5.4: *Two isothermal transitions where on the left, a solid sublimes to a gas, while on the right, it first melts and then vaporizes. (CC0 Bob Belford)*

Figure 12.7.d, Phase diagram of carbon dioxide (left) and water (right).

There are several things to note in figure 12.7.d. First, the solid/liquid equilibrium line has a negative slope for water and a positive slope for carbon dioxide, with the consequence that ice floats. This is very rare, as most solid phases are more dense than liquid, and sink, not float in their own liquid. Second, the normal isobar (1 atm) is below the triple point for carbon dioxide and above the triple point for water, which is why carbon dioxide sublimes and gaseous carbon dioxide can not be cooled to a liquid, while water can form a liquid at atmospheric pressure.

Additional Information

Many substance have more than one stable solid phase and phase diagrams are useful in identifying the conditions required for each phase. For example, water has multiple crystal structures, and a phase diagram of carbon can tell you which conditions favor diamond over graphite

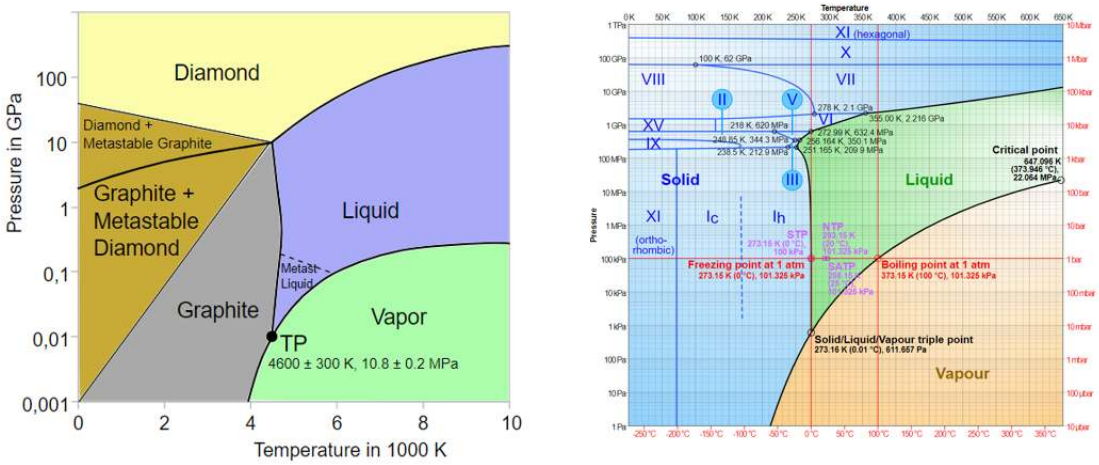


Figure 12.5.5: Phase diagram of Carbon (Public Domain, Wikimedia Commons) and water (CC 3.0, author uncertain, WikiMedia Commons)

As the above two phase diagrams demonstrate, there can be more than one stable phase to a substance, in fact there are 18 phases of water.

In Class Activities

Test Yourself

Homework

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

Images from Chris Schaller, Wikipedia

This page titled 12.5: Phase Diagrams is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

CHAPTER OVERVIEW

13: Solutions

Topic hierarchy

13.1: Prelude
13.2: Units of Concentration
13.3: Solvation Processes
13.4: Pressure and Temperature Effects on Solubility
13.5: Colligative Properties
13.6: Colloidal Mixtures

This page titled 13: Solutions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

13.1: Prelude

Introduction:

Solutions are homogenous mixtures of two or more compounds. They may be solid phase (alloys), liquid phase or gas phase. In the case of liquid phase solutions, the solvent is typically the compound in greater quantity, and the solute in lesser, where the solute is dissolved into the solvent. In aqueous solutions water is the solvent, even if it is in lesser quantities, and in this class we will be dealing mostly with aqueous solutions. The solute can be of a different phase than the solvent

1. **Gas Phase** - like the air, the idea of a solute dissolved in a solvent does not fit this. Gaseous systems are typically described by the partial pressure and mole fraction, review Raoult's Law from your gas phase chapter.
2. **Liquid Phas**e - typically described by solutes dissolved in solvent.
   Solute can be
   - Liquid (alcohol in wine)
   - solid (salt or sugar in water)
   - gas (oxygen in water or blood)
3. **Solid Phase** (may be amorphous or crystalline
   If Crystalline
   - Substitutional (solute takes place of atoms in crystal lattice)
   - Interstitial (solute is in voids of crystal)

Solubility

Solubility is a quantitative measurement of how much of a solute can be dissolved in a solvent. We will go over the units of concentration in the next section. The term solubility often refers to the concentration of a saturated solution

Saturated Solution

A saturated solution has the maximum amount of solute that can exist in equilibrium with undissolved solute. If you add more solute to a saturated solution it does not dissolve, typically falling to the bottom as a precipitate and the concentration of the solution does not change.

Unsaturated Solution

An unsaturated solution can dissolve more solute, and so as you add solute, the concentration of the dissolved particles increases.

Supersaturated Solution

A supersaturated solution is a metastable state which contains more dissolved solute than can exist in equilibrium with undissolved solute. If a small seed crystal is added the dissolved solute in excess of a saturated solution crashes out as is shown in the following video. A metastable state is a state that can be disrupted by a minor disturbance or perturbation. For example, scratching the sides of the glass with a piece of metal could cause the crystals to form.



Video 13.1.1: Supersaturated solution of Sodium Acetate uploaded by dchummer Chemistry (https://youtu.be/FcxZ9DyOaUk)

Miscible Solutions: Soluble in all proportions
Immiscible Solutions: Insoluble, do not mix and form separate layers

Is there an easy way to determine if two liquids are miscible or immiscible?

Like Dissolves in Like:

- Polar liquids dissolve in polar liquids
- Nonpolar liquids dissolve in nonpolar liquids

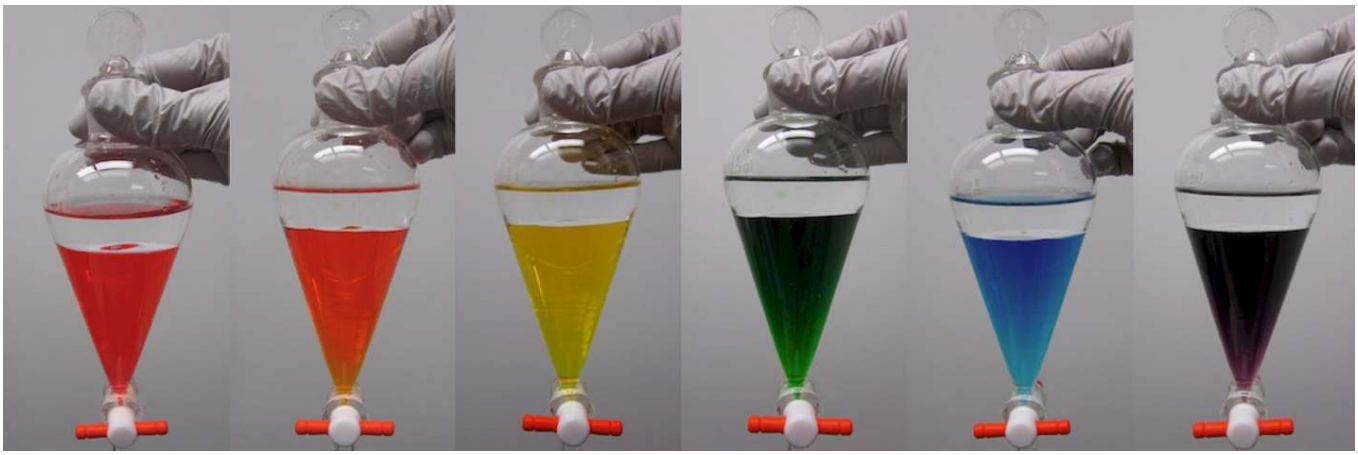


Figure 13.1.1: *Separatory funnels showing immisicible solutions, the bottom layer are aqueous solutions with food coloring added, and the top layer is an organic solvent. The dye molecules are polar and so dissolve in the polar aqueous layer, coloring that layer while making the non-polar layer clear.*

The two solutions in the above separatory funnel are immiscible, and so they form different phases. In this case we are looking at a nonpolar organic solvent with a low density. If the organic solvent was a dense solution like carbon tetrachloride, the clear layer would be at the bottom.

How can you separate two miscible liquids?

Distillation

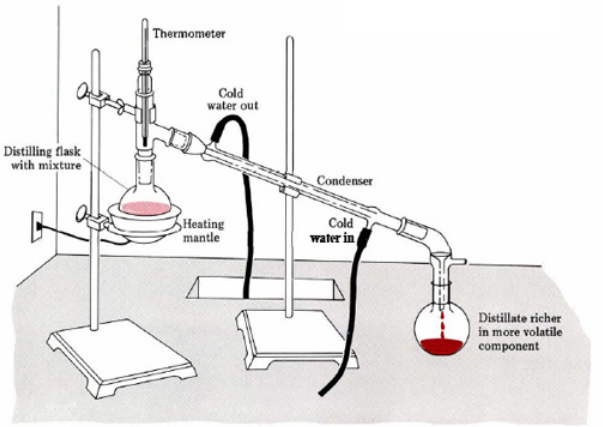


Figure 13.1.2: Distillation apparatus for separating two miscible liquids that have different boiling points.

Two substances with different boiling points are placed in the distilling flask (above figure). As heat is applied, the vapor pressure of the two substances increases and their gas phase molecules rise up and enter the condenser, which cools them, causing condensation and they drip into the collection flask, forming the distillate. At some point the boiling point of the more volatile substance is reached, which then boils and the system stays at its boiling point until it is all boiled. At this point the two compounds have been separated with the more volatile compound being the distillate and collected in the collection flask, while the less

volatile compound stays in the distillation flask. It should be noted that the distillate is not pure as some of the less volatile compound vaporized, and this can be further distilled, producing increasingly pure distillate on the second or third distillation.



Video*13.1.1*: 1:45 min YouTube on Fractional Distillation developed by the Royal Society of Chemistry.

Exercise 13.1.1

Would octane (C_8H_{18}) and Pentane (C_5H_{12}) be miscible or immiscible?

Answer

They are both nonpolar, and would be miscible.

Exercise 13.1.2

If you placed octane and pentane in a still, which would be the distillate?

Answer

Octane has the higher enthalpy of vaporization and lower vapor pressure, and so Pentane would have the higher vapor pressure and boil first. There are two easy to understand reasons why it has a higher vapor pressure (and lower enthalpy of vaporization). First, it is lighter in mass, and so it is easier to vaporize. Second, pentane has weaker intermolecular forces, being smaller in volume, it's valence electrons are held in tighter, making it less polarizable, and so it would have weaker instantaneous-induced dipole intermolecular forces (London Dipsersive Forces) to hold it together..

How do you separate two immiscible fluids?

One way to do this is through a separatory funnel (figure 13.0.1), where the more dense layer is the bottom layer. Note, "like dissolves in like" does not just apply to liquids dissolved in liquids, but also to various solutes. This explains why ionic compounds can be dissolved in water, and so extraction techniques often involve isolating a product from other compounds by extracting it into a solution for which it is preferentially soluble.

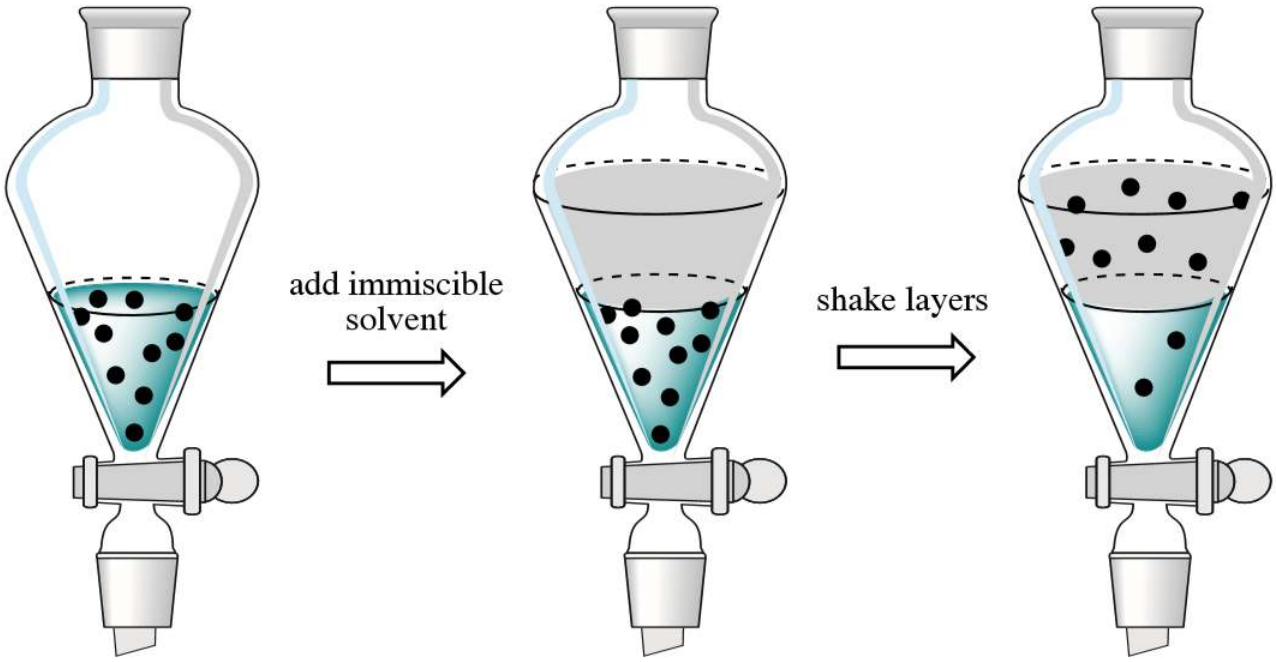


Figure 13.1.2: Consider on the left for the black dots to be the nonpolar product of an aqueous phase reaction, like that between iodide and ferric iron to produce iodine and ferrous iron (eq. 13.0.1). If an immiscilbe nonpolar solvent was added, the nonpolar iodine would have a higher solubility in it than in the polar water phase, and thus would transfer across the boundary and leave the aqueous phase for the organic phase. This could allow you to extract the iodine.

Consider the equation

$$2Fe^{+3} + 2I^{-} \rightarrow 2Fe^{+2} + I_2 \tag{13.1.1}$$

The reactants (Fe^{+3} and I^-) are water soluble through ion-dipole interactions, and one of the products (Fe^{+2}) is also water soluble, but the other product, molecular iodine (I_2) is nonpolar and so is not very soluble in water, but would be soluble in a nonpolar solvent like carbon tetrachloride. So a reaction between water soluble reactants could produce a nonwater soluble product, that in turn could be extracted by dissolving it in a nonpolar solvent and then extracting through a separatory funnel.



***Video*13.1.2:** 3:42 min YouTube on solvent separation with a separatory funnel developed by the Royal Society of Chemistry.

Colligative Properties

- properties of a solvent like the boiling and melting point which for an ideal solution are influenced by the quantity of solute particles, and not the chemical identity of the solute particles. These are covered in section 13.5

Colloids

- homogenous mixtures like solutions, but metastable, that is, they will eventually break into a heterogenous mixture. A foam is a homogeous colloid made of a gas in a liquid, and will eventually fall apart, while oxygen dissolved in water is a pure solution, and will not break. These are covered in section 13.6.

In Class Activities

Test Yourself

Homework

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Lisa Nichols (images repurposed from LibreText site)
- Anonymous

13.1: Prelude is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

13.2: Units of Concentration

Introduction

What does concentration mean?

In the sciences, there are basically two different meanings for concentration; first, how close things are to each other, and second, the composition of substances within a mixture. In General Chemistry 1 we used concepts like density and molarity to describe the first concept, and mass percent and mole fraction to describe the second.

- How dense (packed) things are
  - **Density** ($d = \frac{mass}{volume}$)
  - **Molarity** ($M = \frac{moles}{volume}$),

    Note, the above can be used to describe a pure substance or a mixture. Molarity was very useful for identifying the number of solute particles in a solution as you could only measure the total solution (either its mass or volume), but could not directly measure its components.
- Relative composition of a mixture
  - **Mass Percent** $\left(Mass\ \%_A = 100(\frac{Mass_A}{Mass_{Total}})\right)$
  - **Mole Fraction** $\left(X_A = (\frac{moles_A}{moles_{Total}})\right)$

    Note, the above can be used to describe the relative composition of homogenous mixtures (solutions), but don't really tell you about how close things are to each other. For example, we used the concept of mole fraction to describe the partial pressure of a gas, where the partial pressure was the mole fraction times the total pressure, but that told you nothing about how close the molecules were to each other

    It should also be noted that "percent" is simply the "fraction times 100", and so they are two different ways of stating the same relationship, and that it is a matter of convention to use percent for mass and fraction for the number of molecules, but you could also have "mass fraction" and "mole percent".

Note

When it comes to units of measurement, there are also two fundamentally different ways of mathematically describing the concentrations of things

- One Part to the Whole
  - This is the only kind we have dealt with, and describes things like molarity (mole of a compound to the total volume) and fractions (mole or mass of one compound to the total moles or mass of all compounds)
- One Part to Another Part
  - We will introduce several new measurements, which fit this, like molality (moles of solute to kg solvent), and g solute/100 g solvent. Each of these is representing one entity (the solute) to another entity (the solvent), which is different than relating to the whole (which is the solute and solvent).

Units of Concentration

Molarity M:

$$\text{molarity (M)} = \frac{\text{moles solute}}{\text{liter solution}} \tag{13.2.1}$$

Molarity is useful because by measuring the volume of a solution you can determine the number of solute particles (n=MV, where n=moles solute). Since many reactions occur in solution phases and solutes are often reactants, we used molarity in stoichiometric calculations. We will also learn in the next chapter that the rate of reactions is also dependent on their concentration, and molarity can express that.

NOTE: This is a Part-to-Whole type of calculation, that is, a measurement of the volume (the whole: as the solution is the solvent plus all solutes allows you to determine the moles of a substance (the part). n = MV, where n=moles, M=Molarity and V=Volume. So for example, **when making solutions of a specific molarity, you dilute the solute to a desired volume.**

Molality m:

$$\text{molality (m)} = \frac{\text{moles solute}}{\text{kilogram solvent}} \tag{13.2.2}$$

Molality is the ratio of moles of solute to the mass of solute in Kg. This is often used in calculating how a solute affects a physical property of a solvent, like the boiling or melting point of a solvent. For example, we could determine how much salt is required to lower the freezing point of a specific amount of water by 1 degree.

NOTE: This is a Part-to-Part type calculation, that is, moles solute per kilogram solvent (not solution). So for example, **when making solutions of a desired molality, you add solute to a specific amount (mass) of solvent** (you do not dilute to volume).

Mole Fraction

We used mole fractions in gen chem 1 to describe gas mixtures (sec 10.4.4), where the partial pressure of a gas was its mole fraction time the total pressure.

$$P_A = X_A P_T \tag{13.2.3}$$

$$Mole\ Fraction_A = \left(\frac{mole_A}{moles_{total}} \right) \tag{13.2.4}$$

$$\sum_{n=1}^{all} X_n = 1 \tag{13.2.5}$$

Mole fraction of substance A is often denoted by X_A and the sum of the mole fractions = 1. Although you can have a mass fraction, chemists usually use this for mole fractions.

NOTE: This is a Part-to-Whole type calculation, that is mole of a species divided by the total moles of all species, this is dimensionless.

Mass Percent

$$Mass\%_A = \left(\frac{mass_A}{mass_{total}} \right) 100 \tag{13.2.6}$$

$$\sum_{n=1}^{all} Mass\%_n = 100 \tag{13.2.7}$$

Percentage is related to fraction, it is simply the fraction times 100. Chemists usually use percentage to describe mass fractions. Note, the sum of the mass percents of all substances within a sample = 100%.

Note: This is a Part-to-Whole type calculation, That is, this is 100 times the mass fraction.

Mass Ratio

The ratio of two substances is the amount of one compared to the amount of another. If one of these is the solvent, then the ratio of solute to solvent becomes an indicator of how concentrated the solute is in the solvent. This is not normally used, but may help you understand grams solute per 100 g water (see below).

Note: This is a Part-to-Part type calculation: So mass ratio of a solute in a solvent would be mass solute divided by mass solvent (not solution, as in mass fraction)

Grams Solute per 100 g H_2O (S)

This is often given the symbol (S) and used in graphing properties of solvents, like how a solute concentration effects the boiling point (temperature) of water. It tells you how concentrated a solute is in terms of g solute per 100 g water. This is simply the ratio times 100, and has units g solute/100 g solvent. Note: a rule-of-thumb, is a soluble substance has a solubility greater than 0.1g/100 g solvent, and an insoluble substance is less, but of course, that is all relevant.

$$S = 100(mass\ ratio) = \frac{mass\ solute}{mass\ solvent}(100) \tag{13.2.8}$$

If you dissolve Xg solute into Yg solvent, S = (X/Y)100g

Note: This is a Part-to-Part type calculation. Simply speaking it is the mass ration times 100.

Parts-per notation

These are often called "pseudo-units" and are dimensionless quantities used to describe very dilute solute concentrations. The meaning can be ambiguous, but they are often used in engineering. In this section we will look at aqueous systems.

Parts per million

Often expressed as g solute/10^6g solvent or "medium", where the medium is a sample like dirt or body mass. Note, mass is not a measure of the parts like a number of entities, but this is the convention)

$$ppm = \frac{g\ solute}{10^6 g\ solvent} = \frac{g\ solute}{10^6 g\ medium} \tag{13.2.9}$$

for aqueous solutions we note that the density of water is 1g/ml, so the above equation can be converted to

$$ppm = \frac{mg_{solute}}{L_{water}} \tag{13.2.10}$$

Exercise 13.2.1

Show how to convert g solute/10^6g solvent = mg solute/L water (when the solvent is water)

Answer

$$ppm = \left(\frac{g\ solute}{10^6\ g\ H_2O}\right)\left(\frac{10^3\ g\ H_2O}{L}\right)\left(\frac{10^3 mg\ solute}{g}\right) = \frac{mg\ solute}{L\ H_2O}$$

Exercise 13.2.2

Calculate the concentration of selenium in ppm if 5.4 grams are found in 250 kg of water?

Answer

note 1 kg is 10^3g so 250 kg is 2.5x10^5 g.

$$\left(\frac{5.4\ g\ solute}{2.5x10^5\ g\ H_2O}\right)\left(\frac{10^3\ g\ H_2O}{L}\right)\left(\frac{10^3 mg\ solute}{g}\right) = \frac{22\ mg\ solute}{L\ H_2O} = 22\ ppm$$

Parts per billion

Often expressed as g solute/10^9g solvent (note, mass is not a unit of quantity, but this is the convention)

$$ppb = \frac{g\ solute}{10^9 g\ solvent} \tag{13.2.11}$$

for aqueous solutions we note that the density of water is 1g/ml, so the above equation can be converted to

$$ppb = \frac{\mu g_{solute}}{L_{water}} \tag{13.2.12}$$

Exercise 13.2.3

Show how to convert g solute/10^9g solvent = μg solute/L water (when the solvent is water)

Answer

$$ppb = \left(\frac{g\ solute}{10^9\ g\ H_2O}\right)\left(\frac{10^3\ g\ H_2O}{L}\right)\left(\frac{10^6 \mu g\ solute}{g}\right) = \frac{\mu g\ solute}{L\ H_2O}$$

Worksheet

- Concentration worksheet
- Concentration worksheet key

Note:

If you open a PDF in browser, you can comment on it. Be sure to tag it c1403c13 and to post it to the hypothes.is group UALRChem1403. Contact your instructor if you are not in the group. You can also print the worksheet if that is easier to work from.

Test Yourself

homework

The following problem have Video Solutions in the Answers

Exercise 13.2.4

Concentrated aqueous ammonia is 28% by mass NH_3 and has a density of 0.90g/ml. What is the mole fraction ammonia in concentrated ammonia? Note: Answer contains a video.

Answer

$X_{Ammonia}$ = 0.29 , note how this is close to the mass %, which is because ammonia and water have similar molar masses.



Exercise 13.2.5

Concentrated aqueous ammonia is 28% by mass NH_3 and has a density of 0.90g/ml. What is the molarity of ammonia in concentrated ammonia? Note: Answer contains a video.

Answer

$M_{Ammonia}$ = 15M.



Exercise 13.2.6

Concentrated aqueous ammonia is 28% by mass NH_3 and has a density of 0.90g/ml. What is the molality of ammonia in concentrated ammonia? Note: Answer contains a video.

Answer

$m_{Ammonia}$ = 23 (mol NH_3/kg H_2O)



Contributors and Attributions

- Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 13.2: Units of Concentration is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

13.3: Solvation Processes

Introduction

Solvation, or dissolution, is the process by which a solute dissolves into a solvent.

As indicated in figure 13.2.1, solvation can be considered to occur in three steps.

- Step 1: Separate particles of the solute from each other
- Step 2: Separate particles of the solvent from each other
- Step 3: Combine separated solute and solvent particles to make solution

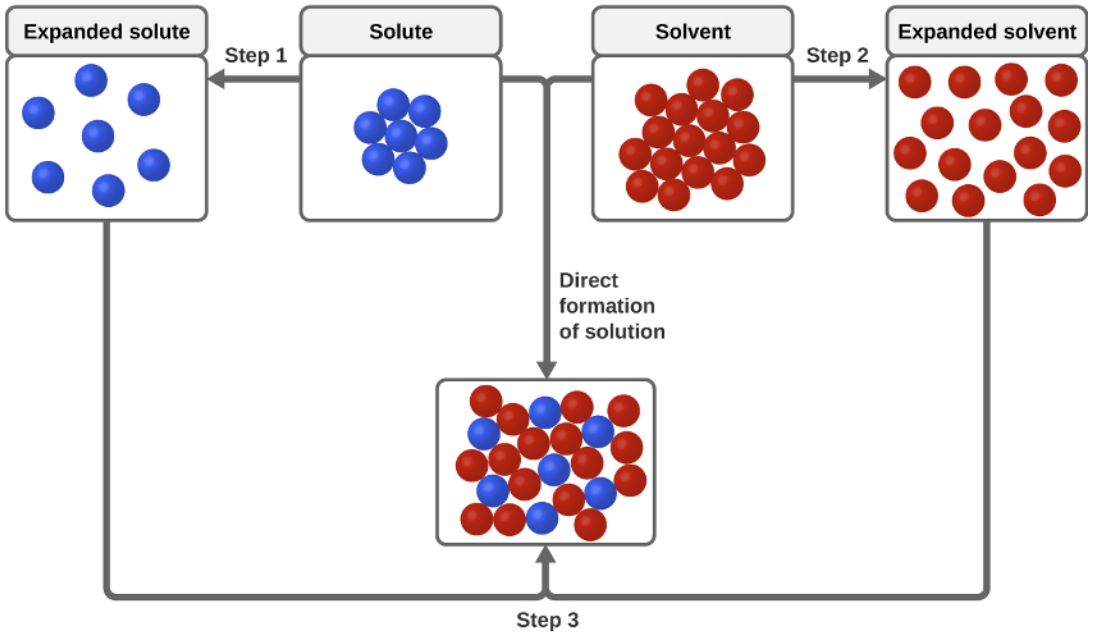


Figure 13.3.1: Visualization of solvation process as taking place in 3 distinct steps.

Note, in the above diagram the first two steps require breaking apart the pure solute and the pure solvent, while the second requires forming the solution.

Energetics of Dissolution

Enthalpy is a state function and thus path independent. So the energetics requires breaking apart the solute (step 1) and the solvent (step 2) and then forming the solution (step 3).

- Step 1: Separate particles of the solute from each other [ENDOTHERMIC]
- Step 2: Separate particles of the solvent from each other [ENDOTHERMIC]
- Step 3: Combine separated solute and solvent particles to make solution [EXOTHERMIC]

Exercise 13.3.1

Why are the first two steps endothermic, but the third exothermic?

Answer

The first law of thermodynamics states that the energy of the universe is conserved, that the universe can be partitioned between a system and the surroundings, and that positive energy is energy added to the system (endothermic) and "negative energy" is energy added to the surroundings (exothermic), which is lost by the system. By "negative energy" we do not mean that energy is negative, but that the flow of energy is from the system to the surroundings and thus the system loses energy. It may be better to say the "flow of energy", but we often associate energy with a reaction, that is the change of

energy of the system during a reaction, and that may be positive or negative, depending on if it is endothermic or exothermic. So lets look at energy from the perspective of the energy associated with each step of the the process.

Since you add energy to break apart something (intermolecular forces in the case of a solute and intramolecular forces in the case of the solvent), the first two steps are endothermic.

The third step is exothermic, which may be easier understood by looking at the opposite process. That is, to break a solution apart into its separate components must require energy, and since energy is conserved, the opposite process, that of forming the solution from its separated pieces must release that energy, and so it is exothermic.

So when is dissolution endothermic and when is it exothermic? From figure 13.1.1 we can see that the direct process is the summation of the three steps. If the endothermic steps (1 & 2) are larger than the exothermic step (2), it is endothermic. If they are less, it is exothermic.

Exothermic Solvation Processes

This is illustrated in the energy cycle of figure 13.2.2. Since enthalpy is a state function the energy going from solvent and solute to solution is independent of the path, and there are two paths, the direct route, represented in green as ΔH_{soln} and that of steps 1,2,3. So

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3. \tag{13.3.1}$$

Since ΔH_3 releases more energy than $\Delta H_1 + \Delta H_2$ absorb, the process is exothermic, and

$$\Delta H_{soln} < 0 \tag{13.3.2}$$

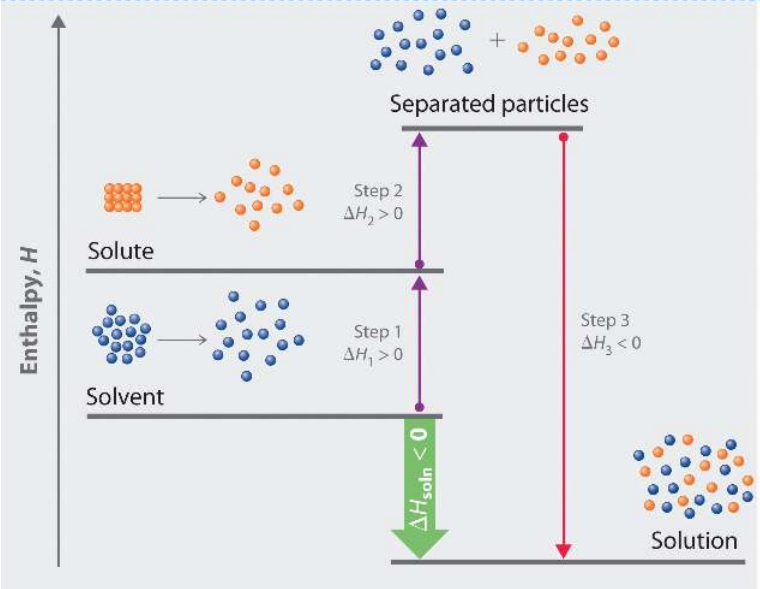


Figure 13.3.2: An exothermic solvation process where the exothermic step releases more energy than the endothermic steps absorb. Such a process will heat the surroundings.

Endothermic Solvation Processes

This is illustrated in the energy cycle of figure 13.2.3 . Here the two endothermic steps absorb more energy than the exothermic step releases, and so the dissolution process is endothermic.

$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$. Since $\Delta H_1 + \Delta H_2$ absorb more energy than ΔH_3 releases, the overall process is endothermic, and

$\Delta H_{soln} > 0$

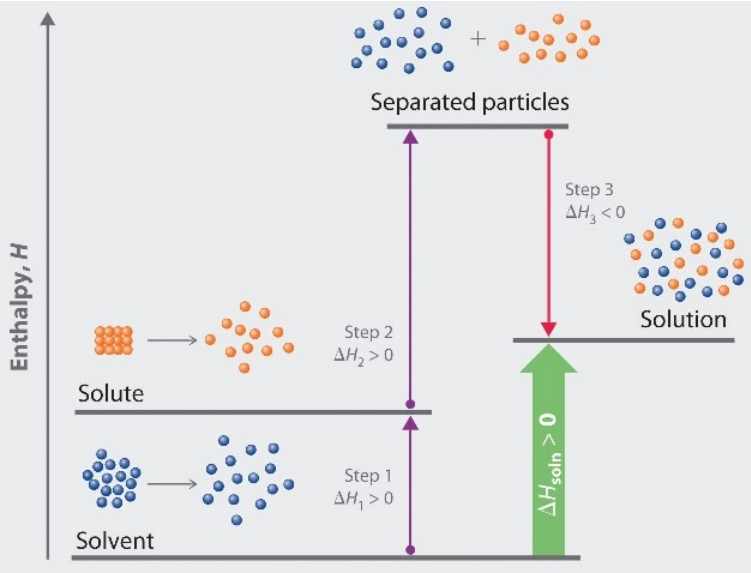


Figure 13.3.3: An endothermic solvation process where the endothermic steps absorb more energy than the exothermic releases. Such a process will cool the surroundings.



Video 13.3.1: 3:48 Minute YouTube by Gydeon Rozen of the Technion Israel Institute of Technology. In the first part they demo the exothermic dissolution of calcium chloride in water, in the second part they demonstrate the endothermic reaction of the dissolution of uera in water.

In Class Activity

Test Yourself

Homework

This page titled 13.3: Solvation Processes is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

13.4: Pressure and Temperature Effects on Solubility

Introduction

In this section we will look at how the pressure and temperature effect solubility.

When we look at pressure effects, we are considering the pressure of a gas over a liquid, and so the solute is necessarily a gas, and we will introduce Henry's law to describe this.

When we look at the temperature effect, the solute can be a solid or a gas, and the temperature effects can often be very different. We will introduce solubility curves to describe the temperature effects, noting that gas solubilities go down as temperature goes up, but solid solubilities usually, but not always increase upon heating.

Pressure Effects on Solubility

When a gas phase molecule hits the surface of a liquid it may be deflected back into the gas or dissolved into the solution, in the latter case becoming a solute particle. If a dissolved molecule reaches the surface of the liquid, a fraction will have enough kinetic energy to escape, and so particles are being exchanged across the liquid/gas boundary all the time. When the rate at which the gas phase particles enter and leave are equal you have a dynamic equilibrium, where the concentration in each phase becomes a constant value. The solubility is a measure of the concentration of the dissolved gas particles in the liquid and is a function of the gas pressure. As you increase the pressure of a gas, the collision frequency increases and thus the solubility goes up, as you decrease the pressure, the solubility goes down..

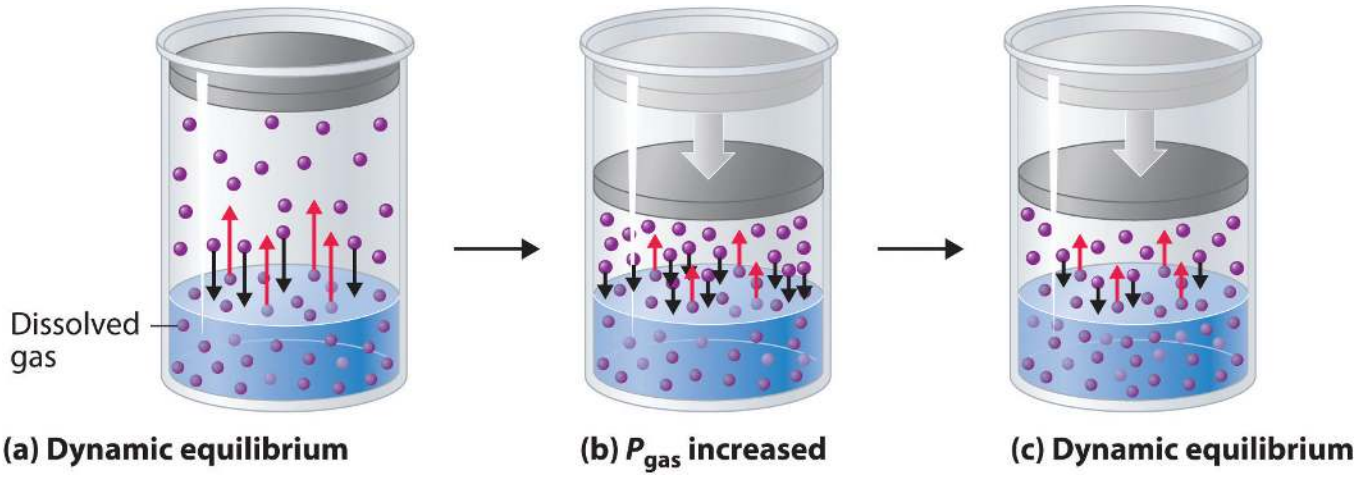


Figure 13.4.1: This figure shows how the solubility of a gas can be understood as a dynamic process where gaseous particles are transitioning across the boundary between the two phases.

Figure 13.3.1 shows a system at equilibrium (a) where the rate across the suface/vapor boundary is constant (red arrows equal black arrows). In (b) the pressure is increased (by decreasing the volume). This increases the concentration in the vapor phase, and so the collision frequency with the liquid increases, causing more to be dissolved. As the concentration in the liquid increases the rate of escape equals, and the concentration rises until the rate of escape equals the rate at which they are entering the liquid, when a new equilbrium occurs (c).

Exercise 13.4.1

What would be the effect if the gas in figure 13.3.1 was reduced in pressure?

Answer

The solubility would decrease because there would be less molecules hitting the surface.

The relationship between the solubility of a gas and its pressure is a linear one, and can be described by Henry's law.



Video 13.4.1: 0:27 professional animation uploaded by kwesiamoa showing how the solubility of a gas is a function of pressure

Henry's Law

Henry's law states that the concentration of a gaseous solute in a liquid is proportional to the absolute pressure. This explains commonly observed phenomena like the degassing of a can of carbonated beverage upon opening. While sealed, there was no room for gas to expand and so the pressure would be high, resulting in a high dissolved concentration. This system was at equilibrium, but once it was opened, the gas pressure dropped and created a state of disequilibrium, with the gas leaving the fluid far mor rapidly than it was entering. Overtime, the system reached a new equilibrium, and the carbonated beverage became "flat".

Henry's Law Constant

$$\underbrace{C = kP}_{\text{Henry's Law}} \tag{13.4.1}$$

In the above equation, C= concentration, k= Henry's Law constant and P is the partial pressure of the gas that dissolves. Henry's law describes the solubility of a specific gas in a specific solvent and is a strong function of the temperature. So a table of Henry's law constants for various gasses must define the solvent and the temperature for which they apply, and care must be taken that these are the same when comparing constants from different sources. The point is that there is no such thing as Henry's law constant for carbon dioxide, there is one for carbon dioxide at 25ºC in water, another in ethanol and another in benzene...

It should be noted that there are many units for concentration and so "C" may mean different things (Molality, Molarity, ppm,...), and of course there are many units for pressure (atm, torr, bar,...), which students often find this confusing. Probably the best way to write out Henry's law is to look at the units of the constant. So for:

k(CO_2) in water at 20ºC = 0.034 $\frac{mol}{kg \cdot bar}$, I would use, m=kP, where m=molality,

for

k(CO_2) in water at 25ºC = 3.92x10^{-2} $\frac{mol}{L \cdot atm}$, I would use M=kP, where M=molarity.

(**The important thing is to always look at the units of k**)

Exercise 13.4.1

What is Henry's Law constant if the solubility of oxygen is 40mg/L water at 1 bar. Express in the given units, and convert to $\frac{mol}{L \cdot atm}$

Answer

$C = kP \; k = \frac{C}{P} = \frac{40 mg\, O_2}{L \cdot bar}$.

To convert to $\frac{mol}{L \cdot atm}$:

$$\frac{40mg\,O_2}{L \cdot bar}\left(\frac{g\,O_2}{10^3\,mg\,O_2}\right)\left(\frac{molO_2}{32g}\right)\left(\frac{bar}{0.987atm}\right) = 1.27x10^{-3}\,\frac{mol}{l \cdot atm}$$

Two State Approach

Even without knowing Henry's Law constant, if you know the solubility at one pressure, you can determine it at another.

$$C_1 = kP_1 \tag{13.4.2}$$

dividing both sides by the concentration at a different pressure

$$\frac{C_1}{C_2} = \frac{kP_1}{C_2}$$

$$substituting\ \ C_2 = kP_2$$

$$\frac{C_1}{C_2} = \frac{\cancel{k}P_1}{\cancel{k}P_2} = \frac{P_1}{P_2}$$

$$C_2 = C_1\frac{P_2}{P_1}$$

Where the subscripts 1 indicates the concentration at one pressure and the subscript 2 indicates the concentration at a different pressure

Exercise 13.4.2

If the solubility of carbon dioxide is 1.45g/L at 25°C and 100 kPa, what is it at 50 kPa? And give answer in units of Molarity.

Answer

Ok, if you think about it, you halved the pressure, so you are going to halve the concentration and it will be 0.725g/L. This is the same as asking what is the volume of 10 grams of a solid of constant density if 20 grams is 10mL. We simply take the two state approach for Henry's Law.

$$\frac{C_1}{C_2} = \frac{kP_1}{kP_2} = \frac{P_1}{P_2}$$

$$C_2 = C_1\frac{P_2}{P_1}$$

$$= 1.45(\frac{g}{L})\frac{50kPa}{100kPa}$$

$$= 0.725\frac{g}{L}$$

In units of molarity

$$M = 0.725\frac{g}{L}\left(\frac{molCO_2}{44.01g}\right) = 0.0165M\ CO_2$$

or 16.5mM CO_2

Temperature Effect on Solubility

The temperature effect depends on the nature of the solute and the solvent, and their interactions. These are completely different between solid solutes and gaseous ones. The propensity of a solid is to become more soluble as temperature goes up, and for a gas to become less soluble. We will revisit this in chapter 18 when we cover entropy and the second law of thermodynamics, which essentially says that a process goes in the direction that increases the entropy of the universe, that is, how dispersed the universe is.

Spontaneous process tend to occur when reactions are exothermic and particles become more dispersed, but sometimes solvation can get real tricky, as dissolving an ion can induce order in the solvent, as when ion-dipole interactions cause the polar molecules to align around the ions. The "Rule of Thumb" is that with increasing temperature gas solubility goes down and solid solubility goes up, but there are cases where the later is not true.

Temperature and Gas Phase Solubility

In chapter 11 we saw that increasing the temperature increased the vapor pressure above the surface of a pure volatile liquid. This was because more molecules had enough kinetic energy to escape the liquid and enter the vapor phase (figure 11.6.5) . In that chapter we were talking about a pure substance, but if a solution with a gas dissolved in it is heated, it too gains kinetic energy, increases the fraction of collisions at the surface that have enough energy to escape the surfaces forces of the solution, and so the concentration of those remaining dissolved goes down. Figure 13.3.2 shows how the solubility of a gas in water goes down as the temperature is raised. This decrease in the solubility of oxygen as temperature goes up is one of the reasons cold water fish like trout can not live in warm water.

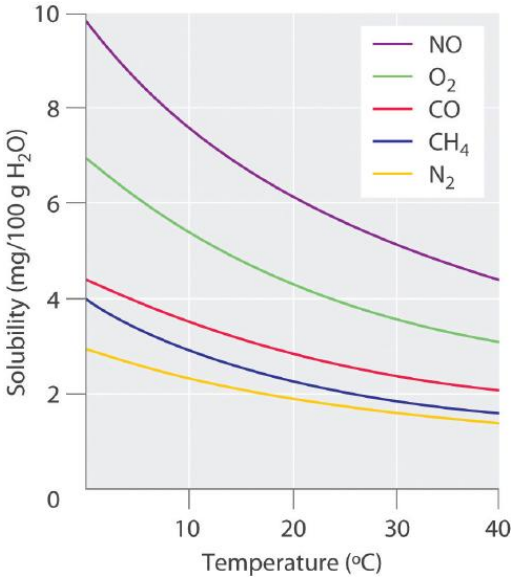


Figure 13.4.2: Solubility of several gasses in water

Temperature and Solid Phase Solubility

Figure 13.3.3 shows the solubility of many ionic and covalent compounds in water. There are a wide range of dependencies on the temperature and although most compounds increase their solubility as heated, some actually show a decrease. We will revisit this material when we get to chapter 18 and cover entropy and Gibb's free energy.

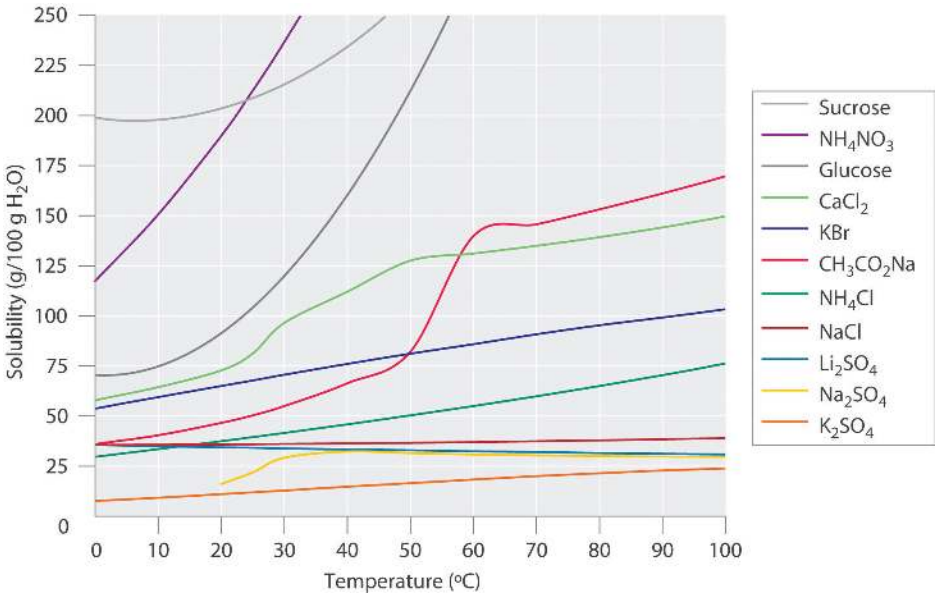


Figure 13.4.3: Solubility of various covalent and ionic solids in water

Some of the molecules in the gas phase condense when they contact the liquid and some in the liquid evaporate into the gas. Thus the molecules can be considered to be partioned across both phases, with some in the liquid and some in the gas phase. For a system at equilibrium the rate they enter the gas phase equals the rate at which they enter the liquid, and so the concentration in both phases is constant.

In Class Activity

Test Yourself

Homework

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 13.4: Pressure and Temperature Effects on Solubility is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

13.5: Colligative Properties

Introduction:

Colligative properties are properties of solutions, that depend on the concentration of the dissolved particles (molecules or ions), but not on the identity of those particles. They often affect solvent properties like boiling and melting point, or the vapor pressure above a fluid. There are four colligative properties we will look at:

- vapor pressure
- boiling point
- freezing point
- osmotic pressure



Figure 13.5.1: *Salt lowers the freezing point of water and so is used to melt ice and snow on roads. Image from Wikipedia*

Vapor Pressure over a Solution

The vapor pressure over a pure liquid was covered in section 11.6 and described by the Clausius-Claperyron equation. When you add a solute to a pure liquid it becomes a solution, and what was a pure liquid is now the solvent that the solute has dissolved into. The solute will affect the vapor pressure above the solution and the effect depends on whether the solute is volatile or nonvolatile. Nonvolatile solutes depress the vapor pressure above the solution, which is only due to the solvent molecules. Volatile solutes that form miscible solutions are more complicated, as each substance has a vapor pressure, with the total vapor pressure being the sum of all the partial vapor pressures.

Nonvolatile Solutes

Nonvolatile solutes do not have an appreciable vapor pressure of their own, and they decrease the vapor pressure of a solvent (over a solution) when added to a solvent. This can be understood by the dynamics depicted in figure 13.5.2 In part (a) you have a pure volatile substance (solvent) and the vapor pressure (P^o) is the equilibrium pressure of the solvent when the rate of evaporation equals the rate of condensation (review 11.6, Vapor Pressure as Equilibrium Pressure). Note there are 5 red lines representing the evaporating molecules and 5 black lines representing the condensing molecules (so the rate of condensation equals evaporation and the number of vapor molecules is constant). A non-volatile solute is introduced (b), and when a solute molecule is near the surface it can't escape. This effectively reduces the surface area for evaporation, and so fewer molecules transfer to the vapor phase, but those condensing have no such reduction in surface area (a vaporized solvent molecule can lose energy and condense if it his a surface solute or solvent molecule). So in (b) there are 6 black arrows entering the liquid, but only 4 red arrows leaving. The system is no longer at equilibrium and more solute condense than evaporate, reducing the vapor pressure until the ate of evaporation equals condensation and a new equilibrium has been reached (c). The result is a reduction in the vapor pressure.

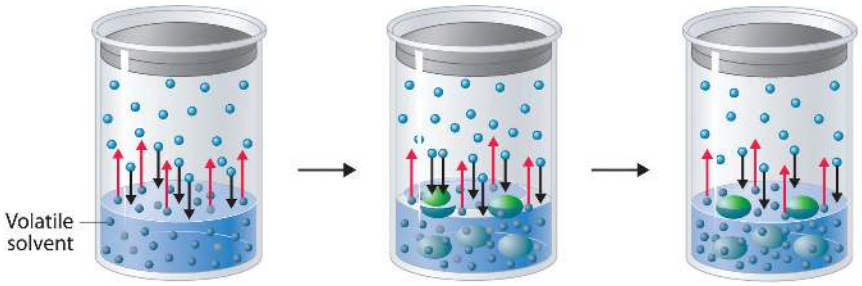


Figure 13.5.2: *Figure showing how introducing a nonvolatile solute (glucose) to a volatile solvent (water) in a closed system reduces the rate of evaporation while not affecting the rate of condensation, resulting in a decrease in the number of vapor particles once a new dynamic equilbrium vapor pressure is achieved.*

Volatile Solutes

If a volatile solute is added to a volatile solvent the total pressure is the sum of the partial pressures of both components. This is usually the case for liquid solutes like that of dissolving ethanol (alcohol) into water, where the vapor above the circuit consists of both ethanol and water molecules. If there are more than two volatile substances in a solution, the total pressure is the sum of the partial pressures of all the substances.

Raoult's Law

Raoult's Law describes the vapor pressure of a volatile substance as the mole fraction of that substance times the vapor pressure of the pure substance.

$$\underbrace{P_{substance} = X_{substance} P^o_{substance}}_{\text{Vapor Pressure of a volatile substance in a solution}} \tag{13.5.1}$$

where,

$P_{substance}$= vapor pressure of a volatile substance in a solution
$X_{substance}$= mole fraction of the volatile substance in a solution
$P^o_{substance}$= vapor pressure of the pure volatile substance

Nonvolatile Solute

For a solution with a nonvolatile solute dissolved in a volatile solvent the vapor pressure is due to the solvent. This is a very simple relationship based on the fraction of particles (mole fraction) that are volatile. If a solution is half solute and half solvent on a mole basis, the vapor pressure above the solution is half that of the pure solvent. If the solution was 90% solvent on a mole basis, it's vapor pressure would be 90% of the pure solvent. In reality, most nonvolatile solutes are solids, and so can not be soluble in all proportions, that is, at some point a solution becomes saturated, and addition of further solute does not add to the solution but precipitates out.

From this we can see two expressions for Raoults law, the first one describing the vapor pressure of a volatile solvent in a solution, and the second the vapor pressure depression due to the nonvolatile solute. These two relationships are displayed by the data in figure 13.5.3

1. Vapor Pressure is proportional to mole fraction of solvent.

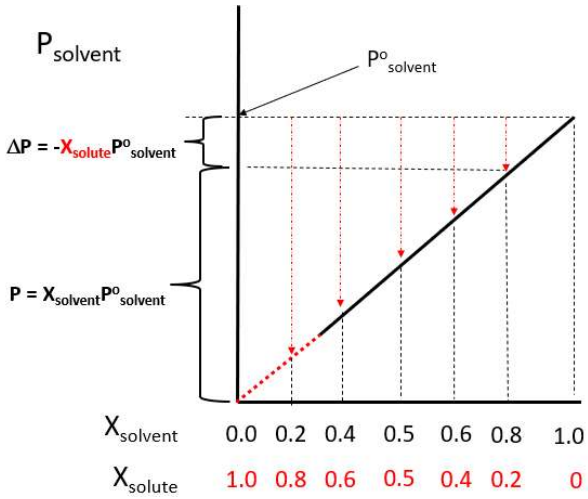
$$\underbrace{P_{solvent} = X_{solvent} P^o_{solvent}}_{\text{Vapor Pressure over solution}} \tag{13.5.2}$$

   the maximum value is that of the pure solvent

2. Vapor Pressure depression is proportional to mole fraction of non-volatile solute.

$$\underbrace{\Delta P_{solvent} = -X_{solute} P^o_{solvent}}_{\text{Vapor Pressure Depression due to non volatile solute}} \tag{13.5.3}$$

Since the solute has no vapor pressure, the depression is proportional to the fraction of the solute. Note the negative sign



$X_{solvent}$	X_{solute}	$P_{solvent}$	$\Delta P_{solvent}$
1	0	$P^o_{solvent}$	0
0.8	0.2	$0.8P^o_{solvent}$	$-0.2P^o_{solvent}$
0.6	0.4	$0.6P^o_{solvent}$	$-0.4P^o_{solvent}$
0.5	0.5	$0.5P^o_{solvent}$	$-0.5P^o_{solvent}$
0.4	0.6	$0.4P^o_{solvent}$	$-0.6P^o_{solvent}$
0.2	0.8	$0.2P^o_{solvent}$	$-0.8P^o_{solvent}$
0	1	0	$-P^o_{solvent}$

Figure 13.5.3: Raoult's Law plot of vapor pressure of volatile solvent with a non-volatile solute. Note this is a hypothetical system where the solute and solvent are soluble in all proportions. In reality, nonvolatile solutes are typically solids and form saturated solutions, and thus there is a limit to the possible mole fractions, which is being represented by the red dots on the graph. Only for misciple liquid/liquid solutions can the graph go from pure solute to pure solvent. P^o represents the vapor pressure of the pure solvent ($X_{solvent}$=1). The table on the right is color coded so you can see how as the mole fraction solute increases, the vapor pressure of the solvent is decreased from that of pure solvent. (CC0; Bob Belford)

Do not be confused by Raoult's law, it is real simple. If you have a solution that is 40% solvent and 60% nonvolatile solute, the vapor pressure is 40% of the pure solvent. If it is 90% solvent, it is 90% of the solvent. That is what Raoult's law and figure 13.5.3 say.

Volatile Solutes

Volatile solute are solutes that have a vapor pressure. These are typically miscible liquids that form solutions of any proportion, and so it is not always useful to distinguish one as the solvent and the other as the solute. The vapor pressure above the solution is the sum of the vapor pressure of each component within the solution (Dalton's Law of Partial Pressure, section 10.4.3)., where the vapor pressure of each component is determined by Raoult's Law. For component A, $P_A=X_AP^0_A$, and for component B, $P_B=X_BP^0_B$ .We will only look at two component systems, but the vapor pressure of a system with more than two volatile solutes is simply the sum of their individual Vapor Pressures.

The vapor pressure above a solution with a volatile solute consists of vapor due to each species, and this usually occurs when miscible liquids are present, like ethanol and water, which can mix in any ration. Figure 3.4.3 shows the Raoult's Law graph of the total vapor pressure for two miscible fluids, toluene ($C_6H_5CH_3$) and benzene (C_6H_6). Note, as you move across the graph the roles of solute and solvent switch. That is, for a solution that is 95% benzene and 5% toluene we would consider benzene to be the solvent, but we would consider toluene to be the solvent for a solution that is 95% toluene and 5% benzene.

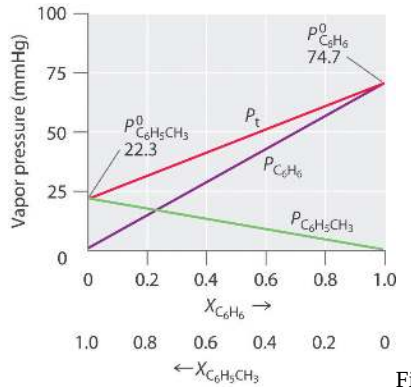


Figure 13.5.4: *Vapor pressure diagram for a solution of two volatile substances. The green line shows the partial pressure of toluene, the purple line of benzene, and the red line is the sum of the two at any specified concentration.*

The total Vapor Pressure is: $P_T = X_{toluene} P^0_{toluene} + X_{benzene} P^0_{benzene}$. (Noting: $X_{toluene} + X_{benzene} = 1$)

Although this looks complicated, it really is not. Each solution follows Raoult's Law where it's vapor pressure is the vapor pressure of the pure substance times the mole fraction of that substance. The total vapor pressure follows Dalton's law of partial pressures, in that the total vapor pressure is the sum of the partial pressures.

Exercise 13.5.1

For a nonvolatile solute, can you derive the equation for the vapor depression dependence on the mole fraction solute (13.4.2)

$$\Delta P_{solvent} = -X_{solute} P^o_{solvent}$$

from the equation for the vapor pressure dependence on the mole fraction solvent (13.4.1)?

$$P_{solvent} = X_{solvent} P^o_{solvent}$$

To do this you need to recognize that

$$X_{solvent} + X_{solute} = 1$$

Answer

$$\begin{aligned} \Delta P &= P_{Final} - P_{Initial} \\ &= P^{(in\ solution)}_{solvent} - P^0_{solvent} \\ &= X_{solvent} P^0_{solvent} - P^0_{solvent} \\ &= P^0_{solvent} (X_{solvent} - 1) \end{aligned} \tag{13.5.4}$$

Noting $X_{solvent} + X_{solute} = 1$ can be arranged to

$$X_{solute} = 1 - X_{solvent} \quad (13.5.5)$$
$$\text{or}$$
$$-X_{solute} = X_{solvent} - 1$$

Substituting eq 13.4.5 into eq 13.4.4 gives eq. 13.4.2

$$\underbrace{\Delta P_{solvent} = -X_{solute} P^o_{solvent}}_{\text{Vapor Pressure Depression due to non volatile solute}}$$

Simply speaking, if a solution is 30% nonvolatile solute its pure vapor pressure depression (-ΔP) is 0.30P$^o_{solvent}$, and its pressure is 70% of the pure P=0.70P$^o_{solvent}$. As is shown in the next exercise, you can't have all mole fraction ranges of figure 13.4.3 with a solid solute, and at some point the solution becomes saturated and a precipitate starts to form. The saturated solution represents the largest possible mole fraction of dissolved solute.

Exercise 13.5.2

What is the maximum amount sucrose can depress the vapor pressure of water at 20^{0}C if the vapor pressure of pure water (P$^o_{water}$) is 17.5 torr and a saturated solution of sucrose has a concentration of S=$\frac{230.9g(C_6H_{22}O_{11})}{100g(H_2O)}$ at that temperature. (Video performs solution, while describing problem).



Answer

1.89 Torr

Real Solutions

There are two comments that should be made on Raoult's Law.

1. Solid solutes are usually nonvolatile, and they can not form solutions at all the concentrations described by Raoult's law, which is indicated by the dashed red line in Figure 13.5.3 That is, at some point a solution becomes saturated and the addition of solute causes a precipitate to form, and so you can not make solutions of all mole fractions This limitation does not happen for miscible substances, but those usually involve volatile solutes, where the total vapor pressure is the sum of the partial pressure do to all volatile species. So the equation works, but the graph can be misleading.

2. Solutions that follow Raoult's Law are considered to be Ideal Solutions, and by this we mean the solute-solvent interactions are the same as solvent-solvent. In reality, most solutions with nonvolatile solutes have stronger solute-solvent interactions than solvent-solvent, which can be considered as a reason why they are soluble. If this happens, then there are greater intermolecular forces for the solution than the pure solvent, and so there is a greater vapor pressure depression than described by Raoult's Law. This is also why there is often a contraction in volume while mixing. That is, the greater the intermolecular forces, the closer the particles are to each other, and the harder it is to vaporize them (so the vapor pressure decreases).

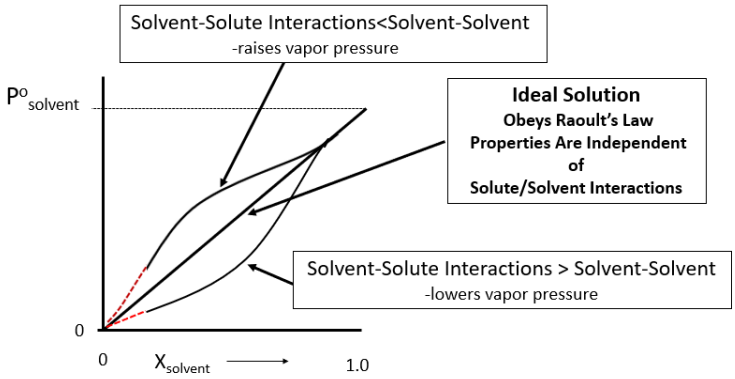


Figure 13.5.5: Limitations of Raoult's Law. Note, for nonvolatile solutes this deviation is usually negative and the vapor pressure depression is greater than given by Raoult's law.(Copyright; Belford CC0)

Note, if the solute-solute and solvent-solvent attractions are greater than the solute-solvent, they tend not to mix, causing an insoluble solid solute, or two immiscible liquids if the solute is a liquid. But things can get complicated. For instance, acetone ($CH_3C(=O)CH_3$) and water are miscible and you can dry wet glassware by adding acetone to it. The acetone does not hydrogen bond and so has a higher vapor pressure than water, and by mixing with the water it weakens the h-bonding effect of the water, allowing the water to evaporate more easily. You need to look at figure 13.5.4 to understand this. Figure 13.5.5 as written is for a nonvolatile solute.

Boiling Point Elevation

The definition of the boiling point is the temperature at which the vapor pressure equals ambient pressure, at which point particles within the bulk of the liquid begin to vaporize. So if a non volatile solute depresses the vapor pressure, you need a higher temperature to bring the vapor pressure up to ambient, and the boiling point is elevated. This is shown in figure 13.5.6 where you see the vapor pressure curve for pure water, and that for an aqueous solution. If we follow the normal isobar (1 atm), the boiling point of pure water is at 100°C, when the water's vapor pressure equals 1 atm. For the solution curve, the vapor pressure is depressed (Raoult's Law), and at 100°C is less than one atm. In order to bring it up to 1 atm, the temperature is raised to about 110°C (T_b), which becomes the boiling point of the solution. This is why we often put salt in water while cooking.

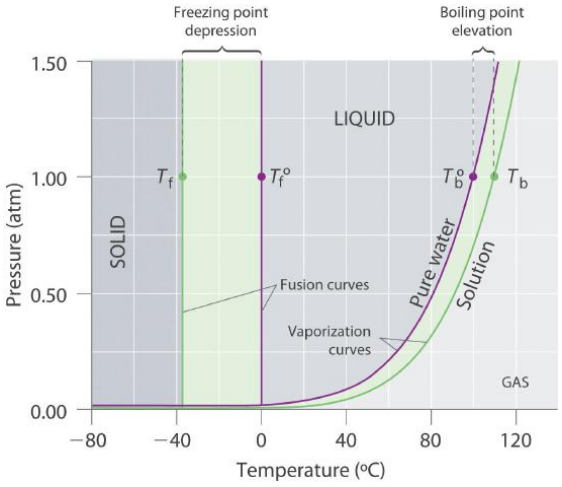


Figure 13.5.6: Plot showing the boiling point elevation and freezing point depression for water.

The amount the boiling point is elevated changes as the concentration of the solution changes and can be given by the following equation.

$$\underbrace{\Delta T = i k_b m}_{\text{Boiling Point Elevation}} \tag{13.5.6}$$

Where,

$$i = \text{Van't Hoff Factor}$$
$$k_b = \text{boiling point elevation constant}$$
$$m = \text{molality} \left(\frac{mole_{solute}}{kg_{solvent}} \right)$$

Note: $\Delta T = T_{bp}(\text{solution}) - T_{bp}(\text{pure solvent})$

Boiling Point Elevation constants can be obtained in table 13.5.2 or through the resources tab on the left of this page.

The Van't hoff factor takes into account the fact ionic compounds break up into individual ions upon dissolution, and colligative properties are an effect of the total number of particles. For covalent compounds i=1, and on a first order of approximation, the van't hoff factor of an ionic compound is equal to the number of ions within its formula

Table13.5.1: Approximate Van't Hoff Factors for various compounds.

Compound	Van't Hoff Factor (Ideal Solution)
$C_{12}H_{22}O_{11}$ (sucrose)	1
NaCl	2
BaF_2	3
X_2Y_3	5

Note: Many books introduce the boiling point elevation equation in the context of nonelectrolytes where the Van't Hoff factor equals one, and then introduce it later when when the solute is an electrolytes. The values above are for "ideal solutions" where the ions of an electrolyte do not interact with each other, and these are valid for dilute solutions, but as the ion concentration increases, the ions start to interact with each other and form clusters, so the true value is less than indicated in table 13.5.1. This will be discussed in more detail in section 13.5.7)

BP Elevation Problems

Exercise 13.5.1

Calculate the Molar Mass of Adrenaline if 0.64g is dissolved in 36.0g of CCl_4 and causes a boiling point elevation of 0.49°C. Obtain k_b from table 13.4.2.



Answer

182 g/mol.

Exercise 13.5.2

You are on a mountain at an elevation wherewater boils at 95°C and want to raise the boiling point to 100°C by adding table salt (NaCl). How much table salt do you need to add to 1 kg of water to reach 100°C?



Answer

285 g NaCl

Freezing Point Depression

Freezing point depression is very similar to boiling point elevation. The freezing point is a temperature at which both a solid and liquid phase can coexist, which is a dynamic equilbrium where the rate of freezing (liquid joining the solid) is equal to the rate of melting (solid joining liquid). As seen in the video below, solute particles are only in the liquid phase, collisons of the solute with the solid do not freeze, and so they reduce the rate of freezing. But since there are no solute in the crystal, the do not affect the rate of melting. As lower temperature favors freezing, the system cools until these two processes become equal.



Video13.5.1: 0.19 min YouTube animation showing how solute particles affect the process of crystalization and thus lower the freezing point.

The equation for freezing point depression is similar to that for boiling point elevation. What is important to realize is that the freezing point is depressed.

$$\Delta T = ik_f m \text{ Freezing Point Depression}$$
$$or$$
$$\Delta T = -ik_f m \text{ Freezing Point Depression} \quad (13.5.7)$$

NOTE: The freezing point is depressed ($\Delta T < 0$) and some tables have the value of k_f as a negative number and some as a positive number, and so you have to look at the value of k to figure if you need a negative sign in the equation. (If k_f is negative, use the top form of eq. 13.4.7, if k_f is positive, use the bottom form of the equation (with the negative sign).

Where,

$$i = \text{Van't Hoff Factor}$$
$$k_f = \text{freezing point point constant}$$
$$m = \text{molality} \left(\frac{mole_{solute}}{kg_{solvent}} \right)$$

$\Delta T = T_{fp}(\text{solution}) - T_{fp}(\text{pure solvent})$

NOTE: The freezing point is depressed ($\Delta T < 0$) and some tables have the value of k_f as a negative number and some as a positive number, and so you have to look at the value of k to figure if you need a negative sign in the equation. (If k_f is negative, use the top form of eq. 13.4.7, if k_f is positive, use the bottom form of the equation (with the negative sign).

Boiling Point Elevation and Freezing Point Depression Constants

Table13.5.2: Boiling Point Elevation Constants (Kb) and Freezing Point Depression Constants (Kf) for Some Solvents

Solvent	Boiling Point (°C)	Kb (°C/m)	Freezing Point (°C)	Kf (°C/m)
acetic acid	117.90	3.22	16.64	3.63
benzene	80.09	2.64	5.49	5.07
d-(+)-camphor	207.4	4.91	178.8	37.8
carbon disulfide	46.2	2.42	−112.1	3.74
carbon tetrachloride	76.8	5.02	−22.62	31.4
chloroform	61.17	3.80	−63.41	4.60
nitrobenzene	210.8	5.24	5.70	6.87
water	100.00	0.5121	0.00	1.86

Note, the above table gives both boiling point elevation constants and freezing point depression constants. The very next section of the chapter goes over freezing point depression.

More on van't Hoff Factor

The van't Hoff factor (i) in the freezing point depression and boiling point elevation equations is typically omitted from the equations for nonelectrolytes, and most textbooks add it on to explain that electrolytes ionize, and the true colligative effect is a result of the total number of ions in the solution. This aligns with the definition of a colligative property not depending on the identity of the solute, just the total number of particles, and we can call this an ideal solution. The actual van't Hoff factor is often less than predicted from table 13.4.1 where an ionic compound breaks up into its ions, and the van't Hoff factor is experimentally determined from the following formula:

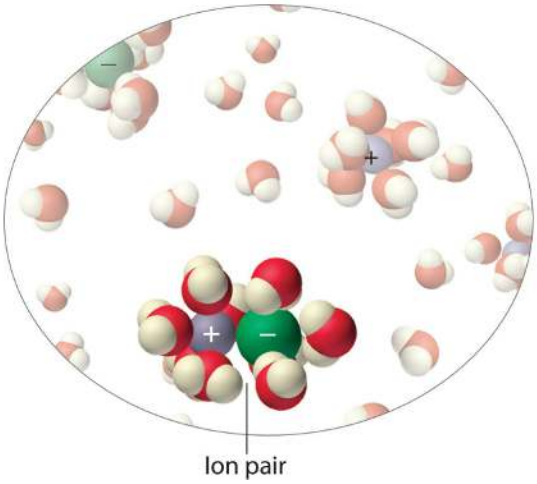
$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}} \tag{13.5.8}$$

Table 13.5.3: van't Hoff Factors for 0.0500 M Aqueous Solutions of Selected Compounds at 25°C

Compound	i (measured)	i (ideal)
glucose	1.0	1.0
sucrose	1.0	1.0
$NaCl$	1.9	2.0
HCl	1.9	2.0
$MgCl_2$	2.7	3.0

Compound	i (measured)	i (ideal)
$FeCl_3$	3.4	4.0
$Ca(NO_3)_2$	2.5	3.0
$AlCl_3$	3.2	4.0
$MgSO_4$	1.4	2.0

For an ideal solution the ions are completely independent, but in a real solution, they can start to interact with each other and form ion pairs, like in figure in the left part of table 13.4.3, which shows two ions interacting with each other, and behaving like a single particle.



m $\left(\frac{mol(NaCl)}{kg(H_2O)}\right)$	i $\left(\frac{\Delta_{fp}(measured)}{\Delta_{fp}(calculated)}\right)$
0.0120	1.94
0.0860	1.87
0.173	1.84
0.349	1.83

Figure 13.5.7: Van't Hoff factor as a function of concentration for sodium chloride. The image on the left shows to ions forming a pair, which sort of acts like a single particle. The more concentrated the solution the greater the propensity to form ion pairs and the less the ions act as discrete particles, resulting in a lowering of i from ideal conditions where every ion acts as an independent particle

Osmosis

Osmosis is a colligative property where an osmotic pressure builds up across a semipermeable membrane that selectively allows solvent molecules to cross but prevents solute molecules from crossing.Osmotic pressure which can be understood through figure 13.4.7. In this image a semipermiable membrane allows water to pass, but does not allow glucose to pass. In the initial state (a) you had pure water and so the height of the two tubes are equal and then instantly add glucose to one side, this reduces the flow from right to left, and so more water enters the right side causing its height to rise to a new equilibrium. The osmotic pressure is technically defined as the pressure required to restore to bring the columns back to the same height (c), which is related to the difference in the height of the column on the right side of (b) and the left side, and the density of the solution. ($\Pi = \rho gh$, where Π is the osmotic pressure, ρ is the density, h is the difference in height of the columns and g is the gravitational constant).

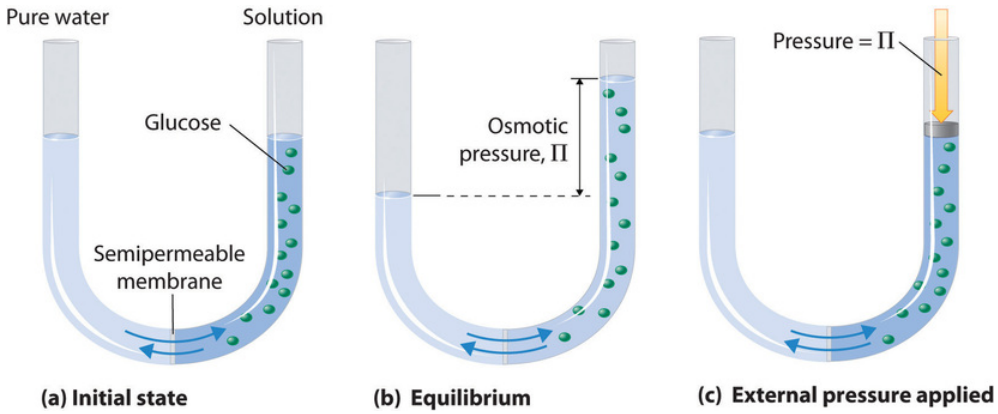


Figure 13.5.7:

From experimental measurements this take a form similar form to the ideal gas law,

$$\Pi V = nRT \tag{13.5.9}$$

which can be rearranged

$$\Pi = \frac{n}{V}RT$$

$$\Pi = MRT \tag{13.5.10}$$

where, M=Molarity of solute in solution, R= Ideal Gas Constant and T=absolute Temperature (Kelvin).

Exercise 13.5.2

What is the osmotic pressure of a solution if you dilute 2.02 g of Urea ($(NH_2)_2CO$) at 20.0°C with water to a volume of 145mL? [Note: the answer has a YouTube Video deriving the solution].

Answer

5.58 atm, see YouTube for derivation



Osmosis is very important in biology as cell membranes are semipermable. When a solution is injected into the blood it must have the same concentration as the cells or osmotic pressure can build up across them

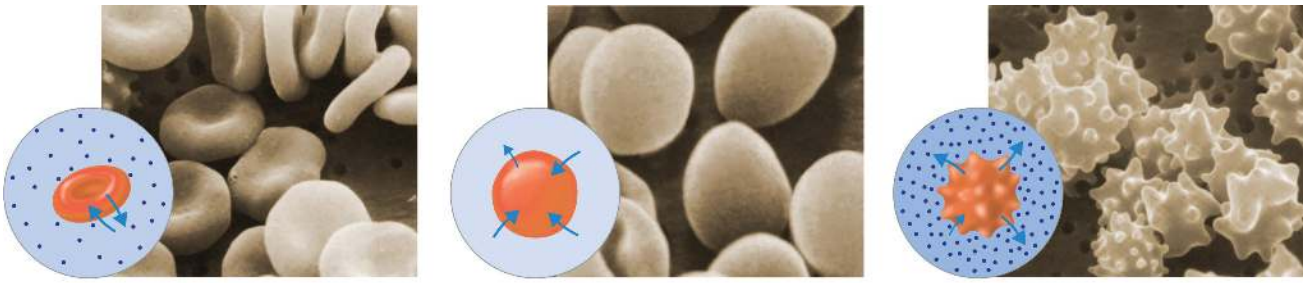


Figure 13.5.7: (a) Isotonic solution where the solution outside has the same concentration as a cell and the osmotic pressure is zero. In distilled water (b), which is a hypotonic fluid, the solute concentration in the cell is higher and so water flows into the cells, potentially rupturing them. In a hypertonic solution (b) the solute concentration is higher than the cell, causeing water to flow out of the cell with the result that they shrivel up.

Worksheets

- Colligative Properties
- Colligative Properties Key

Class Activities

Test Yourself

Homework

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 13.5: Colligative Properties is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

13.6: Colloidal Mixtures

Suspensions and colloids are two common types of mixtures whose properties are in many ways intermediate between those of true solutions and heterogeneous mixtures. A suspension is a heterogeneous mixture of particles with diameters of about 1 µm (1000 nm) that are distributed throughout a second phase. Common suspensions include paint, blood, and hot chocolate, which are solid particles in a liquid, and aerosol sprays, which are liquid particles in a gas. If the suspension is allowed to stand, the two phases will separate, which is why paints must be thoroughly stirred or shaken before use. A colloid is also a heterogeneous mixture, but the particles of a colloid are typically smaller than those of a suspension, generally in the range of 2 to about 500 nm in diameter. Colloids include fog and clouds (liquid particles in a gas), milk (solid particles in a liquid), and butter (solid particles in a solid). Other colloids are used industrially as catalysts. Unlike in a suspension, the particles in a colloid do not separate into two phases on standing. The only combination of substances that cannot produce a suspension or a colloid is a mixture of two gases because their particles are so small that they always form true solutions. The properties of suspensions, colloids, and solutions are summarized in Table 13.10.1.

Table 13.10.1: Properties of Liquid Solutions, Colloids, and Suspensions

Type of Mixture	Approximate Size of Particles (nm)	Characteristic Properties	Examples
solution	< 2	not filterable; does not separate on standing; does not scatter visible light	air, white wine, gasoline, salt water
colloid	2–500	scatters visible light; translucent or opaque; not filterable; does not separate on standing	smoke, fog, ink, milk, butter, cheese
suspension	500–1000	cloudy or opaque; filterable; separates on standing	muddy water, hot cocoa, blood, paint

Colloids and Suspensions

Colloids were first characterized in about 1860 by Thomas Graham, who also gave us Graham's law of diffusion and effusion. Although some substances, such as starch, gelatin, and glue, appear to dissolve in water to produce solutions, Graham found that they diffuse very slowly or not at all compared with solutions of substances such as salt and sugar. Graham coined the word colloid (from the Greek kólla, meaning "glue") to describe these substances, as well as the words sol and gel to describe certain types of colloids in which all of the solvent has been absorbed by the solid particles, thus preventing the mixture from flowing readily, as we see in Jell-O. Two other important types of colloids are aerosols, which are dispersions of solid or liquid particles in a gas, and emulsions, which are dispersions of one liquid in another liquid with which it is immiscible.

Colloids share many properties with solutions. For example, the particles in both are invisible without a powerful microscope, do not settle on standing, and pass through most filters. However, the particles in a colloid scatter a beam of visible light, a phenomenon known as the Tyndall effect,The effect is named after its discoverer, John Tyndall, an English physicist (1820–1893), whereas the particles of a solution do not. The Tyndall effect is responsible for the way the beams from automobile headlights are clearly visible from the side on a foggy night but cannot be seen from the side on a clear night. It is also responsible for the colored rays of light seen in many sunsets, where the sun's light is scattered by water droplets and dust particles high in the atmosphere. An example of the Tyndall effect is shown in Figure 13.10.1.



Figure 13.6.1: Tyndall Effect, the Scattering of Light by Colloids (CC2.0 Pedro Szekely, WikiMedia Commons)

Although colloids and suspensions can have particles similar in size, the two differ in stability: the particles of a colloid remain dispersed indefinitely unless the temperature or chemical composition of the dispersing medium is changed. The chemical explanation for the stability of colloids depends on whether the colloidal particles are hydrophilic or hydrophobic.

Most proteins, including those responsible for the properties of gelatin and glue, are hydrophilic because their exterior surface is largely covered with polar or charged groups. Starch, a long-branched polymer of glucose molecules, is also hydrophilic. A hydrophilic colloid particle interacts strongly with water, resulting in a shell of tightly bound water molecules that prevents the particles from aggregating when they collide. Heating such a colloid can cause aggregation because the particles collide with greater energy and disrupt the protective shell of solvent. Moreover, heat causes protein structures to unfold, exposing previously buried hydrophobic groups that can now interact with other hydrophobic groups and cause the particles to aggregate and precipitate from solution. When an egg is boiled, for example, the egg white, which is primarily a colloidal suspension of a protein called albumin, unfolds and exposes its hydrophobic groups, which aggregate and cause the albumin to precipitate as a white solid.

In some cases, a stable colloid can be transformed to an aggregated suspension by a minor chemical modification. Consider, for example, the behavior of hemoglobin, a major component of red blood cells. Hemoglobin molecules normally form a colloidal suspension inside red blood cells, which typically have a “donut” shape and are easily deformed, allowing them to squeeze through the capillaries to deliver oxygen to tissues 13.6.2 In a common inherited disease called sickle-cell anemia, one of the amino acids in hemoglobin that has a hydrophilic carboxylic acid side chain (glutamate) is replaced by another amino acid that has a hydrophobic side chain. Under some conditions, the abnormal hemoglobin molecules can aggregate to form long, rigid fibers that cause the red blood cells to deform, adopting a characteristic sickle shape that prevents them from passing through the capillaries. The reduction in blood flow results in severe cramps, swollen joints, and liver damage. Until recently, many patients with sickle-cell anemia died before the age of 30 from infection, blood clots, or heart or kidney failure, although individuals with the sickle-cell genetic trait are more resistant to malaria than are those with “normal” hemoglobin.

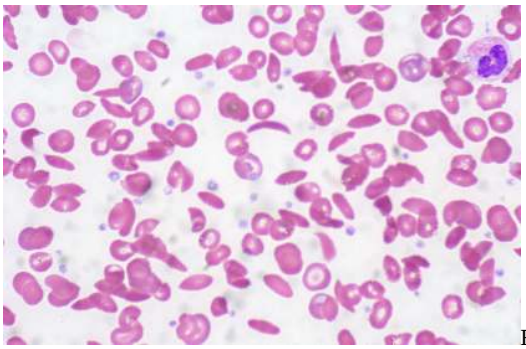


Figure 13.6.2: Sickle cell amenia. (CC2.0, Ed Uthman, WikiMedia Commons)

Figure 13.6.2: Formation of New Land by the Destabilization of a Colloid Suspension. This satellite photograph shows the Mississippi River delta from New Orleans (top) to the Gulf of Mexico (bottom). Where seawater mixes with freshwater from the Mississippi River, colloidal clay particles in the river water precipitate (tan area).

Aggregation and precipitation can also result when the outer, charged layer of a particle is neutralized by ions with the opposite charge. In inland waterways, clay particles, which have a charged surface, form a colloidal suspension. High salt concentrations in seawater neutralize the charge on the particles, causing them to precipitate and form land at the mouths of large rivers, as seen in the satellite view in Figure 13.10.3. Charge neutralization is also an important strategy for precipitating solid particles from gaseous colloids such as smoke, and it is widely used to reduce particulate emissions from power plants that burn fossil fuels.

Aerosols

Aerosols are very important in atmospheric chemistry and much atmospheric chemistry occurs in aerosols. In the next chapter we will study the rates of reactions, and from bimolecular collision theory realize that if two reactants react, they have to collide with each other. We will learn that the more concentrated they are, the higher the collision frequency. From Henry's law we know that many compounds will dissolve in water and so the concentration of many reactants is higher in aerosol than in the raw gas phase, meaning many reactions occur within these tiny airborn particles of water. Smog is fog that contains dangerous solutes like ozone, particulate mater, oxides of nitrogen, volatile organic compounds, and other unhealthy compounds.



Video 13.6.1: 3:50min video by the Center for Aerosol Impacts on Chemistry of the Environment describing soot (https://youtu.be/CT8Bapg6pro)

Today citizens can stream data on air quality to web services, and one such service is Purple Air. Purple air sensors primarly measure particulate matter, which is a major concern out west and their interactive map allows you to zoom in to geographic areas, and there are even two Purple Air sensors in the Little Rock area. The EPA runs Federal Monitoring stations that are much more accurate (and expensive) and their AirData Quality Monitors map allows you to pick specific gases the EPA is monitoring (you need to click the layers icon on their map and choose the monitors you wish to see), but there are monitors here in Little Rock providing data on toxins like Ozone, which is a serious health issue in this region.

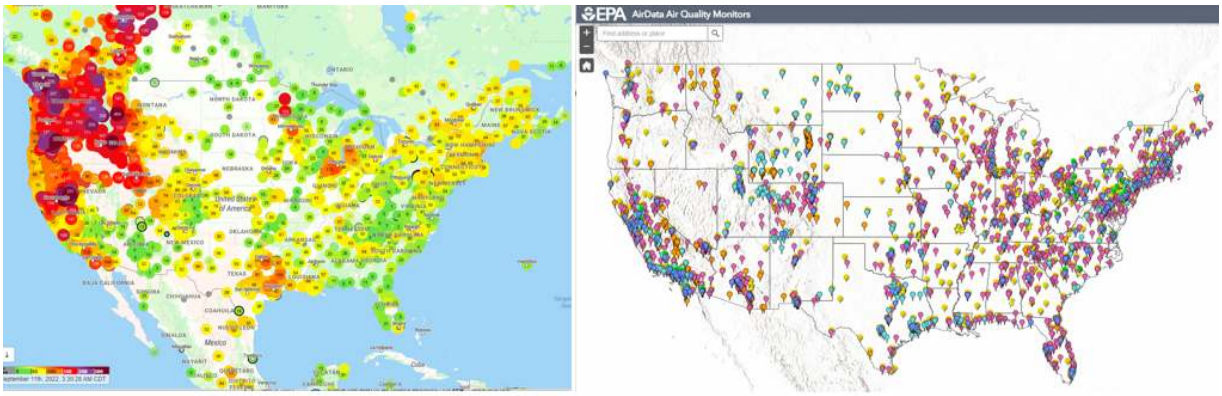


Figure 13.6.3: Two Interactive Air Quality Maps. On the left is the Purple Air Map where citizens can stream data on particulate matter and on the right is the EPA Air Quality Data Map streamed from government sensors. Both maps are interactive, although on the EPA map you need to open up the layers option and choose the types of monitors you want to read(you can zoom down to Little Rock) (CC0, Bob Belford, captured Sep 11, 2022)

Emulsions

Emulsions are colloids formed by the dispersion of a hydrophobic liquid in water, thereby bringing two mutually insoluble liquids, such as oil and water, in close contact. Various agents have been developed to stabilize emulsions, the most successful being molecules that combine a relatively long hydrophobic “tail” with a hydrophilic “head”. Soaps are natural emulsifying agents and detergents are synthetic ones. Figure 13.6.4 shows the similarity in structure between the soap sodium stearate [$NaCH_3(CH_2)_{16}CO_2$,] and detergent sodium dodecyl sulfate [$NaCH_3(CH_2)_{11}OSO_3$], both of which are salts with a charge on one end (the head) and a long tailed (nonpolar) hydrocarbon chain on the other. The charged head is soluble in polar compounds like water while the long hydrophobic head is soluble in non polar compounds like fats and oils.

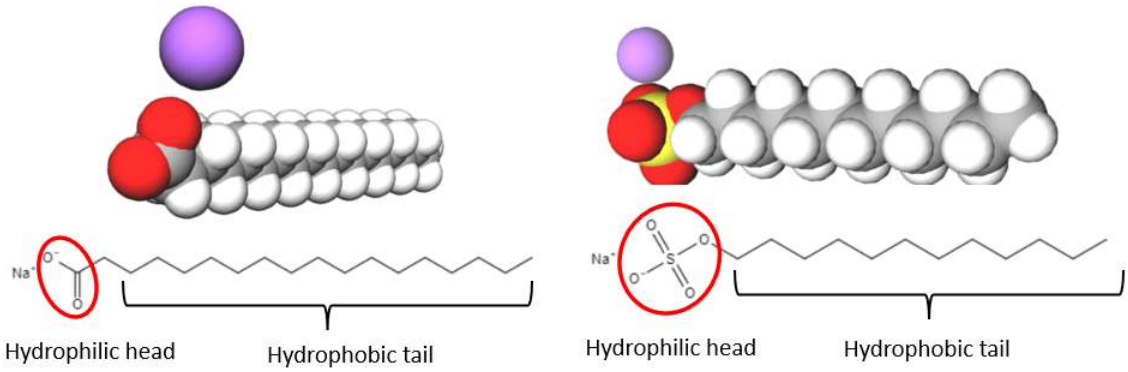
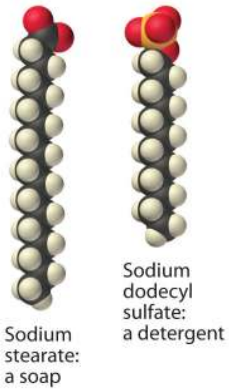


Figure 13.6.4: The soap sodium stearate (left) and the detergent sodium lauryl sulfate y and Paste Caption here. (CC0, Bob Belford using MolView)



When you wash your laundry, the hydrophobic tails of soaps and detergents interact with hydrophobic particles of dirt or grease through dispersion forces, dissolving in the interior of the hydrophobic particle. The hydrophilic group is then exposed at the surface of the particle, which enables it to interact with water through ion–dipole forces and hydrogen bonding. This causes the particles of dirt or grease to disperse in the wash water and allows them to be removed by rinsing. Similar agents are used in the food industry to stabilize emulsions such as mayonnaise.

A related mechanism allows us to absorb and digest the fats in buttered popcorn and French fries. To solubilize the fats so that they can be absorbed, the gall bladder secretes a fluid called bile into the small intestine. Bile contains a variety of bile salts, detergent-like molecules that emulsify the fats.

Micelles

Detergents and soaps are surprisingly soluble in water in spite of their hydrophobic tails. The reason for their solubility is that they do not, in fact, form simple solutions. Instead, above a certain concentration they spontaneously form micelles, which are spherical or cylindrical aggregates that minimize contact between the hydrophobic tails and water. In a micelle, only the hydrophilic heads are in direct contact with water, and the hydrophobic tails are in the interior of the aggregate (part (a) in Figure 13.10.4).

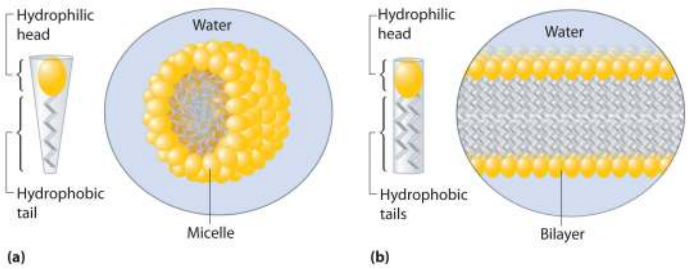


Figure 13.10.4: Micelles and a Phospholipid Bilayer. (a) Soaps and detergents, which contain a single hydrophobic tail on each molecule, form spherical micelles with the intertwined tails in the interior and the hydrophilic head groups on the exterior. (b) Phospholipids, which have two hydrophobic tails, tend to form extended double layers in which the hydrophobic tails are sandwiched between the hydrophilic head groups.

A large class of biological molecules called phospholipids consists of detergent-like molecules with a hydrophilic head and two hydrophobic tails, as can be seen in the molecule of phosphatidylcholine. The additional tail results in a cylindrical shape that prevents phospholipids from forming a spherical micelle. Consequently, phospholipids form bilayers, extended sheets consisting of a double layer of molecules. As shown in part (b) in Figure 13.10.4, the hydrophobic tails are in the center of the bilayer, where they are not in contact with water, and the hydrophilic heads are on the two surfaces, in contact with the surrounding aqueous solution.



Phosphatidylcholine:
a phospholipid

A cell membrane is essentially a mixture of phospholipids that form a phospholipid bilayer. One definition of a cell is a collection of molecules surrounded by a phospholipid bilayer that is capable of reproducing itself. The simplest cells are bacteria, which consist of only a single compartment surrounded by a single membrane. Animal and plant cells are much more complex, however, and contain many different kinds of compartments, each surrounded by a membrane and able to carry out specialized tasks.

Summary

A suspension is a heterogeneous mixture of particles of one substance distributed throughout a second phase; the dispersed particles separate from the dispersing phase on standing. In contrast, the particles in a colloid are smaller and do not separate on standing. A colloid can be classified as a sol, a dispersion of solid particles in a liquid or solid; a gel, a semisolid sol in which all of the liquid phase has been absorbed by the solid particles; an aerosol, a dispersion of solid or liquid particles in a gas; or an emulsion, a dispersion of one liquid phase in another. A colloid can be distinguished from a true solution by its ability to scatter a beam of light, known as the Tyndall effect. Hydrophilic colloids contain an outer shell of groups that interact favorably with water, whereas hydrophobic colloids have an outer surface with little affinity for water. Emulsions are prepared by dispersing a hydrophobic liquid in water. In the absence of a dispersed hydrophobic liquid phase, solutions of detergents in water form organized spherical aggregates called micelles. Phospholipids are a class of detergent-like molecules that have two hydrophobic tails attached to a hydrophilic head. A bilayer is a two-dimensional sheet consisting of a double layer of phospholipid molecules arranged tail to tail with a hydrophobic interior and a hydrophilic exterior. Cells are collections of molecules that are surrounded by a phospholipid bilayer called a cell membrane and are able to reproduce themselves.

Test Yourself

Homework

13.6: Colloidal Mixtures is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

14: Rates of Chemical Reactions

14.1: Prelude
14.2: Rates of Chemical Reactions
14.3: Reaction Conditions and Rate
14.4: Effect of Concentration on Reaction Rate
14.5: Integrated Rate Law
14.6: Energetics and Reaction Rates
14.7: Reaction Mechanisms

This page titled 14: Rates of Chemical Reactions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

14.1: Prelude

Introduction

Kinetics deals with the time evolution of a system that undergoes a change as it approaches equilibrium. Chemical kinetics is the branch of chemistry dealing with the rates of chemical reactions, that is, how fast they proceed. If a system is at equilibrium, there appears to be no reaction occurring on a macroscopic scale. If a reaction is occurring, the system is in a non-equilbrium state, and kinetics is the study of how it evolves over time until equilibrium is achieved. The next chapter will describe systems in equilibrium.

An easy to understand system can be described by the heat transfer from a hot object to a cold object. The hot object cools and the cold object warms until the reach the same temperature, $T_{equilibrium}$. At this point, heat is still being transferred, but the rate between the two objects is the same, and so the temperature does not change.

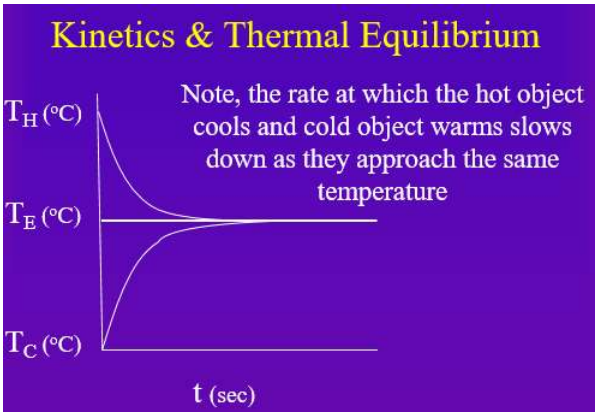


Figure 14.1.1: Kinetics diagram of heat transfer. (Belford)

Calculus is the mathematics that studies how variables change with respect to each other, and kinetics is the study of how something changes with respect to time. In chemical kinetics it is the change of the concentration with respect to time. Figure 14.1.1 shows the kinetics of temperature change as heat is transferred from a hot object to a cold object. The instantaneous slope of the line is called the derivative, and represents the rate of temperature change. Figure 14.1.1 is of interest, because the rate of temperature change is related to the temperature difference. The greater the temperature difference, the faster the rate of change, and as the temperatures of the hot and cold objects approach the same temperature, the slower the rate of change. From calculus, such a dependency results in an exponential/logarithmic relationship, and it is because of this that chemical kinetics often shows exponential relationships that require students to master logarithms. That is, the rate of many chemical reactions depend on the concentration of the chemical, and this often requires students to be able to use both power functions ($f(x)=Ax^m$) and exponential functions ($f(x)=Ae^{mx}$), and their logarithmic relationships.

You need to be familiar with the following relationships

Math Review

Exponentials and Logarithims



Figure 14.1.2: logarithm definiton (Belford)

$10^2=100$ $\log_{10}100 = 2$

Relationships in Base-10 Logarithms

Table 14.1.1: Powers of 10 and logs

Numerical Value	Exponential Form	Logarithm

Numerical Value	Exponential Form	Logarithm
100	10^2	2
10	10^1	1
1	10^0	0
0.1	10^{-1}	−1
0.01	10^{-2}	−2

Comparing logarithms to scientific notation



Video 14.1.1: 3:07 YouTube relating logarithms to scientific notation (https://youtu.be/i9K9fIF__6g)

Note, the log of a number between 1 and 10 is a fraction, and an easy way to understand logarithms is to relate them to scientific notation.

Let's consider the number 26794

It can be expressed in scientific notation or as a log

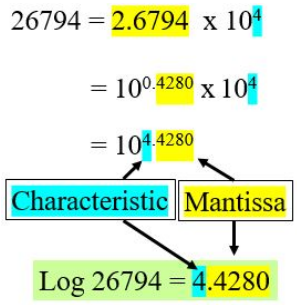


Figure 14.1.3: Writing a number as scientific notation or as a log (Belford)

So logarithms are very similar to scientific notation, where the number being multiplied by 10 to a power is expressed as 10 to the power of a fraction.

You are required to know these operations.

Table 14.1.2: logarithmic operations

$$a^{-n} = \frac{1}{a^n} \qquad \frac{1}{a^{-n}} = a^n$$
$$a^m a^n = a^{(m+n)} \qquad \frac{a^m}{a^n} = a^{(m-n)}$$
$$(ab)^k = a^k b^k \qquad \left(\frac{a}{b}\right)^k = \frac{a^k}{b^k}$$
$$\left(a^m\right)^n = a^{mn} \qquad \left(a^m\right)^{-n} = \frac{1}{a^{mn}}$$

$$\ln xy = \ln x + \ln y \qquad \log xy = \log x + \log y$$
$$\ln \frac{x}{y} = \ln x - \ln y \qquad \log \frac{x}{y} = \log x - \log y$$
$$\ln x^k = k \ln x \qquad \log x^k = k \log x$$
$$\ln \sqrt[k]{x} = \ln x^{\frac{1}{k}} = \frac{1}{k} \ln x \qquad \log \sqrt[k]{x} = \log x^{\frac{1}{k}} = \frac{1}{k} logx$$
$$\ln e^k = k \qquad \log 10^k = k$$
$$\ln x = 2.302585 \ldots \log x \qquad \log x = 0.434294 \ldots \ln x$$

If the above do not make sense to you, try doing them with base 10, or base 2, but something you can do off your head:



Video 14.1.2 4:59 YouTube on manipulating logarithms (https://youtu.be/NP0PAJlmnkg)

For example if $a^m a^n = a^{(m+n)}$ makes no sense to you,
try it with base 10.
$10^2 x 10^3 = 10^{(2+3)} = 10^5 = 100{,}000$

Exercise 14.1.1

Show that $a^m a^n = a^{(m+n)}$ using base 10, with m=2 and n=3
and then
logxy = logx +logY for X=100 and Y=1000

Answer

$10^2 x 10^3 = 10^{(2+3)} = 10^5 = 100{,}000$
(ie., a hundred times a thousand is a hundred thousand)
and
log[(100)(1000) = log(100) + log(1000)
log[(100,000) = log(100) + log(1000
5 = 2 + 3

In Class Activities

Test Yourself

Homework: Section 14.1

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Liliane Poirot

14.1: Prelude is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

14.2: Rates of Chemical Reactions

Introduction

The rate of reaction, often called the "reaction velocity" and is a measure of how fast a reaction occurs. As a reaction proceeds in the forward direction products are produced as reactants are consumed, and the rate is how fast this occurs. Sort of like the speed of a car is how its location changes with respect to time, the rate is how the concentration changes over time. This makes sense, because products are produced as the reaction proceeds and they thus get more concentrated, while reactants are consumed and thus become less concentrated. As the balanced equation describes moles of species it is common to use the unit of Molarity (M=mol/l) for concentration and the convention is to use square brackets [ ] to describe concentration of a species. So the concentration of chemical "A" is denoted as:

$$[\mathbf{A}] \tag{14.2.1}$$

$$\text{with units of } \frac{mols}{l} \text{ for the chemical species "A"}$$

The reaction rate of Chemical "A" is

$$R_A = \frac{\Delta [\mathbf{A}]}{\Delta t} \tag{14.2.2}$$

typically in units of $\frac{M}{sec}$ or $\frac{mol}{l \cdot sec}$ (they mean the same thing), and of course any unit of time can be used, depending on how fast the reaction occurs, so an explosion may be on the nanosecond time scale while a very slow nuclear decay may be on a gigayear scale. It should also be mentioned that in the gas phase we often use partial pressure (P_A), but for now will stick to M/time.

By convention we say reactants are on the left side of the chemical equation and products on the right

$$\text{Reactants} \rightarrow \text{Products} \tag{14.2.3}$$

Reactants are consumed, and so their concentrations go down (is negative), while products are produced, and so their concentrations go up. It is important to keep this notation, and maintain the convention that a Δ means the final state minus the initial state.

1. The Rate of Disappearance of Reactants

$$-\frac{\Delta [Reactants]}{\Delta t} \tag{14.2.4}$$

   Note this is actually positive because it measures the rate of disappearance of the reactants, which is a negative number and the negative of a negative is positive.

2. The Rate of Formation of Products

$$\frac{\Delta [Products]}{\Delta t} \tag{14.2.5}$$

   This is the rate at which the products are formed.

Note: It is important to maintain the above convention of using a negative sign in front of the rate of reactants. Later we will see that reactions can proceed in either direction, with "reactants" being formed by "products" (the "back reaction"). When this happens, the actual value of the rate of change of the reactants $\frac{\Delta [Reactants]}{\Delta t}$ will be negative, and so eq. 14.1.3 will be positive, as it is taking the negative of a negative. We do not need to worry about that now, but we need to maintain the conventions.

Exercise 14.2.1

Write the rate of reaction for each species in the following generic equation, where capital letters denote chemical species

$$A + B \rightarrow C + D \tag{14.2.6}$$

Answer

- rate of disappearance of A

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

- rate of disappearance of B

$$\text{rate} = -\frac{\Delta[B]}{\Delta t}$$

- rate of formation of C

$$\text{rate} = \frac{\Delta[C]}{\Delta t}$$

- rate of formation of D)

$$\text{rate} = \frac{\Delta[D]}{\Delta t}$$

Note

If a chemical species is in the gas phase and at constant temperature it's concentration can be expressed in terms of its partial pressure. Consider gas "A",

$$P_A V = n_A RT \tag{14.2.7}$$

$$[A] = \frac{n_A}{V} = \frac{P_A}{RT}$$

So for systems at constant temperature the concentration can be expressed in terms of partial pressure.

Reaction Graphs

It is common to plot the concentration of reactants and products as a function of time. Figure 14.2.1 shows a simple plot for the reaction

$$A \rightarrow B \tag{14.2.8}$$

Note that this reaction goes to completion, and at t=0 the initial concentration of the reactant (purple [A]) was 0.5M and if we follow the reactant curve (purple) it decreases to a bit over 0.1M at twenty seconds and by 60 seconds the reaction is over and all of the reactant had been consumed. On the other hand we could follow the product concentration on the product curve (green) that started at zero, reached a little less than 0.4M after 20 seconds and by 60 seconds the final concentration of 0.5 M was attained.the there was no [B], but after were originally 50 purple particles in the container, which were completely consumed after 60 seconds. You note from eq. 14.1.7 that for stoichiometric coefficients of A and B are the same (one) and so for every A consumed a B was formed and these curves are effectively symmetric. If the reaction had been $A \rightarrow 2B$ then the green curve would have risen at twice the rate of the purple curve and the final concentration of the green curve would have been 1.0M

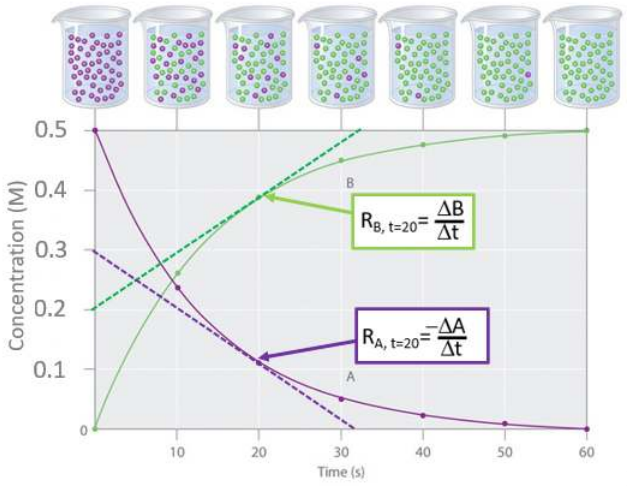


Figure 14.2.1:*Reaction plot of the number of molecules over time*

The rate is technically the instantaneous change in concentration over the change in time when the change in time approaches is technically known as the derivative.

$$\frac{d[A]}{dt} = \lim_{\Delta t \to 0} \frac{\Delta [A]}{\Delta t} \tag{14.2.9}$$

Calculus is not a prerequisite for this class and we can obtain the rate from the graph by drawing a straight line that only touches the curve at one point, the tangent to the curve, as shown by the dashed curves in figure 14.2.1. From this we can calculate the rate of reaction for A and B at 20 seconds

$$R_{A,t=20} = -\frac{\Delta [A]}{\Delta t} = -\frac{0.0M - 0.3M}{32s - 0s} = 0.009\ Ms^{-1}\ \ or\ \ 9\ mMs^{-1} \tag{14.2.10}$$

$$and$$

$$R_{B,t=20} = \frac{\Delta [B]}{\Delta t} = \frac{0.5M - 0.2}{32s - 0s} = 0.009\ Ms^{-1}\ \ or\ \ 9\ mMs^{-1}$$

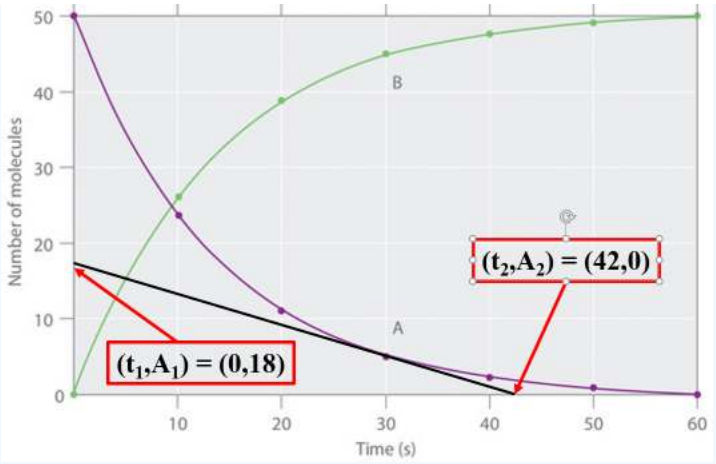
If needed, review section 1B.5.3 on graphing straight line functions and do the following exercise.

Exercise 14.2.2

What is the rate of reaction for the reactant "A" in figure 14.2.1 at 30 seconds?.

Answer

The black line in the figure below is the tangent to the curve for the decay of "A" at 30 seconds. It would have been better to use graph paper with a higher grid density that would have allowed us to exactly pick points where the line intersects with the grid lines. Instead, we will estimate the values when the line intersects the axes.



At 30 seconds the slope of the tangent is:

$$\frac{\Delta[A]}{\Delta t} = \frac{A_2 - A_1}{t_2 - t_1}$$

$$= \frac{(0-18)molecules}{(42-0)sec}$$

$$= -0.43\left(\frac{molecules}{second}\right)$$

$$R = -\frac{\Delta[A]}{\Delta t} = 0.43\left(\frac{\text{molecules consumed}}{second}\right) \tag{14.2.11}$$

NOTE:

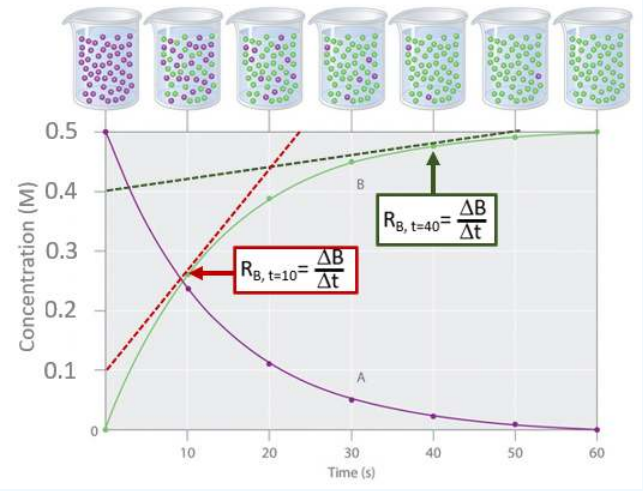
- The value of the rate of consumption of A is a negative number ($A_2 < A_1$)
- Since A→B, the curve for the production of B is symmetric to the consumption of A, except that the value of the rate is positive ($A_1 < A_2$)
- The Y-axis (50 to 0 molecules) is not realistic, and a more common system would be the molarity (number of molecules expressed as moles inside of a container with a known volume).

You should also note that from figure 14.2.1 that the initial rate is the highest and as the reaction approaches completion the rate goes to zero because no more reactants are being consumed or products are produced, that is, the line becomes a horizontal flat line. We shall see that the rate is a function of the concentration, but it does not always decrease over time like it did in this example.

Exercise 14.2.3

Calculate the rates of reactions for the product curve (B) at 10 and 40 seconds and show that the rate slows as the reaction proceeds.

Answer



Tangents to the product curve at 10 and 40 seconds

The red curve represents the tangent at 10 seconds and the dark green curve represents it at 40 seconds.

$$R_{B,t=10} = \frac{0.5-0.1}{24-0} = 20mMs^{-1}$$

$$R_{B,t=40} = \frac{0.5-0.4}{50-0} = 2mMs^{-1}$$

and so the reaction is clearly slowing down over time.

Reaction Rate of Hydrolysis of Aspirin

Lets look at a real reaction, the reaction rate for the hydrolysis of aspirin, probably the most commonly used drug in the world, (more than 25,000,000 kg are produced annually worldwide.) Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid. Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate.

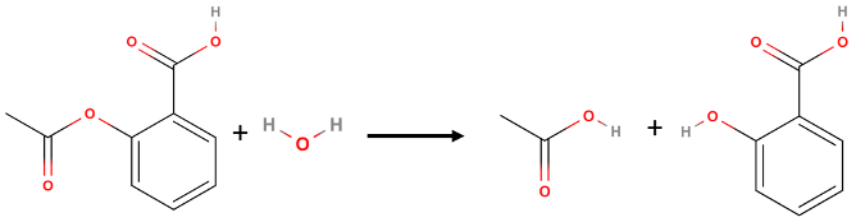


Figure 14.2.2: Hydroloysis of aspirin (acetylsalicylic acid) to acetic acid and salicylic acid (Belford cc 0.0)

Data for the hydrolysis of a sample of aspirin are given below and are shown in the adjacent graph. This data were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	0.00555	0
2.0	0.00551	0.000040
5.0	0.00545	0.00010
10	0.00535	0.00020
20	0.00515	0.00040
30	0.00496	0.00059
40	0.00478	0.00077
50	0.00461	0.00094
100	0.00383	0.00172
200	0.00264	0.00291
300	0.00182	0.00373

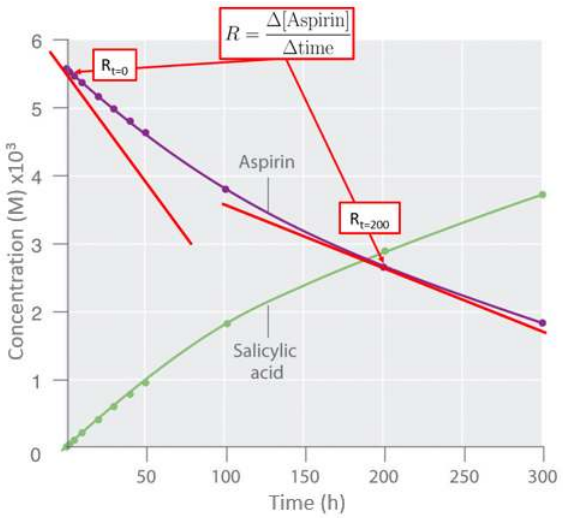


Figure 14.2.3: Graph of concentration vs. time for the hydrolysis of aspirin into salicylic acid showing the rate (tangent to the curve) at t=0 and t=200 hrs.

In addition to calculating the rate from the curve we can also calculate the average rate over time from the actual data, and the shorter the time the closer the average rate is to the actual rate. Let's calculate the average rate for the production of salicylic acid between the initial measurement (t=0) and the second measurement (t=2 hr).

$$Average\ rate_{(t=2.0-0.0\ h)} = \frac{[salicylic\ acid]_2 - [salicylic\ acid]_0}{2.0\ h - 0.0\ h}$$

$$= \frac{0.040 \times 10^{-3}\ M - 0.000\ M}{2.0\ h - 0.0\ h} = 2 \times 10^{-5}\ Mh^{-1} = 20 \mu Mh^{-1}$$

Exercise 14.2.4

What is the average rate of salicylic acid production between the last two measurements of 200 and 300 hours, and before doing the calculation, would you expect it to be greater or less than the initial rate? (You may look at the graph)

Answer

It should be clear from the graph that the rate decreases.

$$rate_{(t=300-200\ h)} = \frac{[salicylic\ acid]_{300} - [salicylic\ acid]_{200}}{300\ h - 200\ h}$$

$$= \frac{3.73 \times 10^{-3}\ M - 2.91 \times 10^{-3}\ M}{100\ h} = 8.2 \times 10^{-6}\ Mh^{-1} = 8 \mu Mh^{-1}$$

Relative Rates

The storichiometric coefficients of the balanced reaction relate the rates at which reactants are consumed and products are produced . If we want to relate the rate of reaction of two or more species we need to take into account the stoichiometric coefficients, consider the following reaction for the decomposition of ammonia into nitrogen and hydrogen.

$$2\,NH_3 \rightarrow N_2 + 3\,H_2 \tag{14.2.12}$$

It is clear from the above equation that for mass to be conserved, every time two ammonia are consumed, one nitrogen and three hydrogen are produced. This means that the rate ammonia consumption is twice that of nitrogen production, while the rate of hydrogen production is three times the rate of nitrogen production.

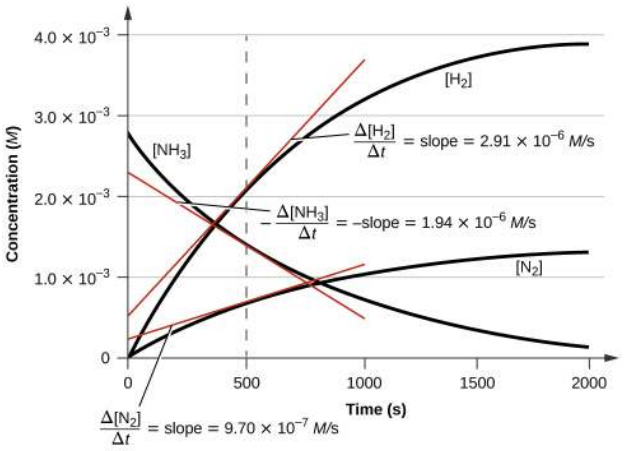


Figure 14.2.2: This graph shows three curves for the concentration of each species in eq. 14.1.8. Note, the slope of the line is drawn in at the tangent to each curve at 500 seconds and they are related to each other by the stoichiometric coefficient of each reactant and product. (Belford)

If you take the value at 500 seconds in figure 14.1.2 and divide by the stoichiometric coefficient of each species, they all equal the same value. Equation 14-1.9 is a generic equation that can be used to relate the rates of production and consumption of the various species in a chemical reaction where capital letter denote chemical species, and small letters denote their stoichiometric coefficients when the equation is balanced.

$$aA + bB \rightarrow cC + dD \tag{14.2.13}$$

We can normalize the above rates by dividing each species by its coefficient, which comes up with a relative rate of reaction

$$\underbrace{R_{relative} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}}_{\text{Relative Rate of Reaction}} \tag{14.2.14}$$

There are two important things to note here:

1. There are actually 5 different Rate expressions for the above equation, The relative rate, and the rate of reaction with respect to each chemical species, A, B, C & D. If you can measure any of the species (A,B,C or D) you can use the above equality to calculate the rate of the other species.
2. In relating the reaction rates, the reactants were multiplied by a negative sign, while the products were not.

Exercise 14.2.5

What is the rate of ammonia production for the Haber process (Equation 14.2.12) if the rate of hydrogen consumption is -0.458M/min?

Answer

https://chem.libretexts.org/@go/page/60725

$$-\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

$$\frac{\Delta[NH_3]}{\Delta t} = -\frac{2}{3}\frac{\Delta[H_2]}{\Delta t}$$

$$= -\frac{2}{3}\left(-0.458\frac{M}{min}\right)$$

$$= 0.305\frac{mol}{L \cdot min}$$

In Class Activity

Test Yourself

Homework: Section 14.2

Contributors

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Liliane Poirot
- Modifications or content borrowed from
  - Paul Flowers et al. Open Stax
  - Joshua Halpern, Scott Sinex, Scott Johnson

This page titled 14.2: Rates of Chemical Reactions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

14.3: Reaction Conditions and Rate

Introduction

In this section we will introduce some of the conditions that influence the rate of reaction. Later in this chapter we will take a deeper look at each of these conditions, and we are covering them now to give you a big picture of where we are going. The four major conditions we will cover are:

1. Concentration
2. Temperature
3. Catalyst
4. Surface Areas (heterogeneous systems)

Note: Many texts also discuss the nature of the reactants, which could be added to the above list.

Concentration

The effects of concentration can be varied. Many reactions require two reactants to collide with each other as reactant bonds are broken and product bonds formed. From bimolecular collision theory the frequency of collisions is not related to the total number of molecules, but how concentrated they are. That is, the more concentrated the higher the collision frequency, and thus the faster the reaction rate. Some other reactions do not require collisions, like radioactive decays where a nonstable nucleus spontaneously decomposes into another nuclide, while giving off a radioactive particle. Here, the rate is dependent on the number of particles and thus the concentration, but not on the collision frequency. The following YouTube demonstrates a reaction rate that is influenced by concentration.



Video \(\PageIndex{1}|) 2:18 YouTube uploaded by Learn Science demonstrating the effect of reactant concentration on reaction rate (https://youtu.be/LEkXQxHtbMM)

Temperature

Increased temperature implies increased kinetic energy and this can increase reaction velocity in several ways. First, there is more energy in collisions, and thus the fraction of collisions with enough energy to initiate a reaction increases. We will look at this in more detail when we get to the Arrhenius equation. Another way temperature increases rate is by increasing the collision frequency. It should be noted that cooling slows down reaction rates, and so refrigerating food slows down the rate at which it gets oxidizes, and allows it to last longer. The following YouTube shows the temperature effect on an Iodide clock reaction,



Video 14.3.2 *2:34 YouTube uploaded by Katherine Mirica demonstrating the temperature effect on a chemical reaction.*

In the lab we will be running a similar experiment to this.

Catalyst

A catalyst influences the mechanism of a reaction. It is a reactant that is consumed in an early step and produced in a later step, and thus can be used over and over. We will be discussing these in great detail when we get to section section 14.5.



Video 14.3.1: 4:13 Royal Society of Chemistry Video on the Decomposition of hydrogen peroxide (https://youtu.be/Ta4DomSDzF8)

Surface Area



Video 14.3.2: 2:46 Royal Society of Chemistry Video on the effect of surface area on reaction rate (https://youtu.be/FBF7auCMy58)

Test Yourself

Homework: Section 14.3

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Liliane Poirot

This page titled 14.3: Reaction Conditions and Rate is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

14.4: Effect of Concentration on Reaction Rate

Rate Law

The Rate Law is a power function that describes the effect of the concentration of the reactants on the rate of reaction for a reaction occurring at constant temperature.

If there is only one reactant it has the form of

$$\begin{aligned} A &\rightarrow Products \\ R &= k[A]^m \end{aligned} \tag{14.4.1}$$

Using the convention introduced in section 14.2.1 of this chapter, R is the rate of reaction, [A]represent the concentration of reactant A, typically in units of molarity (moles reactant per liter), and m is a constant, the order of reaction with respect to A. So the rate law is a power function that describes how R (the dependent variable) depends on the concentration of A (the independent variable)

If there are two reactants, say A and B, then the relationship is extended to two independent variables, each with their own order of reaction

$$\begin{aligned} A + B &\rightarrow Products \\ R &= k[A]^m[B]^n \end{aligned} \tag{14.4.2}$$

Each additional reaction contributes an additional independent variable to this power function, each with its own order of reaction, and so three reactants would have the following relationship

$$\begin{aligned} A + B + C &\rightarrow Products \\ R &= k[A]^m[B]^n[C]^p \end{aligned} \tag{14.4.3}$$

Students often get confused with the "reaction rate" and the "rate constant" and it is good to take a look at each part of the rate law before proceeding.

The variables

In the rate law the rate is dependent on the reaction concentrations so:

- **R the reaction rate is the dependent variable** representing the change in concentration of any species related to time and can be expressed in terms of either reactants or products. This is often confusing for students as you can describe the rate by the consumption of any reactant or the production of any product, and these various rates are all related, as described in section 14.2.3 . If you know the rate of one species, you can calculate the rate of any other, just remember that over time reactants decrease in concentration (have a negative sign) and products increase in concentration.

- **The concentrations [A], [B], [C], ... are the independent variables** (remember [ ] describes concentration). As the concentration of each reactant can be varied, the number of independent variables equals the number of reactant species. Typically the higher the concentration the faster the rate, but this is not always true, and depends on the values of the constants in the rate law.

The Constants

- **m,n,p... t**he power of the power function with respect to each independent variable are called the **"orders of reaction"** They are typically integers and have values starting with zero (in this class we will consider them always to be integers). Each reactant has its own order of reaction, typically represented with a lower case letter. Lets look at the orders of reaction for a single independent variable [A], which has the order of reaction m

$$R = k[A]^m \tag{14.4.4}$$

  - m = 0 (Zero Order Reaction): Here the rate is not affected by the concentration and if you were to double the concentration the rate would not change.

$$R = k \tag{14.4.5}$$

- m = 1 (First Order Reaction): This is a linear relationship and if you double the concentration you double the rate of reaction

$$R = k[A] \tag{14.4.6}$$

- m=2 (Second Order Reaction): This is a squared relationship and if you double the concentration the rate quadruples

$$R = k[A]^2 \tag{14.4.7}$$

- m=3 (Third Order Reaction): This is a cubed relationship and if you double the concentration it goes eight times faster.

$$R = k[A]^3 \tag{14.4.8}$$

- m=n (n^{th} Order Reaction): Very few reactants have orders higher than third, but if you double the concentration it goes 2^n times faster.

$$R = k[A]^n \tag{14.4.9}$$

OVERALL ORDER of REACTION (Θ):

We will use the Greek symbol Theta Θ to describe the sum (Σ) of the order of reaction for all reactants in a chemical reaction

- Θ = m+n for two reactants where ($R = k[A]^m[B]^n$)
- Θ = m+n+p for three reactants where ($R = k[A]^m[B]^n[C]^p$)

- **k is the rate constant.** Actually, as we will see in section 14.6, k is not really a constant but a function of temperature. But right now we are looking at the concentration dependence of the reaction and will not consider the temperature effect. Also,the convention is to use e a lower case k for rate constants, as in the next chapter we will introduce the equilibrium constant (K), and will use that to distinguish it from the rate constant. Likewise, we will use t for time T for temperature.

  The units of k depend on Θ the overall order of reaction (see table below). Lets look at the units without identifying the species. The rate has units of concentration/time $R = \frac{\Delta[concentration]}{\Delta time}$ and each concentration has units of concentration to the power of its order of reaction, so in terms of units we could write:

$$\frac{[concentration]}{time} = k[concentration]^{\theta} \tag{14.4.10}$$

so dimensionally speaking the units of k would be

$$k = \frac{\frac{[concentration]}{time}}{[concentration]^{\theta}} = \frac{[concentration^{1-\Theta}]}{time} \tag{14.4.11}$$

So for a reaction where concentration was in molarity and time in seconds, the units of k ar

$$\frac{M^{(1-\Theta)}}{second} \tag{14.4.12}$$

Let's summarize this in the following table for the reaction, where A, B and C are reactants, and the order of reaction is m for A, n for B and p for C, with an overall order Θ= m+n+p

$$\text{rate} = k[A]^m[B]^n[C]^p \tag{14.4.13}$$

Table 14.4.(1): Example Rate Laws

Rate law	(m)	(n)	(p)	Overall order Θ
$\text{rate} = k$	0	0	0	0
$\text{rate} = k[A]$	1	0	0	1
$\text{rate} = k[A]^2$	2	0	0	2

Rate law	(m)	(n)	(p)	Overall order (Θ)
$\text{rate} = k[A][B]$	1	1	0	2
$\text{rate} = k[A]^2[B]$	2	1	0	3
$\text{rate} = k$	0	0	0	0
$\text{rate} = k[A][B][C]$	1	1	1	3
$\text{rate} = k[A]$	1	0	0	1
$\text{rate} = k[A]^2$	2	0	0	2

It should be noted that most chemical reactions are zero, first or second order.

Experimental Determination of Rate Law

We know the dependent variable (R) is a function of the independent variable, and on a piece of graph paper can plot out this relationship with R on the Y-axis and the independent variable [reactant concentration] on the the x-axis. The problem is, every reactant is an independent variable, and you can only graph one independent variable on a two dimensional plot. So if there is more than one reactant, you have to reduce the number of independent variables to one. If we assume the orders of reaction for each reactant are independent of each other (m does not change n), we can run a series of experiments where we vary one reactant concentration at a time to determine its order of reaction, while keeping all others constant. By successively doing this for all reactants we can determine the order of reaction for all species.

This lesson will start by solving the single reactant rate law. Then show how to reduce multi-reactant problems to single reactant problems. We will also introduce two different techniques for solving these. First the Ratio (Two State) Technique, which works well for "precise data", and then the graphing technique, which needs to be used when the data is unprecise. In the lab we will run an experiment where we have to use the graphing technique.

Single Reactant Rate Law

Consider the reaction:

$$A \rightarrow B \tag{14.4.14}$$

The Rate Law for the above is:

$$R = k[A]^m \tag{14.4.15}$$

We need to solve for k and m. There are two approaches. If we have real good data, we can use the two state method. If we have bad data, like the data you use in lab, we will need to use the graphing technique. Note:, since "m" is in an exponent, we will need to use logarithms, and the relationship $\log a^b = b \log a$.

Exercise 14.4.1

Solve the following equation for m.

$$56.3 = 32\,(0.45^m) \tag{14.4.16}$$

Answer

$$0.45^m = \frac{56.3}{32}$$

$$log 0.45^m = log \frac{56.3}{32}$$

$$m log 0.45 = log \frac{56.3}{32}$$

$$m = \frac{log \frac{56.3}{32}}{log 0.45} = \frac{0.24536}{-0.34679} = -0.7075$$

Graphing Technique

Because the rate law is a power function we need to use logarithms to determine the order of reaction. First take the log of both sides

$$log R = log k[A]^m \tag{14.4.17}$$

Using the relationship lnab = lna + lnb gives

$$logR = logk + log[A]^m \tag{14.4.18}$$

then using the relationship $log[A]^b = blog[A]$ and rearranging gives

$$logR = mlog[A] + logk \tag{14.4.19}$$

which has the form of a straight line with slope=m

y=mx+b

Where, y=logR, x=log[A] and b=logk

To get k you take the antilog of b

$$k = 10^b \tag{14.4.20}$$

Note, you could have used any base to the log scale and ploted

$$lnR = mln[A] + lnk \tag{14.4.21}$$

in which case Y=lnR, X = ln[A] and b= lnk, so k=e^b.

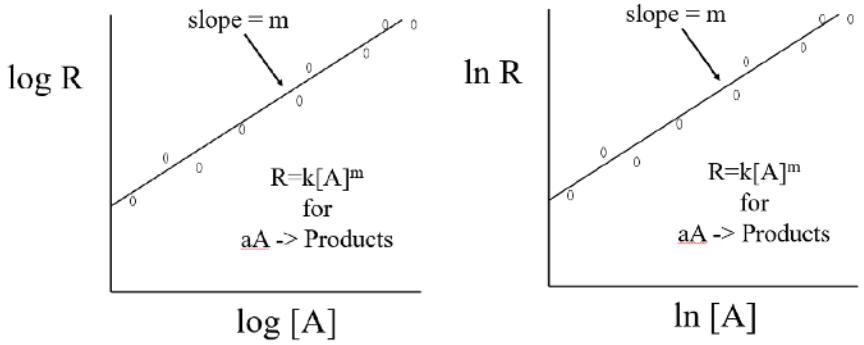


Figure 14.4.1: Log base 10 and natural log plots to determine the order of reaction. Note, both while have the same value of the slope (m) but different y-intercepts (b) of the generic straight line equation of Y=mX+b. For the left plot, k=10^b, for the right plot k=e^b.

Two State Technique

If your data is exact, and all the data is on the line, you can use the two state approach, that is you can simply use the data from only two measurements. So we run an experiment with a known concentration and measure the initial rate (state 1). Now we change the concentration and measure the initial rate (state 2). We divide state one by state 2 as we have done in the other two-state problems like the ideal gas and Henry's Law calculations.

$$\frac{R_1}{R_2} = \frac{k[A_1]^m}{k[A_2]^m}$$

$$\frac{R_1}{R_2} = \left(\frac{[A_1]}{[A_2]}\right)^m$$

$$\log\left(\frac{R_1}{R_2}\right) = m\log\left(\frac{[A_1]}{[A_2]}\right)$$

$$m = \frac{\log\left(\frac{R_1}{R_2}\right)}{\log\left(\frac{[A_1]}{[A_2]}\right)} \tag{14.4.22}$$

Once we calculate m, we can substitute back into one of the states and solve for k (see following worked example)



Video 14.4.1: 11:46 Youtube video on Reaction Rate Law (https://youtu.be/33TkHkWFLPA)

Multi Reactant Systems

Lets look at a system involving three reactants,

$$A + B + C \rightarrow Products \qquad (14.4.23)$$
$$R = k[A]^m[B]^n[C]^p$$

In the above equation we have on dependent variable (the rate), which has a value that depends on three independent variables, the concentrations of chemical species "A" and "B", and "C". Can you think of an equation from General Chemistry 1 that had four variables? How about the Ideal Gas Law? If you review section 10.2 Gas Laws, you will see that historically a series of "empirical gas laws" were experimentally developed that were in essence the ideal gas law with two of the four variables held constant.

- Boyle's Law: P=k$\frac{1}{V}$ (PV=nRT at constant n,T)
- Gay-Lussacs Law: P=k'T (PV=nRT at constant n,V)
- Charles's Law: V=k"T (PV=nRT at constant n,P)
- Avogadro's Law V=k'"n (PV=nRT at consant P,T)

We are going to take the same strategy, although there is a slight difference between the rate law with three reactants and the ideal gas law, in that the ideal gas law was an equation of state and all variables were equal, whereas here the rate is a dependent variable and the concentrations are independent. So you design a series of experiments where two of the concentrations are constant and vary the third to see how it affects the rate. You then sequentially repeat this for the remaining two independent variables, so in essence you need to run three sets of experiments, where in each set only one of the concentrations vary. If your data is exact, you do not need to make a graph, but can use the two state approach.

Table 13.3.3 Rate Data for a Hypothetical Reaction of the Form A + B → Products

Experiment	[A] (M)	[B] (M)	[C](M)	Initial Rate (M/s)
1	0.10	0.10	0.10	0.00475
2	0.20	0.10	0.10	0.019
3	0.20	0.20	0.10	0.152
4	0.20	0.10	0.20	0.038

- **Step 1: Determine m by running set of experiments at constant [B] and [C] constant**.
  This can be done with experiments 1 and 2. TRICK: place the larger concentration in the numerator
  Lets start by looking at the entire rate law

$$\frac{rate_2}{rate_1} = \frac{k[A_2]^m[B_2]^n[C_2]^p}{k[A_1]^m[B_1]^n[C_1]^p} = \frac{k[A_2]^m[0.1]^n[0.1]^p}{k[A_1]^m[0.1]^n[0.1]^p}$$

$$\frac{R_2}{R_1} = \left(\frac{A_2}{A_1}\right)^m \left(\frac{0.1}{0.1}\right)^n \left(\frac{0.1}{0.1}\right)^p$$

$$\frac{R_2}{R_1} = \left(\frac{A_2}{A_1}\right)^m \tag{14.4.24}$$

$$\frac{0.019\ M}{0.00475\ M} = \left(\frac{.20\ M/s}{.10\ M/s}\right)^m$$

$$4 = 2^m$$

$$m = 2$$

Step 2: Determine n by running set of experiments at constant [A] and [C] constant
Experiments 3 and 2

$$\frac{R_3}{R_2} = \left(\frac{B_3}{B_2}\right)^n \tag{14.4.25}$$

$$\frac{0.152\ M}{0.019\ M} = \left(\frac{.20\ M/s}{.10\ M/s}\right)^n$$

$$8 = 2^m$$

$$n = 3$$

NOTE: Dividing R_2 by R_3 (not place the larger concentration in the numerator) would have given $0.125=0.50^n$ for the second to last step and a student may not have recognized that as $1/8=(1/2)^n$, in which case they would need to take the log of both sides to find n.

$$\frac{R_2}{R_3} = \left(\frac{B_2}{B_3}\right)^n \tag{14.4.26}$$

$$\frac{0.019\ M}{0.152\ M} = \left(\frac{0.10\ M/s}{0.20\ M/s}\right)^n$$

$$0.125 = 0.50^m \Rightarrow log(0.125) = log(0.50)^n = nlog(0.50)$$

$$n = \frac{log 0.125}{log 0.50} = \frac{-0.90309}{-0.30103} = 3$$

Step 3: Determine p by running set of experiments at constant [A] and [B] constant
Experiments 4 and 2

$$\frac{R_4}{R_2} = \left(\frac{C_4}{C_2}\right)^p \tag{14.4.27}$$

$$\frac{0.038\ M}{0.019\ M} = \left(\frac{.20\ M/s}{.10\ M/s}\right)^n$$

$$4 = 2^p$$

$$p = 2$$

Step 4: Determine k, the rate constant

$$k = \frac{R}{[A]^m[B]^n[C]^p} = \frac{0.00475 M/s}{[0.1M]^2[0.1M]^3[0.1M]} = 4800 s^{-1} M^{-5} \tag{14.4.28}$$

Note

In the above problems we changed the concentration by orders of 2. This made the math very easy and you could have just looked and seen the order of reaction. But also, it is very easy to change the concentration of a reactant by 2. You simply take some of it and dilute in half, and now the original solution is twice that of the diluted.

- In going from experiment 1 to 2 we doubled the concentration of [A] at constant [B], [C] and the reaction went 4 times as fast, so the order with respect to A is 2, as 2^2=4.
- In going from experiment 2 to 3 we doubled the concentration of [B] at constant [A], [C] and the reaction went 8 times as fast, so the order with respect to B is 3, as 2^3=8.
- In going from experiment 2 to 4 we doubled the concentration of [C] at constant [A], [B] and the reaction went 4 times as fast, so the order with respect to C is 2, as 2^1=2.

Exercise 14.4.2

Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:

$$2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g) \longrightarrow 2\,\mathrm{NOCl}(g) \tag{14.4.29}$$

Trial	[NO] (mol/L)	[Cl_2] (mol/L)	$-\frac{\Delta[\mathrm{NO}]}{\Delta t}$ ($\mathrm{mol\,L^{-1}\,s^{-1}}$)
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Answer

Solution

The rate law for this reaction will have the form:

$$\text{rate} = k[\mathrm{NO}]^m[\mathrm{Cl_2}]^n \tag{14.4.30}$$

***1. Determine the value of* m** (at constant [Cl_2]):

$$\frac{\text{rate}_x}{\text{rate}_y} = \frac{k[\mathrm{NO}]_x^m[\mathrm{Cl_2}]_x^n}{k[\mathrm{NO}]_y^m[\mathrm{Cl_2}]_y^n} \tag{14.4.31}$$

Using the third trial and the first trial:

$$\frac{\text{rate } 3}{\text{rate } 1} = \frac{0.00675}{0.00300} = \frac{\cancel{k}(0.15)^m\ \cancel{(0.10)^n}}{\cancel{k}(0.10)^m\ \cancel{(0.10)^n}} \tag{14.4.32}$$

After canceling equivalent terms in the numerator and denominator, we are left with:

$$\frac{0.00675}{0.00300} = \frac{(0.15)^m}{(0.10)^m} \tag{14.4.33}$$

which simplifies to:

$$2.25 = (1.5)^m \tag{14.4.34}$$

We can use the log of any base to determine the value of the exponent *m*, (we used base 10 in the worked out example above, and will use natural logs here).

$$\ln(2.25) = m\ln(1.5) \tag{14.4.35}$$

$$m = \frac{\ln(2.25)}{\ln(1.5)} \tag{14.4.36}$$

$$m = 2 \tag{14.4.37}$$

We can confirm the result easily, since:

$$1.5^2 = 2.25$$

2. Determine the value of n (at constant [NO]).

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{0.00450}{0.00300} = \frac{\cancel{k(0.10)^m}(0.15)^n}{\cancel{k(0.10)^m}(0.10)^n} \tag{14.4.38}$$

Cancelation gives:

$$\frac{0.0045}{0.0030} = \frac{(0.15)^n}{(0.10)^n} \tag{14.4.39}$$

which simplifies to:

$$1.5 = (1.5)^n \tag{14.4.40}$$

Thus *n* must be 1, and the form of the rate law is:

$$\text{Rate} = k[\text{NO}]^m[\text{Cl}_2]^n = k[\text{NO}]^2[\text{Cl}_2] \tag{14.4.41}$$

3. Determine the numerical value of the rate constant k with appropriate units. Since the overall order of reaction is three, the units are $M^{-2}s^{-1}$, $l^2mol^{-2}s^{-1}$. To determine the value of *k* once the rate law expression has been solved, simply plug in values from any experiment, we will use the first experimental trial because the math is easiest, and solve for *k*:

$$0.00300 \text{ mol L}^{-1} \text{ s}^{-1} = k(0.10 \text{ mol L}^{-1})^2(0.10 \text{ mol L}^{-1})^1 \tag{14.4.42}$$

$$k = 3.0 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1} \tag{14.4.43}$$

In Class Activity

Test Yourself

Homework: Section 14.4

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Liliane Poirot

This page titled 14.4: Effect of Concentration on Reaction Rate is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

14.5: Integrated Rate Law

Introduction

Consider the following generic reaction of chemical species A turning into species B,

$$A \rightarrow B$$

$$R = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t} = k[A]^m \tag{14.5.1}$$

The above equation is a power function relating the rate of reaction to the concentration, with the nature of that relationship being defined by the order of reaction. Yet the rate itself is a function of concentration $R = \frac{\Delta[\ ]}{\Delta t}$, where [ ] represents the concentration of some species (reactant or product). If we express the rate law as the consumption of the reactant [A], the we have one equation with two variables, which we could graph, that is [A] is a function of t.

$$-\frac{\Delta[A]}{\Delta t} = k[A]^m \tag{14.5.2}$$

rearranging to we can look at how the concentration changes over time give"

$$\frac{\Delta[A]}{[A]^m} = -k\Delta t$$

The problem is that it is the change in A as a function of the change in t, which requires calculus to solve, and **calculus is not a prerequisite to this course**. So we are going to memorize the algebraic solutions of the integrated rate law for zero, first and second order reactions.

Optional Background material

For those of you who have had calculus, or wish to get a bearing on where these equations come from, we need to start with the concept of the derivative, which is the rate at an instant in time, that is, as Δt approaches zero.

$$\lim_{\Delta t \to 0} \frac{\Delta[A]}{\Delta t} = \frac{d[A]}{dt} \tag{14.5.3}$$

the rate law becomes.

$$\frac{d[A]}{dt} = -k[A]^m \tag{14.5.4}$$

which from calculus, you can separate the variables and integrate

$$\int \frac{d[A]}{[A]^m} = -\int k\, dt \tag{14.5.5}$$

There is one solution to the right hand side of Equation 14.5.5

$$-\int_{t=0}^{t} kdt = -k(t-0) = -kt \tag{14.5.6}$$

There are two solutions to the left part of Equation 14.5.5. Note, Equation 14.5.7 expresses the equation the way it normally is expressed in calculus classes (the dependent variable is in the numenator $[A]^n$), but in Equation 14.5.5 it is in the denominator ($[A]^{-m}$), and so in comparing these equations $m = -n$.

$$\underbrace{\int_{[A]_0}^{[A]} [A]^n d[A] = \frac{1}{n+1}\left([A]^{n+1} - [A]_0^{n+1}\right)}_{n \neq -1} \tag{14.5.7}$$

when $n = -1$

https://chem.libretexts.org/@go/page/60728

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \ln[A] - \ln[A]_0 \tag{14.5.8}$$

The integrated rate laws you need to know are the solutions to the above equation for $n = 0,\ 1,\ 2$.

Students do not need to know Equation 14.5.3- 14.5.8. These are just being provided so you know that the integrated rate laws come from calculus solutions to the rate equation. You do need to know the solutions for n = 0,1,2. These are covered in table 14.5.1 of the very next section.

Integrated Rate Laws

Most orders of reaction are zero, first or second. Table 14.5.1 gives the solutions to the integrated rate laws, and you need to know these solutions for zero, first and second order reactions. Note, there is a form of each order of reaction that follows the equation of a straight line (y=mx+b).

Table 14.5.1

Order	0	1	2
Integrated Rate Law	[A]= -kt + $[A]_0$	A] = $[A]_0e^{-kt}$ or ln[A] = -kt + $\ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$

Implicit in the above equations is that [A], the dependent variable, represents the concentration at any time (t), the independent variable as a function of the rate constant (k) and the initial concentration at t=0, ($[A]_o$). We could write [A] as $[A]_t$ to indicate that it is the value of [A] at some time t. The nature of that relationship depends on the order of reaction.

Zero Order Reaction

In zero order reactions the reaction rate is independent of the concentration and the rate is the negative of the rate constant, which has units of concentration/time, like M/sec.

$$Rate = \frac{\Delta[A]}{\Delta t} = -k \tag{14.5.9}$$

A plot of the concentration of a reactant gives a linear function where the concentration decreases over time at a constant rate.

$$[A] = -kt + [A]_0 \tag{14.5.10}$$

or

$$[A]_t = -kt + [A]_0$$

$$(y = mx + b)$$

Optional Background material

For those of you who have had calculus, or wish to get a bearing on where these equations come from,

$$\frac{d[A]}{dt} = -k[A]^o = -k \tag{14.5.11}$$

$$d[A] = -kdt$$

$$\int_{[A]_0}^{[A]_t} d[A] = -\int_{t=0}^{t} kdt$$

$$[A]_t - [A]_o = -kt - k(0)$$

$$[A]_t = -kt + [A]_o$$

The rate of a zero order reaction does not depend on the concentration of a reactant and it stays constant until all the limiting reagent is completely consumed.

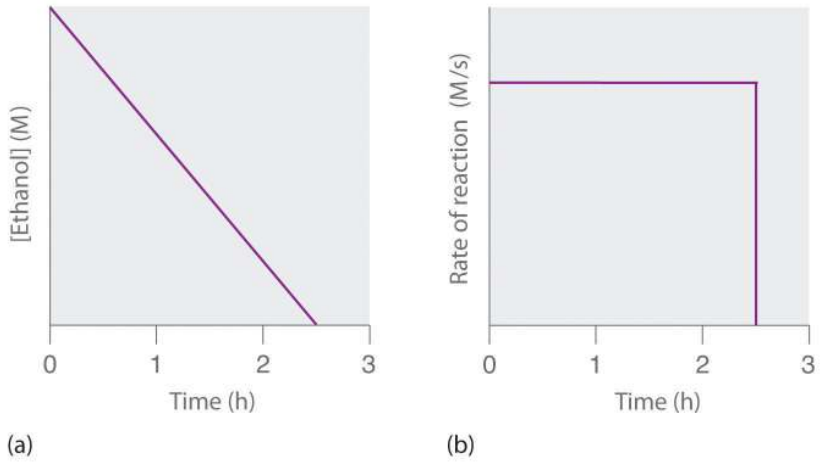


Figure 14.5.1: *The catalyzed oxidation of ethanol is zero order. Note, the slope of the line in (a) is constant, and (b) is a plot of that slope.* (Belford)

Sometimes it is useful to look at this as:

$$\underbrace{[A]}_{\text{concentration at time t}} = \underbrace{[A]_0}_{\text{initial concentration}} - \underbrace{kt}_{\text{amount consumed}} \tag{14.5.12}$$

Where what you have left ([A]) is what you started with ($[A]_0$) minus the amount consumed over a specified period of time (kt) is the amount consumed. This is very simple math, for example, if a student has \$100 in the bank ($[A]_0$) and spends \$10/day (k) for three days (t), they have \$70 left ([A]).

Zero order reactions are often called pseudo zero order as they are the results of the reaction conditions, typically because a reactant is in excess concentrations compared to others, and always break down to other kinetics as the concentration approaches zero (the rate must change as the reactant concentration approaches zero as it is zero when the concentration is zero). Heterogeneous catalysts like enzymes (next section) are often zero order with respect to substrate (reactant) concentration because there are so few active sites compared to the number of substrate (reactant) molecules that the moment one opens up another substrate molecules is ready to fill it, but this breaks down as the substrate concentration approaches zero.

First Order Reaction

In a first order rate law, the rate of consumption of a reactant is proportional to the consumption of a reactant and the rate constant has units of 1/t, like 1/sec.

$$Rate = -\frac{\Delta[A]}{\Delta t} = k[A]^1 = k[A] \tag{14.5.13}$$

rearranging gives,

$$Rate = \frac{\Delta[A]}{\Delta t} = -k[A] \tag{14.5.14}$$

A plot of concentration over times gives a first order reaction gives an exponential decay and a plot of the natural log of concentration over times gives a linear decay. Students in general chemistry need to know the following two equations and do not need to know the optional calculus.find the concentration as a function of time we need to apply calculus (Equation 14.5.7), and the solution for a first order reaction is:

$$[A] = -kt + [A]_0 \tag{14.5.15}$$

$$(y = mx + b)$$

or

$$[A] = [A]_0 e^{-kt} \tag{14.5.16}$$

Optional Background material

For those of you who have had calculus, or wish to get a bearing on where these equations come from,

$$\frac{d[A]}{dt} = -k[A] \tag{14.5.17}$$

$$\frac{d[A]}{[A]} = -kdt$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -\int_{t=0}^{t} kdt$$

$$ln[A]_t - ln[A]_o = -kt - k(0)$$

$$ln[A]_t = -kt + ln[A]_o$$

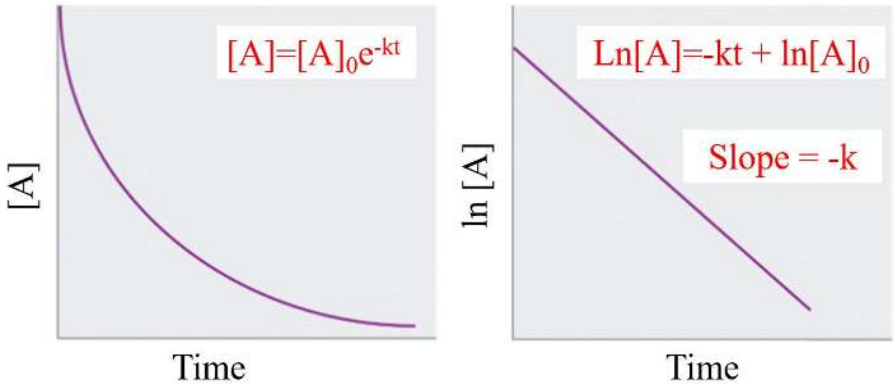


Figure 14.5.2: *wo graphs associated with first order decays. The left graph is the exponential function of the decay of concentration over time, while the right graph is the linear natural log of concentration as a function of time.* (Belford)

Note

There are two forms of a first order decay, exponential and natural log. The one you use depends on what you are solving for.

- Use Exponential form is solving for [A] or $[A]_o$. (**$A=A_0e^{-kt}$**).
- Use Natural log form if solving for k or t. (**$\ln[A] = -kt + \ln[A]_0$**).

Closer look at the exponential form and the fraction remaining or consumed

$$[A] = [A]_0 e^{-kt} \tag{14.5.18}$$

$$\therefore \tag{14.5.19}$$

$$\frac{[A]}{[A]_o} = e^{-kt} \tag{14.5.20}$$

$$\therefore \tag{14.5.21}$$

$$e^{-kt} = \text{ fraction of } [A]_o \text{ remaining} \tag{14.5.22}$$

So one can interpret the exponential form of a first order decay as"

$$\underbrace{[A]}_{\text{concentration remaining}} = \underbrace{[A]_0}_{\text{Initial concentration}} \times \underbrace{e^{-kt}}_{\text{fraction remaining}} \tag{14.5.23}$$

Since the fraction remaining plust the fraction consumed is equal to 1, we can also calculate the fraction consumed

$$\text{fraction consumed} = 1 - e^{-kt} \tag{14.5.24}$$

Note

The fraction remaining or consumed is independent of the initial concentration, and this is only true for first order reactions.

- **Fraction remaining** ($\frac{[A]}{[A]_o}$)=e^{-kt}.
- **Fraction consumed** ($\frac{[A]-[A]_o}{[A]_o}$)=1 - e^{-kt}.

This is important because if we know a first order rate constant we can ask questions like how long does it take for half of a sample to be consumed, and that amount of time is independent of the amount of sample we have. In fact this leads to the concept of half lives, which is a common way of describing a first order reaction rate constant. In fact for many people it is more intuitive than the rate constant, but for first order reactions, as we shall see, the half life is directly related to the rate constant, and if you know the half life, you know the rate constant.

Half Lives and First Order Reactions

The half life, is the amount of time it takes for the concentration to be reduced to one half its original value. In the case of a first order reaction, the half life is independent of the concentration.

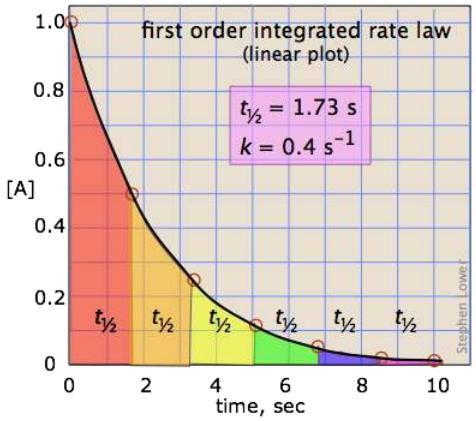


Figure 14.5.3: *The above plot shows that the amount of time it takes for a concentration to decompose to half its original value is independent of the concentration.* (Stephen Lower)

The definition of a half life is the amount of time it takes for a sample to decompose to one half its value. For a single exponential decay this is not a function of the sample size, for other orders of reaction, it is. Mathematically, the half life criteria is

$$at \;\; t = t_{1/2}, \;\; [A] = \frac{[A]_0}{2} \tag{14.5.25}$$

Substituting the half-life criteria ($[A] = \frac{[A]_o}{2}$)into the first order equation ($A=A_oe^{-kt}$) gives:

$$\frac{\cancel{[A]_0}}{2} = \cancel{[A]_0} e^{-kt_{1/2}} = \frac{\cancel{[A]_o}}{e^{kt_{1/2}}} \tag{14.5.26}$$

cancelling $[A]_o$ and taking the reciprocal of both sides gives

$$2 = e^{kt_{1/2}} \tag{14.5.27}$$

Taking the natural log of both sides and rearranging gives:

$$kt_{1/2} = ln2 = 0.693 \tag{14.5.28}$$

So a table of half lives give you the value of the rate constant (the longer the half life the smaller the rate constant)

$$k = \frac{.693}{t_{1/2}} \tag{14.5.29}$$

See Video 14.5.1 for the derivation of Equation ???



Video 14.5.1: 4:01 Youtube on half life and rate contant (https://youtu.be/8ucTs_4IpWs)

So you can write a first order integrated rate law in terms of the rate constant or half life

First Order Reactions	Exponential Form	Natural Log Form
Using rate constant	$A = e^{-kt}$	lnA=-kt + $\ln A_o$
Using half life	$A = e^{-\frac{0.693}{t_{1/2}}t}$	$lnA = -\frac{0.693}{t_{1/2}}t + lnA_o$

Half Lives and Radioactive (Carbon) dating

Carbon-14 undergoes beta (β) decay, in which a neutron is converted to a proton and a high-energy electron that is ejected from the nucleus as a β particle:

$$\underset{\substack{\text{unstable}\\\text{neutron in}\\\text{nucleus}}}{{}^{1}_{0}\text{n}} \rightarrow \underset{\substack{\text{proton}\\\text{retained}\\\text{by nucleus}}}{{}^{1}_{1}\text{p}} + \underset{\substack{\text{beta particle}\\\text{emitted by}\\\text{nucleus}}}{{}^{0}_{-1}\beta} \tag{14.5.30}$$

The general reaction for beta decay is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z+1}\text{X}'} + \underset{\text{beta particle}}{{}^{0}_{-1}\beta} \tag{14.5.31}$$

Although beta decay does not change the mass number of the nucleus, it does result in an increase of +1 in the atomic number because of the addition of a proton in the daughter nucleus. Thus beta decay decreases the neutron-to-proton ratio, moving the nucleus toward the band of stable nuclei. For example, carbon-14 undergoes beta decay to form nitrogen-14:

$${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\beta$$

The parent and the daughter nuclei have the same mass number, 14, and the sum of the atomic numbers of the products is 6, which is the same as the atomic number of the carbon-14 parent. We will cover nuclear reactions in more detail in chapter 21.

The Carbon-14 Cycle

There are two stable isotopes of carbon, carbon-12 (^{12}C) and carbon-13 (^{13}C), and an unstable radioisotope, carbon-14 (^{14}C), which decays with a half life of 5,730 years. Carbon-14 is continually being generated in the upper atmosphere, where cosmic rays generate free neutrons when they collide with nuclei, and ^{14}C is created when one of these neutrons collides with nitrogen (^{14}N) and in essence knocks out a proton as it is absorbed into the nucleus resulting in carbon-14. The unstable ^{14}C radioisotope (radioactive isotope) eventually emits a beta particle and reverts back to ^{14}N, as described in figure 14.5.4

In the upper atmosphere

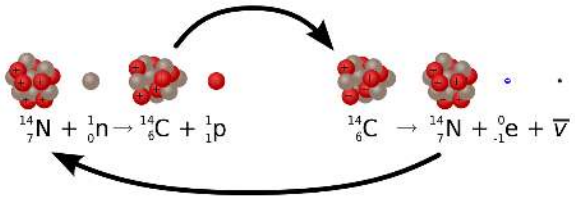


Figure 14.5.4: *The process where carbon-14 is generated through collision of a neutron with nitrogen-14, only to undergo beta decay back to a nitrogen 14* (source)

The result of this process is that the ration of ^{14}C to ^{12}C in the atmosphere is constant, and so living plant matter, which absorbs ^{14}C as it uptakes carbon dioxide in the process of photosynthesis has a constant ration of ^{14}C to ^{12}C. Once a plant dies, no more ^{14}C uptake occurs, and the ration decreases as the ^{14}C particles decay to ^{14}N. This is described in figures 14.5.4and 14.5.5

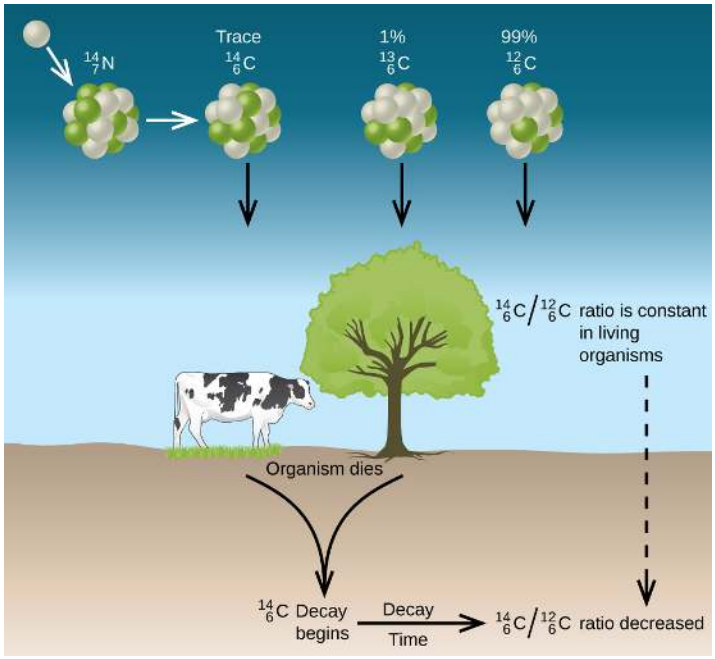


Figure 14.5.5: *Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died). Image used with permission (CC-BY 4.0; OpenStax).*

This allows scientists to determine the age of a plant based artifact by assuming that the current ratio of ^{14}C to ^{12}C in the atmosphere was the same when the plant died. In reality, this ratio can fluctuate, for an example, combustion of fossil fuel can increase the atmospheric concentration of "old carbon". It is also important to note that the decay rate of a sample of carbon-14, that is the number of radiating particles, is proportional to the the concentration of carbon-14 in the sample. So the kinetics measure the rate of radiation, which is equal to the rate of change in carbon-14 to nitrogen-14 if one particle is given off each time a nuclei in the sample decays.

Note

Carbon-14 dating takes some assumptions into account, the major one being that the ratio of ^{14}C to ^{12}C is constant from the time the sample died to the time it was tested. This allows one to postulate that living samples have the same ratio as the sample being tested had when it was alive, and so you have a value for the initial decay rate. This assumption may be in error if the atmospheric carbon dioxide differ over the time span, for example the burning of fossil fuels also produce carbon dioxide, but have a different ratio of ^{14}C to ^{12}C to that of respiration, and so their uptake in photosynthesis could result in an alteration of the ratio. In this class we will ignore these effects, and carbon-14 dating is a valuable tool to determine the age of material that was formed through photosynthesis.

Exercise 14.5.1

In 1988 radiocarbon dating was done on a sample obtained from the Shroud of Turin. At that time, living matter gave off 15.3 disintegrations per minute, and the sample gave off 14.2. How old was the Shroud of Turin in 1988 if the half life of ^{14}C = 5,715 years?



Video 14.5.2: 5:13 Youtube video working out Exercise 14.4.1 (https://youtu.be/MUaa8oY1C4s)

Answer

615 years.

Second Order Reactions

In second order reactions the reaction rate is dependent on the square of the concentration and the rate constant has units of 1/(concentration-time) like $M^{-1}s^{-1}$.

$$Rate = \frac{\Delta[A]}{\Delta t} = -k[A]^2 \tag{14.5.32}$$

A plot of the reciprocal concentration of a reactant gives a linear function with time, where the reciprocal concentration increases over time at a constant rate.

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \tag{14.5.33}$$

$$(y = mx + b)$$

Optional Background material

For those of you who have had calculus, or wish to get a bearing on where these equations come from,

$$\frac{d[A]}{dt} = -k[A]^2 \tag{14.5.34}$$

$$\frac{d[A]}{[A]^2} = -kdt$$

$$\int \frac{d[A]}{[A]^2} = -\int k\,dt$$

$$\int_{[A]_0}^{[A]_t} [A]^{-2} d[A] = -\int_{t=0}^{t} kdt$$

$$\left(\frac{1}{-2+1}\right)\left([A]_t^{-2+1} - [A]_o^{-2+1}\right) = -kt$$

$$-[A]_t^{-1} + [A]_o^{-1} = -kt$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$$

Note, that as the reactant concentration goes down it's reciprocal goes up

And so for second order reactions you plot the reciprocal function

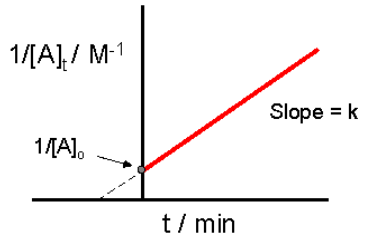
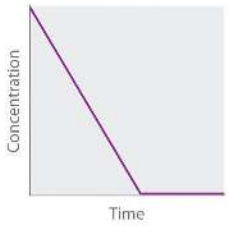
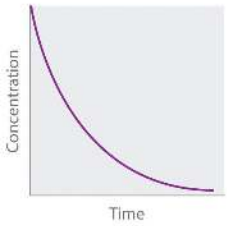
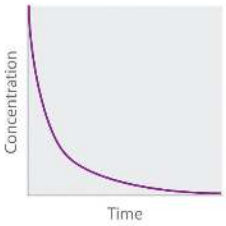
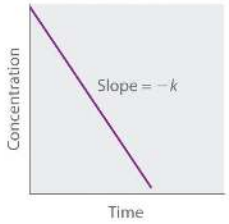
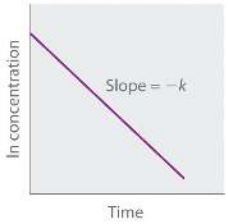
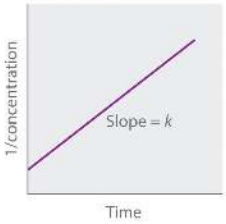


Figure 14.5.6: Second order plots are reciprocal plots. (Belford)

Summary of Rate Laws

	Zeroth Order	First Order	Second Order
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$
Concentration vs. time			
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Straight-line plot to determine rate constant			
Relative rate vs. concentration	[A], *M* / Rate, M/s 1 / 1 2 / 1 3 / 1	[A], *M* / Rate, M/s 1 / 1 2 / 2 3 / 3	[A], *M* / Rate, M/s 1 / 1 2 / 4 3 / 9
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$
Units of *k*, rate constant	M/s	1/s	$M^{-1}\cdot s^{-1}$

The above table summarizes the material in sections 14.4.3.and 14.4.4

Test Yourself

Homework: Section 14.5

(Note, there are around 30 worked problems in the homework, and you need to be able to do them)

Worksheet and Key:

Worksheet 1

Worksheet 1 Key

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Liliane Poirot
- d
-

This page titled 14.5: Integrated Rate Law is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

- **21.1: Radioactivity** is licensed CC BY-NC-SA 3.0.

14.6: Energetics and Reaction Rates

Introduction

In this section we will look at the temperature dependence of the rate law, and the effect of catalysts. Lets start with a simple energetic perspective. We know that the energy change of a reaction can be endothermic or exothermic. We know that enthalpy and internal energy are state functions, and the energy difference between the two state is independent of the path, that is, how the atoms rearranged and what intermediates were formed as they transformed from reactants to products. But there was an actual path, or mechanism by which the connectivity of the atoms of the reactants rearranged to produce the products. What we now want to do is look at the actual path that atoms took, and what we discover is that the rate of reaction is a function of the path, or mechanism. That is, the energy difference is independent of the path, but the rate does depend on the path. Figure 14.5.1 is an energy plot for a reaction as reactants become products that we commonly call an Arrhenius diagram.

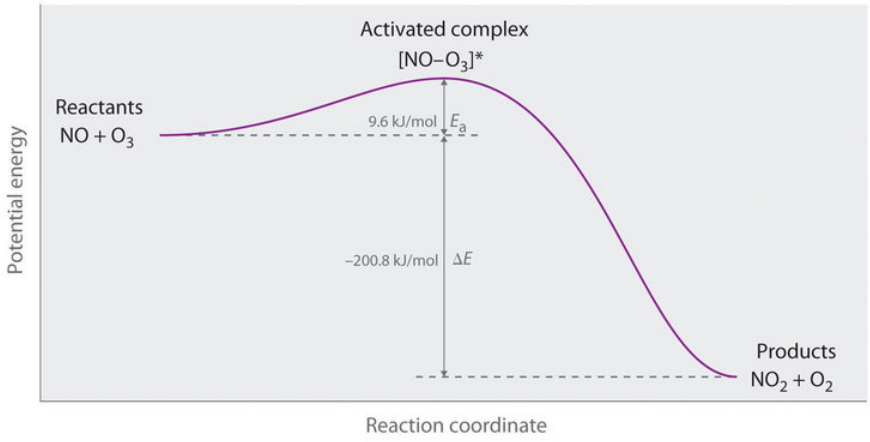


Figure 14.6.1: *Arrhenius diagram for the production of nitrogen dioxide and oxygen from nitric oxide and ozone. In this process 9.6kJ/mol of enegy was required to form the activated complex (transition state) and then -210.4 kJ of energy was released as the product was formed, and so the energy change for the reaction was -200.8kJ*

Figure 14.6.1 is a very important diagram to understand, and it is also a major simplification of what is really happening, but it is very useful. We know from the first law of thermodynamics that energy is conserved and that the energy difference between the final state (products) and the initial state (reactants) is independent of the path. It is also intuitive that energy is added to start breaking bonds (or intermolecular forces) and so a reaction starts with an endothermic step, which will be followed by an exothermic step as products are formed. But what were the states in between? The truth is, reactions can simultaneously proceed along many paths, and in the Arrhenius diagram we have simplified this to just one path, the lowest energy path, which we shall call the reaction coordinate. That is, in reality reactions involve many molecules and they do not all use the same path, but most use the path of lowest energy, which is the one described in the Arrhenius diagram.

This process involves an activated complex, also called the transition state, which is not a stable molecule that you can put in a jar, but a transient structure that exists as atoms rearrange during the transition from reactants to products. In figure 14.6.2 the transition state shows a 5 bonded carbon which is clearly not a real molecule, but representative of this sort of transient pseudo-molecule that exists between reactants and products, as the reaction proceeds from reactants to products.

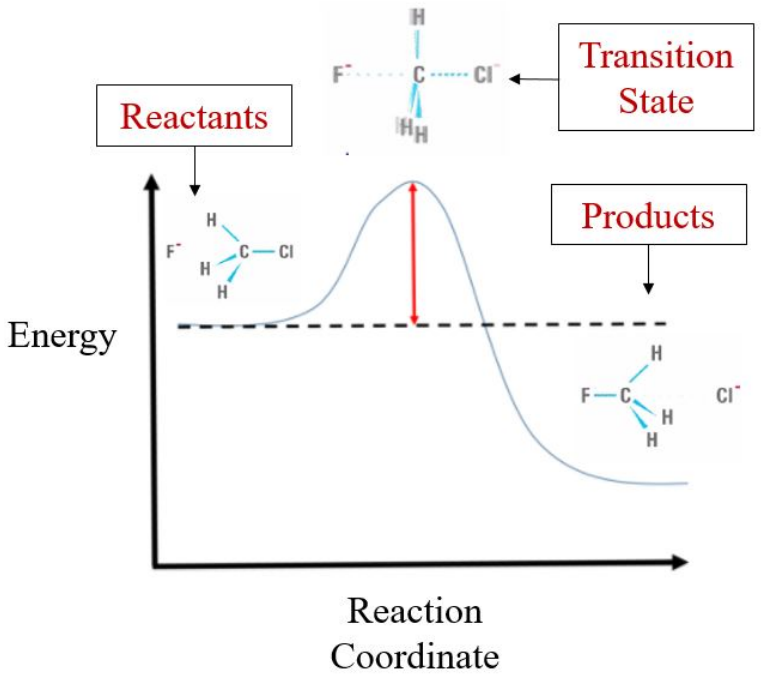


Figure 14.6.2: Note, the transition state had a "5-bonded carbon", which is obviously not a real molecule, but a state representative of the structure of the atoms as they transition between reactants and products.

It may be worth taking a moment to reflect on what are reactants and products. That is, although they are different chemical species, the atoms are the same atoms, it is just the connectivity of their bonds that changes, but the atoms do not change.

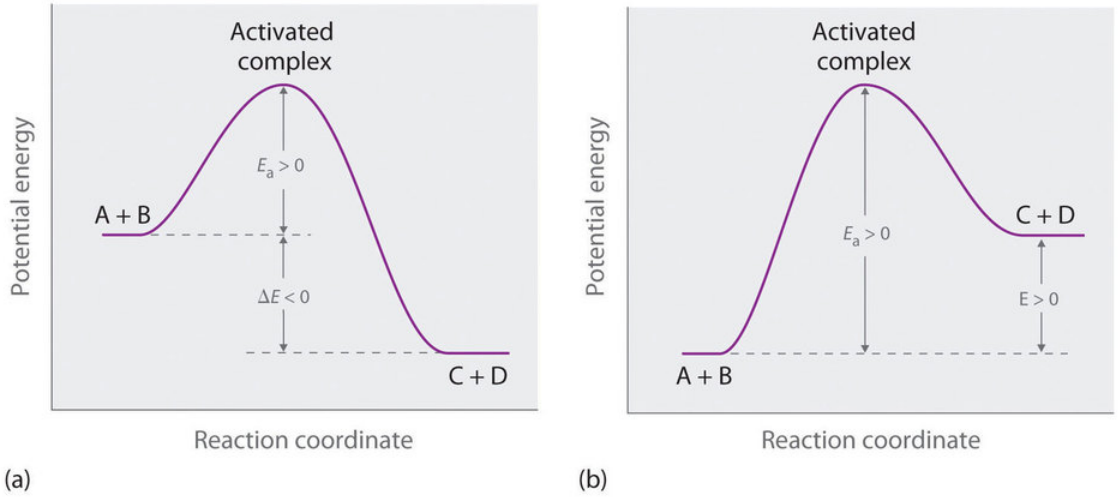


Figure 14.6.3: *Two Arrhenius plots, the one on the left representing an exothermic reaction where energy is released to the envrionment, and the one on the right an endothermic reaction, which absorbs energy. In these diagrams E_a represents the energy of activation, and E represents the energy (enthalpy) of reaction.*

Note, if the energy of activation of an exothermic reaction is less than the energy of reaction, the reaction is self perpetuating. This is the case in figure 14.6.1, where the energy released (-200.8kJ/mol) by some molecules as they react provides the E_a (9.6kJ/mol) others need to react. This is why a piece of paper is stable until it is ignited, when the energy relesed in combustion causes more paper molecules to ignite until it as turned to ashes. The following YouTube video does a good job of describing Arrhenius plots.



Video 14.6.1: 3:43 Animation uploaded by Biotech Review showing Arrhenius plots for both endothermic and exothermic reactions. (https://youtu.be/1_1Ho1LY_Lc)

Rate Constant and Arrhenius Equation

The rate law for a reaction between two substances, A and B, is the following:

$$\text{rate} = k[A]^m[B]^n \tag{14.6.1}$$

Actually, the rate constant is not a constant, but a function of temperature, which is mathematically described by the Arrhenius equation, where R has units of 8.314J/mol-K

$$k = Ae^{-\frac{E_a}{RT}} \tag{14.6.2}$$

Note that the rate constant has two components, the pre-exponential "A" and the exponential $e^{-\frac{E_a}{RT}}$. So the rate law also has a temperature component, which shows up when the Arrhenius equation is substituted for the rate constant in the rate law.

$$\text{rate} = Ae^{-\frac{E_a}{RT}}[A]^m[B]^n \tag{14.6.3}$$

Note, in the above equation, A is the pre-exponential of the Arrhenius equation and [A] is the concentration of reactant A.

Since this is an exponential equation, there are two ways of expressing it.

$$k = Ae^{-\frac{E_a}{RT}} \tag{14.6.4}$$

and

$$lnk = lnA - \frac{E_a}{RT} \tag{14.6.5}$$

which is usually written in the form of a straight line

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A \tag{14.6.6}$$

where ln k is a linear function of the reciprocal temperature $\frac{1}{T}$.

You would use the exponential form if you are solving for k or "A", and the ln form if you are solving for E_a or T.

Pre-exponential

The pre-exponential "A" is a function of two factors, the frequency factor (z) and the steric factor (ρ)

$$k = A e^{-\frac{E_a}{RT}}$$

$A = Z \times \rho$ (frequency factor, steric factor)

The pre-exponential "A" defines the largest possible value of the rate constant, assuming all collisions have enough energy to overcome the activation barrier. For reactions that involve two or more molecules interacting there are two factors involved in the pre-exponential, the frequency factor and the steric factor.

- The **frequency factor** determines the maximum rate of collisions, is a function of particle size, concentration and the rate of diffusion.
- The **steric factor** accounts for orientation, in that not all collisions have the correct orientation to result in a reaction, (see video 14.6.2). The rule of thumb is that the more symmetric a molecule the larger the steric factor (a value of 1 means there is no effect, and the pre-exponential is determined by the collision frequency) and the more complicated a molecule, the smaller the steric factor (which is less than one), because only a fraction of the collisions have the correct orientation.

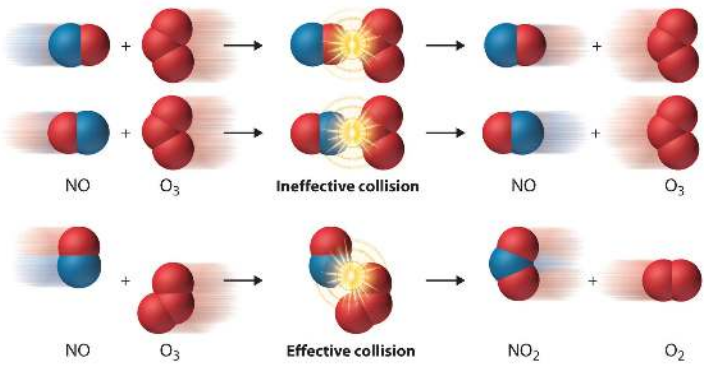


Figure 14.6.4: *Even if all the collisions above have sufficient energy to overcome the activation barrier, not all have the correct orientation. For the above reaction to occur, the nitrogen in NO must colloid with a terminal oxygen in ozone, so the top two collisions will not result in a reaction, while the bottom can, if there is enough energy in the collision to overcome the activation barrier.*

The following YouTube animation also shows the orientational dependence.



Video 14.6.2: *0.38 min YouTube uploaded by Cayerchem showing orientation affect of collisions on the steric factor, in that not all collisions have the correct orientation to allow the reaction to proceed, even if the collision has enough energy to overcome the activation barrier.* (https://youtu.be/IkqoBbFZV4Q)

Exponential

Even if a collision is of the correct orientation it must also have enough energy to overcome the activation barrier, and the fraction of molecules with enough energy is described by the exponential of the arrhenius equation: The second term ($e^{-\frac{E_a}{RT}}$) has a value

between 0 and 1 and accounts for the fraction of molecules that have enough energy to overcome the activation barrier.

$$e^{-\frac{E_a}{RT}} = \frac{1}{e^{\frac{E_a}{RT}}} \tag{14.6.7}$$

Note

R=8.314J/mol-K, and that Energies of activation are often recorded in kJ/mol, and so care must be taken in calculations to convert these to the same value. Since E_a is positive (the energy of activation is endothermic, the energy added to the system to reach the transition state) and K is positive (absolute zero is the coldest temperature possible), the value of $e^{-(E_a/RT)}$ is between 0 and 1

- At extreme high T or Low E_a: $e^{-(E_a/RT)}$ approaches $e^0 = 1$
- At extreme low T or High E_a: $e^{-(E_a/RT)}$ approaches $e^{-\infty} = 0$

Figure 14.5.5 provides a visualization on how this represents the fraction of collisions with enough energy to overcome the activation barrier. The y-axis represents the energy, and the horizontal line E_a represents the energy of activation. The green curves are the energy distribution profiles for a system of particles (say a mol) and at high T (500K) there are more molecules with higher kinetic energy than at low T (300K), and the fraction is the quantity above E_a divided by the entire area under the curve.

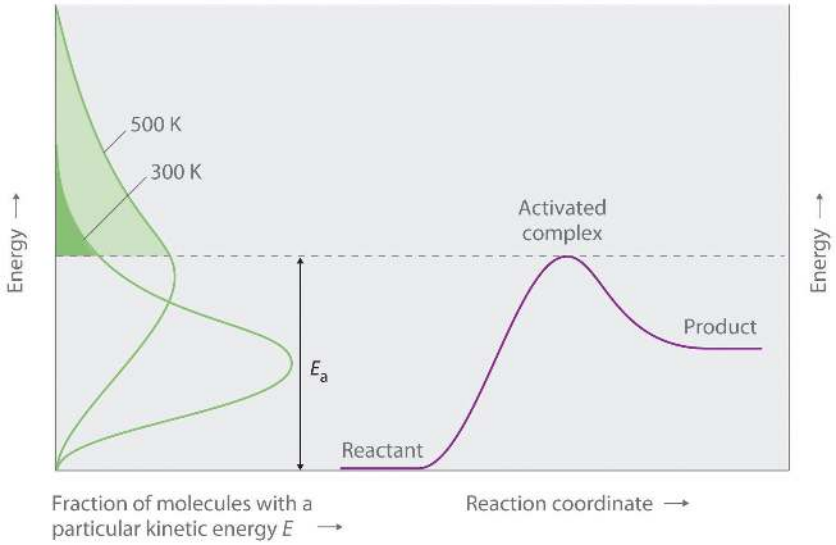


Figure 14.6.5: The area under the green curves are identical, and the fraction of molecules with an energy greater then E_a: is higher for the distribution at 500K then it is at 300K

Arrhenius Eq. Calculations

Calculate the energy of activation if raising the temperature from 30°C to 40°C doubles the rate when all concentrations are maintained constant. You may want to review the material on the Clausius-Claperyon equation in chapter 11 (sec. 11.6.3) describing the vapor pressure above a liquid, as these equations model similiar processes.



Video 14.6.3: 8:32 Youtube video on Arrhenius Eq. Calculations (https://youtu.be/sHQouO_7RJg)

Catalysts

Catalysts speed up the rate of reaction by changing the mechanism by which the reaction occurs. They are involved in multistep processes where they are consumed like a reactant in an early step to create an intermediate, and then are regenerated as a product in a subsequent step. The net effect is that the catalyst is regenerated after it is consumed, and thus can be used over and over. Catalysts also speed up the rate by lowering the activation energy. To indicate the presence of a catalyst they are written over the arrow as in equation 14.5.5, which describes the catalyzed production of B from A, where "Catalyst" is the identity of the catalyst

$$A \overset{Catalyst}{\rightarrow} B \tag{14.6.8}$$

Catalysts:

- Speed up the Rate of Reaction
- Change the mechanism of reaction
- Are not consumed by net reaction
  - Consumed in early steps as intermediate species are formed
  - Regenerated in later steps as intermediate species react
- Lower the Energy of Activation by forming intermediates with lower activation energy

All catalytic processes require the formation of one or more intermediates, which through subsequent steps reproduce the catalyst. Lets look at the simplest possible process, a two step reaction involving a single intermediate (A-CAT), where species A and B react to form C in the presence of a catalyst, CAT

$$A + B \overset{CAT}{\rightarrow} C \tag{14.6.9}$$

This can occur in a two step process where an intermediate A-CAT is formed.

$$\underbrace{A}_{reactant} + \underbrace{CAT}_{catalyst} \rightarrow \underbrace{\text{A-CAT}}_{intermediate} \tag{14.6.10}$$

$$\underbrace{\text{A-CAT}}_{intermediate} + \underbrace{B}_{reactant} \rightarrow \underbrace{C}_{product} + \underbrace{CAT}_{catalyst} \tag{14.6.11}$$

When you add the above two equations you get the net reaction

$$A + B \rightarrow C \tag{14.6.12}$$

NOTE that in the coupled equations neither the catalyst or the intermediate show up in the net equation

- Catalyst: Consumed in Early Step and Produced in Later Step
- Intermediate: Produced in Early Step and Consumed in Later Step

Catalysts and the Arrhenius Equation

Figure 14.6.6 shows an Arrhenius diagram for both a catalyzed reaction (in blue) and a noncatalyzed reactions (in red). What is important to note is that the catalyzed path shows the formation of an intermediate. This is a real molecule and the deeper its well the more stable it is. Since forming the intermediate has a lower activation than the uncatalyzed path, the fraction of collisions with enough energy to overcome the activation barrier is higher, and so the rate is higher.

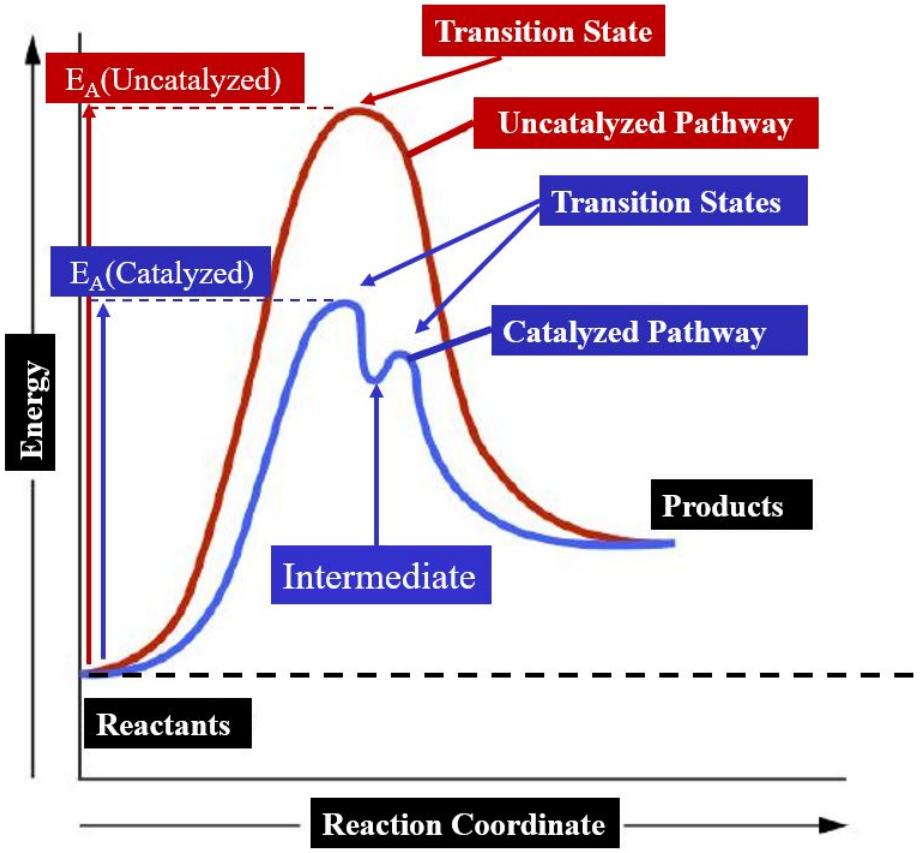


Figure 14.6.6: Arrhenius diagram comparing noncatalyzed reaction (**red**) with catalyzed reaction (**blue**). Note how the catalyzed reaction has an intermediate with a potential well, and that there are two activation energies associated with the intermediate (not shown in diagram). The higher one goes back to reactants and the lower one goes to products. Since the one to products is lower than the one to reactants, that process will tend to be faster.

Lets revisit the Arrhenius Eq (14.5.2)

$$k = Ae^{-\frac{E_a}{RT}}$$

We see there are two ways to increase the fraction of molecules that have enough energy to overcome the activation barrier $e^{-\frac{E_a}{RT}}$, by raising the temperature or by lowering the activation energy, which is what a catalyst does. What needs to be understood is that in a real system, there are often competing reactions that can occur, and raising the temperature increases the rate of all of them, indiscriminately. While a catalyst can be very selective, and lower the activation energy of a specific reaction and thus allow you to increase the rate of a specific process, without increasing the rate of other processes.

It should also be noted that in real reactions there can be many intermediates, as illustrated by the Arrhenius diagram in figure 14.5.7

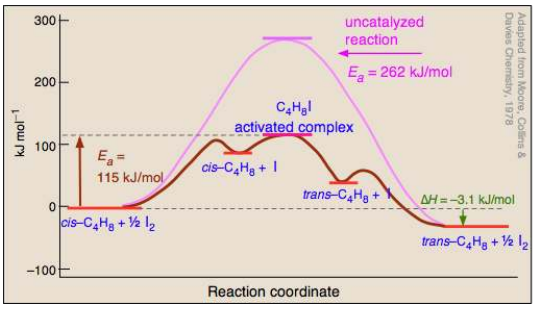


Figure 14.6.7: Iodine catalyzed cis-trans isomerization reaction that involves several intermediates. Even though this reaction creates multiple intermediates, all of the intermittent steps of low energies of activation and so this process is much faster than the uncatalyzed reactions. Also note that during the final step, the molecular iodine is regenerated.

Another advantage of catalysts is that since they are regenerated, they quantity of reagents are decreased, and this fits in with one of the paradigms for green chemistry, which seeks to develop chemical chemical processes that use minimal resources and generate minimal waste.

Two basic types of catalysts

- Homogenous Catalysts
  - Same phase as reactants
  - Typically have a concentration dependence in the rate law
- Heterogeneous Catalysts
  - Different phase than reactants
  - efficiency influenced by surface area between phases.

Homogenous Catalysts

Oxides of nitrogen are byproducts of combustion and are produced by high flying aircraft in the upper atmosphere. The catalytic depletion of Ozone by Nitric Oxide (NO) in the stratosphere can have profound environmental effects because each NO molecule can destroys multiple ozone molecules.



Video 14.6.4: *1:36 min animation uploaded by HerrPingui describing NO catalyzed destruction of ozone* (https://youtu.be/4NWkNEVrjnU)

The equation below describes the catalytic destruction of ozone by nitric oxide (NO). Note that NO is the catalyst and NO_2 is the intermediate

$$\begin{aligned} NO + O_3 &\rightarrow NO_2 + O_2 \\ NO_2 + O &\rightarrow NO + O_2 \end{aligned} \tag{14.6.13}$$

Note that NO is the catalyst and NO_2 is the intermediate, and that the net equation is

$$O_3 + O \overset{NO}{\rightarrow} 2O_2 \tag{14.6.14}$$

Homgenous catalysts are included in the concentration dependence of the rate law

$$R = k[O_3]^m[O]^n[NO]^p \tag{14.6.15}$$

Exercise 14.6.1

Write the follow rate law for the decomposition of hydrogen peroxide by the homogenous catalysts bromine

$$2H_2O_2 \overset{Br_2}{\rightarrow} 2H_2O + O_2$$

Answer

$$R = k[Br_2]^m(H_2O_2]^n$$

Note that in a homogenous system, the catalyst concentration affects the rate of reaction, and so it is in the reaction law expression, like any other reactant. But it is a catalyts, because it is regenerated in a subsequent step.

Heterogeneous Catalysts

Heterogeneous catalyst involve more than one phase, and so the surface area between the phases influences the rate. Typical heterogeneous catalysts are solids that react with reactants that are in the liquid of gaseous phase, and since the catalyst is a solid, its concentration is constant and it does not appear in the rate equation.

The nickel catalyzed hydrogenation of ethylene ($H_2C{=}CH_2$) to ethane (H_3CCH_3) is an example of a heterogeneous catalyst,



Figure 14.6.5: 3:00 min by XhwmAuecicL describes the catalytic hydrogenation of ethylene into ethane. (https://youtu.be/wWc1c-gpD6Q)

Note, ethylene is stable in the presence of hydrogen and this makes sense, as there is no way the small diatomic hydrogen can approach both carbons in a single collision, split apart and form a bond with each. But by adsorbing into the catalytic surface they can then split apart and approach the carbons. It should be noted that the process of a gas reacting with a solid catalyst can be viewed to take place in three generic process, although as the video above shows, step 2, the actual reaction can be viewed to take place in multiple steps. But all heterogeneous catalysts must undergo the following 3 processes.

Process 1: Adsorption - reactants adsorb onto surface of heterogeneous catalyst
Process 2: Reactants interact and form products (which can involve multiple steps)
Process 3: Desorption - products leave catalytic surface, rejuvenating the catalyst so it can repeat the process and adsorb more reactants.

Poisoning a Catalyst occurs when a compound irreversibly adsorbs onto the surface and thus reduces the amount of active surface area. Many catalysts have active sites, which are specific regions of a molecule that has catalytic action. Enzymes are biological

catalysts, most of which are made of proteins.

Enzymes

Enzymes are biological protein based catalysts. The following video shows an enzyme catalyzed reaction. Although many of the details in this video are advanced for this class, it gives you a good feel for the specificity of catalysts, and how catalytic reactions can involve multiple steps.



Figure 14.6.6: 4.51 min YouTube uploaded by RCSBProteinDataBank (Research Collaboratory for Structural Bioinformatics) showing an enzyme catalyzed reaction. Note, in the video the catalyzed Arrhenius plot at around 1.47 min does not show an intermediate. As you continue watching the video you realize that for the Arrhenius plot to accurately show intermediates, there would need to be many many of them, so the plot is just showing a lowering of the activation energy. (https://youtu.be/yk14dOOvwMk)

Test Yourself

Homework: Section 14.5

WorkSheets and Keys:

- WorkSheet Arrhenius Eq.
- WorkSheet Arrhenius Eq. Key

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Liliane Poirot

This page titled 14.6: Energetics and Reaction Rates is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

14.7: Reaction Mechanisms

Introduction

Reaction Mechanism describe how a reaction actually proceeds, that is, what molecules colloid or spontaneously react. Most reactions are multistep, consisting of a series of coupled elementary reactions or steps, with each step typically involving one or two reactants.

An elementary reaction is a single step reaction involving 1 species decaying, or 2 or 3 molecules simultaneously colliding.

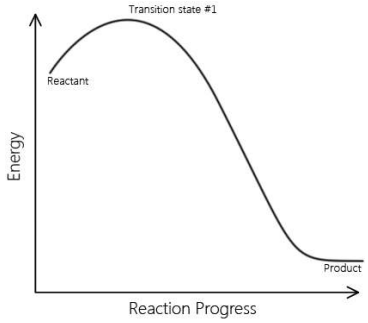
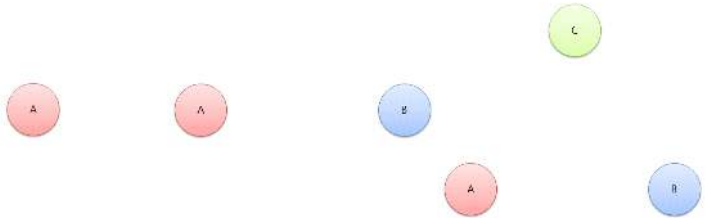


Figure 14.7.1: Arrehnius diagram for an elementary step involving one species

Molecularity

For an elementary step, the molecularly describes the number of particles involved in that step, and the order of reaction for each species is the stoichiometric coeficient of that species in the actual elementary step. The molecularity is the number of species involved with an elementary reaction. Molecularity can be described as unimolecular, bimolecular, or termolecular. Termolecular reactions are very rare as they require 3 particles colloiding with the correct orientation at the exact same time. Most reactions are unimolecular or bimolecular.



Unimolecular Reaction *Bimolecular Reaction* *Termolecular Reaction*

Figure 14.7.2: Illustrations of unimolecular, bimolecular and termolecular reactions

Unimolecular Elementary Reactions

These involve one species that spontaneously reacts, like the radioactive decay of an unstable radioisotope. The rate is proportional to the concentration

$$\begin{aligned} &A \rightarrow Products \\ &R = k[A] \end{aligned} \tag{14.7.1}$$

That is, the coeficient of a unimolecular elementary reaction is its coeficient, and if we integrated the above equation we would have an exponential decay.

Bimolecular Elementary Reactions

A bimolecular collision requires two chemicals to colloid and from collision theory the rate is proportional to the concentration of each colliding chemical with an overall order of reaction equal to two. That is, if the colliding molecules are the same species, the order of reaction is 2 for that species.

$$2A \rightarrow Products$$
$$R = k[A]^2 \tag{14.7.2}$$

$$A + B \rightarrow Products$$
$$R = k[A][B] \tag{14.7.3}$$

Termolecular Elementary Reactions

A termolecular elementary reaction requires 3 species to colloid at the same time with the proper orientation and energy, and is thus very rare. But they can occur, especially under conditions of high pressure and high temperature where there is a high collision frequency and a lot of energy in collisions. From collision theory the overall molecularity is three, with the order of reaction for each species being the number of colliding particles of that species in the termolecular collision.

$$3A \rightarrow Products$$
$$R = k[A]^3 \tag{14.7.4}$$

$$2A + B \rightarrow Products$$
$$R = k[A]^2[B] \tag{14.7.5}$$

$$A + B + C \rightarrow Products$$
$$R = k[A][B][C] \tag{14.7.6}$$

Higher order reactions do not occur, and it should be emphasized the termolecular elementary reactions are rare. Table 14.6.1 summarizes the molecularity of elementary reactions.

Table 14.6.1 Common Types of Elementary Reactions and Their Rate Laws

Elementary Reaction	Molecularity	Rate Law	Reaction Order
A → products	unimolecular	rate = k[A]	first
2A → products	bimolecular	rate = k[A]^2	second
A + B → products	bimolecular	rate = k[A][B]	second
2A + B → products	termolecular	rate = k[A]^2[B]	third
A + B + C → products	termolecular	rate = k[A][B][C]	third

Multistep Reactions

Most reactions occur in two or more coupled steps,

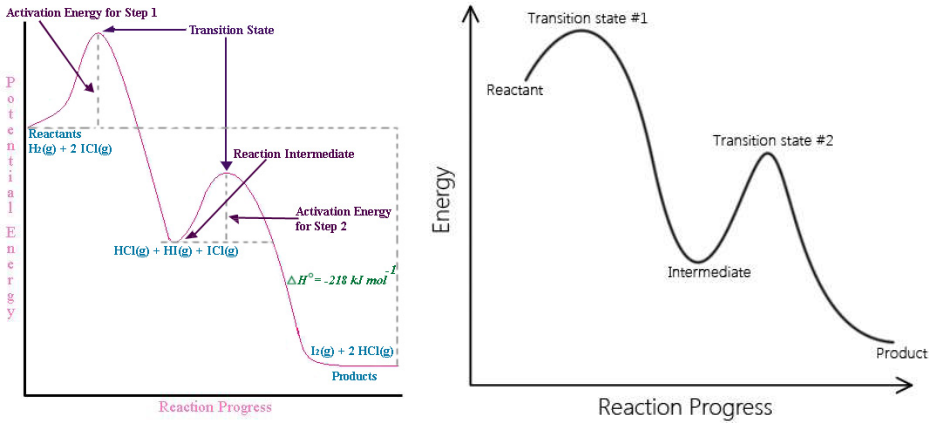


Figure 14.7.3: In a two step process an intermediate is formed in the first elementary step, which is then consumed in the second elementary step. A reaction mechanism is a series of coupled elementary steps (typically first or second order) where intermediates are created in one step and consumed in a subsequent step. Note, each step has its own energy of activation, and the intermediate can go forward or backwards (to produce products or reactants respectively).

In real mechanisms there can be many intermediates, but to illustrate this we will look at a two step mechanism for the formation of Iodine and Hydrogen chloride gas.

$$H_2(g) + 2ICl(g) \rightarrow I_2(g) + 2HClg \tag{14.7.7}$$

This process occurs in two bimolecular mechanistic (elementary) steps:

$$H_2 + ICl \rightarrow HCl + HI \tag{14.7.8}$$
$$HI + ICl \rightarrow HCl + I_2 \tag{14.7.9}$$

In the first step HCl and the intermediate HI are formed from the bimolecular reaction of H_2 and ICl. In the second elementary step, the HI (intermediate) collides with another ICl in a second bimolecular collision to form HCl and I_2. The net result is the reaction

$$H_2(g) + 2ICl(g) \rightarrow I_2(g) + 2HClg \tag{14.7.10}$$

The first two equations (14.6.7 & 14.6.8) are elementary steps of a reaction mechanism and you can determine the rate equation for each step from the stoichiometric coefficients of the elementary steps

$R_1 = k_1[H_2][ICl]$
$R_2 = k_2[HI][ICl]$

Where, k_1 & k_2 are the rate constants for the first and second steps respectively, and note that the rate equation for the second step has HI in it, which is not a reactant, but an intermediate.

NOTE: Equation 14.6.9 is a balanced chemical equation and not an elementary step of a mechanism, so you can not calculate the order of reactions from its coeficients. What you need to do is run experiments like in section 14.3 of this chapter where you hold hydrogen constant and change the ICl concentration to determine the order of reaction with respect to ICl, and then hold the ICl constant and change the hydrogen concentration to determine the order of reaction with respect to hydrogen.

In the next section we will see that the slow step is the rate determining step, and by comparing the results of experiments on eq. 14.6.9 to the predicted results of 14.6.7 and 14.6.8, we can identify the real mechanism

Mechanisms Based on Rate Determining Step

The observed rate of reaction for a serious of sequentially coupled elementary steps is based on the slow step, otherwise known as the Rate Determining Step.



Figure 14.7.4: In this diagram the small funnel has a smaller diameter and thus the speed at which the fluid flows is based on which step the small funnel is in. The same principle holds for kinetics where we consider the Slow step to be the rate determing step, and the rate law is based on the molecularity of the rate determing step. We will look at two simple processes, the first step is the slow step, and the second step is the slow step.

Rule: In Multi-step Mechanisms the Rate Law is Based on the Elementary Reactions of the Slow Step.

1. First Step Slow Step

When the first step is the slow step the rate law is simple based on the first step, and the subsequent steps (however many) have no effect. Consider a two step mechanism for the following reaction

$$NO_2 + CO \rightarrow NO + CO_2 \tag{14.7.11}$$

Step 1 (**Slow**):

$$\mathrm{NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO} \tag{14.7.12}$$

Step 2 (fast):

$$\mathrm{NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2} \tag{14.7.13}$$

The above mechansim would result in an observed rate law based on the slow step:

$$\mathrm{rate}_{observed} = k_1 [\mathrm{NO_2}]^2 \tag{14.7.14}$$

Note, the rate law can not be determined from the balanced equation (14.6.10)

2. Second Step Slow Step

Consider the equation

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O \tag{14.7.15}$$

Step 1 (Fast):

$$\mathrm{NO + NO \xrightarrow{k_1} N_2O_2} \tag{14.7.16}$$

Step 2 (Slow)

$$\mathrm{N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O} \tag{14.7.17}$$

Step 3 (Fast)

$$\mathrm{N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O} \tag{14.7.18}$$

The Rate Law is

$$Rate = k_2[N_2O_2][H_2] \tag{14.7.19}$$

But N_2O_2 is an intermediate!

To solve this problem we are going to assume that the products in the first step can form reactants and reach a psuedostate of equilibrium, that is, their rate of formation equals their rate of dissociation, which is also known as the steady state approximation. So eq14.6.15 can be rewritten as

$$\mathrm{NO} + \mathrm{NO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{N_2O_2} \tag{14.7.20}$$

where k_1 is the forward rate constant of the first step, and k_{-1} is the backward (reverse) rate constant of the first step. The steady state or psuedoequilbrium approximation says that since the second step is so slow, the forward and reverse rate of the first step become equal

$$Rate_{Forward} = Rate_{Backward}$$

$$k_1[NO]^2 = k_{-1}[N_2O_2] \tag{14.7.21}$$

Solving equation 14.6.20 for N_2O_2 gives:

$$[N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2 \tag{14.7.22}$$

Substituting N_2O_2 from equation 14.6.21 into equation 14.6.18 gives

$$Rate = \frac{k_1 k_2}{k_{-1}}[NO]^2[H_2]$$

$$= k_{obs}[NO]^2[H_2] \tag{14.7.23}$$

Note, since the third step was fast, it did not influence the observed rate constant. What the steady state approximation is saying is that the first step rapidly comes to a steady concentration, and we can treat the forward and backward reactions of the first step as if they are at equilibrium. In the next chapter we will look at the behavior of reactions at equilibrium.

In-Class Activity

Test Yourself

Homework: Section 14.6

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Liliane Poirot

This page titled 14.7: Reaction Mechanisms is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

CHAPTER OVERVIEW

15: Equilibria

Topic hierarchy

15.1: Chemical Equilibrium
15.2: Equilibrium Constant and Reaction Quotient
Clicker1
15.3: Determining an Equilibrium Constant
15.4: Using Equilibrium Constants in Calculations
15.5: Equilibrium Constants and Coupled Reactions
15.6: Disturbing a Chemical Equilibrium

This page titled 15: Equilibria is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

15.1: Chemical Equilibrium

Introduction

It was believed that all chemical reactions were irreversible until 1803, when French chemist Claude Louis Berthollet introduced the concept of reversible reactions. Initially he observed that sodium carbonate and calcium chloride react to yield calcium carbonate and sodium chloride; however, after observing sodium carbonate formation around the edges of salt lakes, he realized that large amount of salts in the evaporating water reacted with calcium carbonate to form sodium carbonate, indicating that the reverse reaction was occurring.

Chemical reactions are represented by chemical equations. These equations typically have a unidirectional arrow ($\rightarrow$) to represent irreversible reactions. Other chemical equations may have a bidirectional harpoons ($\rightleftharpoons$) that represent reversible reactions (not to be confused with the double headed arrows $\leftrightarrow$ used to indicate resonance of Lewis dot structures).

Before proceeding, we need to define some conventions for reversible reactions, as either reactants or products can be created.

$$Reactants \underset{k_{Backwards}}{\overset{k_{Forward}}{\rightleftharpoons}} Products \tag{15.1.1}$$

This means reactants are on the left side of the chemical equation and products are on the right, even if products react and produce reactants.

Irreversible Reactions

A fundamental concept of chemistry is that chemical reactions occurred when reactants reacted with each other to form products. These unidirectional reactions are known as irreversible reactions, reactions in which the reactants convert to products and where the products *cannot* convert back to the reactants. These reactions are essentially like baking. The ingredients, acting as the reactants, are mixed and baked together to form a cake, which acts as the product. This cake cannot be converted back to the reactants (the eggs, flour, etc.), just as the products in an irreversible reaction cannot convert back into the reactants.

An example of an irreversible reaction is combustion. Combustion involves burning an organic compound—such as a hydrocarbon—and oxygen to produce carbon dioxide and water. Because water and carbon dioxide are stable, they do not react with each other to form the reactants. Combustion reactions take the following form:

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O \tag{15.1.2}$$

Reversible Reactions

In reversible reactions, the reactants and products are never fully consumed; they are each constantly reacting and being produced. A reversible reaction can take the following summarized form:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D \tag{15.1.3}$$

This reversible reaction can be broken into two reactions.

Reaction 1:

$$A + B \overset{k_1}{\longrightarrow} C + D \tag{15.1.4}$$

Reaction 2:

$$C + D \overset{k_{-1}}{\longrightarrow} A + B \tag{15.1.5}$$

These two reactions are occurring ***simultaneously***, which means that the reactants are reacting to produce the products, as the products are reacting to produce the reactants.



Video15.1.1 1:47 min Youtube from University of Surrey. This youtube shows a dynamic equilibrium involing the evaporation and condensation of water in a closed system (https://youtu.be/JsoawKguU6A).

Kinetics and Equilibrium

Consider the simplest reversible reaction of the form

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \tag{15.1.6}$$

The Rates are

$$\underbrace{R_F = k_1[A]^m}_{\text{Forward Rate}} \text{ and } \underbrace{R_B = k_{-1}[B]^n}_{\text{Backward Rate}} \tag{15.1.7}$$

This system is described in figure 15.1.1, where initially (at t=0), [A] = $[A]_0$ and [B] = 0, and the rate of consumption of A production of B is the greatest (the curves are steepest at t=0).

As soon as B accumulates the rate of the back reaction increases (producing A and consuming B) and this occurs until equilibrium is achieved, when, the forward rate equals the backward rate (also called the reverse rate). At this point the slope of the line equals zero as each species is being produced and consumed at the same rate.

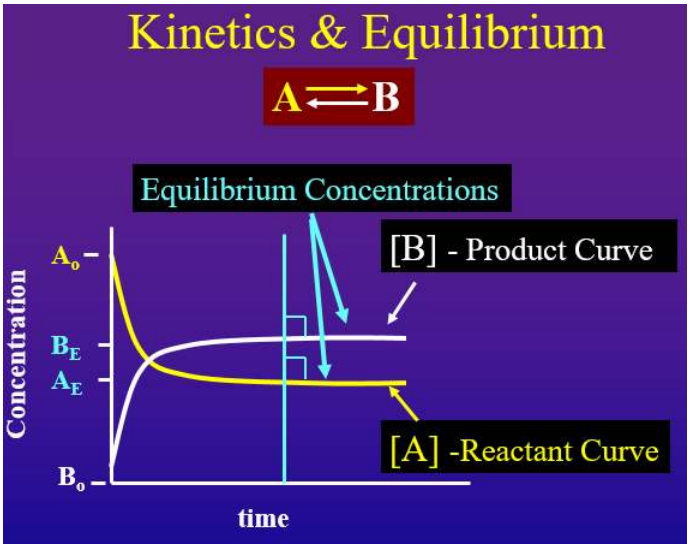


Figure15.1.1: graph showing relationship between kinetics and equilibrium.

At equilibrium, the backward rate equals the forward rate.

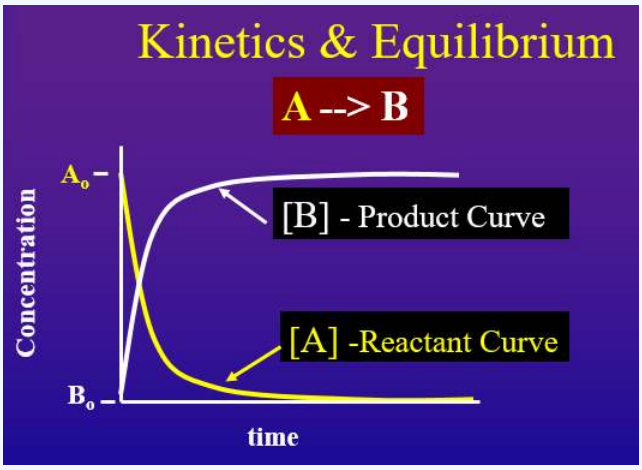
$$R_F = R_B$$

$$k_1[A]^m = k_{-1}[B]^n \tag{15.1.8}$$

Exercise 15.1.1

What would figure 15.1.1 look like if the reaction was irreversible?

Answer



All the reactant would disappear, and you could have 100% yield.

Chapter 14 described Kinetics and how fast a reaction proceeds. If a reaction is reversible, it will proceed until equilbrium is achieved, and at the point in time, the concentration of the reactants and products stays constant.

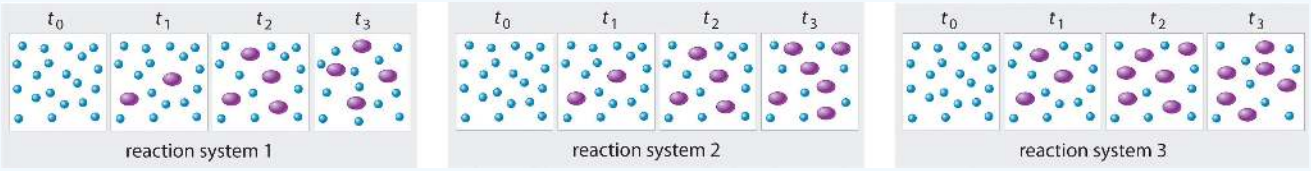
> *At equilibrium, the forward reaction rate is equal to the reverse reaction rate.*

Example 15.1.1

The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation:

$$2A \rightleftharpoons B \tag{15.1.9}$$

where the blue circles are A and the purple ovals are B. Each set of panels shows the changing composition of one of the three reaction mixtures as a function of time. Which system took the longest to reach chemical equilibrium?



Given: three reaction systems

Asked for: relative time to reach chemical equilibrium

Strategy:

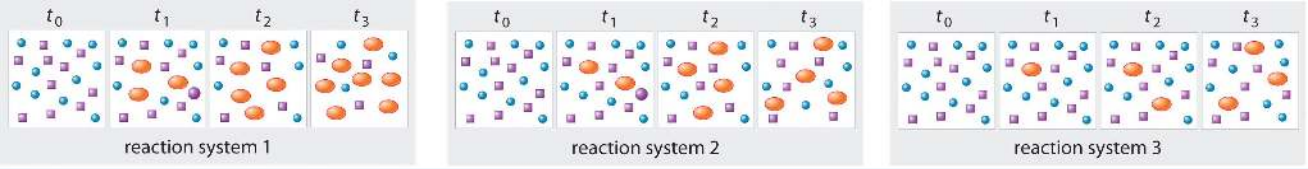
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

Solution:

In systems 1 and 3, the concentration of A decreases from t_0 through t_2 but is the same at both t_2 and t_3. Thus systems 1 and 3 are at equilibrium by t_3. In system 2, the concentrations of A and B are still changing between t_2 and t_3, so system 2 may not yet have reached equilibrium by t_3. Thus system 2 took the longest to reach chemical equilibrium.

Exercise 15.1.2

In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is A + B ⇌ C. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown hdo we know for a fact has reached equilibrium?



Answer

system 2

Test Yourself

Homework

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 15.1: Chemical Equilibrium is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

15.2: Equilibrium Constant and Reaction Quotient

Introduction

In this section we will mathematically describe the concentrations of products and reactants for a system that has reached equilibrium in terms of an Equilibrium constant. We use K (capital K) for the equilibrium constant and it is unitless, and we use small k for rate constants, and it has units.

$$aA + bB \rightleftharpoons cC + dD$$

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{15.2.1}$$

Where a, b, c & d are the stoichiometric coefficients of the chemical species A,B,C & D respectively.

NOTE: K is unitless and we use [A] to represent the concentration of "A", but this is really a simplification, and equilibrium constants are calculated using “effective concentrations,” or activities, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M. As shown in Equation 15.2.2, the units of concentration cancel, which makes K unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{[A]\ \cancel{M}}{[1]\ \cancel{M}} = [A]\frac{\frac{mol}{\cancel{L}}}{\frac{mol}{\cancel{L}}} = [A](unitless) \tag{15.2.2}$$

Equilbrium and Rate Constants

Capital K = Equilibrium constant and is unitless

Small k = Rate constant and has units

(which depend on overall order of reaction)

Equilibrium Constant and Kinetics

Consider the general equation

$$aA + bB \underset{k_r}{\overset{k_f}{\rightleftharpoons}} cC + dD$$

At equilibrium, the rate of the foward reaction equals the rate of the reverse (or back reaction).

$$Rate_{forward} = Rate_{reverse}$$

$$k_f[A]^m[B]^n = k_r[C]^p[D]^q \tag{15.2.3}$$

Rearranging

$$K = \frac{k_f}{k_r} = \frac{[C]^p[D]^q}{[A]^m[B]^n} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{15.2.4}$$

To understand why the stoichiometric coefficients are the exponents in the equilibrium constant while the rate law has experimentally determined orders of reaction, you need to take into account that the actual stoichiometric equation is the result of a series of coupled mechanistic equations, and for each elementary mechanistic step the order of reaction is the coefficient. This will be revisited later when equilibrium constants of coupled equations are covered, and right now this can be considered to be a consequence of the conservation of mass.

There is also a sleight of hand in Equation 15.2.4, in that small k's have units and capital K's do not, that is the rate is not really of the concentration, but the "effective concentration" or activity. In this class we will ignore this, and treat rate constants as having units, and equilibrium constants as not having units.

In-Class Activity

Magnitude of K

The magnitude of K tells you if you have a Products, Reactants or a mixture of products and reactants once a reaction is over and equilibrium is reached. The Rule of thumb is that products are favored for K>1000, reactants are favored if K<0.001 and a mixture if 0.001<K<1000.

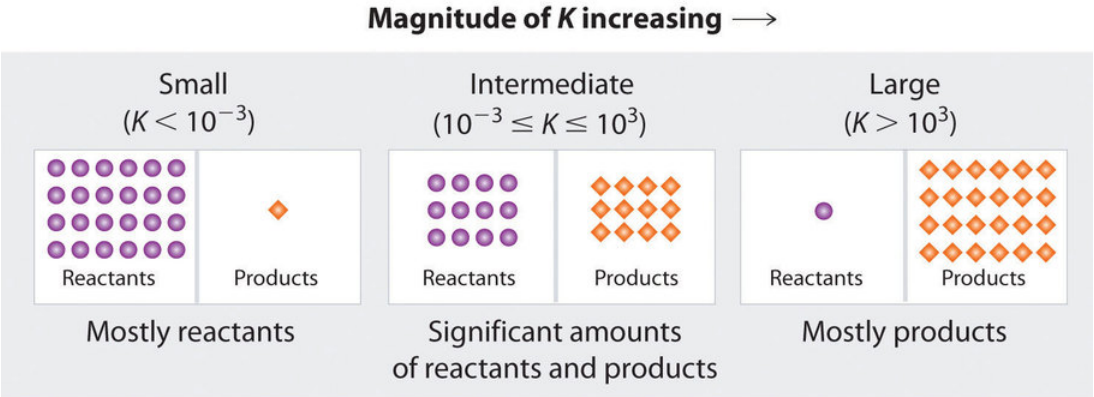


Figure15.2.1: Composition of equilibrium mixtures as a function of K

Table 15.2.1: Equilibrium Constants for Selected Reactions*

Reaction	Temperature (K)	Equilibrium Constant (K)
$S_{(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$	300	4.4×10^{53}
$2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O(g)$	500	2.4×10^{47}
$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$	300	1.6×10^{33}
$H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)}$	300	4.1×10^{18}
$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$	300	4.2×10^{13}
$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$	300	2.7×10^{8}
$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$	100	1.92
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	300	2.9×10^{-1}
$I_{2(g)} \rightleftharpoons 2I_{(g)}$	800	4.6×10^{-7}
$Br_{2(g)} \rightleftharpoons 2Br_{(g)}$	1000	4.0×10^{-7}
$Cl_{2(g)} \rightleftharpoons 2Cl_{(g)}$	1000	1.8×10^{-9}
$F_{2(g)} \rightleftharpoons 2F_{(g)}$	500	7.4×10^{-13}

*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.

Notice in Table 15.2.1 that equilibrium constants decrease going down the table from very large numbers 10^{53} to very small fractions, 10^{-13}. The reactions on the top essentially go to completion and are called "product favored reactions" because they favor the production of products at equilibrium, and the ones at the bottom are often called "reactant favored reactions", because as written, they favor reactants, and essentially do not make any products. Also note that the equilbrium constant is a function of temperature and thus the temperature is also given in the table.

Product Favored Reactions

K>>1: The reaction essentially goes to completion. These are essentially irreversible in the sense that reactants form products, but products do not form reactants.

Consider the simple reaction

$$aA \rightleftharpoons B \tag{15.2.5}$$

$$K = \frac{[B]^b}{[A]^a}$$

for K>>1
the numerator must be much greater than the denominator, so [B] > [A] at equilibrium.

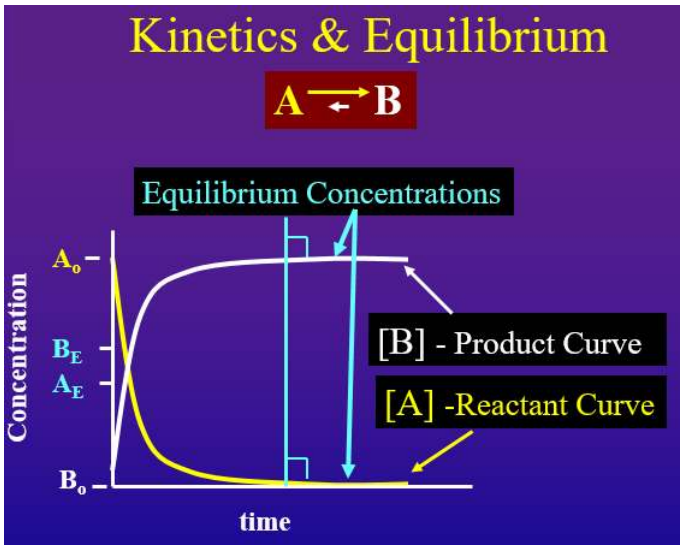


Figure15.2.2: *The flat part of this curve shows when equilibrium is reached and the reaction is over and essentially all of the reactant (A) has converted to product (B). The above curve has a 1:1 ratio, and so the final [B] is roughly equal to the initial [A].*

If the reaction in figure 15.2.2 was A $\rightarrow$ 2B, the final B concentration would approach double the original A concentration.

Combustion of a hydrocarbon to carbon dioxide and water is a product favored reaction, and once the reaction is over all of the reactant will be converted to carbon dioxide and water.

Reactant Favored Reactions

K<<1 (a very small fraction), essentially nothing happens. These are essentially irreversible in the sense that products would form reactants, and reactants do nothing.

Consider the simple reaction

$$aA \rightleftharpoons B \tag{15.2.6}$$

$$K = \frac{[B]^b}{[A]^a}$$

for K<<1
the numerator must be much smaller than the denominator,
so [B] < [A] at equilibrium.

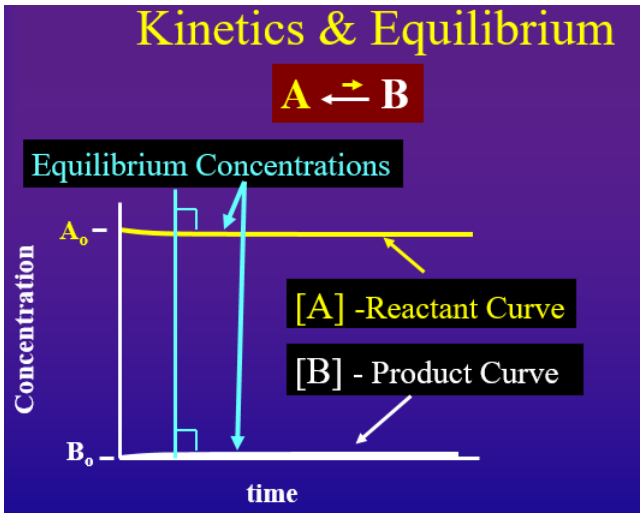


Figure15.2.3: Shows that for a reactant favored reaction, essentially nothing happens. In general chemistry 1 you learned that silver chloride is an insoluble salt, and very little would dissolve if you added it to water. This would be reflected by it having a very small equilibrium constant. In fact, K for silver chloride dissolving in water is 1.8×10^{-10}.

Reaction Mixtures

Reactions that result in a mixture of products and reactants have K around one, and as a rule of thumb we say if K is between and thousand and a thousandth, (1,000>K>1/1000), both reactants and products exist once the reaction is over.

Consider the gas phase formation of sulfur trioxide from sulfur dioxide and water which has a K near 1.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

In Figure15.2.4, you have two kinetics plots for the above reaction. In (a) you start with O_2 & SO_2 with no SO_3 and so the reaction must go in the forward direction and make SO_3, which it does until you reach equilibrium (realize the flat part of each reaction curve means the change in concentration of that species is zero, so it is not being consumed or produced). In (b) you start with SO_3 and no O_2 or SO_2 and so the back reaction must occur forming the "reactants" O_2 and SO_2.

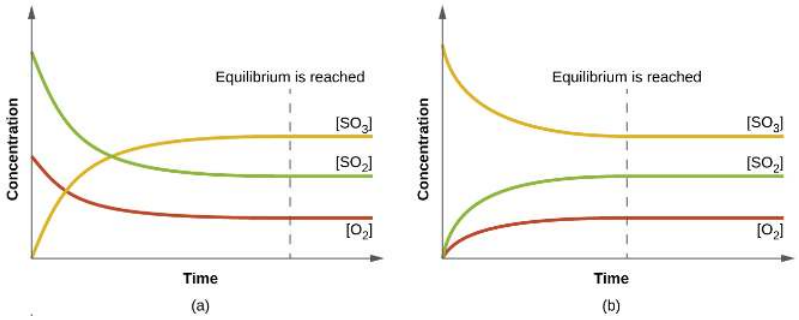


Figure15.2.4: Kinetics curves showing forward and back reactions for the following reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$, (a) is forward, (b) is backwards. Note in (b) that SO_2 and O_2 both start at zero concentration and that from the balanced equation, the rate of SO_2 production is twice that of O_2 and so at any point in time, the SO_2 concentration is twice thed O_2 concentration. Image used with permission (CC BY-3.0; OpenStax)

It should be noted that once equilibrium is reached, the equilibrium constant expression for the above two curves must equal, as expressed in Equation 15.2.7.

$$\left(\frac{[SO_3]^2}{[O_2][SO_2]^2}\right)_{(a)} = \left(\frac{[SO_3]^2}{[O_2][SO_2]^2}\right)_{(b)} \tag{15.2.7}$$

Note, the above graph may be misleading, the above concentrations for each species do not need to be equal, but their values as expressed in the equilibrium constant expressions (Equation 15.2.7) do need to be equal.

Write the equilibrium constant for each reaction.

- $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
- $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons CO_{2(g)}$
- $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 15.2.1. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

The only product is ammonia, which has a coefficient of 2. For the reactants, N_2 has a coefficient of 1 and H_2 has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[NH_3]^2}{[N_2][H_2]^3} \tag{15.2.8}$$

The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and O_2, with a coefficient of $\frac{1}{2}$. Thus the equilibrium constant expression is as follows:

$$\frac{[CO_2]}{[CO][O_2]^{1/2}} \tag{15.2.9}$$

This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for O_2. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2

$$\frac{[CO]^2[O_2]}{[CO_2]^2} \tag{15.2.10}$$

Exercise 15.2.1

Write the equilibrium constant expression for each reaction.

a. $N_2O_{(g)} \rightleftharpoons N_{2(g)} + \frac{1}{2}O_{2(g)}$
b. $2C_8H_{18(g)} + 25O_{2(g)} \rightleftharpoons 16CO_{2(g)} + 18H_2O_{(g)}$
c. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

Answer a

$$K = \frac{[N_2][O_2]^{1/2}}{[N_2O]}$$

Answer b

$$K = \frac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$$

Answer c

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

Example 15.2.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Given: systems and values of K

Asked for: composition of systems at equilibrium

Strategy:

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

a. Only system 4 has $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K \ll 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

Exercise 15.2.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{15.2.11}$$

Values of the equilibrium constant at various temperatures were reported as

- $K_{25^\circ C} = 3.3 \times 10^8$,
- $K_{177^\circ C} = 2.6 \times 10^3$, and
- $K_{327^\circ C} = 4.1$.

a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
b. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer a

327°C, where K is smallest

Answer b

25°C

K for Reverse Reactions

If you write a reaction backward K is the reciprocal

Forward Reaction

$$a[A] + b[B] \rightleftharpoons c[C] + d[D] \tag{15.2.12}$$

$$K_{forward} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Reaction written backwards

$$c[C]+d[D] \rightleftharpoons a[A]+b[B] \tag{15.2.13}$$

$$K_{backward} = \frac{[A]^a[B]^b}{[C]^c[D]^d}$$

Therefore

$$K_{forward} = \frac{1}{K_{backward}} \tag{15.2.14}$$

Heterogeneous Equilibria

Solid and pure liquids (not solutions) have constant densities and therefore their concentrations are constant and do not change as a reaction proceeds and thus they are not kept in the equilibrium constant. In the following reaction the iron and iron (II) oxide have constant densities, which don't change as they get consumed or produced, and thus they can be omitted in the equilibrium calculations. Note, they need to be present, but their concentrations are always the same.

$$Fe(s)+CO_2(g) \rightleftharpoons FeO(s)+CO(g) \tag{15.2.15}$$

$$K = \frac{[CO]}{[CO_2]}$$

Solubility of salts is a common heterogeneous equilibria and will be studied in depth in chapter 17.

Exercise 15.2.1

Write the equilibrium constant expression for the solubility of lead(II) iodide.

Answer

The reaction is

$$PbI_2(s) \rightleftharpoons Pb^{+2}(aq)+2I^-$$

$$K = [Pb^{+2}][I^-]^2]$$

Excess Reagents

If a chemical species involved in a reaction is in great excess compared to the other species, its concentration remains constant and so like solids and pure substances, its concentration does not effectively change. This typically happens when a reaction involves a solvent, such as in the case of aqueous acid base reactions involving the protonation or deprotonation of water.

$$HA(aq)+H_2O(l) \rightleftharpoons H_3O^+(aq)+A^-(aq) \tag{15.2.16}$$

At first glance this gives an equilibrium constant of

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \tag{15.2.17}$$

But lets look at a dilute solution at say pH = 2, where $[H_3O^+] = 10^{-pH} = 0.01M$ and $[H_2O] = 55.56M$

$$[H_2O] = \frac{1000g\ H_2O}{L}\left(\frac{molH_2O}{18g}\right) = 55.5\bar{5}M \tag{15.2.18}$$

and so the water concentration is of the order of 10,000 more concentrated the the acid, and its concentration essentially stays constant. This results in an acid dissociation constant where the water is absorbed into K_a (a constant divided by a constant is a constant) and we will cover this in great detail in chapter 16.

$$K_a = \frac{K}{[H_2O]} = \frac{[H_3O^+][A^-]}{[HA]} \tag{15.2.19}$$

So if one reagent is of orders magnitude greater than the others, as if often the case when a solvent is involved in a reaction, its concentration is effectively constant and you can remove it from the equilibrium constant

Gas Phase Equilibria

For the generic equation,

$$aA + bB \rightleftharpoons cC + dD \tag{15.2.20}$$

The equilibrium constant for a gas is K_p:

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} \tag{15.2.21}$$

This can be related to the concentration based equilibrium constant, K_c.

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{15.2.22}$$

By the relationship

$$K_p = K_c(RT)^{\Delta n} \tag{15.2.23}$$

where,

$$\Delta n = \sum \text{Product Stoichiometric Coef} - \sum \text{Reactant Stoichiometric Coef}$$

Note, Equation 15.2.23 can be derived from the Ideal gas equation of state

$$P_A V = n_A RT \tag{15.2.24}$$

$$\therefore$$

$$[A] = \frac{n_A}{V} = \frac{P_A}{RT}$$

In video 15.2.1, Equation 15.2.23 is derived by substituting Equation 15.2.24 into Equation 15.2.22



Video15.2.1 : 5.06 min YouTube showing derivation of eq. 15.2.15

Example 15.2.3: The Haber Process for making ammonia

The equilibrium constant for the reaction of nitrogen and hydrogen to give ammonia is 0.118 at 745 K. The balanced equilibrium equation is as follows:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{15.2.25}$$

What is K_p for this reaction at the same temperature?

Given: equilibrium equation, equilibrium constant, and temperature

Asked for: K_p

Strategy:

Use the coefficients in the balanced chemical equation to calculate Δn. Then use Equation ??? to calculate K from K_p.

Solution:

This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so $\Delta n = (2-4) = -2$. We know K, and $T = 745\ K$. Thus, from Equation ???, we have the following:

$$\begin{aligned} K_p &= K(RT)^{-2} \\ &= \frac{K}{(RT)^2} \\ &= \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745\ K]\}^2} \\ &= 3.16 \times 10^{-5} \end{aligned}$$

Because K_p is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

Exercise 15.2.3

Calculate K_p for the reaction

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

Answer

$K_p = 1.2 \times 10^3$

Note: A deeper dive

The above derivation works and is taught in most freshmen chemistry courses, but note, as derived, the K_p would have units of $(RT)^{\Delta n}$. Just as the concentration is really a relative concentration (activity), we need to realize the pressure terms are also relative, and a more formal approach would be to treat the pressure as

$$P_A^a = \left(\frac{P_A}{P^0}\right)^0, \text{where} P^a \text{is the standard pressure (1 bar=0.987 atm)} \tag{15.2.26}$$

Lets look at

$$aA \rightleftharpoons bB \tag{15.2.27}$$

now

$$K_P = \frac{\left(\frac{P_B}{P^0}\right)^b}{\left(\frac{P_A}{P^0}\right)^a}$$

which is unitless, noting for gas Z

$$P_Z = \frac{n_Z}{V}RT = [Z]RT(atm)$$

substituting for P_A *and* P_B *gives*

$$K_P = \frac{\left(\frac{[B]RT\ (atm)}{P^0(\ atm)}\right)^b}{\left(\frac{[A]RT\ (atm)}{P^0(\ atm)}\right)^a} \tag{15.2.28}$$

$$= \frac{[B]^b}{[A]^a}\left(\frac{(RT)^b}{(RT)^a}\right)\left(\frac{(P^0)^a}{(P^0)^b}\right)$$

noting $P^0 = 1$ atm, so last term of above eq. is 1

$$K_P = K_C(RT)^{b-a}, or$$
$$K_P = K_C(RT)^{\Delta n}\ where$$
$$\Delta n = b - a(\text{products minus reactants}) \tag{15.2.29}$$

Equation 15.2.15 of above derivation shows why the eq $K_p = K_c(RT)^{\Delta n}$ has no units, even though it looks like RT has units (they canceled out in step 15.2.15).

Note the following problem involves three phases

Exercise 15.2.1

Write the equilbrium constant expression for the following reaction

$$Mg(s) + 2HCl(aq) \rightleftharpoons MgCl_2(aq) + H_2(g) \tag{15.2.30}$$

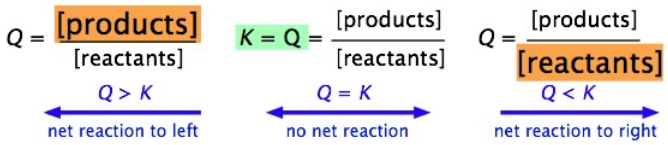
Answer

$$K = \frac{[MgCl_2][P_{H_2}]}{[HCl]^2} \tag{15.2.31}$$

Reaction Quotient

The reaction quotient (Q) describes the state of a system with respect to equilibrium, and tells you if a chemical reaction will proceed, and if so, in what direction. Mathematically, it is the equlibrium constant expression, but using the concentrations of any system, whether it is at equilibrium, or not. For a chemical reaction to occur, Q ≠ K. There are three possiblities.

- Q=K, No reaction, system is at equilbrium
- Q>K, Product loaded, reactants are produced until Q=K
- Q<K, Reactant loaded, products are produced until Q=K



Product Loaded Systems

For a product loaded system, Q>K.

What does this mean? It means the reaction will not proceed as written, in fact the opposite will happen, and you will make reactants.

The concept is simple, and you have "loaded" your system with products it will make reactants. That is, what you call reactants (the species on the left hand side of the equation) are not reactants, but products, and you make them.

Reactant Loaded Systems

For a reactant loaded system, Q<K.

What does this mean? It means the reaction will proceed as written, and reactants will form products.

Reaction Quotient Calculations



Catalysts

Catalysts do not change the value of the equilibrium constant, they speed up the rate at which a reaction reaches equilibrium. That is, they speed up both the forward and the reverse reactions. Lets go back to eq. 15.2.4, where k_{For} is the forward rate constant, and k_{Rev} is the reverse rate constant. General chemistry students need to know that catalysts do not effect the equilibrium constant, but they do not need to derive this equation.

$$K = \frac{k_{For}}{k_{Rev}} = \frac{Ae^{-\frac{E_{a,For}}{RT}}}{Ae^{-\frac{E_{a,Rev}}{RT}}} = e^{\frac{E_{a,Rev}-E_{a,For}}{RT}} \tag{15.2.32}$$

We know that catalysts change the rate constant by lowering the activation energy. Lets say D is the amount the activation energy is lowered, so the catalyzed activation energy, $E_{a\text{-}CAT} = E_a - D$, and:

$$E_{a-CAT,For} = E_{a,For} - D \;\; and \;\; E_{a-CAT,Rev} = E_{a,Rev} - D \tag{15.2.33}$$

substituting for K_{cat}:

$$K_{CAT} = e^{\frac{E_{a-CAT,Rev}-E_{a-CAT,For}}{RT}} = e^{\frac{E_{a,Rev}-D-(E_{a,For}-D)}{RT}} = e^{\frac{E_{a,Rev}-E_{a,For}}{RT}} = K \tag{15.2.34}$$

Worksheets:

- Equilibrium Constant Worksheet 1:
- Equilibrium Constant Worksheet 1 Key:

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

Test Yourself

Homework

This page titled 15.2: Equilibrium Constant and Reaction Quotient is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

Clicker1

Clicker1 is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

15.3: Determining an Equilibrium Constant

Overview

In general chemistry 1 we calculated % Yield based on the complete consumption of the limiting reagent. We know now that only product favored reactions with large equilibrium constants go to completion, and in this section we will learn how to calculate the equilibrium constant for a reaction that does not go to completion. In the next section we will show how we can use the equilibrium constant to calculate the equilibrium concentration of all species if we mix reactants, products, or a mixture of the two.

Extent of Reaction & RICE Diagram

To calculate the equilibrium constant we need to know what we started with, and the concentration of just one species at equilibrium. In section 14.1 we looked at **relative reaction rates** and saw that the rates of consumption and production of the various species were related to each other by the stoichiometric coefficients. If we had pure ammonia it must be **reactant loaded** (Q<K), and we know that for every two ammonia consumed, we would make one nitrogen and three hydrogen, and the reaction would proceed until Q=K. If we consider x to be the "extent of reaction", then the amount of ammonia consumed would be -2x, while the amount of nitrogen and hydrogen produced would be x and 3x respectively. So x, the extent of reaction is a measure of how far the system is from equilibrium, and if K was a large number, the reaction would proceed and create lots of products, but if K was a small fraction, very few products would be produced before Q=K and equilibrium is achieved.

$$2NH_3 \rightarrow N_2 + 3H_2 \tag{15.3.1}$$

On the other hand, if we had no ammonia and a mixture of nitrogen and hydrogen, then the system is "**product loaded**" (Q>K) and they would react to produce two ammonia for every three hydrogen and one nitrogen consumed, with the reaction proceeding until equilibrium is achieved (Q=K). If we had a mixture of all three species it could be either reactant loaded, product loaded, or at equilibrium. If it is not at equilibrium, a reaction occurs until equilibrium is achieved. Since this reaction can go in the forward or reverse direction, we need a convention, and we will always call the species on the left the reactant, and the species on the right the product, and if the reverse reaction occurs and we make reactants, the value of x, the extent of reaction, will be a negative number.

Generic RICE Diagram

For the generic reaction

$$aA + bB \rightleftharpoons cC + dD \tag{15.3.2}$$

the RICE diagram is:

Reactants	aA +	bB		cC	dD
Initial	$[A]_{Initial}$	$[B]_{Initial}$		$[C]_{Initial}$	$[D]_{Initial}$
Change	-ax	-bx		+cx	+dx
Equilibrium	$[A]_{Eq}$	$[B]_{Eq}$		$[C]_{Eq}$	$[D]_{Eq}$

noting that:

$$\begin{aligned} [A]_{Eq} &= [A]_{Initial} - ax \\ [B]_{Eq} &= [B]_{Initial} - bx \\ [C]_{Eq} &= [C]_{Initial} + cx \\ [D]_{Eq} &= [D]_{Initial} + dx \end{aligned} \tag{15.3.3}$$

So if we know both the initial and equlibrium concentrations of one species, we can calculate x from the above equation for that species, and then use that value of x to calculate the equilibrium concentration of the other species

Once we know the equilibrium concentration of all species, we can calculate K.

$$K = \frac{[C]_{eq}^{c}[D]_{eq}^{d}}{[A]_{eq}^{a}[B]_{eq}^{b}} \tag{15.3.4}$$

Solved Problem

Calculate the equilibrium constant for the following equation if 0.063 mol NO(g) is produced after 0.100 mol of NO, 0.050 mol of H_2 and 0.100 mol H_2O(g) are mixed in a 1 L container.

$$2NO(g) + 2H_2 \rightleftharpoons N_2 + 2H_2O \tag{15.3.5}$$

Before proceeding to watch the video, think about what you have been given. First, you know the balanced equation and have the initial concentration of all species and the equilibrium concentration of one. This means you have the data you need. Second, you note there is initially no nitrogen, and so the reaction must move in the forward direction and x is positive. Note, if you wrote the reaction backwards, so the Nitrogen was a reactant, then the back reaction would have occurred and x would be negative.



In-Class Activity

This page titled 15.3: Determining an Equilibrium Constant is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

15.4: Using Equilibrium Constants in Calculations

This page is under construction

Overview

In the last section we used the initial concentrations and the equilibrium concentration of one species to calculate the equilibrium constant. In this section we use the equilibrium constant to calculate the equilibrium concentration of all species. If K is a very large number, we have a product favored reaction and we do not need to do an equilibrium calculation, we simply base the theoretical yield on the complete consumption of the limiting reagent. But if K is a small number, or if you mixed "products" instead of "reactants", the reaction may not go to completion in the general Chemistry 1 sense, and you need to do an equilibrium calulation to calculate the final reactant and product.

- If the reaction proceeds as written (forming products and consuming reactants) the extent of reaction (x) is positive.
- If the reverse reaction procees (forming reactants and consuming products) the extent of reaction (x) is negative.

The overall strategy for these problems is to set up an RICE diagram and solve for x, the extent of reaction. Once you know x, you can calculate the equilibrium (final) concentration of each chemical species. This process is similiar to that in the last section (15-3), but you are now using the equilibrium constant expression to solve for the extent of reaction and not K, and then you use that value to calculate the equilbrium concentration of each species.

Generic RICE Diagram

For the generic reaction

$$aA + bB \rightleftharpoons cC + dD \tag{15.4.1}$$

the RICE diagram is:

Reactants	aA +	bB	⇌	cC	dD
Initial	$[A]_{Initial}$	$[B]_{Initial}$		$[C]_{Initial}$	$[D]_{Initial}$
Change	-ax	-bx		+cx	+dx
Equilibrium	$[A]_{Eq}$	$[B]_{Eq}$		$[C]_{Eq}$	$[D]_{Eq}$

noting that:

$$\begin{aligned} [A]_{Eq} &= [A]_{Initial} - ax \\ [B]_{Eq} &= [B]_{Initial} - bx \\ [C]_{Eq} &= [C]_{Initial} + cx \\ [D]_{Eq} &= [D]_{Initial} + dx \end{aligned} \tag{15.4.2}$$

We know the equilbrium constant is:

$$K = \frac{[C]_{eq}^{c}[D]_{eq}^{d}}{[A]_{eq}^{a}[B]_{eq}^{b}} \tag{15.4.3}$$

substituting the above relationship into eq. 15.4.2 gives us a single equation with just one unknown, x, which means we can algebraically solve for x.

$$K = \frac{([C]_{Initial} + cx)^{c}([D]_{Initial} + dx)^{d}}{([A]_{Initial} - ax)^{a}([B]_{Initial} - bx)^{b}} \tag{15.4.4}$$

Solving Equilibrium Problems

Lets take a closer look at eq 15.4.4 and solve for x, first we realize this is a polynomial equation where the degree (maximum power of x) is determined by the sum of the stoichiometric coefficients of either the numerator (products) or denominator

(reactants), depending on which is larger.

$$a_n x^n + \ldots + a_2 x^2 + a_1 x + a_0 \tag{15.4.5}$$

This will make sense as you work through the problems, but the bottom line is these can become very complicated to solve and in this class we are going to look at several simple cases that are easy to solve.

Quadratic Polynomials

Quadratic equations are polynomial equations of degree 2.

$$ax^2 + bx + c = 0 \tag{15.4.6}$$

These occur for the following types of reactions (note, the highest sum of stoichiometric coefficients on either the reactant or product side is 2, and so the polynomial is quadratic)

$$\begin{aligned} A + B &\rightleftharpoons C + D \\ A + B &\rightleftharpoons C \\ 2A &\rightleftharpoons C + D \\ A &\rightleftharpoons C + D \end{aligned} \tag{15.4.7}$$

There will be two approaches we can use, the quadratic formula, and complete the square.

Quadratic Formula

From algebra there are two roots to the quadratic equation, $ax^2 + bx + c = 0$ that can be determined from the quadratic formula.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{15.4.8}$$

These two roots occur because there are two solutions to a square root. One of the answers will make no sense, typically giving a negative concentration for one species, meaning you consumed more of it than you have, which is impossible.

Note, if your reaction is product loaded, that is, you start with more products than you would have at equilibrium, the correct solution would be the one that has a negative x, if you set up the RICE diagram so that reactants are consumed and products are produced, that is, you are consuming the things on the right side of the equation, not producing them.

Consider the following problem: Calculate the equilibrium concentration of all species if 1 mol of $COCl_2$ is placed in a 10 L container and undergoes the following reaction.

Problem 15.4.1:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2 \tag{15.4.9}$$

In the following video this problem is solved, and it was noted that the $COCl_2$ must be a reactant and so the equation was written backwards and the reciprocal of K was used.



Video 15.4.1: Solution for Problem15.4.1, with the equation rewritten so the $COCl_2$ is a reactant. Note how the extent of reaction (x) is a positive number.

After watching the above video, you should try and solve it as written in equation 15-4.9, that is, while treating $COCl_2$ as a product, even though it is obviously a reactant. In this case, the solution that makes sense will have a negative value for x, the extent of reaction. This has been done with the following



Video 15.4.2: Solution for Problem15.4.1, with the equation written with the $COCl_2$ as product, even though it is obviously a reactant. Note how the extent of reaction (x) is a negative number

In the above two videos we knew the $COCl_2$ was a product because there was no CO or Cl_2 and therefor they could not be reactants, and thus the system had to be product loaded (as written n eq. 15-4.9). As K = 26.7 we know that at equilibrium there can be substantial amounts of both products and reactants coexisting at equilibrium, and if we had mixed similar quantities of all three species we would not have known ahead of time if the reaction would go to the right (reactant loaded - forming products), or to the left (product loaded - forming reactants). So in solving these problems you need to be prepared to check both roots of the square root term in the quadratic formula. Since your calculator gives the positive root, it is probably best to use that one first, and then if the answer makes no sense, go back and recalculate, using the other root.

Complete the Square

If two reactants create two products, and the species mixed are in stoichiometric proportions, you can simplify the problem where the equilibrium constant equals a single expression to the power of two.

$$K = (expression\ of\ x)^2 \tag{15.4.10}$$

This is a much easier mathematical problem to solve than the quadratic equation, as you simply take the square of both sides and then algebraically solve for x. The technique works if you start with just reactants, or just products, or a mixture of the two, as long as they are in stoichiometric proportions.

Consider the following reaction

$$H_2(g) + Br_2(g) \leftrightharpoons 2HBr(g) \tag{15.4.11}$$

There are three types of problems we can use complete the square and avoid using the quadratic formula

1. Mix equal amounts of bromine and hydrogen
2. Mix any amount of hydrogen bromide gas
3. Mix equal amounts of bromine and hydrogen, along with any amount of hydrogen bromide gas.

(Note: from general chemistry1, HBr(aq) is hydrobromic acid, but HBr(g) is hydrogen bromide (gas).

Problem 15.4.1: Calculate the equilibrium concentration of all species if the initial concentrations of hydrogen and bromide react 0.6 M and that of HBr is 1.25M and K = 50 for the reaction as written in equation 15-4.10.

$$K = \frac{[HBr]_{eq}^2}{[H_2]_{eq}[Br_2]_{eq}} = \frac{([HBr]_{Initial} + 2x)^2}{([H_2]_{Initial} - x)([Br_2]_{Initial} - x)} \tag{15.4.12}$$

since $H_2 = Br_2$, everything in the right becomes a single expression, as can be seen by substituting in actual values.

$$K = \frac{\left([1.25]_{Initial} + 2x\right)^2}{\left([0.6]_{Initial} - x\right)^2} = \left(\frac{\left([1.25]_{Initial} + 2x\right)}{\left([0.6]_{Initial} - x\right)}\right)^2 \tag{15.4.13}$$

Now you simply take the square root of both sides:\

$$\sqrt{K} = \frac{[1.25]_{Initial} + 2x}{[0.6]_{Initial} - x} \tag{15.4.14}$$

Video 15-4.3 shows how to solve this problem



Video 15.4.3: Solution to a complete the square problem15.4.1:

Complete the Cube (or higher degree polynomials)

If n reactants create n products, and the species mixed are in stoichiometric proportions, you can simplify the problem where the equilibrium constant equals a single expression to the power of n.

$$K = (expression\ of\ x)^n \tag{15.4.15}$$

Lets consider a problem where three reactants form three products and they were mixed in stoichiometric proportions. This results in a cubic equation, and we will solve by completing the cube.s.

Consider the following reaction

$$Cl_2(g) + 2HBr(g) \leftrightharpoons Br_2(g) + 2HCl(g) \tag{15.4.16}$$

Problem 15.4.2: Calculate the equilibrium concentration of all species if the initial concentrations of chlorine if 2.00 moles of chlorine and 4.00 moles of hydrogen bromide are added to a 10.0 liter container and K = 15.

Since we start with no products we know this is a reactant loaded system and will proceed to the right, meaning the extent of reaction will be a positive number. We also know that since K = 15, which is greater than 0.001 and less than 1,000, that there will be substantial amounts of reactants and products coexisitng at equlibrium, and so we have an equilibrium problem. That is for example, if K = 10^{15} we could treat this as a general chemistry 1 problem and say the amount of product produced is based on the complete consumption of the limiting reagent, and if K = 10^{15} we could say that no reaction occurs.

$$K = \frac{[Br_2]\,[HCl]_{eq}^2}{[Cl_2]_{eq}[HBr]_{eq}^2} = \frac{\left([Br_2] + x\right)\left([HCl]_{Initial} + 2x\right)^2}{\left([Cl_2]_{Initial} - x\right)\left([HBr]_{Initial} - 2x\right)^2} \tag{15.4.17}$$

substituting the initial concentrations:

$$K = \frac{\left([0] + x\right)\left([0] + 2x\right)^2}{\left([0.200] - x\right)\left([0.400] - 2x\right)^2} = \frac{(x)\,(2x)^2}{\left([0.200] - x\right)\left([0.400] - 2x\right)^2} \tag{15.4.18}$$

Bringing the right hand side to a common power

$$K = \frac{x^3}{([0.200] - x)^3} = \left(\frac{x}{0.200 - x}\right)^3 \tag{15.4.19}$$

Now you simply take the cube root of both sides, and then solve for x:

$$\sqrt[3]{K} = \frac{x}{0.200 - x} \tag{15.4.20}$$

Please watch the following YouTube if you need help solving this problem



Video 15.4.4

,@api,deki,files,126256,UALR_Worksheet_15-4.pdf ,@api,deki,files,126257,UALR_Worksheet_15-4KEY.pdf

Method of Successive Approximations

Lets look at the RICE diagram again for the generic reaction

$$aA + bB \leftrightharpoons cC + dD \tag{15.4.21}$$

Table 15.4.2: Generic RICE Diagram

Reactants	aA +	bB	⇌	cC	dD
Initial	$[A]_{Initial}$	$[B]_{Initial}$		$[C]_{Initial}$	$[D]_{Initial}$
Change	-ax	-bx		+cx	+dx
Equilibrium	$[A]_{Eq}$	$[B]_{Eq}$		$[C]_{Eq}$	$[D]_{Eq}$

noting that:

$$\begin{aligned} [A]_{Eq} &= [A]_{Initial} - ax \\ [B]_{Eq} &= [B]_{Initial} - bx \\ [C]_{Eq} &= [C]_{Initial} + cx \\ [D]_{Eq} &= [D]_{Initial} + dx \end{aligned} \tag{15.4.22}$$

where,

x=extent of reaction

and

$$K = \frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b} = \frac{([C]_i - cx)^c ([D]_i - dx)^d}{([A]_i - ax)^a ([B]_i - bx)^b} \tag{15.4.23}$$

In the method of successive approximations you make an intelligent estimate of what x would be, plug it into the above equation and calculate the value.

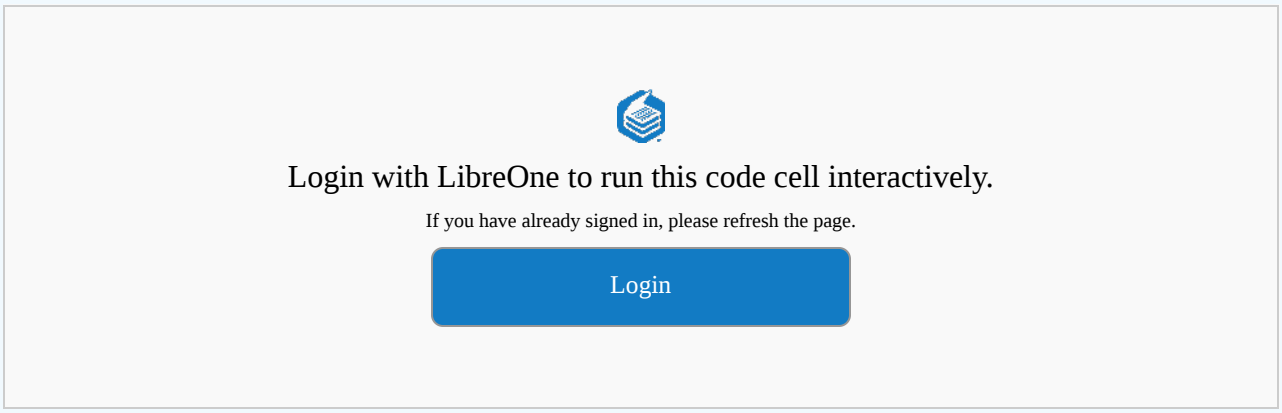
Python Script 15.4.1

The following python script was developed by Elena Lisitsyna and Bob Belford and can be activated by clicking which allows you to input the chemical identities, stoichiometric coefficients, initial concentrations and an equilibrium constant for the above equation. You can then iteratively input different extent of reactions until the value of x gives the equilibrium constant you want. Once you are happy with the K based on your extent of reaction you can input what you think are the equilibrium concentrations and the program will compare those values to the values based on the K you choose to use.

If there is only one reactant or product you can name the second nothing, give it a concentration of 1 and a coefficient of zero. Any comments can be sent to Bob Belford, rebelford@ualr.edu

Python Program - (click here)

To start the program click "Run" and it may take a little time to load the kernal the first time, but once loaded it is fast.




```
#Start
import math

def checkStr(a):
    while a.isnumeric() == True:
        a = input("Please type the full name or formula. Input the name: ")
    return a

def checkInt(a):
    try:
        val = int(a)
    except ValueError:
        a = input("Has to be a positive number. Please input a different value:
    return int(a)

def checkFloat(a):
    try:
        val = float(a)
    except ValueError:
        a = input("Has to be a positive number. Please input a different value:
    return float(a)
```

```
def getReaction():
#Get coefficients and names
    global reactName1, reactName2, prodName1, prodName2, reactCoef1, reactCoef2,

    a = input("Input the name of reactant # 1: ")
    reactName1 = checkStr(a)

    a = input("Input the coefficient of {}: ".format(reactName1))
    reactCoef1 = checkInt(a)

    a = input("Input the name of reactant # 2: ")
    reactName2 = checkStr(a)

    a = input("Input the coefficient of {}: ".format(reactName2))
    reactCoef2 = checkInt(a)

    a = input("Input the name of product # 1: ")
    prodName1 = checkStr(a)

    a = input("Input the coefficient of {}: ".format(prodName1))
    prodCoef1 = checkInt(a)

    a = input("Input the name of product # 2: ")
    prodName2 = checkStr(a)

    a = input("Input the coefficient of {}: ".format(prodName2))
    prodCoef2 = checkInt(a)

    #Output the reaction
    print(" ")
    print ("Check the reaction:")
    print(reactCoef1, reactName1, "+", reactCoef2, reactName2, "\u21CC", prodCoe

    print(" ")
    print("Type 1 to continue to the next step")
    print("Type 2 to input the values again")
    while True:
        proceed = input ("Type '1' or '2': ")
        if proceed == "1":
            print (" ")
            getConc()
            break
        elif proceed == "2":
            print (" ")
            getReaction()
            break
```

```
        else:
            print (" ")
            print ("'1' and '2' are the only acceptable inputs for this step.")

def getConc():
#get concentrations of all reactants and products
    global reactConc1, reactConc2, prodConc1, prodConc2

    a = (input("Input the initial concentration of {} in units of M: ".format(re
    reactConc1 = checkFloat(a)

    a = (input("Input the initial concentration of {} in units of M: ".format(re
    reactConc2 = checkFloat(a)

    a = (input("Input the initial concentration of {} in units of M: ".format(pr
    prodConc1 = checkFloat(a)

    a = (input("Input the initial concentration of {} in units of M: ".format(pr
    prodConc2 = checkFloat(a)

    #check for no reaction
    if reactConc1*reactConc2 == 0 and prodConc1*prodConc2 == 0:
        print ("No reaction. Try again.")
        getConc()

def getK():
    global guessX, concGuessR1, concGuessR2, concGuessP1, concGuessP2

    a = float (input("Input your estimated extent of reaction: "))
    guessX = checkFloat(a)
    concGuessR1 = float(reactConc1 - (reactCoef1*guessX))
    concGuessR2 = float(reactConc2 - (reactCoef2*guessX))
    concGuessP1 = float(prodConc1 + (prodCoef1*guessX))
    concGuessP2 = float(prodConc2 + (prodCoef2*guessX))
    #check for division by 0
    if concGuessR1 != 0 and concGuessR2!=0:
        calcK = float(((concGuessP1**prodCoef1)*(concGuessP2**prodCoef2))/((conc
    else:
        print (" ")
        print ("Unable to calculate K (division by 0). Try again.")
        getK()
    #check if calculated K is a negative number
    if calcK<0:
        print ("Your estimated extent of reaction requires you to consume more o
        print ("Please try again.")
        getK()
    else:
```

```
    #compare K
        print ("K_real = ", realK)
        print ("K_calculated = ", calcK)
        compareK = (math.log10(calcK))-(math.log10(realK))
        #print (compareK)
        if compareK < 0:
            compareK = int(compareK*(-1)) #remove negative sign, round to the ne
            #print (compareK)
            print ("Your calculated K is apriximatelly {} orders of magnitude sm
        elif compareK > 0:
            compareK = int(compareK)
            print ("Your calculated K is apriximatelly {} orders of magnitude la
        else:
            print ("Good job! Your calculated K is equal to K_real")

        print (" ")
        print ("Type 1 to input the estimated extent of reaction again")
        print ("Type 2 to continue to the next step")
        while True:
            proceed = input ("Type '1' or '2': ")
            if proceed == "1":
                print (" ")
                getK()
                break
            elif proceed == "2":
                print (" ")
                print ("--- STEP 3 ---")
                print ("Your estimated extent of reaction is {}".format(guessX))
                print ("Your value of K is {}".format(calcK))
                print ("Calculate equlibrium concentrations of all reactants and
                getEqConc()
                break

            else:
                print (" ")
                print ("'1' and '2' are the only acceptable inputs for this step

def getEqConc():
    #asking for eq.conc calculated by student
    reactEqConc1 = input ("Input the equilibrium concentration of {} in units of
    reactEqConc2 = input ("Input the equilibrium concentration of {} in units of
    prodEqConc1 = input ("Input the equilibrium concentration of {} in units of
    prodEqConc2 = input ("Input the equilibrium concentration of {} in units of
    #printing student calculated values and python calculated values
    print (" ")
    print ("Your value of the equilibrium concentration of {} is {}M".format(rea
    print ("Based on your calculated K, the equilibrium concentration of {} shou
```

```
    print (" ")
    print ("Your value of the equilibrium concentration of {} is {}M".format(rea
    print ("Based on your calculated K, the equilibrium concentration of {} shou
    print (" ")
    print ("Your value of the equilibrium concentration of {} is {}M".format(pro
    print ("Based on your calculated K, the equilibrium concentration of {} shou
    print (" ")
    print ("Your value of the equilibrium concentration of {} is {}M".format(pro
    print ("Based on your calculated K, the equilibrium concentration of {} shou

print ("--- STEP 1 ---")
getReaction()

print (" ")
print ("--- STEP 2 ---")
realK = float (input("Input K_real: "))
getK()
print (" ")
print ("Click 'restart & run all' to start over")

#End
```

```
Hello world!
```

In-Class Activity

Test Yourself

Homework

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 15.4: Using Equilibrium Constants in Calculations is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

15.5: Equilibrium Constants and Coupled Reactions

Coupled Equations

Chemists frequently need to know the equilibrium constant for a reaction that has not been previously studied. In section 5.7: Hess's Law, we learned that **for coupled reactions enthalpies are additive**. In this section we shall see that **for coupled reactions equilibrium constants are multiplicative**. Thus just as we could calculate the enthalpy of reaction for a reaction we had not studied, we can also calculate the equilibrium constant, if we know the equilibrium constants of the coupled reactions that add up to the desired reaction.

Multi-step Equilibrium Rules

1. The equilibrium constant for a reaction written backwards is the reciprocal of the constant for the reaction written in the forward direction

$$aA \rightleftharpoons bB \quad K_{forward} = \frac{[B]^b}{[A]^a}$$

$$bB \rightleftharpoons aA \quad K_{backwards} = \frac{[A]^a}{[B]^b} = \frac{1}{K_{forward}} \tag{15.5.1}$$

2. The equilibrium constant of two or more coupled reactions is the product of the equilibrium constant for each coupled step.

$$aA \rightleftharpoons bB \quad K_1 = \frac{[B]^b}{[A]^a}$$

$$bB \rightleftharpoons cC \quad K_2 = \frac{[C]^c}{[B]^b} \tag{15.5.2}$$

$$\tag{15.5.3}$$

the sum of reaction 1 and 2 is

$$aA \rightleftharpoons cC \quad K_3 = \frac{[C]^c}{[A]^a} \tag{15.5.4}$$

and $K_3 = K_1 K_2$ where the intermediate B cancels out.

$$K_1 K_2 = \frac{\cancel{[B]^b}}{[A]^a} \frac{[C]^c}{\cancel{[B]^b}} = \frac{[C]^c}{[A]^a} = K_3$$

To illustrate this procedure, let's consider the reaction of N_2 with O_2 to give NO_2. This reaction is an important source of the NO_2 that gives urban smog its typical brown color. The reaction normally occurs in two distinct steps with NO (in red to identify it) being the intermediate that allows the two reactions to be added to a third reaction. In the first reaction (step 1), N_2 reacts with O_2 at the high temperatures inside an internal combustion engine to give NO. The released NO then reacts with additional O_2 to give NO_2 (step 2). The equilibrium constant for each reaction at 100°C is also given.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \qquad K_1 = 2.0 \times 10^{-25} \qquad \text{(step 1)}$$

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \quad K_2 = 6.4 \times 10^{9} \qquad \text{(step 2)}$$

Summing reactions (step 1) and (step 2) gives the overall reaction of N_2 with O_2:

$$N_{2(g)} + 2O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_3 = ? \qquad \text{(overall reaction 3)}$$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2} \tag{15.5.5}$$

What is the relationship between K_1, K_2, and K_3, all at 100°C? The expression for K_1 has $[NO]^2$ in the numerator, the expression for K_2 has $[NO]^2$ in the denominator, and $[NO]^2$ does not appear in the expression for K_3. Multiplying K_1 by K_2 and canceling the $[NO]^2$ terms,

$$K_1K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3 \tag{15.5.6}$$

Thus the product of the equilibrium constant expressions for K_1 and K_2 is the same as the equilibrium constant expression for K_3:

$$K_3 = K_1K_2 = (2.0 \times 10^{-25})(6.4 \times 10^{9}) = 1.3 \times 10^{-15} \tag{15.5.7}$$

The equilibrium constant for a reaction that is the sum of two or more reactions is equal to the product of the equilibrium constants for the individual reactions. In contrast, recall that according to Hess's Law, ΔH for the sum of two or more reactions is the sum of the ΔH values for the individual reactions.

YouTube Demonstration



Video\PageIndex{1}\: 4.47 min YouTube showing how to calculate K for an unknown equation if it is known for coupled equations that can be added to form the unknown equation.

Examples

Example 15.5.1

The following reactions occur at 1200°C:

1. $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \qquad K_1 = 9.17 \times 10^{-2}$
2. $CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)} \qquad K_2 = 3.3 \times 10^{4}$

Calculate the equilibrium constant for the following reaction at the same temperature.

3. $CO_{(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \qquad K_3 = ?$

Given: two balanced equilibrium equations, values of K, and an equilibrium equation for the overall reaction

Asked for: equilibrium constant for the overall reaction

Strategy:

Arrange the equations so that their sum produces the overall equation. If an equation had to be reversed, invert the value of K for that equation. Calculate K for the overall equation by multiplying the equilibrium constants for the individual equations.

Solution:

The key to solving this problem is to recognize that reaction 3 is the sum of reactions 1 and 2:

$$CO_{(g)} + \cancel{3H_{2(g)}} \rightleftharpoons \cancel{CH_{4(g)}} + H_2O_{(g)} \tag{15.5.8}$$

$$\cancel{CH_{4(g)}} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + \cancel{3H_{2(g)}} + H_{2(g)} \tag{15.5.9}$$

$$CO_{(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \tag{15.5.10}$$

The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:

$$K_3 = K_1K_2 = (9.17 \times 10^{-2})(3.3 \times 10^4) = 3.03 \times 10^3 \tag{15.5.11}$$

Exercise 15.5.1

In the first of two steps in the industrial synthesis of sulfuric acid, elemental sulfur reacts with oxygen to produce sulfur dioxide. In the second step, sulfur dioxide reacts with additional oxygen to form sulfur trioxide. The reaction for each step is shown, as is the value of the corresponding equilibrium constant at 25°C. Calculate the equilibrium constant for the overall reaction at this same temperature.

1. $\frac{1}{8}S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)} \qquad K_1 = 4.4 \times 10^{53}$
2. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_2 = 2.6 \times 10^{12}$
3. $\frac{1}{8}S_{8(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_3 = ?$

Answer

$K_3 = 1.1 \times 10^{66}$

In-Class Activity

Deep Dive

We are now in a position to understand why the equilibrium constant can be determined can be determined from the stoichiometric coefficients, while the order of reaction had to be determined experimentally. This is because a real reaction occurs through a mechanism of one or more coupled elementary steps where the order of reaction is the stoichiometric coefficient of the actual mechanistic (elementary) step, and the values of the intermediates cancel out as the successive equilibrium constants cancel out.

Lets review section 14.2.2, Multistep Reactions, for the following reaction:

$$H_2(g) + 2ICl(g) \rightarrow I_2(g) + 2HClg \tag{15.5.12}$$

we postulated **two elementary steps**, where **HI** is the intermediate.

$$H_2 + ICl \rightarrow HCl + HI \tag{15.5.13}$$
$$HI + ICl \rightarrow HCl + I_2 \tag{15.5.14}$$

Now from section 15.1.4: Kinetics and Equilibrium, we saw that at equilibria the rate forward = the rate backward,

$$aA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} bB \tag{15.5.15}$$

The Rates are

$$\underbrace{R_F = k_1[A]^m}_{\text{Forward Rate for mechanistic step}} \quad \text{and} \quad \underbrace{R_B = k_{-1}[B]^b}_{\text{Backward Rate for mechanistic step}} \tag{15.5.16}$$

but if these are mechanistic steps, the orders of reaction are the stoichiometric coefficients

$$\underbrace{R_F = k_1[A]^a}_{\text{Forward Rate for mechanistic step}} \quad \text{and} \quad \underbrace{R_B = k_{-1}[B]^b}_{\text{Backward Rate for mechanistic step}} \tag{15.5.17}$$

If we now look at eq. 15.2.4 from the perspective of a mechanistic step we see that

$$K = \frac{k_f}{k_r} = \frac{[B]^b}{[A]^a} \tag{15.5.18}$$

So:.

$$H_2 + ICl \rightleftharpoons HCl + HI \quad K_1 = \frac{[HCl][HI]}{[H_2][ICl]} \tag{eq.15.5.9(above))}$$

$$HI + ICl \rightleftharpoons HCl + I_2 \quad K_2 = \frac{[HCl][I_2]}{[HI][ICl]} \tag{eq.15.5.10(above))}$$

Summing the above two equations gives equation 15.5.8

$$H_2 + 2ICl \rightleftharpoons I_2 + 2HCl \quad K_3 = \frac{[I_2][HCl]^2}{[H_2][ICl]^2} \tag{eq.15.5.8(above))}$$

$$K_3 = K_1 K_2 = \left(\frac{[HCl][HI]}{[H_2][ICl]}\right)\left(\frac{[HCl][I_2]}{[HI][ICl]}\right) = \frac{[I_2][HCl]^2}{[H_2][ICl]^2} \tag{15.5.19}$$

In summary: You can use the stoichiometric coefficients in calculating the powers in equilibrium constants because real reactions have a mechanism involving one or more coupled elementary steps, and the order of reaction is based on the stoichiometric coefficient of the elementary step. Intermediates cancel out because they are formed in an early step (where they are on the numerator of the rate constant) and are then consumed in a subsequent step (where they appear in the denominator), and thus the equilibrium constant is the product concentrations to the power of their coefficients, divided by the reactant concentrations to the power of their coefficients.

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 15.5: Equilibrium Constants and Coupled Reactions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

15.6: Disturbing a Chemical Equilibrium

Introduction

Hopefully you have come to realize that if you mix reactants a reaction will occur until a state of dynamic equilibria is achieved, at which time the rate of forward reaction equals that of the reverse reaction, and so you see no observable change in the concentration of chemical species, that is, no further reaction occurs. We have used the concept of the reaction quotient to describe how your initial mixture relates to equilibrium. That is, if Q<K, products are formed (until Q=K), if Q>K, reactants are formed until Q=K, and of course, if Q=K, no reaction occurs. In this section we will look at systems at equilibrium, and see how they respond if they are perturbed from this equilibrium state. That is, Le Chatlier's principle states that if you have a system at equilibrium, and you then perturb it and induce a state of disequilibrium, the system will react in a manner that allows it to return to equilibrium.

This principle can be extended to non-chemical systems, like for example, the temperature of your home. If you like your room to be at a temperature of 70 deg F, and your system is perturbed by either a cold front or a heat wave occurring, you will react to return your equilibrium state by either turning on the heat, or the air conditioning respectively.

We need to remember that for a chemical system, equilibrium is attained when the forward rate equals the backward rate. So for the reaction

$$aA \rightleftharpoons bB \tag{15.6.1}$$
$$R_F = R_B \quad (at\ equlibrium)$$

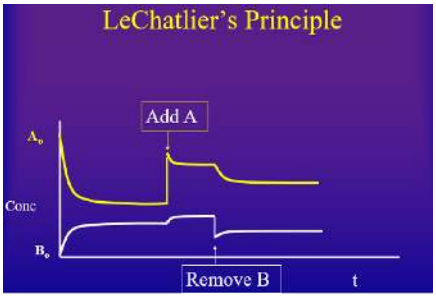
$$k_1[A]^m = k_{-1}[B]^n \quad (at\ equlibrium) \tag{15.6.2}$$

So there are two ways we can perturb a system at equilibrium, that is, make $R_f \neq R_b$. The first is to change the concent of reactants or products so the rates don't equal, and the second is by changing the Temperature, which changes the value of k ($k = Ae^{-\frac{E_a}{RT}}$). If the system is a gaseous system, changes in pressure can change the concentration, and so general chemistry texts typically give three perturbations that you are expected to understand.

1. Δ[Concentration]
2. ΔP (for gaseous systems, which can change the concentration)
3. ΔT (this changes the value of k, and thus K, as $K = \frac{k_f}{k_b}$

Concentration

The concentration dependence is the easiest to understand. If you have a system, and then add something, the system will react to consume what you added, until equilibrium is achieved. On the other hand, if you have a system at equilibrium and you remove something, the system will produce what you removed until a new equilibrium is achieved. There is a virtual lab at the bottom of this page where you can change concentration of a reactant or product at equilibrium, causing a state of disequilibrium and allow you to observe how the system returns to equilibrium



Pressure

There are two pressure effects. The first is adding or subtracting a single gas, and the second is changing the volume of a closed system, which changes the total pressure

Change Partial Pressure of a Single Gas

This is actually the same thing as changing the concentration of a species, and typically done by adding or removing a gas phase species. For gas A:

$$P_A V = n_A RT \tag{15.6.3}$$

so

$$[A] = \frac{n_A}{V} = \frac{P_A}{RT} \tag{15.6.4}$$

Change in Total Pressure

If you change the volume of a closed system at constant temperature you change the total pressure according to Boyle's Law (PV=Constant), and so you change the concentration of all species. This will change the value of the the sum of the stoichiometric coefficients on the reactant side do not equal their sum on the product side.

- **If you increase pressure by contracting the system the equilibrium will shift to the side with fewer species.**
- **If you decrease pressure by expanding the system the equilibrium will shift to the side with more species.**

Case

Case 15.6.1:: Doubling the Volume (Halves the pressure)

Consider the formation of ammonia

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \tag{15.6.5}$$

There are 4 species on the left, and two on the right,

(A) In what direction does the reaction proceed if we half the pressure by doubling the volume?

It moves the equilibrium to the left, creating more species.

Lets look at the math. initially we are at equilbrium

$$K = \frac{[NH_3]^2_{eq}}{[N_2]_{eq}[H_2]^3_{eq}}$$

If we double the volume , then the new volumes are the initial divided by two and Q, the reaction quotient becomes:

$$Q = \frac{\left(\frac{[NH_3]_{eq}}{2}\right)^2}{\left(\frac{[N_2]_{eq}}{2}\right)\left(\frac{[NH_3]_{eq}}{3}\right)^3} = \left(\frac{\left(\frac{1}{2}\right)^2}{\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)^3}\right)\left(\frac{[NH_3]^2_{eq}}{[N_2]_{eq}[H_2]^3_{eq}}\right) = 4K_{eq}$$

That is, Q>K and it moves to the left as we predicted, forming reactants until Q=K.

Case 15.6.2: Halving the Volume (Doubles the pressure)

Consider the formation of ammonia

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \tag{15.6.6}$$

There are 4 species on the left, and two on the right,

(A) In what direction does the reaction proceed if we double the pressure by halving the volume?

It moves the equilibrium to the right, reducing the total number of species.

Lets look at the math. initially we are at equilbrium

$$K = \frac{[NH_3]^2_{eq}}{[N_2]_{eq}[H_2]^3_{eq}}$$

If we double the volume , then the new volumes are the initial divided by two and Q, the reaction quotient becomes:

$$Q = \frac{(2[NH_3]_{eq})^2}{(2[N_2]_{eq})(2[H_2]_{eq})^3} = \left(\frac{(2)^2}{(2)(2)^3}\right)\left(\frac{[NH_3]_{eq}^2}{[N_2]_{eq}[H_2]_{eq}^3}\right) = \frac{1}{4}K_{eq}$$

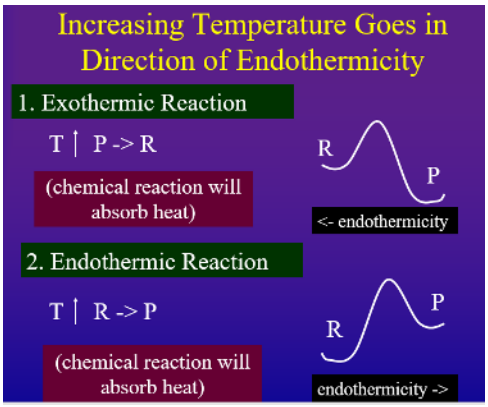
That is, Q<K and it moves to the right as we predicted, forming products until Q=K.

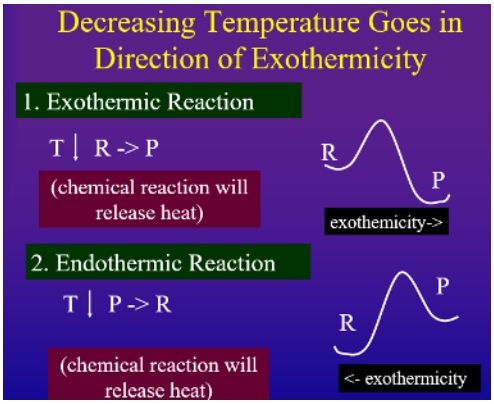
Change in Temperature

Every reaction has a direction of endothermicity and a direction of exothermicity. That is, an "endothermic reaction" is endothermic in the forward direction and exothermic in the reverse. Likewise, an "exothermic" reaction is exothermic in the forward direction, but endothermic in the reverse. According to Le Chatlier's principle if you add heat to the system, it will try and absorb it but going in the direction of endothermicity. On the other hand, if you remove heat from a system it will try and replace the heat by shifting in the direction of exothermicity.

- **Increasing Temperature Shifts Equilibrium in Direction of Endothermicity to absorb heat added**
- **Decreasing Temperature Shifts Equilibrium in Direction of Exothermicity to replace heat removed**

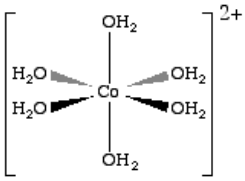
Probably the easiest way to look at this is to draw the Arrhenius diagram as in figures

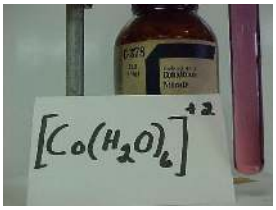




Interactive Cobalt(II) Chloride(aq) Virtual Lab

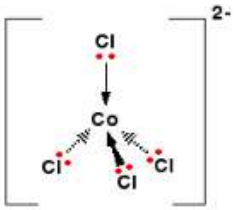
When the cobaltous cation (Co^{+2}) dissolves in water it does not exist as a free ion, but forms a pink octahedral coordination complex with six water molecules, which is called hexaaquacobalt(II) ion, That is, the metal has empty d-orbitals of the cobalt ion accepts the lone pair electrons of a water molecules and forms a covalent bond, where both electrons come from the water. In fact six water molecules bond to each cobalt(II) cation, along the Cartesian axes, forming a pink octahedral complex (fig. *.*), which has the formula $[Co(H_2O)_6]^{+2}$. These are an important class of compounds as most metals form complexes with water, and this is a topic that was avoided in general chemistry 1. As we shall learn later this semester, coordination complexes are often highly colored, and thus easily observed. So in this virtual lab, we will take advantage of the color of coordination complexes to investigate Le Chatlier's principle. We can start by looking at a pink solution formed by the dissolution of cobalt (II) in water.

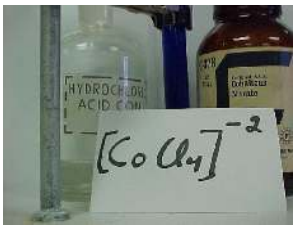




Aqueous Co^{+2} actually covalently bonds to 6 water molecules forming a pink \([Co(H_2O)_6]^{+2}) solution

In the presence of chloride a blue tetrahedral complex form, called tetrchlorocobalt(II) ion is formed

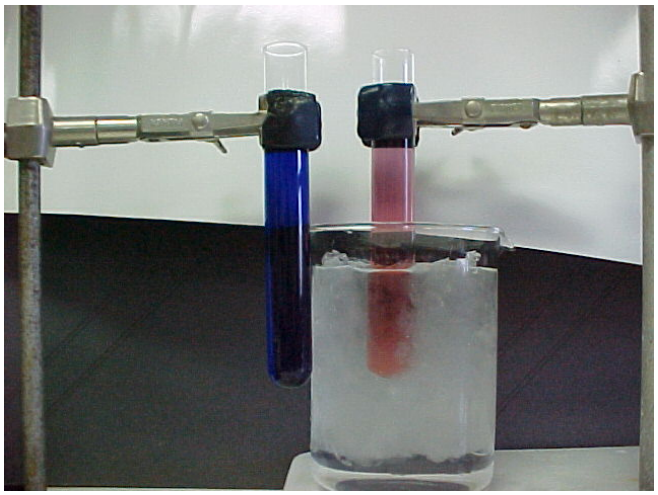


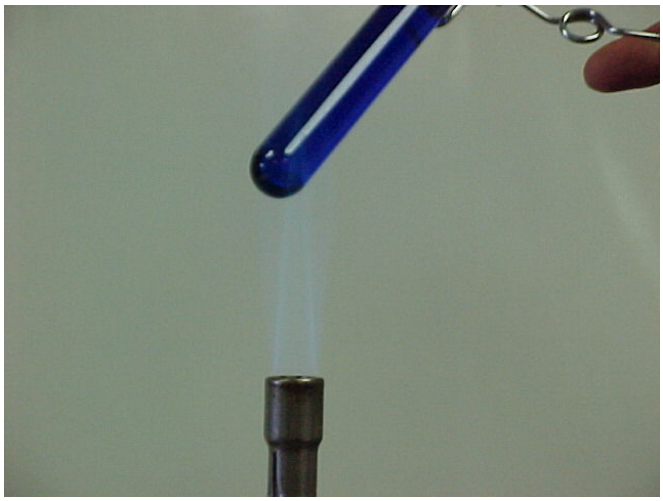


Aqueous Co^{+2} actually covalently bonds to 6 water molecules forming a pink $[Co(H_2O)_6]^{+2}$ solution

The reaction of HCl and Co(aq) is thus described by the following equation and a good visual demonstration of Le Chatlier's principle as the solution is pink when reactant concentrations are high, and blue when product concentrations are high.

$$\underbrace{[Co(H_2O)_6]^{+2}(aq)}_{pink} + 4HCl(aq) \rightleftharpoons \underbrace{[Co(Cl)_2]^{-2}}_{blue} + 6H_2O + 4H^+ \tag{15.6.7}$$





The equilibrium is also shifted by raising or lowering the temperature. On the left the blue solution was cooled and it turned pink. On the right the pink solution was heated and it turned blue.

In the virtual lab perform the following activities.

1.Note the color of 100 ml 1M $CoCl_2$. At equilibrium, do you think K for pure $CoCl_2$ favors reactants or products.

2. Predict how adding 12 M HCl would influence the equilibrium. Right click on the 100 ml 1M $CoCl_2$ and duplicate, so you have two bottles. Now add 100 mL in 10 mL increments of 12M HCl to one of the bottles. Compare the two bottles.

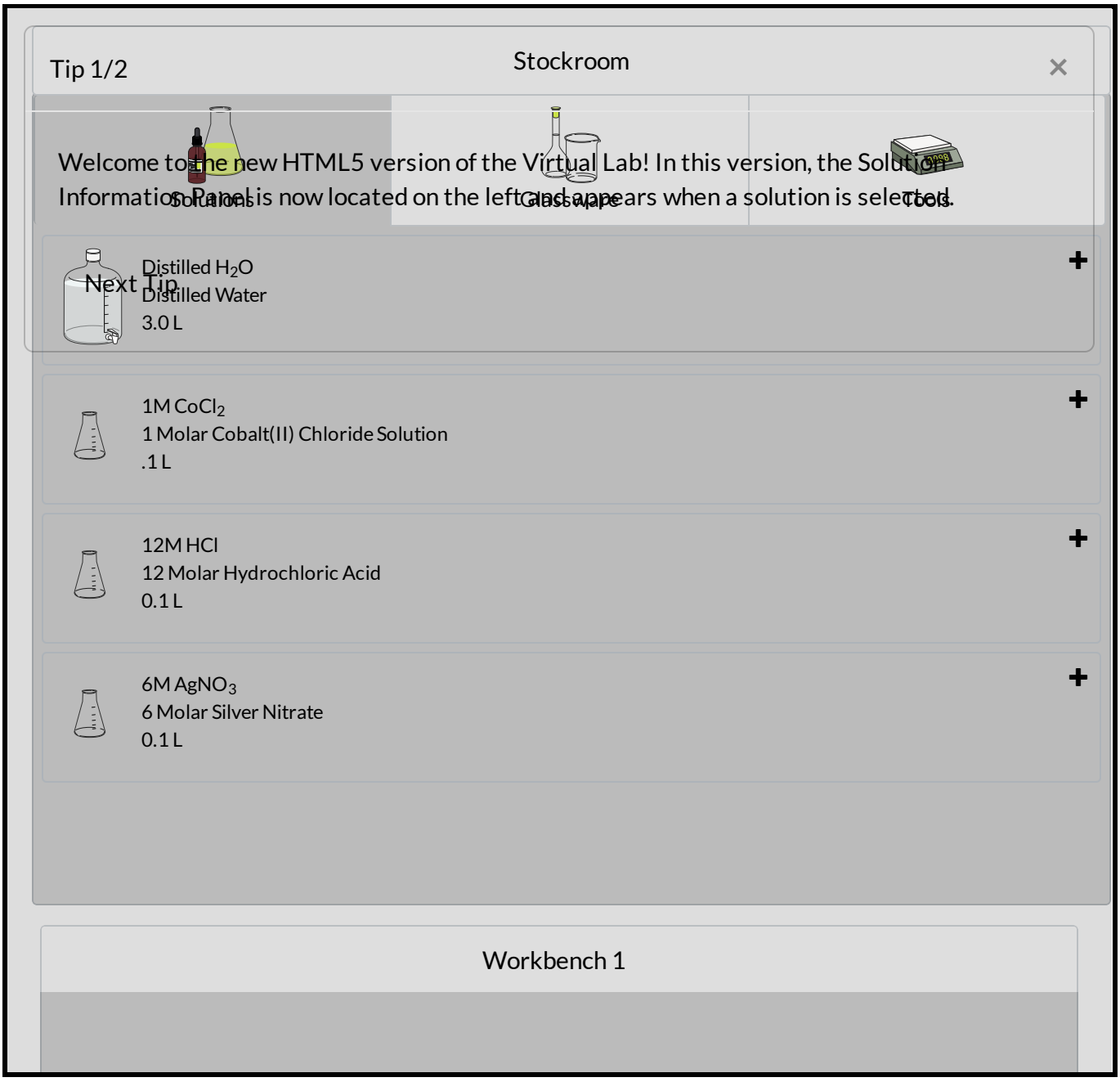
3. Pour 100 ml of the blue solution into an empty 250 ml Erlenmeyer flask. Predict what would happen if you added silver nitrate, noting that silver reacts with chloride according the the following equation:

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s) \tag{15.6.8}$$

Add 100 mL in 10 mL increments of 6M $AgNO_3$ to the blue flask containing 100 mL of the reaction solution.

4. Determine if the reaction is exothermic or endothermic by changing the temperature. Note, the virtual lab operates at an ambient temperature of 25°C. You can quickly change the temperature and isolate it from the surroundings by right clicking on a solution and choosing thermal properties. You then click "Insulated from surroundings" and type in the temperature you want.

$$\underbrace{[Co(H_2O)_6]^{+2}(aq)}_{pink} + 4HCl(aq) \rightleftharpoons \underbrace{[Co(Cl)_2]^{-2}}_{blue} + 6H_2O + 4H^+ \tag{15.6.9}$$



In Class Activity

Please click the following link, it should open the clicker question in a new page. Please return to this page once we after we have discussed the results

CLICKER LINK

This page titled 15.6: Disturbing a Chemical Equilibrium is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

CHAPTER OVERVIEW

16: Acids and Bases

Topic hierarchy

16.1: Brønsted-Lowry Concept of Acids and Bases
16.2: Water and the pH Scale
16.3: Equilibrium Constants for Acids and Bases
16.4: Acid-Base Properties of Salts
16.5: Acid-Base Equilibrium Calculations
16.6: Molecular Structure, Bonding, and Acid-Base Behavior
16.7: Lewis Concept of Acids and Bases

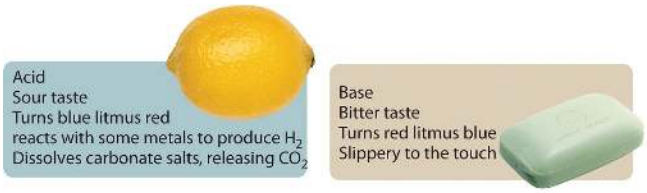
This page titled 16: Acids and Bases is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

16.1: Brønsted-Lowry Concept of Acids and Bases

Introduction

Acids and bases are common substances and the concept of acids and bases have evolved as science progressed. There are three definitions that you will be required to know by the end of this chapter, the Arrhenius, Brønsted-Lowry and Lewis. In general chemistry 1, Section 3.5 you learned how to balance Acid Base Reactions and may want to review that section. There are 4 videos for balancing:

1. Strong Acid and Strong Base
2. Strong Acid and Weak Base
3. Strong Base and Weak Acid
4. Weak Acid and Weak Base



In this section we will take a deeper look into the nature of acids and bases

Autoionization of water

Neutral water does not consist of pure H_2O, as sometimes when two water molecules collide a proton is transferred from one molecule to another.

$$\mathrm{H_2O}\,(l) + \mathrm{H_2O}\,(l) \rightarrow \mathrm{H_3O^+}\,(aq) + \mathrm{OH^-}\,(aq) \tag{16.1.1}$$

Note, when this happens, the number of positive charged hydronium ions equals the number of negatively charged hydroxide ions, and so even though there are charged particles, the water is still neutral.



Video16.1.2 (https://youtu.be/iqINYjHyimY): 10 Youtube uploaded by akumich showing the formation of hydronium ions and hydroxide ions as protons are transferred between water molecules.

The above animation and the longer video it links to does a good job of showing the transient nature of the actual hydronium or hydroxide ions in neutral water. That is, as soon as a hydroxide is formed, its negative net charge will grab a proton from another water molecule to become neutral (but form another hydroxide), and in a similar manner each hydronium will give its extra proton to another water molecule, becoming neutral while forming another hydronium. And of course the hydronium and hydroxide ions will react with each other to form neutral water. It also needs to be emphasized that the concentration of hydronium and hydroxide is 0.0000001 M (10^{-7}M) in pure water, which is why most collisions are with other water molecules.

Arrhenius Concept of Acids and Bases

The Arrhenius Definition is based on the autoionization of water and is limited because it can only describe acids and bases in aqueous environments. Arrhenius defined an acid to be a compound that dissolves in water to make hydronium ions and a base as a compound that dissolves in water to yield hydroxide anions.

Arrhenius Acid

An Arrhenius Acid is something that gives a proton to water. So for an Arrhenius Acid:

$$H_3O^+(aq) > OH^- \tag{16.1.2}$$

Note, the solution is still neutral because whatever gave the proton to water became negative. HCl acts as an Arrhenius acid when dissolved in water, and every time an HCl molecule gives a proton to a water molecule it not only forms hydronium but also chloride

$$\underset{an\ Arrhenius\ acid}{HCl_{(g)}} \xrightarrow{H_3O_{(l)}} H^+_{(aq)} + Cl^-_{(aq)} \tag{16.1.3}$$

Arrhenius Base

An Arrhenius base is something that forms hydroxide when added to water. So for an Arrhenius Base:

$$H_3O^+(aq) < OH^- \tag{16.1.4}$$

$$\underset{an\ Arrhenius\ base}{NaOH_{(s)}} \xrightarrow{H_2O_{(l)}} Na^+_{(aq)} + OH^-_{(aq)} \tag{16.1.5}$$

NaOH is an Arrhenius Base as dissolving it in water produces hydroxide ions.

Note, there is another type of base, which is typified by ammonia and the amines, which have a nitrogen with a lone pair of electrons. These grab a proton from neutral water forming hydroxide

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{16.1.6}$$

Bronsted Concept of Acids and Bases

An Arrhenius Acid is something that donates a proton to water, and Bronsted-Lowry Concept extends this to any substance, where an acid is a proton donor and a base is a proton acceptor.

- Acid = Proton Donor
- Base=Proton Acceptor

Consider the reactions of ammonia with water and HCl. In the first reaction ammonia is both an Arrhenius and a Bronsted base, in the second it is only a Bronsted base.

$$\underset{\substack{both\ Arrhenius\ and\\ Bronsted\ base}}{NH_3(g)} + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{16.1.7}$$

$$\underset{only\ a\ Bronsted\ base}{NH_3(g)} + HCl(aq) \rightleftharpoons NH_4^+(aq) + Cl^-(aq) \tag{16.1.8}$$

So Arrhenius acids are a subset of Bronsted acids, where water is the proton acceptor.

Conjugate Acid-Base Pairs

Note when molecule "A" gives a proton to molecule "B", molecule molecule "A" acted as an acid and molecule "B" acted as a base. After this reaction, lets call molecule "A" as "a" to indicate that it is minus a proton, and "B" as "b", to indicate that it has received a proton. Well, now "b" is a base and has an extra proton it can give away (becoming "B") and "a" is a base, which can accept a proton and become "A". So "a" and "b" are the conjugate base and conjugate acid of the acid "A' and base"B". This is demonstrated in figure 16.1.2

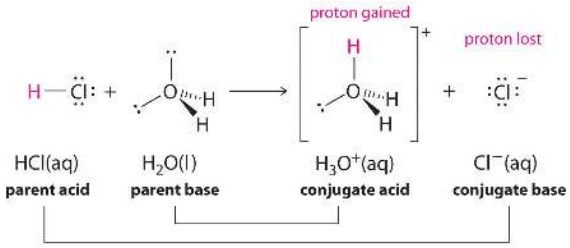


Figure 16.1.2: Acid/base conjugate pair relationship

From figure 16.1.2 you can see that hydronium is the conjugate acid of water, and chloride is the conjugate base of HCl. This is important as it can be used to explain the acid/base behavior of salt solutions.

Polyprotic Acids and Bases

An acid that can donate more than one proton is a polyprotic acid, and a base that can accept more than one proton is a polyprotic base

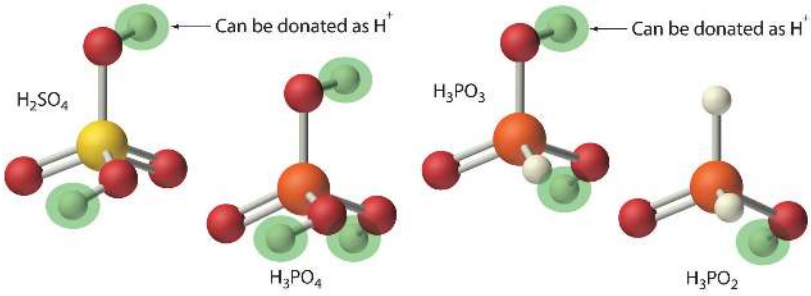


Figure16.1.3: Note, not all protons are acidic. In the case of oxyacids, where oxygen is attached to a non-metal, only the protons attached to the oxygen are acidic. This is why H_3PO_3 and H_3PO_2 are diprotic and monoprotic respectively.

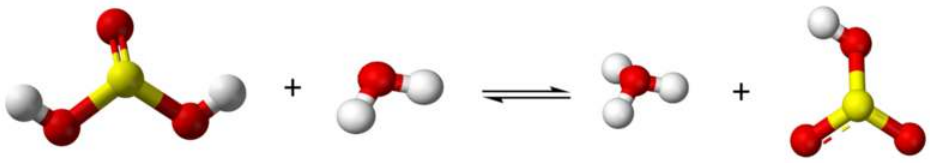
- monoprotic acids, HCl, $HC_2H_3O_2$ (acetic acid only has one acidic proton)
- diprotic acids - H_2SO_4, H_2CO_3, H_2SO_3 ,H_3PO_3,
- triprotic acids - H_3PO_4, H_3AsO_4, H_3BO_3

- monoprotic bases: NaF, NaCl, NaBr (soluble salts)
- diprotic bases, $Ba(OH)_2$, Na_2SO_4, (any anion with a [-2] charge can accept two protons to become neutral
- triprotic bases, Na_3PO_4, K_3AsO_4, Na_3BO_3, (any anion with a [-3] charge)

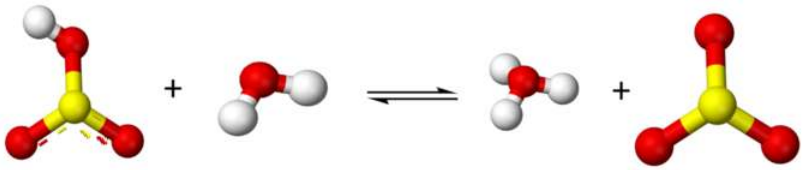
Note: Polyprotic acids and bases react stepwise forming intermediates:

Diprotic Acid

Sulfurous acid is a diprotic acid and forms one intermediate, bisulfite (HSO_3^-) (or hydrogen sulfite)



$$H_2SO_3 + H_2O \rightleftharpoons H_3O^+ + HSO_3^- \tag{16.1.9}$$

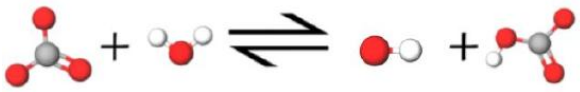


$$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{2-} \tag{16.1.10}$$

Because sulfurous acid is a weak acid you have an equilibrium with all three species existing, H_2SO_3, HSO_3^- and SO_3^{-2}.

Diprotic Base

The carbonate ion, CO_3^{2-}, is an example of a diprotic base and note it has one intermediate, bicarbonate (HCO_3^-) .



$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \tag{16.1.11}$$

and



$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^- \tag{16.1.12}$$

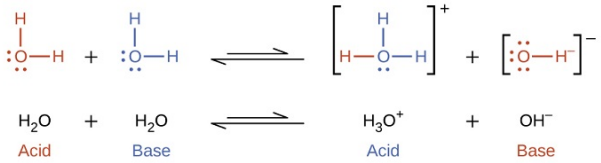
At equilibrium you would have a mixture of all three species, H_2CO_3, HCO_3^- and CO_3^{-2}.

Amphiprotic

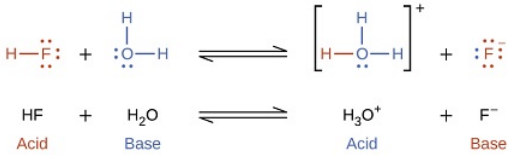
Substances that can donate or accept protons are called amphiprotic, and thus can act as both a Bronsted acid or a Bronsted base. Note, there is a similiar term called amphoteric, which means a substance can be an acid or a base. All amphiprotic substances are amphoteric, but there are some amphoteric substances within the Lewis Acid/Base scheme that do not involve proton transfer. These will be covered in the last section of this chapter.

Water

Self-ionization involves water acting as both an acid and a base

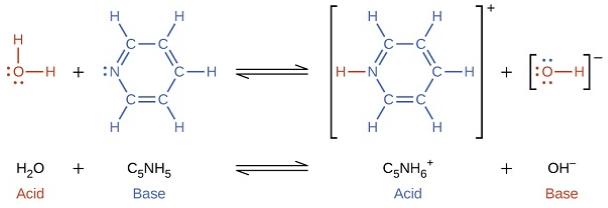


In the presence of the acid HF, water functions as a base and receives a proton forming its conjugate acid (hydronium).



$$K = \frac{[H_3O^+][F^-]}{[HF]}$$

In the presence of the base pyridine (C_5H_5N) water functions as an acid, forming its conjugate base (hydroxide).



$$K = \frac{[C_5NH_6^+][OH^-]}{[C_5NH_5]}$$

Acid Salts

A close look at polyprotic acids and bases show that when an ion has an ionizable proton it is amphiprotic. Thus in the above examples, bisulfite and bicarbonate are amphiprotic, but they are charged ions and so exist as salts like, $NaHCO_3$ and $NaHSO_3$.

$$NaHCO_3(s) \xrightarrow{H_2O(l)} Na^+(aq) + HCO_3^-(aq) \tag{16.1.13}$$

$$\mathrm{HCO_3^- + H_2O} \overset{bicarbonate\ as\ acid}{\rightleftharpoons} \mathrm{CO_3^{-2} + H_3O^+} \tag{16.1.14}$$

$$\mathrm{HCO_3^- + H_2O} \overset{bicarbonate\ as\ base}{\rightleftharpoons} H_2CO_3 + \mathrm{OH^-} \tag{16.1.15}$$

NOTE: Acid Salts may be acidic or basic. The term Acid Salt just means that you have an ionic compound with an anion that can donate a proton. The acidity or basicity depends on the strength of the equilibrium constants and will be covered later in this chapter.

I do not believe there are things like base salts, which implies a cation that accepts protons. When we get to the structure of acids and their strengths, we will see that it is hard to pull a proton away from a negative ion, and so the greater the charge of the ion the weaker its strength. But you can still pull a positive charge away from a negative species, but adding a positive charge to a positive species seems highly unlikely.

Test Yourself

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 16.1: Brønsted-Lowry Concept of Acids and Bases is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

16.2: Water and the pH Scale

Introduction

We have all heard of the pH scale, neutral water has a pH =7, acid is lower and bases are higher. We may also know the pH of some common substances as shown in figure 16.2.1.

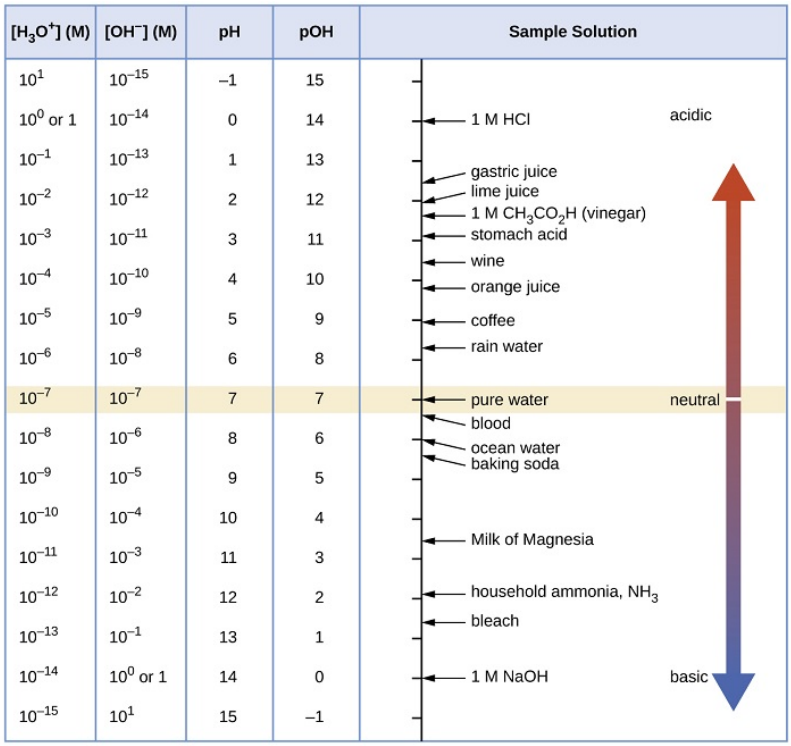


Figure 16.2.1 Table relating ph to concentrations for various substances.

Most chemistry students know the mathematical equation pH=-log[H^+], but what does it mean? For starts, pH is a way to measure the concentration of substances that are very dilute, and in this section we shall seek to develop an understanding of pH

Autoionization Constant (K_W)

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{16.2.1}$$

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \tag{16.2.2}$$

Note, in the equilibrium chapter we were told to ignore pure solid and liquid substances in heterogeneous equilibria because their density is constant, and thus their concentration is constant, but this is not a heterogeneous mixture, but a homogenous solution. The K for the above value is a very small number and so the number of water molecules that dissociates is so small that it is negligible compared to the initial water constant, and thus the water concentration can be considered constant. Thus the water concentration is integrated into the Ionization constant and K_w is defined as:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{16.2.3}$$

For neutral water

$$[H_3O^+] = [OH^-] \tag{16.2.4}$$

substituting

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^2 = [OH^-]^2 = 1.0 \times 10^{-14} \tag{16.2.5}$$

Taking the square root of both sides gives

$$[H_3O^+] = [OH^-] = 1x10^{-7} \tag{16.2.6}$$

Note, for pure water the concentration is

$$\text{Concentration of pure water} = \left(\frac{1000g}{l}\right)\left(\frac{mol}{18.015g}\right) = 55.56\frac{mol}{l} \tag{16.2.7}$$

So the fraction dissociated is

$$\frac{[H_3O^+]}{[H_2O]} = \frac{1x10^{-7}}{55.56} = 1.8x10^{-9} \tag{16.2.8}$$

(or taking the reciprocal, means that for every 556,000,000 molecules of water, one forms a hydronium ion. This allows us to say that the concentration of the water is constant. Also, note from the introduction, that this is a dynamic not static system, we are not saying that some molecules are always hydronium or hydroxide, but that molecules are rapidly interacting and a specific oxygen atom may at a given time have one, two or three protons associated with it, although the vast majority is 2, to the point that the concentration of hydronium or hydroxide in a liter is 10^{-7}moles.

pH, pOH and pK_w

Noting

$$[H_3O^+][OH^-] = K_w = 10^{-14} \tag{16.2.9}$$

we can take the log of both sides and multiply by minus 1, this gives us

$$pH + pOH = 14 \tag{16.2.10}$$

So if you know either hydronium or hydroxide, you know the other.

pH & Significant Figures

Note, pX is the log of how many times you divide by 10 (while log is how many times you multiply by 10). That is, it is an operation, not a number.

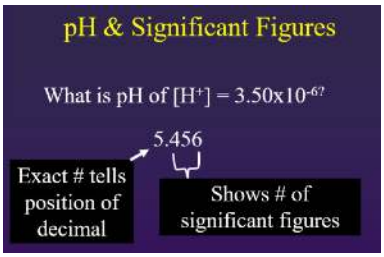


Figure16.2.2 Showing significant figures for logarithms

Why do we need to define things this way?

What is the pH of 0.1M HCl and 0.1M NaOH? (Noting that they both have one sig fig for the concentration).

For 0.1M HCL, pH= -log(0.1)=1, so the [HCl]=.1 and its pH = 1

For 0.1M NaOH], pOH=-log(0.1)=1, which means the pH=13, (remember pH+pOH=14), but 13 has two sig. figures, so you must use the convention in figure 16.2.2, and the answers are pH=1.0 for 1MHCL, and pH=13.0 for 1M NaOH.

(Realize that pH=13 equates to the decimal 0.0000000000001 or $\frac{1}{10^{13}}$, that is, it is not a measured number, but the number of times you divided by 10.

Measuring pH

There are two basic ways to measure pH

1. With an Indicator

Indicators are chemicals that change color at specific pHs. The basic idea is that an indicator is an acid or a base that has a different color in the protonated or unprotonated state, and changes that state at a defined pH.

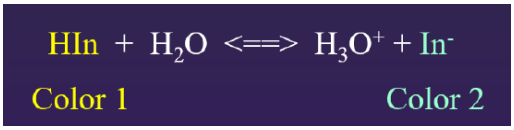


Figure shows an acidic indicator where the acid has a different color than its conjugated base. At low pH there are lots of hydronium and so it stays protonated. As the pH raises the hydronium ion concentration goes down and the hydroxide goes up, pulling the protons from the indicator.

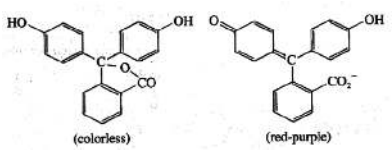


Figure Phenolphthalein is a common indicator which is clear below a pH of around 9, and becomes pink after that.

A list of indicators can be found here.

2. With a pH Meter

A pH probe is an electronic device that measures the pH. These are very common and they should always be checked against standard solutions of known pH and calibrated if they read incorrectly. The workings of pH probes will be covered in analytical chemistry, but the following 2:30 min Youtube from Oxford Press does a good job in explaining how the pH probe works.



Video 16.2.1 2:30 YouTuve describing the operation of a pH probe developed by Oxford University Press (https://youtu.be/aIn4D2QXUy4).

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 16.2: Water and the pH Scale is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

16.3: Equilibrium Constants for Acids and Bases

Introduction

In general chemistry 1 we calculated the pH of strong acids and bases by considering them to completely dissociate, that is, undergo 100% ionization. We will now look at weak acids and bases, which do not completely dissociate, and use equilibrium constants to calculate equilibrium concentrations. We could solve all these problems using the techniques from the last chapter on equilbria, but instead we are going to develop short cut techniques, and identify when they are valid. But first, we need to define what are equilibrium constants for acid base reactions.

Weak Acids

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \tag{16.3.1}$$

At first glance this gives an equilibrium constant of

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \tag{16.3.2}$$

But we can consider the water concentration constant because it is much greater than of acid that has ionized. There are two factors at work here, first that the water is the solvent and so [H_2O] is larger than [HA], and second, that [HA] is a weak acid, and so at equilibrium the amount ionized is smaller than [HA]. It should be noted that this is a homogenous equlibria, and although we are ignoring the water and treating it as a liquid, it is for a different reason than was used in the last chapter for heterogeneous equilibria.

This results in Acid Dissociation Constant (K_a) for aqueous systems:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{16.3.3}$$

where, $K_a = K[H_2O]$

K_a is only used for weak acids. Strong acids have a large K_a and completely dissociate and so you just state the reaction goes to completion.

Weak Bases

There are two types of weak bases, those as modeled by ammonia and amines, which grab a proton from water, and the conjugate bases of weak acids, which are ions, and grab the proton to form the weak acid.

Type 1:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq) \tag{16.3.4}$$

Note, in this reaction the base removes a proton from the water and following the same logic for weak acids, we consider the water concentration to stay constant because only a small fraction of it reacts with the weak base, so:

$$K_b = \frac{[HB^+][OH^-]}{[B]} \tag{16.3.5}$$

An example of the first type would be that of methyl amine, CH_3NH_2.

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq) \tag{16.3.6}$$

$$K = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = 5.0x10^{-4}$$

Type 2:

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq) \tag{16.3.7}$$

$$K_b' = \frac{[HA][OH^-]}{[A^-]} \tag{16.3.8}$$

where K_b is the basic equilibrium constant of the conjugate base A^- of the weak acid HA

Acid Base Conjugate Pairs

We will use $K_{(a \text{ or } b)}$ to represent the acid or base equilibrium constant and $K'_{(b \text{ or } a)}$ to represent the equilibrium constant of the conjugate pair.

For an Acid Base Conjugate Pair

$$K_a K_{b'} = K_w \tag{16.3.9}$$

Consider the generic acid HA which has the reaction and equilibrium constant of

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq),\ K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{16.3.10}$$

its conjugate base A^- has the reaction and equilibrium constant of:

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq), K_b' = \frac{[HA][OH^-]}{[A^-]} \tag{16.3.11}$$

$$K_a K_b' = \left(\frac{[H_3O^+]\ \cancel{[A^-]}}{\cancel{[HA]}}\right)\left(\frac{\cancel{[HA]}[OH^-]}{\cancel{[A^-]}}\right) = [H_3O^+][OH^-] = K_w = 10^{-14} \tag{16.3.12}$$

So there is an inverse relationship across the conjugate pair

- **The Stronger an Acid the Weaker it's Conjugate Base**
- **The Weaker an Acid the Stronger it's Conjugate Base**
- **The Stronger the Base the Weaker it's Conjugate Acid**
- **The Weaker the Base the Stronger it's Conjugate Acid**

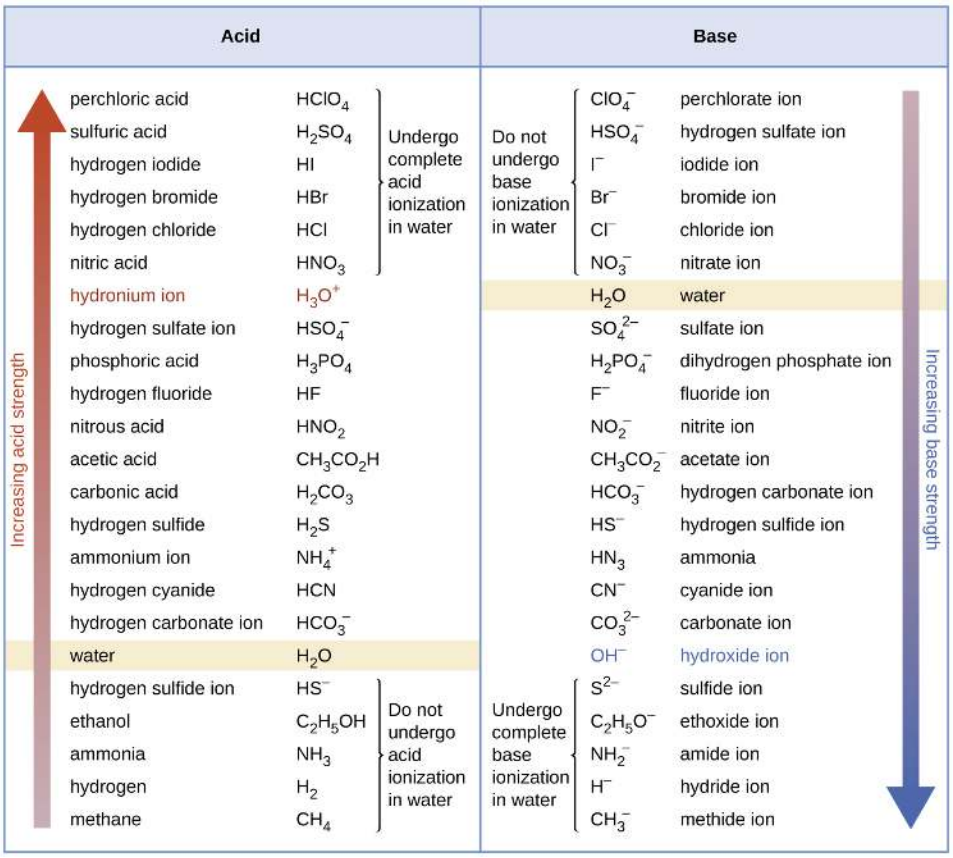


Figure16.3.1: Relationship between acid or base strength and that of their conjugate base or acid.

K_a and K_b Values for PolyProtic Acids

PolyProtic Acids

It is always harder to remove a second proton from an acid because you are removing it from a negative charged species, and even harder to remove the third, as you are removing it from a dianion.

Consider a triprotic acid

$$H_3A + H_2O \rightleftharpoons H_2A^- + H_3O^+ \quad K_{a1} \tag{16.3.13}$$

$$H_2A^- + H_2O \rightleftharpoons HA^{-2} + H_3O^+ \quad K_{a2} \tag{16.3.14}$$

$$HA^2 - + H_2O \rightleftharpoons A^{-3} + H_3O^+ \quad K_{a3} \tag{16.3.15}$$

$$K_{a1} > K_{a2} > K_{a3} \tag{16.3.16}$$

pK_a and pK_b

Because pK_a and pK_b values are so small they are often recorded a pX values, where pX= -logX. So

pK_a = -logK_a and K_a =10^{-pka}
pK_b = -logK_b and K_b =10^{-pkb}

Table of K_a

Table 16.3.1: Table of Acid Ionization Constants

Name	Formula	Conjugate Base	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}	K_{a4}	pK_{a4}
Acetic acid	CH_3CO_2H	$CH_3CO_2^-$	1.75×10^{-5}	4.756						
Arsenic acid	H_3AsO_4	$H_2AsO_4^-$	5.5×10^{-3}	2.26	1.7×10^{-7}	6.76	5.1×10^{-12}	11.29		
Benzoic acid	$C_6H_5CO_2H$	$C_6H_5CO_2^-$	6.25×10^{-5}	4.204						
Boric acid	H_3BO_3	$H_2BO_3^-$	5.4×10^{-10}*	9.27*	>1 × 10^{-14}*	>14*				
Bromoacetic acid	CH_2BrCO_2H	$CH_2BrCO_2^-$	1.3×10^{-3}	2.90						
Carbonic acid	H_2CO_3	HCO_3^-	4.5×10^{-7}	6.35	4.7×10^{-11}	10.33				
Chloroacetic acid	CH_2ClCO_2H	$CH_2ClCO_2^-$	1.3×10^{-3}	2.87						
Chlorous acid	$HClO_2$	ClO_2^-	1.1×10^{-2}	1.94						
Chromic acid	H_2CrO_4	$HCrO_4^-$	1.8×10^{-1}	0.74	3.2×10^{-7}	6.49				
Citric acid	$C_6H_8O_7$	$C_6H_7O_7^-$	7.4×10^{-4}	3.13	1.7×10^{-5}	4.76	4.0×10^{-7}	6.40		
Cyanic acid	HCNO	$HCNO^-$	3.5×10^{-4}	3.46						
Dichloroacetic acid	$CHCl_2CO_2H$	$CHCl_2CO_2^-$	4.5×10^{-2}	1.35						
Fluoroacetic acid	CH_2FCO_2H	$CH_2FCO_2^-$	2.6×10^{-3}	2.59						
Formic acid	CH_2O_2	CHO_2^-	1.8×10^{-4}	3.75						
Hydrazoic acid	HN_3	N_3^-	2.5×10^{-5}	4.6						
Hydrocyanic acid	HCN	CN^-	6.2×10^{-10}	9.21						
Hydrofluoric acid	HF	F^-	6.3×10^{-4}	3.20						
Hydrogen selenide	H_2Se	HSe^-	1.3×10^{-4}	3.89	1.0×10^{-11}	11.0				
Hydrogen sulfide	H_2S	HS^-	8.9×10^{-8}	7.05	1×10^{-19}	19				

* Measured at 20°C, not 25°C.

‡ Measured at 18°C, not 25°C.

Name	Formula	Conjugate Base	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}	K_{a4}	pK_{a4}
Hydrogen telluride	H_2Te	HTe^-	2.5×10^{-3}‡	2.6‡	1×10^{-11}	11				
Hypobromous acid	HBrO	BrO^-	2.8×10^{-9}	8.55						
Hypochlorous acid	HClO	ClO^-	4.0×10^{-8}	7.40						
Hypoiodous acid	HIO	IO^-	3.2×10^{-11}	10.5						
Iodic acid	HIO_3	IO_3^-	1.7×10^{-1}	0.78						
Iodoacetic acid	CH_2ICO_2H	$CH_2ICO_2^-$	6.6×10^{-4}	3.18						
Nitrous acid	HNO_2	NO_2^-	5.6×10^{-4}	3.25						
Oxalic acid	$C_2H_2O_4$	$C_2HO_4^-$	5.6×10^{-2}	1.25	1.5×10^{-4}	3.81				
Periodic acid	HIO_4	IO_4^-	2.3×10^{-2}	1.64						
Phenol	C_6H_5OH	$C_6H_5O^-$	1.0×10^{-10}	9.99						
Phosphoric acid	H_3PO_4	$H_2PO_4^-$	6.9×10^{-3}	2.16	6.2×10^{-8}	7.21	4.8×10^{-13}	12.32		
Phosphorous acid	H_3PO_3	$H_2PO_3^-$	5.0×10^{-2}*	1.3*	2.0×10^{-7}*	6.70*				
Pyrophosphoric acid	$H_4P_2O_7$	$H_3P_2O_7^-$	1.2×10^{-1}	0.91	7.9×10^{-3}	2.10	2.0×10^{-7}	6.70	4.8×10^{-10}	9.32
Resorcinol	$C_6H_4(OH)_2$	$C_6H_4O_2H^-$	4.8×10^{-10}	9.32	7.9×10^{-12}	11.1				
Selenic acid	H_2SeO_4	$HSeO_4^-$	Strong	Strong	2.0×10^{-2}	1.7				
Selenious acid	H_2SeO_3	$HSeO_3^-$	2.4×10^{-3}	2.62	4.8×10^{-9}	8.32				
Sulfuric acid	H_2SO_4	HSO_4^-	Strong	Strong	1.0×10^{-2}	1.99				
Sulfurous acid	H_2SO_3	HSO_3^-	1.4×10^{-2}	1.85	6.3×10^{-8}	7.2				

* Measured at 20°C, not 25°C.

‡ Measured at 18°C, not 25°C.

Name	Formula	Conjugate Base	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}	K_{a4}	pK_{a4}
meso-Tartaric acid	$C_4H_6O_6$	$C_4H_5O_6^-$	6.8×10^{-4}	3.17	1.2×10^{-5}	4.91				
Telluric acid	H_2TeO_4	$HTeO_4^-$	2.1×10^{-8}‡	7.68‡	1.0×10^{-11}‡	11.0‡				
Tellurous acid	H_2TeO_3	$HTeO_3^-$	5.4×10^{-7}	6.27	3.7×10^{-9}	8.43				
Trichloroacetic acid	CCl_3CO_2H	$CCl_3CO_2^-$	2.2×10^{-1}	0.66						
Trifluoroacetic acid	CF_3CO_2H	$CF_3CO_2^-$	3.0×10^{-1}	0.52						
* Measured at 20°C, not 25°C.										
‡ Measured at 18°C, not 25°C.										

Source of data: *CRC Handbook of Chemistry and Physics*, 84th Edition (2004).

Table of K_b

Table16.3.2 Base Ionization Constants

Name	Formula		K_b	pK_b
Ammonia	NH_3	NH_4^+	1.8×10^{-5}	4.75
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3^+$	7.4×10^{-10}	9.13
n-Butylamine	$C_4H_9NH_2$	$C_4H_9NH_3^+$	4.0×10^{-4}	3.40
sec-Butylamine	$(CH_3)_2CHCH_2NH_2$	$(CH_3)_2CHCH_2H_3^+$	3.6×10^{-4}	3.44
tert-Butylamine	$(CH_3)_3CNH_2$	$(CH_3)_3CH_3^+$	4.8×10^{-4}	3.32
Dimethylamine	$(CH_3)_2NH$	$(CH_3)_2H_2^+$	5.4×10^{-4}	3.27
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3^+$	4.5×10^{-4}	3.35
Hydrazine	N_2H_4	$N_2H_5^+$	1.3×10^{-6}	5.9
Hydroxylamine	NH_2OH	NH_3OH^+	8.7×10^{-9}	8.06
Methylamine	CH_3NH_2	$CH_3NH_3^+$	4.6×10^{-4}	3.34
Propylamine	$C_3H_7NH_2$	$C_3H_7NH_3^+$	3.5×10^{-4}	3.46
Pyridine	C_5H_5N	$C_5H_6N^+$	1.7×10^{-9}	8.77
Trimethylamine	$(CH_3)_3N$	$(CH_3)_3NH^+$	6.3×10^{-5}	4.20

Source of data: *CRC Handbook of Chemistry and Physics*, 84th Edition (2004).

Weak Acid pH Calculations

We typically write the acid dissociation as:

$$HA \rightleftharpoons H^+ + A^- \tag{16.3.17}$$

Noting that water is omitted and hydronium is written as H^+ (implicitly meaning H_3O^+ and not a free proton). This gives the following equilibrium constant

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{16.3.18}$$

If we know K we can determine the pH or hydronium ion concentration using a rice diagram where we start with pure acid and measure determine how much dissociates.

Table 16.3.3: Weak Acid RICE Diagram

Reaction	HA	H^+	A^-
Initial	$[HA]_i$	0	0
Change	-x	+x	+x
Equilibrium	$[HA]_i$-x	x	x

Noting that $x = 10^{-pH}$ (at equilibrium) and substituting, gives

$$K_a = \frac{x^2}{[HA]_i - x} \tag{16.3.19}$$

Now by definition, a weak acid means very little dissociates and if x<< $[HA]_{initial}$ we can ignore the x in the denominator. The rule of thumb we will for this approximation is if $[HA]_{initial}$ >100K_a we will ignore x in the denominator and simplify the math

$$If\ [HA]_i > 100K_a \tag{16.3.20}$$

$$then$$

$$[HA]_i - x \approxeq [HA]_i$$

$$and$$

$$K_a = \frac{x^2}{[HA]_i}$$

This allows us to avoid the quadratic equation and quickly solve for the hydronium ion concentration

$$[H^+] = x = \sqrt{K_a[HA]_i} \tag{16.3.21}$$

and we can calculate pH for a weak acid

$$pH = -log[H^+] = -log\sqrt{K_a[HA]_i} \tag{16.3.22}$$

Weak Base pH Calculations

A base reacts with water to accept a proton:

$$B + H_2O \rightleftharpoons BH^+ + OH^- \tag{16.3.23}$$

The water is omitted from the equilibrium constant expression giving.

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{16.3.24}$$

If we know K we can determine the pOH from the rice diagram, and once we know pOH, we can determine pH (because pH + pOH =14). So we follow a similiar calculation as that of the weak acid, but now we are calculating [OH^-] and not [H^+].

Table 16.3.3: Weak Acid RICE Diagram

Reaction	B	H_2O	BH^+	OH^-
Initial	$[B]_i$		0	0
Change	-x		+x	+x
Equilibrium	$[B]_i$-x		x	x

Noting that $x = 10^{-pOH}$ (at equilibrium) and substituting, gives

$$K_b = \frac{x^2}{[B]_i - x} \tag{16.3.25}$$

Now by definition, a weak base means very few protons are accepted and if x<< $[B]_{initial}$ we can ignore the x in the denominator. The rule of thumb we will for this approximation is if $[B]_{initial}$ >100K_b we will ignore x in the denominator and simplify the math

$$If\ [B]_i > 100K_b \tag{16.3.26}$$

$$then$$

$$[B]_i - x \approxeq [B]_i$$

$$and$$

$$K_b = \frac{x^2}{[B]_i}$$

This allows us to avoid the quadratic equation and quickly solve for the hydroxide ion concentration

$$[OH^-] = x = \sqrt{K_b[B]_i} \tag{16.3.27}$$

and we can calculate pOH for a weak acid

$$pOH = -log[OH^-] = -log\sqrt{K_b[B]_i} \tag{16.3.28}$$

and now we can calculate pH

$$pH = 14 - pOH \tag{16.3.29}$$

$$or$$

$$pH = 14 + log\sqrt{K_b[B]_i}$$

Diprotic Acid pH Calculation

Consider a generic diprotic acid H_2A, like carbonic acid, H_2CO_3. Remember that diprotic acids donate protons stepwise and there is an amphoteric intermediate HA^-, so in the reaction of a diprotic acid there are 5 chemical species, H_2A, HA^-, A^{-2}, H^+ and OH^-.

$$H_2A \rightleftharpoons H^+ + HA^- \quad K_1 = \frac{[H^+][HA^-]}{[H_2A]} \tag{16.3.30}$$

$$HA^- \rightleftharpoons H^+ + A^{-2} \quad K_2 = \frac{[H^+][A^{-2}]}{[HA^-]}$$

From section 16.3.5 (K_a for polyprotic acids) and from table 16.3.1 (table of K_a) we see $K_{a1}>>K_{a2}$ and we can ignore the effect of the second dissociation on the hyrdonium ion concentration, so if $[H_2A]_{initial} > 100K_{a1}$ we can use the weak acid approximation to solve for hydronium. Othewise we need to solve the quadratic equation

$$[H^+] = [HA^-] = \sqrt{k_{a1}[H_2A]_i} \tag{16.3.31}$$

The H_2A can now be determined

$$[H_2A] = H_2A]_i - [H^+] \tag{16.3.32}$$

From K_2 we can calculate A^{-2} as $[H^+] = [HA^-]$ and they cancel

$$K_2 = \frac{\cancel{[H^+]}[A^{-2}]}{\cancel{[HA^-]}} \tag{16.3.33}$$

$$so$$

$$[A^{-2}] = K_2$$

and we can get hydroxide from the water ionization constant K_w

$$K_w = [H^+][OH^-] \tag{16.3.34}$$

$$so$$

$$[OH^-] = \frac{K_w}{[H^+]}$$

Percent Ionization and Dilution

Before completing this section we want to look at the effect of dilution on percent ionization and our rule of thumb that we can ignore the extent of dissociation when $[HA]_i > 100K_a$. For the generic acid:

$$HA \rightleftharpoons H^+ + A^- \tag{16.3.35}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

We can write the RICE diagram

Table 16.3.3: Weak Acid RICE Diagram

Reaction	HA	H^+	A^-
Initial	$[HA]_i$	0	0
Change	-x	+x	+x
Equilibrium	$[HA]_i$-x	x	x

noting that the amount ionized is x=$[A^-]$, where $[A^-]$ is the amount that formed the conjugate base.

So we can define the percent ionization of a weak acid as

$$\%I = \frac{[A^-]}{[HA]_i}(100) \tag{16.3.36}$$

Let's calculate the % Ionization of 1.0M and 0.01 M Acetic acid (K_a=1.8x10^{-5}). Since both of these concentrations are greater than 100K_a, we will use the relationship

$$[A^-] = [H^+] = \sqrt{K_a[HA]_i} \tag{16.3.37}$$

$$\%I = \frac{[A^-]}{[HA]_i}(100) = \frac{[\sqrt{K_a[HA]_i}]}{[HA]_i}(100) \tag{16.3.38}$$

For 1.0 M Acetic Acid

$$\%I = \frac{\sqrt{1.8x10^{-5}[1.0]}}{[1.0]}(100) = 0.42 \tag{16.3.39}$$

For 0.01M Acetic Acid

$$\%I = \frac{\sqrt{1.8x10^{-5}[0.01]}}{[0.01]}(100) = 4.2 \tag{16.3.40}$$

Note that as the solution becomes more dilute the percent ionization goes up, and the 0.01 M solution is barely greater than 100K_a , given less than 5% ionized, and our shortcut is saying this in negligible.

Now lets look at 0.0001M Acetic Acid. If we used the above formula we would get 42% ionized, and so x is not insignificant compared to the initial concentration and we would need to use the quadratic formula to solve the RICE diagram.

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 16.3: Equilibrium Constants for Acids and Bases is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

16.4: Acid-Base Properties of Salts

Introduction

Salts can be neutral, acidic or basic. The ions of the salt are the conjugate base and conjugate acid of the acid and base that formed the salt, and the question is, do they react with water to form their parent base and acid?

Let's look at the generic reaction

$$\underset{acid}{HA(aq)} + \underset{base}{B(aq)} \rightleftharpoons \underset{conjugate\ acid}{BH^+(aq)} + \underset{conjugate\ base}{A^-(aq)} \tag{16.4.1}$$

So the salt (**BH^+)(A^-)** is made of the conjugate acid of B (ie., BH^+), and the conjugate base of A (ie., A^-). Noting the stronger the acid or base, the weaker it's conjugate (base or acid). Using Acid Ionization Constants (K_a, Table 16.3.1) and Base Ionization Constants (K_b, Table 16.3.2), one can calculate the conjugate acid ionization constant (K'_a) and the conjugate base ionization constant (K'_b) using the relationships $K_aK'_b = K_w$ and $K_bK'_a = K_w$

Conjugate Base Ionization Constant

Using the Acid Ionization Constants from Table

$$K_b^{'} = \frac{10^{-14}}{K_a} \tag{16.4.2}$$

Exercise 16.4.1

What is the ionization constant for acetate?

Answer

Acetate is the conjugate base of acetic acid, and from table 16.3.1 $K_a = 1.75 \times 10^{-5}$.

$$K_b^{'}(C_2H_3O_2^-) = \frac{10^{-14}}{1.75 \times 10^{-5}} = 5.71 \times 10^{-10} \tag{16.4.3}$$

Conjugate Acid Ionization Constant

$$K_a^{'} = \frac{10^{-14}}{K_b} \tag{16.4.4}$$

Exercise 16.4.2

What is the ionization constant for ammonium?

Answer

Ammonium is the conjugate acid of ammonia, and from Table 16.3.2 $K_b = 1.8 \times 10^{-5}$.

$$K_a^{'}(NH_4^+) = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \tag{16.4.5}$$

Four Types of Salt Solutions

Since acids and bases can be weak or strong there are four types of salts that can result, and these will result in neutral, acidic or basic solutions. That is, the acid can be Strong (SA) or Weak (WA) and the base can be Strong (SB) or Weak (WB).

1. **Salt of Strong Acid and Strong Base**
2. **Salt of Strong Acid and Weak Base**
3. **Salt of Weak Acid and Strong Base**
4. **Salt of Weak Acid and Weak Base**

Neutral Salt (Strong Acid/Strong Base)

Review Acid Base Conjugate pairs figure 16.3.1 for the relationship between conjugate pair strengths.

These are neutral since the anion and cation are both weak as they are the conjugates of a strong acid and strong base. That is, they are stable in water and do not react with water to form the original acid or base.

Example NaCl, which is formed by the reaction of the strong acid HCl and the strong base NaOH.

$$NaCl(aq) \rightarrow Na^(aq) + Cl^-(aq) \tag{16.4.6}$$

$$Na^+(aq) + H_2O(l) \rightarrow \text{no reaction} \tag{16.4.7}$$

$$Cl^-(aq) + H_2O(l) \rightarrow \text{no reaction} \tag{16.4.8}$$

so it is neutral



Acidic Salt (Strong Acid/Weak Base)

These are acidic since the cation is the conjugate acid of a weak base, and the weaker the base, the stronger the acid

Example: Ammonium Chloride which is formed from the reaction of HCl (strong acid) and ammonia (weak base).

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq) \tag{16.4.9}$$

$$Cl^-(aq) + H_2O(l) \rightarrow \text{no reaction} \tag{16.4.10}$$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \tag{16.4.11}$$

so it is acidic, and

$$K_a^{'}(NH_4^+) = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \tag{16.4.12}$$

YouTube Link for above video without questions.

Basic Salt (Weak Acid/Strong Base)

These are basic because the anion is the conjugate base of a weak acid

Example: Sodium fluoride is formed from the reaction of acetic acid (weak acid) and sodium hydroxide (strong base).

$$NaF(aq) \rightarrow Na^+(aq) + F^-(aq) \tag{16.4.13}$$

$$Na^+(aq) + H_2O(l) \rightarrow \text{no reaction} \tag{16.4.14}$$

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq) \tag{16.4.15}$$

$$K_b^{'}(F^-) = \frac{10^{-14}}{6.3 \times 10^{-4}} = 1.6 \times 10^{-11} \tag{16.4.16}$$



Variable A/B Salt (Weak Acid/Weak Base)

These may be acidic or basic as both the cation and the anion interact with water. If the acid that makes the salt is stronger then it is acidic, because it's conjugate base is weaker. And if the base that makes the salt is stronger, it is basic, because its conjugate is weaker.

$$NH_4F(aq) \rightarrow NH_4^+(aq) + F^-(aq) \tag{16.4.17}$$

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq) \tag{16.4.18}$$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \tag{16.4.19}$$

Noting: $K_b(NH_3) = 1.8 \times 10^{-5}$ $K_a(HF) = 6.3 \times 10^{-4}$

So $K_a(HF) > K_b(NH_3)$

and students may think it is acidic because the acid that made the salt is stronger then the base, but it is acidic because the base's conjugate (an acid) is stronger than the acid's conjugate (a base).

$$K_a'(NH_4^+) = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \tag{16.4.20}$$

$$K_b'(F^-) = \frac{10^{-14}}{6.3 \times 10^{-4}} = 1.6 \times 10^{-11} \tag{16.4.21}$$

That is, $K'a\ (NH_4^+) > K'_b(F^-)$

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 16.4: Acid-Base Properties of Salts is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

16.5: Acid-Base Equilibrium Calculations

In this section we will apply equilibrium calculations from chapter 15 to Acids, Bases and their Salts. Although RICE diagrams can always be used, there are many conditions where the extent of ionization is so small that they can be simplified. After a review of the percent ionization, we will cover strong acids and bases, then weak acids and bases, and then acidic and basic salts. We will usually express the concentration of hydronium in terms of pH.

Strong Acids

For the generic reaction of a strong acid K_a is a large number meaning it is a product favored reaction that goes to completion and we use a one way arrow.

$$HA(aq) + H_2O(l) \rightarrow H_3O^+(aq) + A^-(aq) \tag{16.5.1}$$

The acid undergoes 100% ionization, meaning the equilibrium concentration of $[A^-]_e$ and $[H_3O^+]_e$ both equal the initial Acid Concentration $[HA]_i$, and so there is no need to use an equilibrium constant.

Some **common strong acids** are **HCl, HBr, HI, HNO_3, $HClO_3$ and $HClO_4$**.

H_2SO_4 is often called a strong acid because the first proton is kicked off (K_{a1}=1x10^2), but the second is not 100% ionized (K_{a2}=1.0x10-^{2}), but it is also not weak. We will cover sulfuric acid later when we do equilibrium calculations of polyatomic acids.

NOTE: You do not need an Ionization Constant for these reactions

Exercise 16.5.1

What is the pH of 0.025M HCl?

Answer

pH = -log $[H_3O^+]_e$ = -log0.025 = 1.60

Strong Bases

Just like strong acids, strong Bases 100% ionize (K_B>>0) and you solve directly for pOH, and then calculate pH from pH + pOH =14.

There are two basic types of strong bases, soluble hydroxides and anions that extract a proton from water. Some anions interact with more than one water molecule and so there are some polyprotic strong bases.

Alkali metal hydroxides

Alkali metal hydroxides release hydroxide as their anion

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq) \tag{16.5.2}$$

Heavier alkaline earth hydroxides

Calcium, barium and strontium hydroxides are strong diprotic bases

$$Ca(OH)_2(aq) \rightarrow Ca^{+2}(aq) + 2OH^-(aq) \tag{16.5.3}$$

Soluble hydrides

Soluble hydrides release hydride ion to the water which reacts with the water forming hydrogen gas and hydroxide. This can be seen as a two step process.

$$\begin{aligned} NaH(aq) &\rightarrow Na^+(aq) + H^-(aq) \\ H^-(aq) + H_2O(l) &\rightarrow H_2(g) + OH^-(aq) \end{aligned}$$

Net Equation

$$NaH(aq) + H_2O(l) \rightarrow Na^+(aq) + H_2(g) + OH^-(aq) \tag{16.5.4}$$

Exercise 16.5.2

What is the pH of a solution made by dissolving 1.2g NaH into 2.0 liter of water?

Answer

1.2 g sodium hydride in two liters results in a 0.025M NaOH that would have a pOH of 1.6. From that the final pH is calculated using pH + pOH = 14.

$$\frac{(1.2gNaH)}{2.0L}\left(\frac{molNaH}{24.0g}\right)\left(\frac{molOH^-}{molNaH}\right)=0.025MOH^-$$
$$pOH=-log0.025=1.60$$
$$pH=14-pOH=14-1.60=12.40$$

Note this could have been done in one step

$$pH=14+log(\frac{(1.2gNaH)}{2.0L}\left(\frac{molNaH}{24.008g}\right)\left(\frac{molOH^-}{molNaH}\right))=12.40$$

Soluble oxides

Soluble oxides are diprotic and react with water very vigorously to produce two hydroxides. For example CaO reacts with water to produce aqueous calcium hydroxide. This reaction has been used in chemical heaters and can release enough heat to cause water to boil.

$$CaO(aq)\rightarrow Ca^{+2}(aq)+O^{-2}(aq)$$
$$O^{-2}(aq)+H_2O(l)\rightarrow 2OH^-(aq)$$

Net Equation

$$CaO(aq)+H_2O(l)\rightarrow Ca^{+2}+2OH^-(aq) \tag{16.5.5}$$

Exercise 16.5.3

What is the pH of a solution made by dissolving 1.21g calcium oxide to a total volume of 2.00 L?

Answer

$$\frac{(1.21gCaO)}{2.00L}\left(\frac{molCaO}{56.08g}\right)\left(\frac{2molOH^-}{molCaO}\right)=0.0216MOH^-$$
$$pOH=-\log 0.0216=1.666$$
$$pH=14-1.666=12.334$$

Note this could have been done in one step

$$pH=14+log(\frac{(1.21gCaO)}{2.00L}\left(\frac{molCaO}{56.08g}\right)\left(\frac{2molOH^-}{molCaO}\right))=12.334$$

Soluble nitrides

Soluble nitrides are triprotic, nitrides (N^{-3}) react very vigorously with water to produce three hydroxides. For example Li_3N reacts with water to produce aqueous lithium hydroxide and ammonia. This is a violent reaction, which makes sense as the [-3] charge is going to have a very strong pull on the hydrogens as it forms ammonia.

$$Li_3N(aq)\rightarrow 3Li^+(aq)+N^{-3}(aq)$$
$$N^{-3}(aq)+3H_2O(l)\rightarrow 3OH^-(aq)+NH_3(aq)$$

Net Equation

$$Li_3N(aq)+3H_2O(l)\rightarrow 3Li^+(aq)+3OH^-(aq)+NH_3(aq) \tag{16.5.6}$$

Exercise 16.5.4

What is the pH of a solution made by dissolving 1.2g lithium nitride to a total volume of 2.0 L?

Answer

$$\frac{(1.2gLi_3N)}{2.0L}\left(\frac{molLi_3N}{34.83g}\right)\left(\frac{3molOH^-}{molLi_3N}\right)=0.0517MOH^-$$
$$pOH=-log0.0517=1.29$$
$$pH=14-1.29=12.71$$

Note this could have been done in one step

$$pH=14+log(\frac{(1.2gLi_3N)}{2.0L}\left(\frac{molLi_3N}{34.83g}\right)\left(\frac{3molOH^-}{molLi_3N}\right))=12.71$$

Weak Acids

There are two types of weak acid calculations, and these are analogous to the two type of equilibrium calculations we did in sections 15.3 and 15.4.

- Type 1: Determine K_a for an unknown acid from initial concentration and final concentration of one species, typically hydrogen, as defined by the pH. This is analogous to the work in section 15.3, except that it is applied to acids.
- Type2: Calculate final pH from initial concentration and K_a. This is analogous to section15.4 but is applied only to acids, and we will look for simplifications of the RICE diagram so we do not have to solve the quadratic equation.

Calculating K_a

In these problems you typically calculate the K_a of a solution of known molarity by measuring it's pH. You will want to be able to do this without a RICE diagram, but we will start with one for illustrative purpose.

$$HA \rightleftharpoons H^+ + A^- \tag{16.5.7}$$

Starting with an ICE diagram.

	HA	H^+	A^-
Initial	$[HA]_i$	0	0
Change	-x	+x	+x
Equilibrium	$[HA]_i$-x	x	x

From the ice diagram it is clear that

$$K_a = \frac{x^2}{[HA]_i - x} \tag{16.5.8}$$

and you should be able to derive this equation for a weak acid without having to draw the RICE diagram. Noting that $x = 10^{-pH}$ and substituting, gives

$$K_a = \frac{(10^{-pH})^2}{[HA]_i - 10^{-pH}} \tag{16.5.9}$$

Predicting pH

The second type of problem is to predict the pH of a weak acid solution if you know K_a and the acid concentration. K_a values for many weak acids can be obtained from table 16.3.1 There are two cases

- Case I: **[HA]>100 K_a** , then $H^+ = \sqrt{K_a[HA]_i}$ and $pH = -log\sqrt{K_a[HA]_i}$
  - In this case the percent ionized is small and so the amount ionized is negligible to the initial acid concentration. This shortcut used the complete the square technique and its derivation is below in the section on percent ionization, as it is only legitimate if the percent ionization is low.
- Case2: HA$\not>$100K_a , in which case you need to solve the quadratic equation of the RICE diagram for x, noting x = $[H^+]$.
  - In this case the percent ionized is not negligible, and you can not use the approximation used in case 1. Review section 15.4 for case 2 problems.

Note, the approximation [HA]>K_a is usually valid for two reasons, but realize it is not always valid.

1. "Weak" in "weak acid" means K_a is small. That is the definition of a weak acid, (and a strong acid has a large K_a).
2. Most acid concentrations in the real world are larger than K_a values, and there is a limit to how dilute an acid can get and still affect the pH. That is, as you dilute an acid the pH rises, but you can not raise it above 7, the value of neutral water. (Even strong acids have no effect when their concentration is below 10^{-7}M.

Percent Ionization

The "Case 1" shortcut $[H^+] = \sqrt{K_a[HA]_i}$ avoided solving the quadratic formula for the equilibrium constant expression in the RICE diagram by removing the "-x" term from the denominator and allowing us to "complete the square". This is only valid if the percent ionization is so small that x is negligible to the initial acid concentration. We said this is acceptable if 100K_a <$[HA]_i$. We will now look at this derivation, and the situations in which it is acceptable.

$$K_a = \underbrace{\frac{x^2}{[HA]_i - x} \approx \frac{x^2}{[HA]_i}}_{\text{true if x<<}[HA]_i} \tag{16.5.10}$$

solving the simplified version for x and noting that $[H^+]$=x, gives:

$$x^2 = K_a[HA]_i$$
$$x = \sqrt{K_a[HA]_i}$$
$$[H^+] = \sqrt{K_a[HA]_i} \tag{16.5.11}$$

To understand when the above shortcut is valid one needs to relate the percent ionization to the $[HA]_i > 100K_a$ rule of thumb.

Percent Ionization %I:

$$\%I = \frac{x}{[HA]_i} = \frac{[A^-]}{[HA]_i}100 \tag{16.5.12}$$

One way to understand a "rule of thumb" is to apply it. Table 16.5.2 tabulates hydronium concentration for an acid with $K_a=10^{-4}$ at three different concentrations, where $[HA]_i$ is greater than, less than or equal to 100 K_a. What is important to understand is that under the conditions for which an approximation is valid, and how that affects your results. In condition 1, where the approximation is valid, the short cut came up with the same answer for percent ionization (to three significant digits). In column 2 which was the limit, there was an error of .5% in percent ionization and the answer was valid to one sig. fig. but in case 3, which was clearly not valid, you got a completely different answer. To get a real feel for the problems with blindly applying shortcuts, try exercise 16.5.5, where $[HA]_i << 100K_a$ and the answer is complete nonsense.

Column	Relative magnitudes of $[HA]_i$ to $K_a=10^{-4}$	% Ionization (rounded to three significant figures)
1	$[HA]_i > 100K_a$	0.990
2	$[HA]_i = 100K_a$	0.990

3	$[HA]_i < 100K_a$

Table16.5.2 Comparison of hydronium ion and percent ionizations for various concentrations of an acid with K $K_a=10^{-4}$. In the above table, $H^+ = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$ became $H^+ = \frac{-K_a \pm \sqrt{(K_a)^2+4K_a[HA]_i}}{2a}$. Note complete the square gave a nonsense answer for row three, as the criteria that $[HA]_i$ >100K_a was not valid.

One other trend comes out of this table, and that is that the **percent ionization goes up and concentration goes down**.

Exercise 16.5.5

When $[HA]_i$ >100K_a it is acceptable to use $[H^+] = \sqrt{K_a[HA]_i}$. Use this equation to calculate the percent ionization for a 1x10^{-6}M solution of an acid with a K_a = 1x10^{-4}M, and discuss (explain) the answer.

Answer

$$[H^+] = \sqrt{10^{-4}10^{-6}} = 10^{-5}$$

$$\%I = \frac{x}{[HA]_i} = \frac{[A^-]}{[HA]_i}100$$

$$\frac{10^{-5}}{10^{-6}}100 = 1,000\%$$

The above answer is obvious nonsense and the reason is that the initial acid concentration greater than 100 times the ionization constant, in fact, it was less. So the percent ionization was not negligible and this problem had to be solved with the quadratic formula.

Exercise 16.5.6

What is the pH if 10.0 g Acetic Acid is diluted to 1.00 L?

Answer

From table 16.3.1 the value of K is determined to be 1.75x10^{-5} ,and acetic acid has a formula weight of 60.05g/mol, so

$$[HC_2H_3O_2] = \left(\frac{10.0gHC_2H_3O_2}{1.00L}\right)\left(\frac{molHC_2H_3O_2f}{60.05g}\right) = 0.167M$$

$$pH = -log\sqrt{1.75x10^{-5}[0.167]} = 2.767. \quad (16.5.13)$$

Weak Bases

There are two types of weak base calculations, and these are analogous to the two type of equilibrium calculations we did in sections 15.3 and 15.4.

- Type 1: Determine K_b for an unknown base from initial concentration and final concentration of one species, Typically the final concentration is expressed in terms of pH, but the equilibrium involves hydroxide not hydronium, and so you use the relationship pH+pOH=14, or $[H_3O^+][OH^-]=10^{-14}$ to relate hydroxide to hydronium.
- Type2: Calculate final pH or pOH from initial concentrations and K_b. This is analogous to section15.4 but is applied only to bases, and we will look for simplifications of the RICE diagram so we do not have to solve the quadratic equation.

Calculating K_b

In these problems you typically calculate the K_a of a solution of know molarity by measuring it's pH. You will want to be able to do this without a RICE diagram, but we will start with one for illustrative purpose.

$$B + H_2O \rightleftharpoons BH^+ + OH^- \quad (16.5.14)$$

We will start with an ICE diagram, note, water is omitted from the equilibrium constant expression and ICE diagram because it is the solvent and thus its concentration is so much greater than the amount ionized, that it is essentially constant. This is similar to what we did in heterogeneous equilibiria where we omitted pure solids and liquids from equilibrium constants, but the logic is different (this is a homogeneous equilibria and water is the solvent, it is not a separate phase).

	B	BH^+	OH^-
Initial	$[B]_i$	0	0
Change	-x	+x	+x
Equilibrium	$[B]_i$-x	x	x

From the ice diagram it is clear that

$$K_b = \frac{x^2}{[B]_i - x} \tag{16.5.15}$$

and you should be able to derive this equation for a weak acid without having to draw the RICE diagram.

Noting that $x = 10^{-pOH}$ and substituting, gives

$$K_b = \frac{(10^{-pOH})^2}{[B]_i - 10^{-pOH}} \tag{16.5.16}$$

Note, if you are given pH and not pOH, you simple convert to pOH, pOH=14-pH and substitute.

Predicting pOH

The second type of problem is to predict the pH or pOH for a weak base solution if you know K_b and the initial base concentration. K_b values for many weak bases can be obtained from table 16.3.2 There are two cases

- Case I: **[B]>100 K_b** , then $OH^- = \sqrt{K_b[B]_i}$ and $pOH = -log\sqrt{K_b[B]_i}$
  - In this case the percent ionized is small and so the amount ionized is negligible to the initial base concentration
- Case2: B$\not>$100K_b , in which case you need to solve the quadratic equation of the RICE diagram for x, noting x = $[OH^-]$.
  - In this case the percent ionized is not negligible, and you can not use the approximation used in case 1. Review section 15.4 for case 2 problems.

Note, the approximation [B]>K_b is usually valid for two reasons, but realize it is not always valid.

1. "Weak" in "weak base" means K_b is small. That is the definition of a weak base, (and a strong base has a large K_b).
2. Most base concentrations in the real world are larger than K_b values, and there is a limit to how dilute a base can get and still affect the pH (or pOH), as it can not reduce the pH below 7, the value of neutral water. (Even strong bases have no effect when their concentration is below 10^{-7}M.)

Exercise 16.5.7

What is the pH if 10.0 g Methyl Amine (CH_3NH_2) is diluted to 1.00 L? (Obtain K_b from Table 16.3.1)

Answer

From Table 16.3.1 the value of K_b is determined to be $4.6x10^{-4}$,and methyl amine has a formula weight of 31.053 g/mol, so

$$[CH_3NH_2] = \left(\frac{10.0g[CH_3NH_2}{1.00L}\right)\left(\frac{mol[CH_3NH_2}{31.053g}\right) = 0.322M$$

$$pOH = -log\sqrt{4.6x10^{-4}[0.322]} = 1.92 \tag{16.5.17}$$

$$pH = 14 - 1.92 = 12.08.$$

pH of Basic Salts

Salts of a weak acid and a strong base form basic solutions because the conjugate base of the weak acid removes a proton from water. in section 16.4.2.3 we determined how to calculate the equilibrium constant for the conjugate base of a weak acid. The example of sodium fluoride was used, and it was noted that the sodium ion did not react with water, but the fluoride grabbed a proton and formed hydrofluoric acid. We used the relationship $K_aK_b' = K_w$ for a acid/ conjugate base pair (where the prime designates the conjugate) to calculate the ionization constant for the anion. So there is a second step to these problems, in that you need to determine the ionization constant for the basic anion of the salt.

so

$$K_b' = \frac{10^{-14}}{K_a} \tag{16.5.18}$$

If $[A^-]_i > 100K_b'$, then:

$$[OH^-] = \sqrt{K_b'[A^-]_i} = \sqrt{\frac{K_w}{K_a}[A^-]_i} \tag{16.5.19}$$

$$pOH = -log\left(\sqrt{\frac{K_w}{K_a}[A^-]_i}\right)$$

$$pH = 14 - pOH$$

$$pH = 14 + log\left(\sqrt{\frac{K_w}{K_a}[A^-]_i}\right)$$

Exercise 16.5.8

What is the pH of a 0.100 M solution of sodium hypobromite? You can get K_a for hypobromous acid from Table 16.3.1 .

Answer

First calculate the hypobromite ionization constant, noting $K_aK_b' = K_w$ and $K^a = 2.8x10^{-9}$ for hypobromous acid

$$K_b' = \frac{10^{-14}}{K_a} = \frac{10^{-14}}{2.8x10^{-9}} = 3.6x10^{-6} \tag{16.5.20}$$

Since $[Br^-] < 100K_a$

$$p[OH^-] = -log\sqrt{(3.6x10^{-6})(0.100)} = 3.22 \tag{16.5.21}$$

$$pH = 14 - pOH = 14 - 3.22 = 11$$

pH of Acidic Salts

Salts of a weak base and a strong acid form acidic solutions because the conjugate acid of the weak base protonates water. In section 16.4.2.2 we determined how to calculate the equilibrium constant for the conjugate acid of a weak base. The example of ammonium chlorides was used, and it was noted that the chloride ion did not react with water, but the ammonium ion transferred a proton to water forming hydronium ion and ammonia. The equilibrium constant for the acidic cation was calculated from the relationship $K_a'K_b = K_w$ for a base/ conjugate acid pair (where the prime designates the conjugate).

The calculation of the pH for an acidic salt is similar to that of an acid, except that there is a second step, in that you need to determine the ionization constant for the acidic cation of the salt from the basic ionization constant of the base that could have formed it.

so

$$K_a' = \frac{10^{-14}}{K_b} \tag{16.5.22}$$

If $[BH^+]_i > 100K_a'$, then:

$$[H^+] = \sqrt{K_a'[BH^+]_i} = \sqrt{\frac{K_w}{K_b}[BH^+]_i} \tag{16.5.23}$$

$$pH = -log\sqrt{\frac{K_w}{K_b}[BH^+]_i}$$

Exercise 16.5.9

What is the pH of a 0.100 M solution of hydroxylammonium chloride (NH_3OHCl), the chloride salt of hydroxylamine? You can get Kb for hydroxylamine from Table 16.3.2 .

Answer

First calculate the hydroxylammonium ionization constant, noting $K_a'K_b = K_w$ and $K_b = 8.7x10^{-9}$ for hydroxylamine.

$$K_a' = \frac{10^{-14}}{K_b} = \frac{10^{-14}}{8.7x10^{-9}} = 1.1x10^{-6} \tag{16.5.24}$$

Since $[NH_3OH^+] < 100K_a$

$$p[H^+] = -log\sqrt{(1.1x10^{-6})(0.100)} = 3.50 \tag{16.5.25}$$

pH of Polyprotic Acids

In section 15.1.2.2 we discussed polyprotic acids and bases, where there is an equilbiria existing between the acid, the acid salts and the salts. In a diprotic acid there are two species that can protonate water, the acid itself, and the ion formed when it loses one of the two acidic protons (the acid salt anion). Generically, this can be described by the following reaction equations:

$$H_2A(aq) + H_2O)l) \rightleftharpoons HA^-(aq) + H_3O^+(aq), \text{ where } K_{a1} = \frac{[HA^-][H_3O^+]}{H_2A} \tag{16.5.26}$$

$$HA^-(aq) + H_2O(l) \rightleftharpoons A^{-2}(aq) + H_3O^+(aq), \text{ where } K_{a2} = \frac{[A^-2][H_3O^+]}{HA^-} \tag{16.5.27}$$

Note, in the first equation we are removing a proton from a neutral molecule while in the second we are removing it from a negative anion. As the protons are being removed from what is essentially the same compound, coulombs law indicates that it is tougher to remove the second one because you are moving something positive away from a negative anion. This means the second ionization constant is always smaller than the first. Another way to look at that is through the back reaction. Would the proton be more attracted to HA^- or A^{-2}? As the attraction for the minus two is greater than the minus 1, the back reaction of the second step is greater, indicating a small K. So,

$$K_{a1} > K_{a2} \tag{16.5.28}$$

Note, not only can you determine the concentration of H^+, but also OH^-, H_2A, HA^- and A^{-2}.

Rule of Thumb: If $K_{a1} > 1000K_{a2}$ you can ignore the second ionization's contribution to the hydronium ion concentration, and if $[HA]_i > 100K_{a1}$ the problem becomes fairly simple.

Consider H_2A:

Only the first ionization contributes to the hydronium ion concentration as the second ionization is negligible.

For first ionization

$H_2A(aq) + H_2O(l) \rightleftharpoons HA^-(aq) + H_3O^+(aq)$			
	H_2A	HA^-	H_3O^+
Initial	$[H_2A]_i$	0	0
Change	-x	+x	+x
Equilibrium	$[H_2A]_i$-x	x	x

Since $K_{a1} > 1000K_{a2}$ the acid salt anion HA^- and H_3O^+ concentrations come from the first ionization. That is, the amount of the acid salt anion consumed or the hydronium ion produced in the second step (below) is negligible and so the first step determines these concentrations.

$$[H^+] = [HA^-] = \sqrt{K_{a1}[H_2A]_i} \tag{16.5.29}$$

Knowing hydronium we can calculate hydorixde"

$$[OH^-] = \frac{K_w}{[H^+]} \tag{16.5.30}$$

Since the second ionization is small compared to the first, we can also calculate the remaining diprotic acid after the first ionization

$$[H_2A]_e = [H_2A]_i - x \tag{16.5.31}$$

For the second ionization we will use "y" for the extent of reaction, and "x" being the extent of reaction which is from the first ionization, and equal to the acid salt anion and the hydronium cation (from above)

$HA^-(aq) + H_2O(l) \rightleftharpoons A^{-2}(aq) + H_3O^+(aq)$			
	HA^-	A^{-2}	H_3O^+
Initial	x	0	x
Change	-y	+y	+y
Equilibrium	x-y	y	x+y

$$
\begin{aligned}
K_{a2} &= \frac{[A^{-2}][H_3O^+]}{HA^-} \\
&= \underbrace{\frac{[x+y][y]}{[x-y]} \approx \frac{[x][y]}{[x]}}_{\text{negliible second ionization (y<<x)}} \\
K_{a2} &= y \\
\therefore & \\
[A^{-2}] &= K_{a2}
\end{aligned}
\tag{16.5.32}
$$

Exercise 16.5.10

Calculate the concentration of all species in 0.50 M carbonic acid. See Table 16.3.1 for Acid Ionization Constants.

Answer

From Table 16.3 $K_{a1} = 4.5x10^{-7}$ and $K_{a2} = 4.7x10^{-11}$. So both $[H_2A]_i$ 100>K_{a1} and K_{a1} >1000K_{a2} .

$$[H^+] = [HA^-] = \sqrt{K_{a1}[H_2A]_i}$$

$$= \sqrt{(4.5x10^{-7})(0.50)} = 4.7x10^{-4}M$$

$$[OH^-] = \frac{10^{-14}}{4.74x10^{-4}} = 2.1x10^{-11}M$$

$$[H_2A]_e = 0.5 - 0.00047 = 0.50$$

$$[A^{-2}] = K_{a2} = 4.7x10^{-11}M$$

Contributors and Attributions

- Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 16.5: Acid-Base Equilibrium Calculations is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

16.6: Molecular Structure, Bonding, and Acid-Base Behavior

Introduction

When looking at acid base behavior there are several principles one needs to consider before proceeding. First, all reactions are in theory reversible, and so one should always look at the back reaction, that is the reaction of the conjugates, even if it does not occur. Is the conjugate stable? Does it have a stable or reactive structure? One should also look at charge distribution as it clearly influences reactivity. So you are sort of looking at two things, how stable a species is (what structures and feature lead to nonreactivity) and how unstable a species is (what structures and features lead to an unstable species that is going to react).

The second thing is sort of common sense, but worth stating. The stronger the bond that holds hydrogen to an atom, the weaker the acid. That is, weakly bonded hydrogens are more acidic than strongly bonded ones.

Binary compounds of hydrogen

Binary compounds are compounds between two different types of elements, and can consist of more than two atoms. Binary compounds with hydrogen can be acidic (proton donors), basic (proton acceptors), or not show acidic or basic properties. The behavior is defined by the direction of the dipole moment, as indicated in figure 16.6.1, where acidic compounds occur when hydrogen is attached to something more electronegative and basic compounds occur when the bond is to something less electronegative.

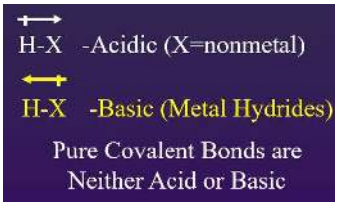


Figure16.6.1: Rule of thumb showing acidity/basicity as a function of polarity. Note, basic hydrides are when you have an ionic compound.

Basic Hydrides

Basic hydrides occur when hydrogen is attached to a highly electropositive element where the difference in electronegativity is great enough to form an ionic compound (review section 8.7.2). That is, when it forms the hydride ion H^-. Soluble hydrides are strong bases (review section 16.5.3.1), and the basicity can be viewed as a property of fact that the small hydride ion is very reactive and grabs a proton from water.

$$H^-(aq) + H_2O(aq) \rightarrow H_2(g) + OH^-(aq) \tag{16.6.1}$$

It needs to be emphasized that hydride is a reactive anion, and so any water soluble hydride will release hydride that can react with water to form hydrogen and hydroxide. These are strong bases.

Acidic Hydrides

These occur when a hydrogen atom is attached to a nonmetal, where the more electronegative nonmetal pulls electron density from the hydrogen making it more positive and thus potentially more reactive. But there is no one factor alone that defines the acid strength of a hydride, although there are some periodic trends we can see, and these can be understood in terms of trends in electronegativity and bond strength, noting the latter can often be correlated to bond lengths and the sizes of atoms.

Periodic Trend for Acidic Hydrides

Figure 16.6.2 shows the ionization constants for non-metal binary hydrides and two periodic trends become obvious. Note, the hydrides in red have large ionization constants and so are considered as strong acids.

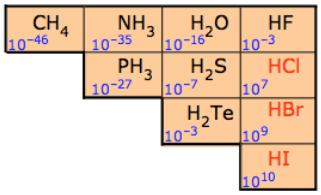


Figure16.6.2:Periodic trends acid strength in terms of equilibrium constants

1. Going across a period the acid strength increases as there is an increase in electronegativity and the molecule gets more polar, with the hydrogen getting a larger partial positive charge. Note, ammonia is a base and actually accepts protons, and methane is symmetric

2. Going down a group the acid strength increases because the bond strength decreases as a function of increasing size of the nonmetal, and this has a larger effect than the electronegativity. In fact HF is a weak acid because it is so small that the hydrogen-fluorine bond is so strong that it is hard to break. Remember, the weaker the bond, the strong the acid strength. This is further illustrated in figure 16.6.3 where the weakest bond has produces the strongest acid.

Relative Acid Strength	HF	<<	HCl	<	HBr	<	HI
H–X Bond Energy (kJ/mol)	570		432		366		298
K_a	10^{-3}		10^{7}		10^{9}		10^{10}

Table16.6.1Acid strength as function of bond energy

Binary Compounds of Oxygen

Binary compounds of oxygen involving metals are basic and known as basic anhydrides, while binary compounds of oxygen with nonmetals are acidic and known as acid anhydrides.

Basic Anhydrides

In section 16.5.2.4 we noted that soluble metal oxides are strong bases and release the oxide ion (O^{-2}) into water and that pulls a proton from the water

$$O^{-2}(aq) + H_2O(l) \rightarrow 2OH^-(aq) \tag{16.6.2}$$

$$and$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

So a metal oxide like CaO can be viewed as $Ca(OH)_2$ with the water removed. Note we used the word "soluble" and many oxides are insoluble, as we shall see in the next chapter (for example, the equilibrium constant for the solubility of aluminum oxide is 1.9×10^{-33} and so it is not a strong base because it does not dissolve). But soluble metal oxides are strong bases because the oxide pulls a proton from the water.

Acid Anhydrides

Acid anhydrides react with water to form oxyacids. This is an important class of acids, where the oxygens are attached to a nonmetal and the acidic hydrogens are attached to the oxygen. This also explains the origins of acid rain, and as nonmetal oxides are formed in the combustion process and can then combine with atmospheric water.

$$\text{nonmetal oxide} + \text{water} \rightleftharpoons \text{oxyacid} \tag{16.6.3}$$
$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \tag{16.6.4}$$
$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq) \tag{16.6.5}$$
$$SO_3(g) + H_2O(l) \rightleftharpoons H_2SO_4(aq) \tag{16.6.6}$$
$$N_2O_3(g) + H_2O(l) \rightleftharpoons 2HNO_2(aq) \tag{16.6.7}$$
$$N_2O_5(l) + H_2O(l) \rightleftharpoons 2HNO_3(aq) \tag{16.6.8}$$

Note, 79% of the atmosphere is nitrogen and the dominant combustion biproduct of nitrogen is NO, with smaller amounts of N_2O and NO_2. The NO is further oxidized to NO_2, and the NO and NO_2, combine to form N_2O_3, which is the acid anhydride of nitrous acid. So nonmetal oxides produce oxyacids in nature and these are an important class of acids that you need to be familiar with.

Oxyacids

Oxyacids are compounds of the general formula H_nXO_m, where X is a nonmetal and the acidic hydrogens are attached to oxygen (not the nonmetal). As seen above, these can be formed by the reaction of nonmetal oxides with water. There are two trends on the acid strength of Oxyacids that you need to be familiar with.

1. Homologous structure (nonmetals of the same periodic group that have identical numbers of H and O)
2. Structures with the same central atom that have varying numbers of oxygens.

These, along with the binary hydrides are often referred to as inorganic acids, in contrast to the carboxylic acids (see below), which are often referred to as organic acids.

Oxyacids with Homologous Structures

These are structures of the same formula but different nonmetals, like hypochlorous, hypobromous and hypoiodous acids (HClO, HBrO & HIO, with the generic structure of HXO, where X is a halogen). Now note, we write the acidic hydrogen first because it is like the cation of an analogous salt, but it is really covalently bonded to the oxygen and not the nonmetal (X), so the structure is of the form H-O-X. What is important to note here is that the acidic bonds that need to be broken are all between hydrogen and oxygen, and so are of the same basic bond length, and the strength is influenced by the electronegativity of X's ability to pull electron density towards it. This is called an inductive effect as the nonmetal's electronegativity induces the effect across the oxygen and makes the oxygen-hydrogen bond more polar. Thus the trend is increasing strength in the direction of increasing electronegativity.

HOX	Electronegativity of X	K_a
HOCl	3.0	4.0×10^{-8}
HOBr	2.8	2.8×10^{-9}
HOI	2.5	3.2×10^{-11}

Table16.6.2: Relationship of electronegativity to acid ionization constant. Note this is an inductive effect, and unlike the binary hydride, the hydrogen is not bonded to the nonmetal, with the result that the trend is the opposite of the trend in table 16.6.1.

HClO>HBrO>HIO (table 16.6.2)
HI>HBr>HCl>>HF (table 16.6.1)

Oxyacids with Same Central Atom

Here we are looking at the trend for acids like perchloric, chloric, chlorous and hypochlous, and see the greater the number of oxygens the stronger the acid. This can be explained in several ways. The most valid deals with the inductive effect, where oxygen is the second most electronegative element, and so the more oxygens attached to the nonmetal of the acid, the greater their pull on electron density across the OH bond, and the more polar the bond. This can be seen in figure 16.6.3.

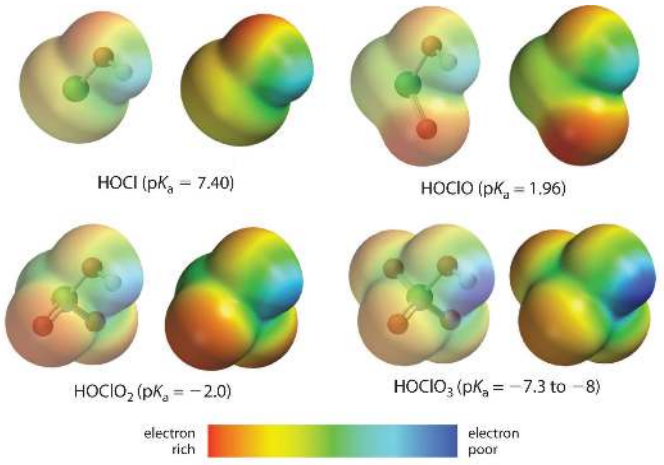


Figure16.6.3: Increasing number of oxygens increases K_a as evidenced by the decreased electron density on the acidic hydrogen (which is most blue in $HClO_4$). Note, $K_a = 10^{-pK_a}$, and so the larger pK_a , the smaller K_a .

Another facet deals with the stability of the conjugate anion, that is, how strong is the back reaction. For example, in hypochlorite (ClO^-), the negative charge is spread over two nuclei and is thus more concentrated than in other oxyanions of chlorine, like perchlorate (ClO_4^-), where it is spread out over 5 nuclei. This increased charge density makes the back reaction stronger in hypochlorite than perchlorate, and so the forward reaction would be weak, making perchlorate stronger in the forward direction.

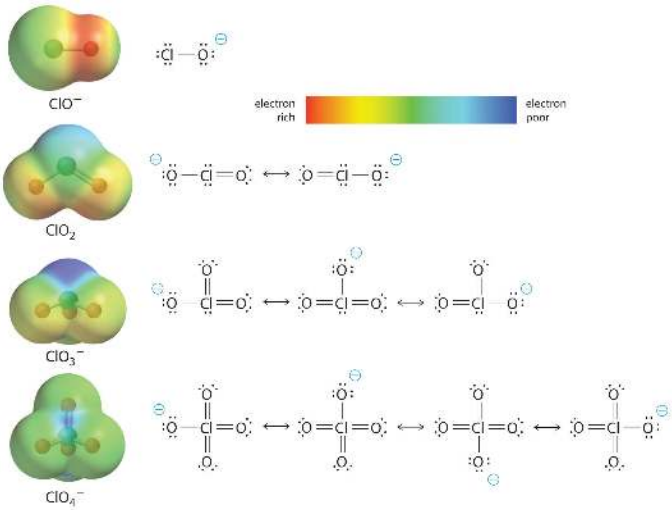


Figure16.6.4: This figure shows two things. First, the larger the ion the more dispersed the charge and thus the less the charge density, making the perchlorate the more stable anion. The second argument this image puts forth is that the greater the number of resonance structures the more dispersed the charge density, which is correct, but I would argue against the resonance structures as drawn. These structures follow the lowest formal charge of the chlorine, but invoke pi bonds when there are no unhybridized p orbitals to make them. This is an interesting issue that chemist argue about, and represent a shortcoming of Lewis dot structures.

Carboxylic Acids

Many organic acids have the carboxylic acid functional group (COOH) that is important to be able to identify. In gen chem 1 you were required to memorize several of these, like acetic acid, oxalic acid and phthalic acid.

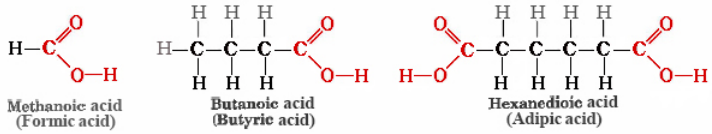


Figure16.6.5: Some organic acids that show the caboxylic acid group in red. Note, Adipic acid is a diprotic acid because it has two carboxylic groups. The hydrogens in black are strongly held and not acidic, while the ones in red are acidic.

https://chem.libretexts.org/@go/page/60748

Resonance Stabilization

Resonance structures are a shortcoming of Lewis dot structures that treat a bond as an electron pair shared between two nuclei, and if electrons are shared between more than two nuclei, you need to draw a resonance structure. If the species is an ion, and the charge can be distributed across multiple nuclei, the charge density is lowered and species is more stable. Figure 16.6.5 shows this effect for the carboxylate ion of the back reaction, where in truth the charge of the extra electron is delocalized over three nuclei (the carbon and the two oxygens) via a pi bond that is represented by both resonance structures. This means the ion is more stable (less reactive), making the back reaction weaker, and thus the forward reaction stronger.

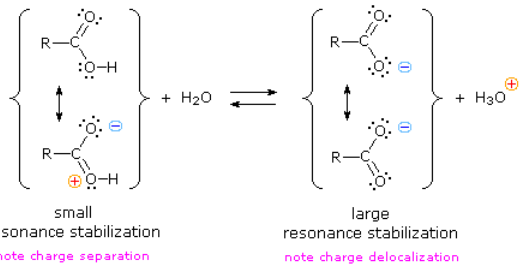


Figure16.6.5: Illustration of effect of resonance structures on carboxylic acid/carboxylate reactions.

It is important to remember that when looking at chemical structure of an acid, you also need to look at its conjugate base. In this example, the carboxylate group on the product side (conjugate base of the weak carboxylic acid) is stabilized by charge delocalization, making the back reaction weaker, and thus contributes to increasing acid strength (the forward reaction).

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 16.6: Molecular Structure, Bonding, and Acid-Base Behavior is shared under a CC BY-NC-SA 3.0 license and was authored, remixed, and/or curated by Robert Belford.

16.7: Lewis Concept of Acids and Bases

Introduction

Lewis Acid base theory is more general than the Bronsted-Lowery theory, and will be used extensively in organic chemistry. A Lewis acid is defined as an electron pair acceptor, and a Lewis base as an electron pair donor.

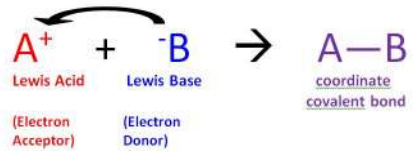


Figure16.7.1: General schema for Lewis acid base reaction.

- Lewis Acid: a species that accepts an electron pair (i.e., an electrophile) and will have vacant orbitals, or the ability to form a vacant orbital.
- Lewis Base: a species that donates an electron pair (i.e., a nucleophile) and will have lone-pair electrons

In a Lewis Acid Base reaction a bond is formed where both electrons come from the Lewis base, and this is called a coordinate covalent bond (or dative covalent bond).

Lewis Acids

There are three general types of Lewis Acids, that is, chemical species that can accept electrons.

1. Molecules with an incomplete octet
2. Molecules with double bonds
3. metal ions with vacant d-orbitals.

Incomplete Octets

Boron Trifluoride is an exception to the octet rule and has an incomplete octet, and can thus accept electrons to form a bond. In the process it goes from sp^2 hybrid to sp^3 hybrid.

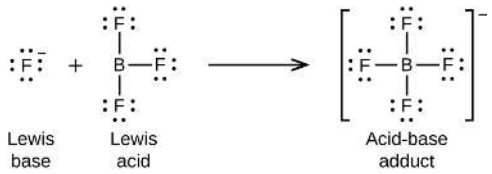


Figure16.7.2: General reaction scheme where a molecule with an incomplete octet functions as a Lewis Acid

Double Bonds

A double bond has 4 electrons shared between 2 atoms in a PI and sigma orbital. If you break the pi bond and move the two electrons to a non-bonding orbital on one atom, the other atom develops an incomplete octet and can function as a Lewis acid. This is shown in figure 16.7.3 where the pi electrons move onto the oxygen, allowing the sulfur to receive electrons from a Lewis base.

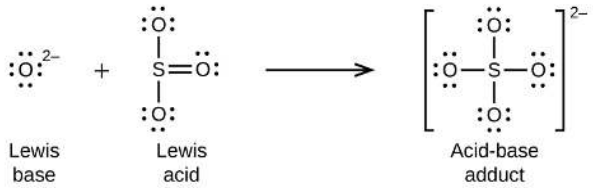


Figure16.7.3: General reaction scheme where a molecule with a double bond functions as a Lewis Acid

Metal Cations

Many metals have vacant d-orbitals that can accept electrons and thus behave as Lewis Acids. In fact, most metals react with water when they dissolve in water to form what is called a complex ion. For example, aluminum(III) is not a free ion, but a complex with 6 water molecules. Complex ions can be highly colored and will be covered in a later section of this text.

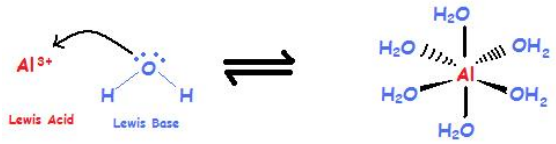


Figure16.7.4: General reaction scheme where a molecule with a double bond functions as a Lewis Acid

Lewis Bases

Lewis bases are molecules that have a lone pair of electrons that can be donated to a coordinate covalent bond. If you look at the Lewis dot structure of the bases in table 16.3.2 you will see that all of those bases have a nitrogen with a lone pair of electrons. This is the electron donor that forms the coordinate covalent bond. If the electron donor is a proton, then it is also a Bronsted base (proton acceptor).

Lewis Acid Base Reactions

Lewis acid base reactions involve the formation of a coordinate covalent bond between the Lewis Acid (that accepts the electrons), and the Lewis base (that donates the electrons). Bronstead acid/base reactions are a subset of Lewis acid/base reactions where the coordinate covalent bond is formed with a proton accepting the electrons (Lewis Acid electron acceptor/ Bronstead Acid proton donor) from the base (Lewis Base electron donor/Bronstead proton acceptor). In the Bronstead acid/base theory a proton is transferred from the base to the acid, causing the charge to change of the subsequent conjugate acid and base, which in turn can form salts. Lewis acid base theory extends the concept of acid base reactions beyond this paradigm and is useful in predicting where bonds will form in many types of synthesis reactions. It should also be noted that the most primitive concept of acid/base reaction is the Arrhenius, which in itself is a subset of the Bronstead concept, involving the equilibrium of hydronium and hydroxide ion concentrations within water. So Lewis acid/base concept is the most general of the three concepts we use in describing acid base reactions.

The following animation should help make clear the types of Lewis acid/base reactions you are required to know and demonstrates how the Bronstead acid/base concept is a subset of the more general Lewis acid/base concept.



Video16.7.1: 1:31 YouTube uploaded by Douglas Mulford describing the above types of Lewis Acid base Reactions (https://youtu.be/6b3xELvF_ns).

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has

both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 16.7: Lewis Concept of Acids and Bases is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

CHAPTER OVERVIEW

17: Aqueous Equilibria

Topic hierarchy

17.1: Common Ion Effect
17.2: Controlling pH- Buffer Solutions
17.3: Acid-Base Titrations
17.4: Solubility of Salts
17.5: Precipitation Reactions
17.6: Equilibria Involving Complex Ions
17.7: Solubility and Complex Ions

This page titled 17: Aqueous Equilibria is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

17.1: Common Ion Effect

The common ion effect is an application of Le Chatelier's Principle to the equilibrium concentration of ionic compounds. We will look at two applications of the common ion effect.

Application 1: Equilibrium of Acid/Base Buffers

Type 1: Weak Acid/Salt of Conjugate base

$$HA \leftrightharpoons H^+ + A^- \tag{17.1.1}$$

Le Chatelier's Principle states that if we added the conjugate base of a weak acid to a solution of the weak acid the equilibrium would move to the left to consume that added A^-, and the pH would go up as the solution becomes less acidic. This can be done by adding a soluble salt that contains the common ion. Lets start with a solution of 1.0M Hydrofluoric acid and look at the common ion effect by adding 0.10 mole of sodium fluoride to one liter of the solution.

Initially we have:

Rice	HF	H^+	F^-
Initial	1.0	0	0
Change	-x	+x	+x
Equilibrium	1.0-x	x	x

Table 17.1.1: RICE diagram for pure HF

We can obtain K from table 16.3.1 and since $[HF]_i >_a 100K$ we can ignore the amount HF ionized and $pH = -log\sqrt{K_a[HA]_i}$

$$pH = -\log\sqrt{6.3x10^{-4}(1.0)} = 1.60 \tag{17.1.2}$$

After adding 0.10mol NaF to one liter

	HF	H^+	F^-
Initial	1.0	0	0.10
Change	-x	+x	+x
Equilibrium	1.0-x	x	0.10+x

Table 17.1.2: ICE diagram for pure HF and a salt with its common ion (fluoride)

Noting we can ignore the x in [0.1+x] and [1.0-x] terms because according to Le Chatelier's Principle they will be even smaller because the 0.10 M fluoride pushes the equilibrium to the left.

$$K_a = \frac{x[0.10+x]}{[1.0-x]} \approx \frac{x(0.10)}{1.0} \tag{17.1.3}$$

Noting x =H^+,and pH=-log H^+,equation 17.1.3 can be rewritten in terms of pH.

$$pH = -log\left(\frac{1.0K_a}{0.1}\right) = -log\left(\frac{1.0(6.3x10^{-4})}{0.1}\right) = 2.20 \tag{17.1.4}$$

Exercise 17.1.1

Explain how equations 17.1.2 and 17.1.4 demonstrate Le Chatelier's Principle in terms of the common ion effect.

Answer

Eq. 17.1.2 has a pH of 1.60 and represents pure 1M hydrofluoric acid. Eq. 17.1.4 represents that solution after adding 0.10 mole of the common ion fluoride (via sodium fluoride) and that had a pH of 2.20. The solution with the common ion had a higher pH, which means the hydronium ion concentration went down when you added the common ion, which means the reaction consumed the added ion and shifted to the left, as predicted by Châtelier's Principle.

Lets take a closer look at eq. 17.1.4 and the ICE diagram for an acid and its salt. Generically, it would be written as:

	HA	H^+	A^-
Initial	$[HA]_i$	0	$[A^-]_i$
Change	-x	+x	+x
Equilibrium	$[HA]_i$-x	x	$[A^-]_i$+x

Table 17.1.3 Generic ICE diagram for acid and its salt.

$$K_a = \frac{[H^+]_e[A^-]_e}{[HA]_e} = \frac{x([A^-]_i + x)}{[HA]_i - x} \approx \frac{x[A^-]_i}{[HA]_i} \tag{17.1.5}$$

What is this saying? It is stating that if the common ion suppresses the ionization to such an extent that you can use the initial concentrations as your equilibrium concentrations. **This simplifies the calculations.**

Type 2: Weak Base/Salt of Conjugate Acid

Just as a salt can have the anion of an acid, it can also have the cation that is formed when a weak base reacts with water

$$B + H_2O \leftrightharpoons BH^+ + OH^- \tag{17.1.6}$$

Lets look at the analogous problem for the type 1 acid, but not use the ICE diagram, by considering the weak base ammonia and it's salt, ammonium chloride.

$$NH_3(aq) + H_2O(l) \leftrightharpoons NH_4^+(aq) + OH^-(aq) \tag{17.1.7}$$

We would predict that adding ammonium ion would suppress the ionization of ammonia and thus consume hydroxide, lowering the pH. So what would be the effect of adding 0.10mol of the soluble salt ammonium chloride to a liter of 1.0M ammonia, assuming no change in volume.

Initially, $pOH = -log\sqrt{K_b[NH_4^+]}$

$$pH = 14 - \left(-log\sqrt{1.8x10^{-5}[0.1]}\right) = 11.11 \tag{17.1.8}$$

After adding Salt and using the logic of eq. 17.1.5:

$$K_b = \frac{[BH^+]_e[OH^-]_e}{[B]_e} \approx \frac{x[BH^+]_i}{[B]_i} = \frac{[x][NH_4^+]_i}{[NH_3]_i} \tag{17.1.9}$$

noting x = [OH-] and $x = \frac{K_b[NH_3]}{[NH_4^+]}$

$$pH = 14 - (-log\frac{K_b[NH_3]}{[NH_4^+]}) = 14 + log\frac{1.8x10^{-5}[1.0]}{[0.10]} = 10.26 \tag{17.1.10}$$

So the effect is the same as it was with the acid and its salt. That is, adding a salt with a common ion to a base suppresses the ionization of the base, and so the pH of the salt solution is lower than of the base.

In the next section we will see that these solutions function as buffers, as the acid and its conjugate base can coexist, (or the base and its conjugate acid), and this means the solution can have an acid and a base to neutralize any external acid or base that can be added to them. Buffers are important, but before we cover them we will cover the common ion effect on salt solutions.

Application 2: Solubility of Salts

The effect of adding a soluble salt with a common ion to an insoluble salt of that ion, which causes more of the insoluble salt to precipitate out (ie., suppresses its ionization). OK, this sounds complicated, but it is actually easy to understand. Lets look at barium sulfate, which in chapter 3.4 we learned was an insoluble salt. What does that mean? It means K is a small number and so little barium dissolves, and in fact for barium sulfate, K= 1.1x10^{-10}.

$$BaSO_4(s) \rightleftharpoons Ba^{+2}(aq) + SO_4^{-2}(aq)$$
$$K = [Ba^{+2}][SO_4^{-2}]$$

Remember this is for a saturated solution, which describes the maximum concentration of dissolved ions that can exist in equilibrium with a solid, and gives a barium concentration of 10 micromolar.

$$[Ba^{+2}] = [SO_4^{-2}] = \sqrt{K} = \sqrt{1.1x10^{-10}} = 1.0x10^{-5}M \tag{17.1.11}$$

Le Chatelier's Principle says that if we add a soluble salt of one of the ions we can push the reaction in the direction that consumes that ion, and reduce the concentration of the other ion. So for example, if you want to remove more of a toxic compound like barium from a solution, you could add a soluble sulfate salt, like sodium sulfate.

What is the maximum possible concentration of barium in a solution that is 0.10M Na_2SO_4 .

	$BaSO_4$	Ba^{+2}	SO_4^{-2}
Initial	Solid	0	0.10M
Change	-x	+x	+x
Equilibrium	Solid	x	0.10+x

Table 17.1.2 Note, since barium is a solid it is not part of the equilibrium expression, and K describes the concentration of ions in a saturated solution, so we are writing "solid" to indicate that the concentration of the ions is that which would be in a saturated solution where solid barium sulfate is present. Note for a saturated solution of pure barium sulfate x=1.0x10^{-5}, and when we add sodium sulfate the common ion moves the equilibrium to the left, and the value of x becomes even smaller, and so we can ignore it in the equilibrium expression.

$$K = [Ba^{+2}][SO_4^{-2} = x(0.10 + x) \approx x(0.10) \tag{17.1.12}$$

This gives

$$Ba^{+2} = x = \frac{K}{0.10} = \frac{1.1x10^{-10}}{0.10} = 1.1x10^{-9}M \tag{17.1.13}$$

This means you can remove toxic metals like barium from water by adding a soluble salt of their counter ion that makes an insoluble salt with the metal. Barium sulfate is an insoluble salt and sodium sulfate is a soluble salt, and they have the common ion sulfate. Pure barium sulfate is 10 micromolar, and by adding sodium sulfate (a soluble salt) so the sulfate ion concentration is 0.1 M the barium concentration is reduced to 1.1 nanomolar.

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 17.1: Common Ion Effect is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

17.2: Controlling pH- Buffer Solutions

Introduction

A buffer is a solution that maintains a constant pH when an external acid or base is added to it. This is done by having an internal acid and base within the buffer solution, and the internal acid and base can not neutralize each other (they must be a conjugate pair). That is, the internal acid and base make the buffer, and then if you add an external acid or base, they neutralize it.

Three Requirements for a Buffer

1. Internal Acid- that neutralizes an external base that has been added to the solution, preventing the base's hydroxide from raising the pH.
2. Internal Base- that neutralizes an external acid that has been added to the solution, preventing acid's hydronium from lowering the pH.
3. The internal acid and base can't neutralize each other.

An acid/base conjugate pair fulfills these requirements: Thus there are two types of buffers

Two Types of Buffers

Buffer Type I: A Weak acid and its conjugate base

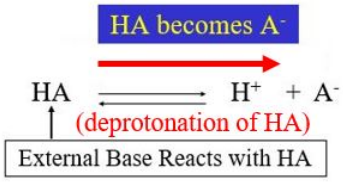
$$HA \leftrightharpoons H_3O^+ + A^- \tag{17.2.1}$$

Adding a Base converts HA to A$^-$.

ex:

$$HA + NaOH \rightarrow NaA + H_2O \tag{17.2.2}$$

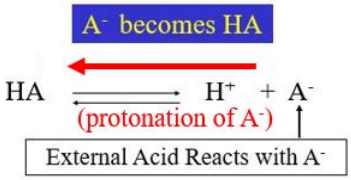
note, we often omit the spectator ions (sodium) in these equations, and are implying that A$^-$ is the anion of a salt.



Adding an Acid converts A$^-$ to HA.

ex:

$$HCl + A^- \rightarrow HA + Cl^- \tag{17.2.3}$$



The total concentration of an acid and its conjugate base are constant, it is just shifting between the protonated and nonprotonated form.

note, we often omit the sodium (spectator ion) in these equations

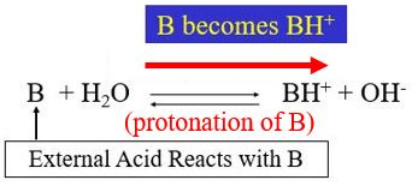
Buffer Type II: A Weak base its conjugate acid

$$B + H_2O \leftrightharpoons BH^+ + OH^- \tag{17.2.4}$$

Adding an Acid converts B to BH$^+$.

ex:

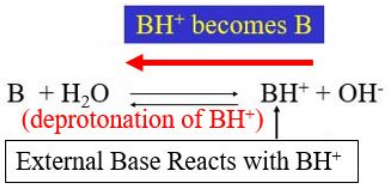
$$HCl + NH_3 \rightarrow NH_4^+ + Cl^- \tag{17.2.5}$$



Adding a Base converts BH^+ to B.

ex:

$$HCl + A^- \rightarrow HA + Cl^- \tag{17.2.6}$$



The total concentration of an acid and its conjugate base are constant, it is just shifting between the protonated and nonprotonated form.

Note, we often omit the sodium (spectator ion) in these equations

Two Ways to Make a Buffer

1. Mix a weak acid (or base) with a soluble salt of its conjugate.
   A solution that is made by diluting 0.5 mol of acetic acid and 0.5 mol of sodium acetate to one liter forms a buffer that is 0.5 molar in acetic acid and sodium acetate
2. Partially neutralizing an acid (or base)
   Neutralizing 500 mL of 2M acetic acid with 500 mL of 1M NaOH creates a solution that is .5 molar in acetic acid and sodium acetate (see exercise 17.2.1)

Exercise 17.2.1

What is the concentration of a solution made by neutralizing 500.0 ml of 2.0M acetic acid with 500.0 ml 1.0M sodium hydroxide, assume the volume of the solutions are additive (500ml + 500ml = 1,000ml)

Answer

$$HC_2H_3O_2 + NaOH \rightarrow NaC_2H_3O_2 + H_2O \tag{17.2.7}$$

Initial moles acetic acid = 0.5000(2.0) = 1.0 mol
Initial moles sodium hydroxide = 0.5000(1.0) = 0.50 mol

Final mols sodium acetate formed after complete consumption of limiting reagent (sodium hydroxide)

$0.50molNaOH) \left(\frac{1molNaC_2H_3O_2}{1molNaOH}\right) = 0.50molNaC_2H_3O_2$

Final mols excess reagent (acetic acid) after complete consumption of limiting reagent

$1.0molHC_2H_3O_2 - 0.50molNaOH) \left(\frac{1molHC_2H_3O_2}{1molNaOH}\right) = 0.50molHC_2H_3O_2$

The final concentration is the moles per liter, or $\frac{n}{V_T}$ where the total volume is 500.0ml+500.0ml = 1.0000L.

$$[NaC_2H_3O_2] = \frac{0.50molNaC_2H_3O_2}{1.0000L} = 0.50MNaC_2H_3O_2 \tag{17.2.8}$$

$$HC_2H_3O_2] = \frac{0.50molHC_2H_3O_2}{1.0000L} = 0.50MHC_2H_3O_2$$

Note: When mixing solutions of acids and bases the concentration of the species are being changed by two different factors, chemical reaction and diluting. Even if you added water and it did not react, the concentration would go down.

Buffer (Henderson Hasselbach) Equation

The buffer equation is also known as the Henderson-Hasselbach equation is an expression of the equilibrium constant in terms of pValues, and making the assumption that the extent of reaction is negligible when you solve the ICE diagram for an acid or base in equilibrium with its conjugate (see section 17.1.2.1)

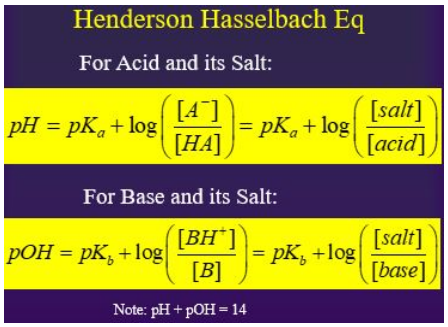
$$K_a = \frac{[H^+]_e[A^-]_e}{[HA]_e} = \frac{x([A^-]_i + x)}{[HA]_i - x} \approx \frac{x[A^-]_i}{[HA]_i} \tag{17.2.9}$$

That is, we can use the initial acid and salt concentration

$$K_a = \frac{[H^+]_e[A^-]_i}{[HA]_i} \tag{17.2.10}$$

One can then rearrange and solve for pH with the Henderson Hasselbach eq. Note, the analogous problem could be solved for a base and its salt, in which case you use pOH and K_b.

$$pH = pK_a + log\frac{[A^-]}{HA} \tag{17.2.11}$$



There are two important characteristics of a buffer, the pH it maintains, and how much external acid or base it can handle, its capacity. The Henderson Hasselbach equation is preferred over eq 17.2.8 not only because hydronium ion concentration is typically measured in terms of pH, but also because it makes it easy to identify the pH it works at, and the buffer capacity, how much external acid or base it can neutralize,

Buffer pH

The ideal pH or pOH for a buffer to work at is the pK value of the acid or base that makes the buffer. Lets consider an acid and its salt, but realize we could apply this to a base and its salt. When the concentration of the acid equals the salt, the buffer can neutralize equal amounts of an external acid or base. At this point the $log\frac{[salt]}{acid} = log1 = 0$ and pH=pK_a .

$$pH = pK_a + \log\frac{[salt]}{\cancel{acid}} \tag{17.2.12}$$

This can can also be seen by Equation 17.2.10where [A^-] = [HA] and

$$K_a = \frac{[H^+]_e\ \cancel{[A^-]_i}}{\cancel{[HA]_i}} \tag{17.2.13}$$

> **Note**
>
> **Note**: Equations 17.2.12and 17.2.13are for solutions where the acid and its salt are of equal concentrations, and only then is $pH = pK_a$. To get a buffer at a different concentration the ratio of the salt to the acid (or base) needs to be adjusted.

So the strategy for picking a buffer is choose an acid with a pK_a close to the desired pH and then adjust the salt to acid ratio until they equal. Also note, if

$$[salt] > [acid]\ then\ \frac{[salt]}{[acid]} > 1\ and\ log\frac{[salt]}{[acid]} \text{is a positive number and pH is greater than pK}_{a} \quad (17.2.14)$$

$$[salt] < [acid]\ then\ \frac{[salt]}{[acid]} < 1\ and\ log\frac{[salt]}{[acid]} \text{is a negative number and pH is less than pK}_{a}$$

Note, like any logarithm, you can write this in the log form, on in the power form

$$\frac{[A^-]}{[HA]} = 10^{pH-pKA} \quad (17.2.15)$$

Exercise 17.2.1

Acetic acid has a K_A of 1.75x10^{-5}, which gives it a pK_A of 4.76. This would make it a good acid to make a buffer with a pH of 5. What would be the acetate concentration if the acetic acid concentration is 0.10M?

Answer

$$pH = pK_a + log\frac{[acetate]}{[acetic\ acid]} \quad (17.2.16)$$

$$\therefore$$

$$\frac{[acetate]}{[acetic\ acid]} = 10^{pH-PK_a}$$

$$[acetate] = [acetic\ acid]10^{pH-pK_a}$$

$$[acetate] = [0.10]10^{5-4.76} = 0.174$$

Note: Since the buffer was at a higher pH than K_a, the acetate concentration (conjugate base) is greater than the acetic acid concentration.

Exercise 17.2.2

What would be the acetate concentration for a buffer with 0.10M acetic acid to have a pH of 10.

Answer

For starts, pK_A of acetic acid is 4.76 (exercise 17.2.2 above) and so this is a very bad choice, but lets take a look. Following the same logic as the problem above,

$$[acetate] = [acetic\ acid]10^{pH-pK_a} \quad (17.2.17)$$

$$[acetate] = [0.10]10^{10-4.76} = 17,000M$$

Note: from problem 17.2.2 the acetate concentration of a 0.10M acetic acid solution would be 17,000M, which is impossible, and so this buffer can not be made.

Can you make a buffer with an acid that has a pH of 10, that is, with a pH of 10?

Sure, you just need an acid with a pKa around 10, which means it's conjugate base has a Kb around 4, that is, the conjugate base is a stronger base than the acid is an acid. Do exercise 17.2.3

Exercise 17.2.3

Go to table 16.3.1 and find an appropriate acid where a 0.10 molar solution of that acid could make a buffer with a pH of 10.

Answer

Phenol has a K_a of 1.0 x 10^{-10} and equal molar of phenol and its salt would work. Lets use hypoidous acid, pK_a = 10.5

$$[hypoiodite] = [hypoiodus\ acid]10^{pH-pK_a} \quad (17.2.18)$$

$$[IO^-] = [0.10]10^{10-10.5} = 0.032M$$

Note: The table of acid ionization constants used to solve16.3.1 problem 17.2.3 had both K_a and pK_a values, and if you are looking for an acid to make a buffer, looking at the pK_a is much easier.

Note: In exercise 17.2.1 the pH we wanted the buffer at was greater than K_a and the resulting salt concentration in the buffer was higher than the acid, but in problem 17.2.3 the pH we wanted was lower than the K_a and so the acid concentration of the buffer was greater than the salt.

Note: You need to do this for bases. If asked to calculate and appropriate base and conjugate acid pair to make a buffer of a certain pH, it is probably easier to convert the question to pOH. That is, in these equations, you are dealing with pOH.

Exercise 17.2.4

What is the base to salt ratio for a buffer of propylamine with a pH of 10?. Use table 16.3.2 to get the K_b value of propylamine

Answer

From table 16.3.2 the pK_b value for propylamine is 3.46, and a solution with a pH of 10 has a pOH of 4, so this is a reasonable choice.

$$pOH = pK_b + log\frac{[C_3H_7NH_3^+]}{[[C_3H_7NH_2]} \tag{17.2.19}$$

$$\therefore$$

$$\frac{[C_3H_7NH_3^+]}{[[C_3H_7NH_2]} = 10^{pOH-PK_b}$$

$$\text{taking the reciprocal of both sides to get the base to salt ratio}$$

$$\frac{[C_3H_7NH_2]}{[[C_3H_7NH_3^+]} = 10^{PK_b-pOH}$$

$$= 10^{3.46-4} = 0.29$$

Buffer Capacity

The buffer capacity deals with how much of an external acid or base can be neutralized so effectively that the pH does not change, and this deals with the concentrations of the acid and salt in the logarithmic term of the Henderson Hasselbach equation.

$$pH = pK_a + \log\frac{[salt]}{[acid]} \tag{17.2.20}$$

The greater the concentration of the salt and the acid, the stronger the buffer. Consider two buffers of acetic acid

Buffer 1: [HA] = 2.0M, [A^-]= 1.0M

$$pH = -\log(1.75x10^{-5}) + log\frac{[1.0]}{[2.0]} = 4.76 - .30 = 4.46 \tag{17.2.21}$$

Buffer 2: [HA] = 0.0020M, [A^-]= 0.0010M

$$pH = -\log(1.75x10^{-5}) + log\frac{[0.001]}{[0.002]} = 4.76 - .30 = 4.46 \tag{17.2.22}$$

Both buffers have exactly the same pH, but buffer one is clearly stronger and has 1 mole of an internal base and 2 moles of an internal acid to react with an external base or acid, while buffer two only has 0.001 and 0.002 moles respectively.

Note: If $[HA] \neq [A^-]$ the strength of a buffer with respect to external acids and bases are different. For the above two buffers, there was more acid than conjugate base, and so they had a greater capacitance towards an external base than an external acid.

Note: when [HA]=[A^-],the capacity to neutralize an external acid and base are the same, and the pH=pK_a. This is one of the reasons one chooses an acid whose pK_a equals the pH the buffer needs to maintain.

The concept of buffer capacity is the same for weak bases and their conjugate acids, except that you use pOH and pK_b in the equations, and sometimes those get tricky as you convert them back to pH.

Test Yourself

Homework: Section 17.2

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 17.2: Controlling pH- Buffer Solutions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

17.3: Acid-Base Titrations

Introduction

Titrations are an analytical technique most commonly used to calculate the concentration of an unknown (the analyte) with a known (the standard, or titrant). The principle is fairly simple, if you know the stoichiometry of a reaction and the quantity of one species, you can calculate the quantity of the other, the trick is to figure out when they are in stoichiometric proportions. One technique is to use an indicator, which is another substance that changes color when the reaction is completed. There are many types of titrations (acid-base, redox), they all involve a reaction where you add one reactant incrementally until they are in stoichiometric proportions, and then knowing the moles of the titrant, you can calculate the moles of the analyte. If the analyte is a solid and you measure it's mass, information on its molar mass can also be obtained.

There are two basic types of acid base titrations, indicator and potentiometric. In an indicator based titration you add another chemical that changes color at the pH equal to the equivalence point, when the acid and base are in stoichiometric proportions. In a potentiometric titration you record the pH as you add titrant, and if the analyte is a weak acid or base you can determine its K_a or K_b.

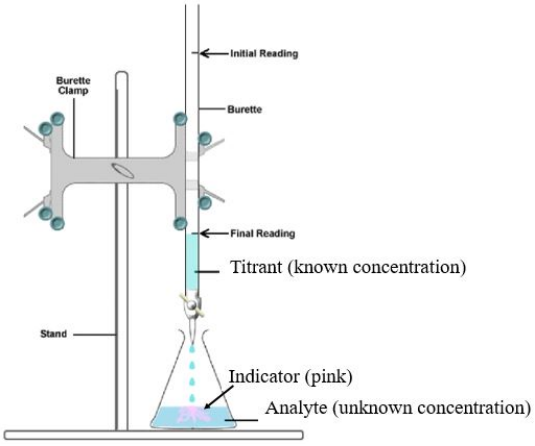


Figure 17.3.1: Generic apparatus for an acid base titration. You take a known volume of analyte (substance of unknown concentration) and add a titrant (substance of know concentration) until the indicator indicates the reaction is over. The trick is to pick the right indicator, which changes color when the reactants and products are in stoichiometric proportions.

Relating Titrations to Stoichiometric Equations

Relating titrations to stoichiometry and limiting reagent problems. Consider the titration of HCl with NaOH, that is, HCl is the analyte and NaOH is the titrant.

$$\mathrm{HCl} + \mathrm{NaOH} \rightarrow \mathrm{NaCl} + \mathrm{H_2O} \tag{17.3.1}$$

As you titrate this you have four types of stoichiometric relationships

1. Initially - Pure HCl (you have added no NaOH)
2. HCl is the excess reagent, NaOH is the limiting reagent (you have not added enough NaOH to react with all the HCl)
3. HCl and NaOH are in stoichiometric proportions (you have added just enough NaOH to neutralize the HCl, but none extra)
4. NaOH is the excess reagent and HCl is the limiting reagent (once you have neutralized all the HCl, any more NaOH is excess).

So the objective of the titration is to find part 3, when the acid and base are in stoichiometric proportions, and knowing the quantity of titrant at that point allows one to calculate the moles of analyte.

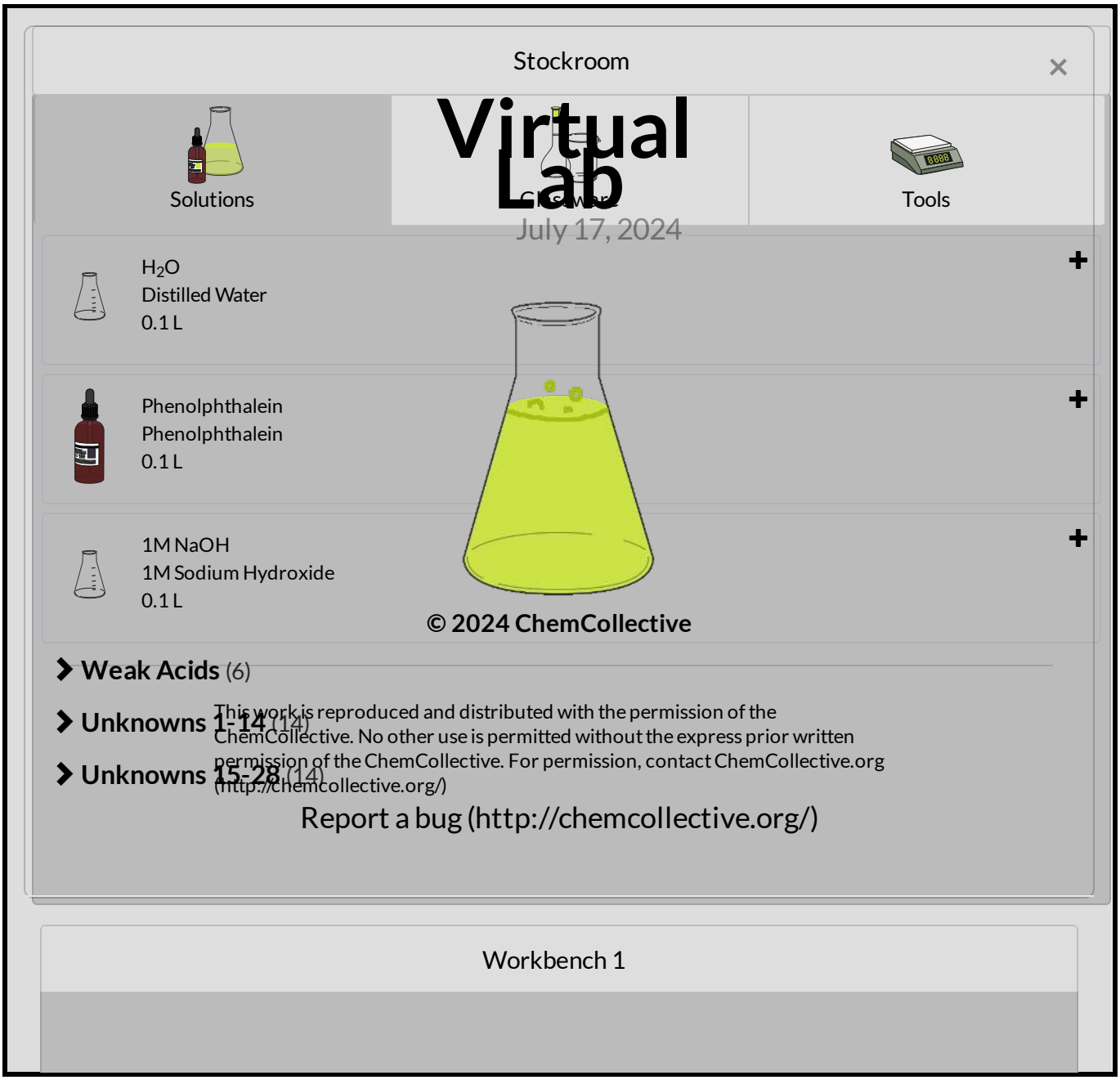
Running a Titration



4:50 min YouTube by RSC. Note, this is a very good video, but there was a potential mistake in that they did not flush out the bottom of the stopcock, but since this was an overshoot run, it made no difference. That is, below the stopcock fluid collects, and you should run the titrant through the burette to make sure no air bubbles get trapped.

Virtual Lab

Try your own titration with the following virtual lab



Four Basic Types of Acid-Base Titrations

Table 17.3.1 shows the four types of titrations, and you note that the titrant (compound in the burette that is added to the analyte) is always strong, while the analyte can be strong or weak. This is because in running a titration it is imperative that the titrant completely react, that way you can say that the moles hydronium or hydroxide added is equal to the molarity times the volume (n=MV) of the titrant. This allows you to calculate the amount of salt produced by the complete consumption of the titrant (up to the triple point). If that salt then reacts to form the acid of it's conjugate relationship, you can calculate the "initial" concentration based on the amount of titrant added.

Table 17.3.1: The four basic types of titrations. Key to the

Type	Analyte	Titrant
SA/SB	Strong Acid	Strong Base

Type	Analyte	Titrant
WA/SB	Weak Acid	Strong Base
SB/SA	Strong Base	Strong Acid
WB/SA	Weak Base	Strong Acid

Strong Acid-Base (SA/SB & SB/SA)

We will treat both SA/SB and SB/SA calculations concurrently because these are essentially general chemistry 1 limiting reagent problems. You simple calculate the moles acid and the moles base, and base the pH on the concentration of the excess reagent. Because these reactions go to completion they **do not form buffers**.

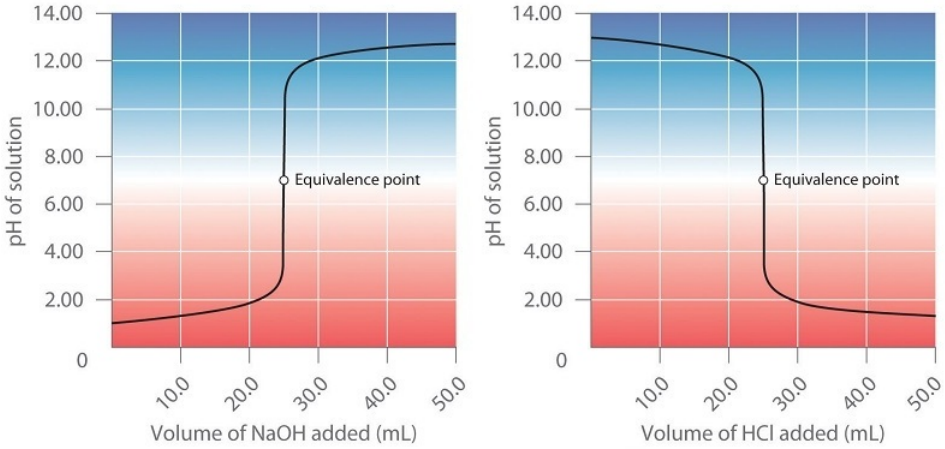
Initially, before any titrant is added, the pH is that of a pure acid or pure base, and the hydronium/hydroxide ion concentration is that of the pure acid or pure base.

Before Equivalence point

The Analyte is the Excess Reagent, and so you need to calculate the moles excess analyte and divide by the total volume, and from that answer the question, which is usually, what is the pH.

$$[Analyte]_{excess} = \frac{(n_{analyte} - n_{titrant})}{V_T} = \frac{(M_{analyte}V_{analyte}) - (M_{titrant}V_{titrant})}{V_{analyte} + V_{titrant}} \tag{17.3.2}$$

Note, in Figure$17.3.2a$, the pH < 7 because the analyte is an acid and you have not neutralized it all, while in Figure$17.3.2b$the pH > 7 because the analyte is a base, and you have not neutralized it all



Figure$17.3.2$: Titration curves for (a) strong acid with strong base and (b) strong base with strong acid.

Equivalence Point

At the equivalence point moles acid = moles base and the pH = 7 because the salt of a strong acid and a strong base is neutral (the ions do not protonate or remove a proton from water)

After Equivalence Point

The Titrant is the Excess Reagent, and so you need to calulate the moles excess titrant and divide by the total volume, and from that answer the question, which is usually, what is the pH.

$$[Titrant]_{excess} = \frac{(n_{titrant} - n_{analyte})}{V_T} \tag{17.3.3}$$

$$= \frac{(M_{titrant}V_{titrant}) - (M_{analyte}V_{analyte})}{V_{analyte} + V_{titrant}} \tag{17.3.4}$$

Note, in Figure$17.3.2a$, the pH > 7 because the titrant is a base and you have added more than was required to neutralize the analyte (acid), while in Figure$17.3.2b$ the pH < 7 because the titrant is an acid and you have added more than was required to neutralize all the analyte (base).

Weak Acid with Strong Base

There are four parts to the titration curve of a weak acid (analyte) with a strong base(titrant).

1. Initial pH (pH of a weak acid)
2. Buffer Equation (Henderson Hasselbach Eq.)
3. Equivalence Point (salt of weak acid)
4. Excess Base (pH based on concentration of excess titrant)

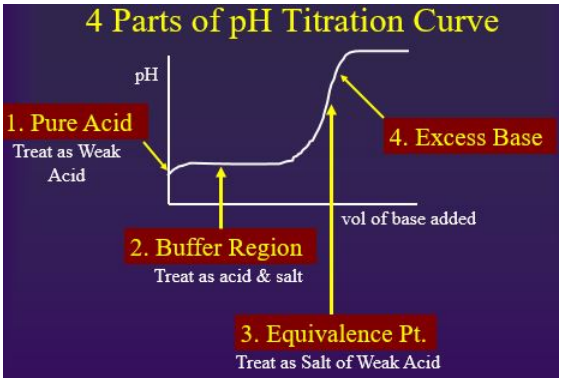


Figure17.3.3: Four parts of the titration curve for a weak acid being titrated with a strong base. Notice that two parts are points (1 & 3) and two parts are regions (2 & 4).

NOTE: A typical question is like: What is the pH when Xml (V_b) of Y molar (M_b) strong base has been added to Q ml ((V_a) of R molar (M_a) weak acid. The first step is to figure out what region of the titration curve you are in, and then solve the problem. This can be done through the relationship $n_a = n_b$ (moles acid = moles base), which for liquids is $M_aV_a = M_bV_b$. Note, this even works for polyprotic acids, that will have more than one equivalence point (see below).

Pure Acid

Treat as a weak acid (section 16.5.4.2)

$$pH = -\log \sqrt{K_a[HA]_i} \tag{17.3.5}$$

Buffer Region

In Section 17.2.3 it was shown that one way to make a buffer is to partially neutralize and acid and so in the buffer region we can use the Henderson Hasslebach equation.

$$pH = pK_a + \log \frac{[A^-]}{HA} \tag{17.3.6}$$

If we know the volume of base to reach equivalence (V_{eq}), we can express the ratio $\frac{[A^-]}{HA}$ as the ratio of the volume of base added at any point (V_b) to the volume of remaining base that would need to be added to completely neutralize the acid ($V_{eq} - V_b$), or

$$\frac{[V_b]}{V_{eq} - V_b}. \tag{17.3.7}$$

So

$$pH_{\text{at point b}} = pK_a + \log \frac{[V_b]}{V_{eq} - V_b} \tag{17.3.8}$$

Equation 17.3.8 not only simplifies the calculation, but allows you to determine the pH of a buffer in a titration even if you do not know the concentration of the acid or the base, as long as you know the volume of base required to neutralize the acid.. The

derivation of this simplification is described in the following YouTube.



Half Equivalence

In section 17.2.5 we discussed buffer pH and that the $pH = pK_a$ if $[HA] = [A^-]$. In a titration this is known as half equivalence or half titer, which is the volume required to titrate off half of the titratable protons (of a monoprotic acid, or the first proton of a polyprotic acid). That is, at half equivalence, $V_b = \frac{V_{eq}}{2}$.

$$\begin{aligned} pH_{\text{at half titer}} &= pK_a + \log \frac{[V_b]}{V_{eq} - V_b} \\ &= pK_a + \log \frac{\frac{V_{eq}}{2}}{V_{eq} - \frac{V_{eq}}{2}} \\ &= pK_a + \log \frac{\frac{V_{eq}}{2}}{\frac{V_{eq}}{2}} \\ &= pK_a + \log(1) \\ &= pK_a + 0 \\ &= pK_a \end{aligned} \tag{17.3.9}$$

Why is this important? This means that if you know the concentration of an acid, you can calculate its pK_a by neutralizing half of it, and then reading the pH. If you do not know its concentration, you can titrate it, find how much base it took to neutralize it (the equivalence point), and then add half of that amount of base to another sample of the same volume of acid, and the pH is its pKa.

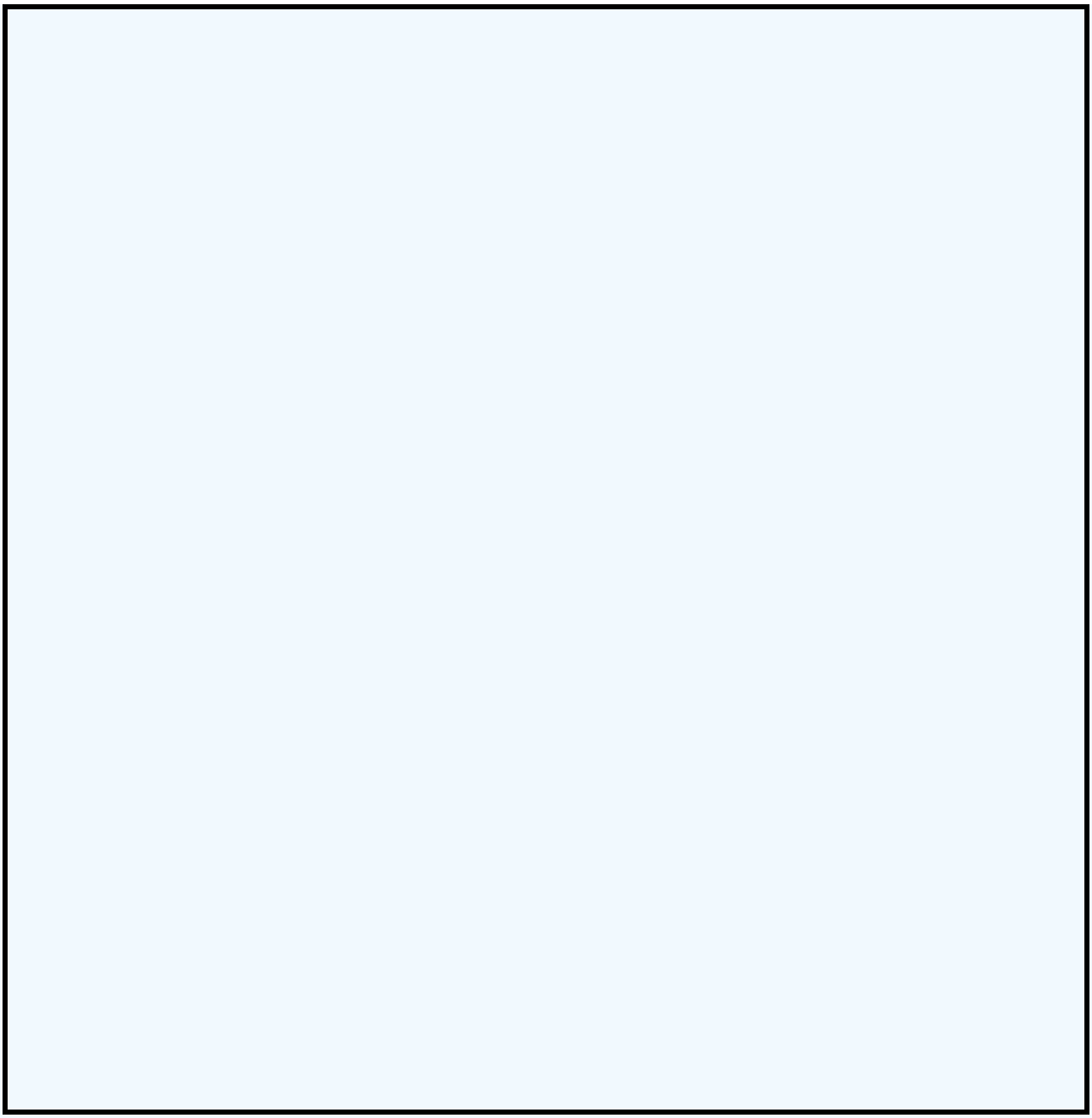
Virtual Lab 17.3.1

With just one measurement, calculate the room temperature K_a for hydrofluoric acid using the virtual lab below.

Activate Virtual Lab

Note: The virtual lab uses thermodynamic equations to calculate equilibrium conditions and operates at an ambient temperature of °C. You can rightclick on a flask and adjust its temperature directly, and you can also isolate it from the surroundings. The equilibrium constant is a function of temperature, and so you need to adjust it to 25 °C to get the correct answer, which should be 6.61×10^{-4}.

There is a short animation on how to use the virtual lab on the UALR lab page in LibreText and additional material is available at the ChemCollective.



The Chemcollective Virtual laboratory was developed by Professor David Yaron's research group at Carnegie Mellon University.

Exercise 17.3.2

What is the pH of an acetic acid solution after 20 mL of an NaOH was added if the equivalence point required 50 ml on NaOH?

Answer

Since it took 50 ml to neutralize, we can easily see that 25 ml would have neutralized half of it, and at 20 ml we have neutralized $\frac{20}{50}$ or 2/5, and have not neutralized $\frac{50-20}{50}$ or 3/5. The fraction neutralized has been converted to the salt, and the fraction remaining is still a weak acid, so pH=pK_a+log2/3, or to do it the long way:

$$\begin{aligned} pH &= pK_a + \log \frac{[A^-]}{[HA]} \\ &= pK_a + \log \frac{V_b}{V_e - V_b} \\ &= -\log 1.75 \times 10^{-5} + \log \frac{20}{50-20} \\ &= 4.76 + (-0.40) \\ &= 4.36 \end{aligned}$$

This makes sense, because you have not reached half equivalence, where the $pH = pK_a$.

Equivalence Point

At the equivalence point the weak acid is in stoichiometric proportions to the strong base, and so it is completely converted to its salt, meaning you have the salt of a weak acid (review section 16.5.6).

$$[OH^-] = \sqrt{\left(\frac{K_w}{K_a}\right)[A^-]_i} \tag{17.3.10}$$

At the equivalence point moles $HA_{initial}$ = moles Base added , so $M_A V_{A,initial} = M_B V_{B.equivalence}$, which is the moles A^- created, because all the HA has been converted to A^-.

As you added the base to the weak acid you did two things

1. Neutralized the Acid
2. Diluted the Acid

Taking this into account and noting that the total volume is the volume of the initial acid $V_{A,i}$ and the base added $V_{B,e}$ to neutralize it

$$[OH^-] = \sqrt{\frac{K_w}{K_a}\left(\frac{M_A V_{A,i}}{V_T}\right)} = \sqrt{\frac{K_w}{K_a}\left(\frac{M_A V_{A,i}}{V_{A,i} + V_{B,e}}\right)} \tag{17.3.11}$$

or, since the definition of the equivalence point is moles $HA_{initial}$ = moles base added, this can also be expressed in the molarity of the base.

$$[OH^-] = \sqrt{\frac{K_w}{K_a}\left(\frac{M_B V_{B,e}}{V_{A,i} + V_{B,e}}\right)} \tag{17.3.12}$$

It does not matter which form of the above equations you use

$$pOH = -\log \sqrt{\frac{K_w}{K_a}\left(\frac{M_B V_{B,e}}{V_{A,i} + V_{B,e}}\right)} \tag{17.3.13}$$

(convert to pH if needed)

Excess Base Region

In the excess base region you have added more strong base than there was weak acid and so this is a limiting reagent problem, and since all the strong base converts to hydroxide, you simply need to find the excess moles strong base and divide by the total concentration to get the hydroxide concentration

$$[OH^-] = \frac{n_{OH^-,(excess)}}{V_T} = \frac{M_B V_B - M_B V_{eq}}{V_B + V_{A,i)}}$$

$$[OH^-] = \frac{M_B\,(V_B - V_{eq})}{V_B + V_{A,i)}} \tag{17.3.14}$$

(convert to pH if needed)

Titration Problems

General Strategy

Find out what part of the curve you are in, and then use the appropriate equation. If you have not added base $V_b = 0$, it is trivial and you are solving the pH for a weak acid. If you have added base, (V_b) there are three possibilities

1. $\mathbf{V_b < V_{b.eq}}$ **: Buffer region**, base is the limiting reagent and there is un-neutralized weak acid.
2. $\mathbf{V_b = V_{b,eq}}$ **: Equivalence point**, base and weak acid are in stoichiometric proportions and the weak acid has been converted to its salt.
3. $\mathbf{V_b > V_{b.eq}}$ **: Excess base region**, additional base has been added beyond the amount required to neutralize the acid.

So the first thing you do is identify $V_{b.eq}$.

This is done by calculating the volume of base required to reach the equivalence point, that is, at the equivalence point the moles acid equals the moles base. (Note, you use this even if it is a polyprotic acid, in which case there will be more than one equivalence point.

$$\begin{aligned} n_a &= n_b \\ M_a V_{a,i} &= M_b V_{b,eq} \\ V_{b,eq} &= \frac{M_a V_{a,i}}{M_b} \end{aligned} \tag{17.3.15}$$

The following problem covers all the regions of the titration curve.

Video Tutorial on Titration problem

Calculate the pH when 50.0 mL of 0.15M acetic acid is titrated with 0.15M NaOH after the following volumes of NaOH have been added.

(a). 0 ml NaOH, (b). 20. ml NaOH (c). 25 ml NaOH (d). 50.0 mL NaOH (e). 70. ml NaOH



Final pH Values: (a) 2.78, (b) 4.56, (c) 4.74, (d) 8.81 and (e) 12.40

Weak Base with Strong Acid

The titration of a weak base with a strong acid has similar features to the titration of a weak acid in a strong base but the curves sort of go in the opposite directions. That is, you start with a weak base, and when you neutralize it the salt is acidic (not basic as it is for titrating a weak acid), and of course the excess acid region now is acidic.

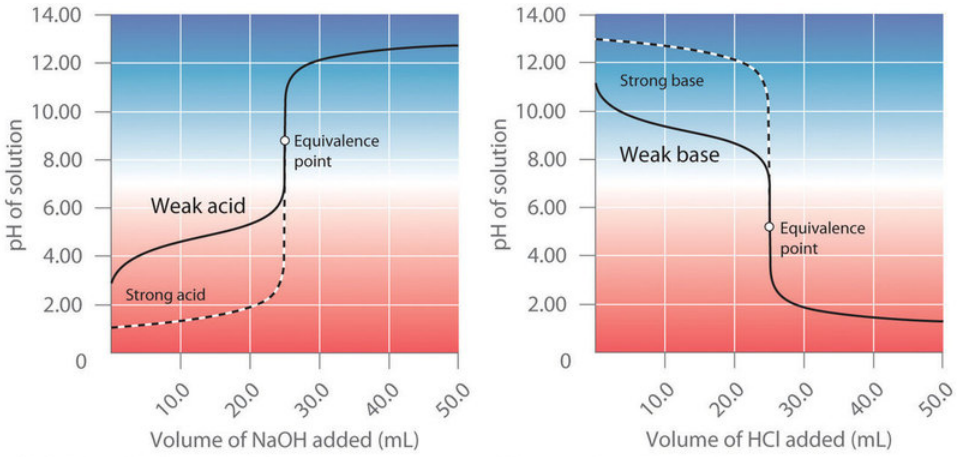


Figure17.3.4: Comparison of the titration of a weak base to that of a weak acid.

Since this is analogous to the previous section we will only write out the equations that were derived above, but their derivations are similar, it is just that the role of the acid and base switched.

Pure Base

Salt of Weak Base (review section 16.5.5 and 16)

$$pOH = -\log \sqrt{K_b [B]_i} \tag{17.3.16}$$

(convert to pH if needed)

Buffer Region

Buffer of Weak Base and its Salt (review section 17.2.2.2 and 17.2.4)

$$pOH = pK_b + log \frac{[BH^+]}{B} \tag{17.3.17}$$

(convert to pH if needed)

Equivalence point

Salt of Weak Base (review section 16.5.7)

$$[H^+] = \sqrt{\left(\frac{K_w}{K_b}\right)[B]_i} \tag{17.3.18}$$

Excess Acid Region

$$[H^+] = \frac{M_A\left(V_A - V_{eq}\right)}{V_A + V_{B,i)}} \tag{17.3.19}$$

Reflections on Titration Curves

Figure $PageIndex5$ shows the titration curves of different weak acids and weak bases of varying concentrations. There are several things we notice from these curves, and two are worth further discussion. The first is that the flat region of the curve is near the midpoint, or at half titer, and this is useful in understanding the pH a buffer can maintain constant. The second the equivalence point, and this can be used to understand how an indicator works, and what indicators are appropriate for what buffers.

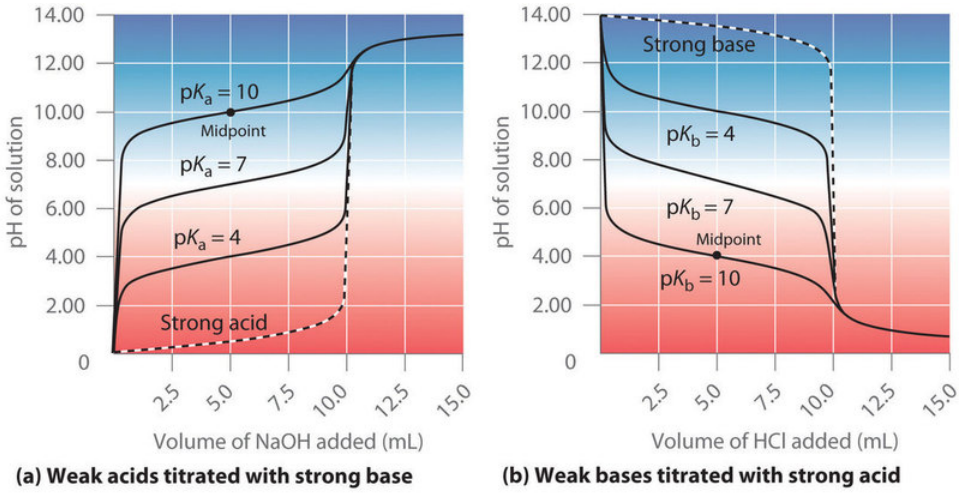


Figure $PageIndex5$: Titration curves for weak acids and base of various strengths.

Buffer pH

The flat region of the curve is the buffer region because moving along the x-axis (adding an acid or base) has the smallest change along the Y axis (Δ pH, and the titration curves for all of the acids and bases in figure 17.3.5 are flattest at half titer. It is clear that the pH at which the above buffers operate varies as the ionization constants vary, and the above diagram demonstrates the logic behind the rules in section 17.2.4.1 for and choosing a buffer, that is, you pick an acid with a K value near the pH (or pOH) and adjust the conjugate pair until it reaches that value.

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \tag{17.3.20}$$

.

Note: the titration curve is flattest at half equivalence. This can be demonstrated by the Henderson Hasselbach Equation.

At any time $n_{HA} + n_{A^-} = n_{HA(initial)}$, because you started with pure HA and every time an NaOH reacted with an HA, the number of HA went down by one and A^- went up by one.

Thought Experiment

Consider a hypothetical titration with just 100 HF molecules (pK_a =3.20) to see why the curve is flattest at half. Note, although the Henderson Hasselbach equation is written in terms of concentration, we can use the number of particles as the volume cancels out in the ratio term

$$\frac{[A^-]}{[HA]} = \frac{[\frac{n_{A^-}}{V_T}]}{[\frac{n_{HA}}{V_T}]} = \frac{n_{A^-}}{n_{HA}}$$

and the Henderson Hasselbach Equation can be written as:

$$pH = pK_a + \log \frac{n_{A^-}}{n_{HA}}.$$

Consider a hypothetical titration with just 100 HF

n_{HF}	n_{F^-}	$pH = pK_a + \log \frac{n_{A^-}}{n_{HA}}$	pH
50	50	$pH = 3.20 + \log \frac{50}{50}$	3.2
49	51	$pH = 3.20 + \log \frac{51}{49}$	3.217
4	96	$pH = 3.20 + \log \frac{96}{4}$	4.58
3	97	$pH = 3.20 + \log \frac{97}{3}$	4.71

Table$PageIndex1$: Hypothetical titration on absurd atom level to give a feel for the ratio term of the buffer equation.

What this shows is that the equation is flattest near half equivalence, which is when it is the best buffer, and so even though there was still an HF to neutralize the 96th NaOH added, the pH went up by 0.13, as compared to 0.017 at half equivalence.

Indicators

Acid base indicators are acids and bases that undergo a color change as they gain or lose a proton, and very dilute solutions of the colored form can be seen by the unaided eye. These are typically organic molecules in nature, and they can be used to estimate the equivalence point if the pH at which they change color is the pH of the equivalence point. Note, when you use an indicator you have an **End Point**, which is when you stop a titration because the indicator changed color. The **Equivalence Point** is when the moles acid equals moles base. If the end point of an indicator is at the same pH as the equivalence point, that indicator can be used to determine when the equivalence point is reached.

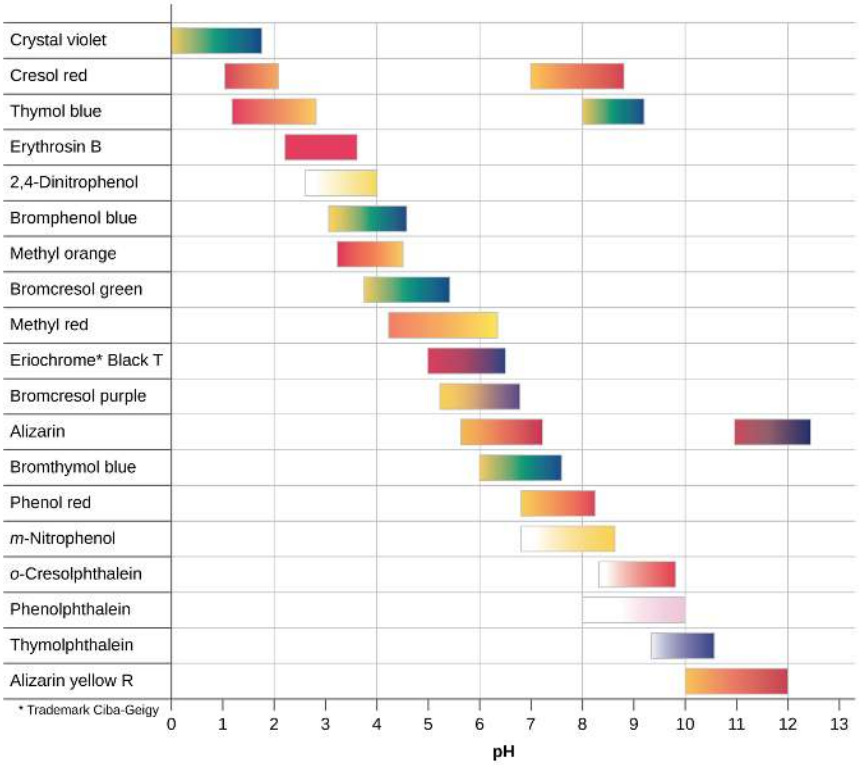


*Table*17.3.2: *Color changes for some common pH indicators as a function of pH. Note, some diprotic indicators have different colors for the acidic, acid salt, and salt forms.*

The trick is to identify the pH at the equivalence point (the salt of the compound you are titrating) and pick an indicator that changes pH over that range. A properly picked indicator will change color over a drop, as the line is almost vertical at the equivalence point. An improperly picked indicator will change color very slowly, for example, if you used Bromocresol purple which goes from yellow to purple over the pH range of 5 to 7 (table 17.3.2) and applied it to acetic acid (figure 17.3.6), it would start to change colors around 15 mL and would finish around 25. But an indicator like phenylphthalein would change color at 25 mL.

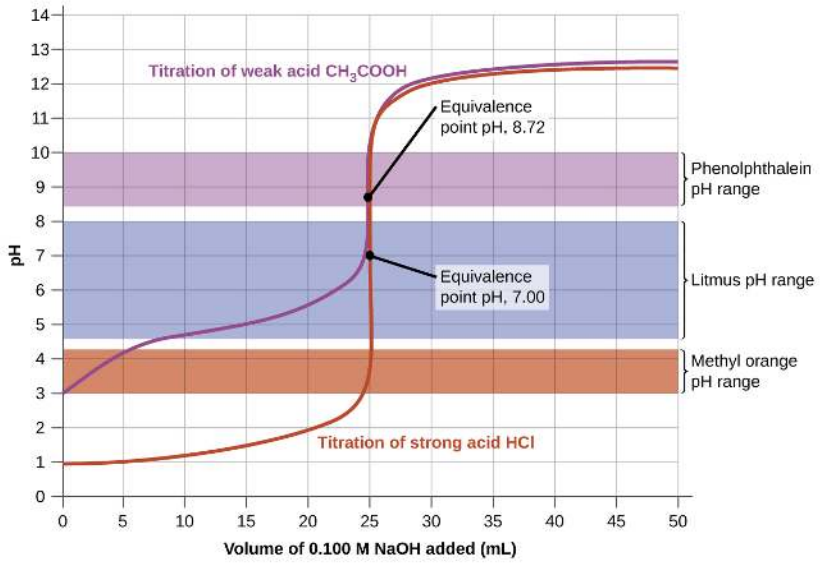


Figure 17.3.6: Titration curves of acetic acid and HCl.

Polyprotic Titration Curves

Polyprotic acids were covered in sections 16.1.2,16.3.5 and 16.5.8 and it was shown that each proton had its own ionization constant, with

$$K_{a1} > K_{a2} > K_{a3} \tag{17.3.21}$$

. This results in a titration curve like that of figure 17.3.7. If each subsequent K_a is at least a 1000 times smaller than the previous than the protons are taking off stepwise, then there would be a unique equivalence point for each step. In a monoprotic titration and base after the equivalence point is excess and the solution quickly becomes basic. But if there is a leveling off, that could indicate another titratable proton.

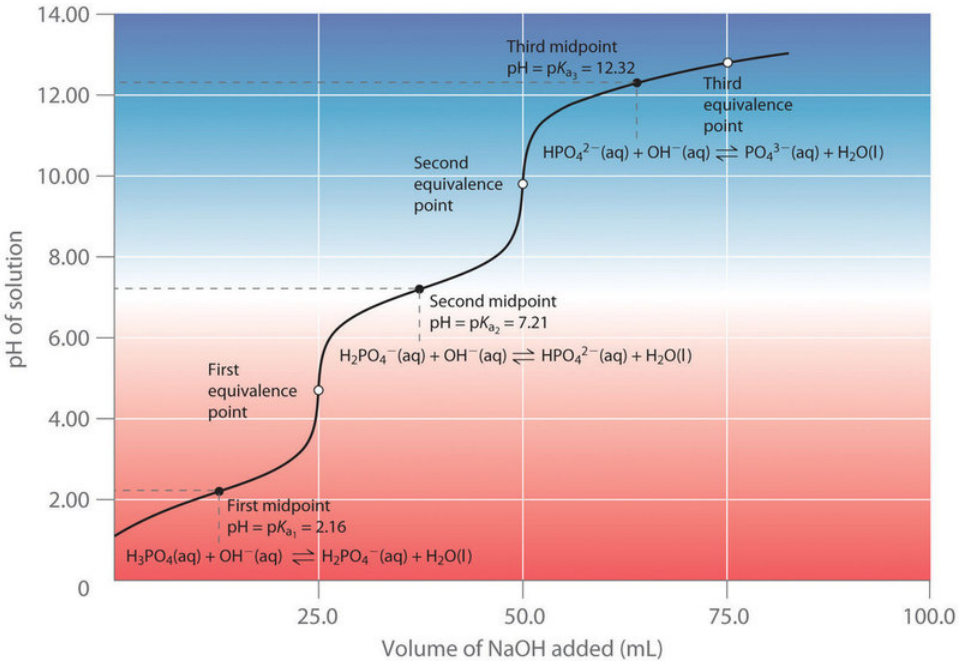


Figure $PageIndex7$: Polyprotic titration curve for phosphoric acid.

Note, if the K_a values of two successive deprotonations are close to each other, the curve begins to look more like a line and you do not have distinct equivalence points where just one acid salt exists.

Test Yourself

Homework: Section 17.3

Contributors and Attributions

- Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 17.3: Acid-Base Titrations is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

17.4: Solubility of Salts

Introduction

In general chemistry 1 students memorized a series of solubility rules (section 3.4.3) to predict if an ionic compound was soluble or not. Using these rules we would predict that insoluble salts formed precipitates and soluble salts dissolved. In this section we will apply chemical equilibria to the concept of solubility and introduce a type of equilibrium constant, the solubility constant, to allow us to calculate how soluble a salt really is.

Solubility Equilibrium defines the dynamic equilibria between a precipitate and its dissolved ions when the rate of dissolution equals the rate of crystallization and the resulting solution is a saturated solution, that contains the maximum concentration of dissolved ions that coexist with the undissolved solute (precipitate).

What do we mean by solubility of a salt? If I say one mole of sodium sulfate dissolves in water I am really meaning for every mole of sodium sulfate that dissolves, two moles of sodium are formed and one mole of sulfate. We will use the concept of solubility to describe the moles the salt that dissolves to form a saturated solution, and the actual ion concentration depends on the formula.

Solubility Product

This is the equilibrium constant for the process of dissolution. Consider the generic salt

$$M_xA_y(s) \leftrightharpoons xM^{+m}(aq) + yA^{-n}(aq) \tag{17.4.1}$$

Noting from charge neutrality that x(+m)+y(-n)=0, then the equilibrium constant expression is:

$$K_{sp} = [M^{+m}]^x[A^{-n}]^y \tag{17.4.2}$$

The solid reactant is not part of the equilibrium, and it is called the solubility product because it is the product of the concentration of all the ions a salt breaks into. It is important to realize this is a heterogeneous equilibrium that defines a saturated solution and the solid is part of the process, although it does not influence the equilibrium concentration. That is, if all the solid is dissolved, you may have an unsaturated solution, and the solubility product defines the concentration of a saturated solution. At the end of this chapter is a solubility product table for ionic compounds at 25°C.

Lets look at the solubility product for Calcium phosphate

$$Ca_3(PO_4)_2(s) \leftrightharpoons 3Ca^{+2} + 2PO_4^{-3} \tag{17.4.3}$$

$$K_{sp}(Ca_3(PO_4)_2) = [Ca^{+2}]^3[PO_4^{-3}]^2 \tag{17.4.4}$$

Solubility Calculations

As in most equilibrium calculations, there are two types of problems. Knowing K, what are the equilibrium concentrations, and knowing the equilibrium concentration of one thing, what is K

Solubility of a Salt

The solubility of a salt is "x" (from the ICE table), but we will not be using ICE tables in solubility product calculations, and are just using it now to explain what is going on. From the following ICE table you can see that for every x moles of the calcium phosphate that dissolves per liter (its solubility), the solution gains 3 times that many moles of calcium and twice that many of phosphate, and there is no calcium phosphate floating around, just calcium and phosphate.

ICE Table	$Ca_3(PO_4)_2(s)$	$\leftrightharpoons$	Ca^{+2}	PO_4^{-3}
Initial	[solid]		0	0
Change	still solid		+3x	+2x
Equilibrium	still solid		3x	2x

That is, x the extent of reaction is a ICE diagram is the solubility of a salt. So you do not use a rice diagram, you say that for every x moles of solid that dissolves, the ions are that times the number of the ions in the formula So for Calcium phosphate

$$[Ca^{+2}] = 3x \ and \ [PO_4^{-3}] = 2x] \tag{17.4.5}$$

$$K_{sp}(Ca_3(PO_4)_2) = [3x]^3[2x]^2 = 108x^5 \tag{17.4.6}$$

Solving for the solubility (x) and noting that K_{sp}(calcium phosphate) = 2.07 × 10^{-33}

$$x = \sqrt[5]{\frac{K_{sp}}{108}} = \left(\frac{2.07x10^{-33}}{108}\right)^{\frac{1}{5}} = 1.14x10^{-7} = 114nM \tag{17.4.7}$$

So there are three questions that can be answered here

1. The solubility of calcium phosphate is 114nM in water (x)
2. The solubility of calcium is 341 nM in water (3x)
3. The solubility of phosphate is 228 nM in water (2x)

Exercise 17.4.1

Which is more soluble, silver thiocyanide (K_{sp} = 1.1 x 10^{-12}) or silver sulfite (K_{sp} = 1.50 x 10^{-14})

Answer

Silver sulfite, you can only compare K_{sp} values if the number of ions are the same, see video below.

For silver thiocyanide,

$$K_{sp} = [Ag^+][SCN^-] = x^2$$

$$x = \sqrt{k_{sp}} = \sqrt{1.1x10^{-12}} = 1.0x10^{-6}$$

For silver sulfite,

$$K_{sp} = [Ag^+][SO_3^{-2}]^2 = x(2x)^2 = 4x^3 \tag{17.4.8}$$

$$x = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.50x10^{-14}}{4}}$$

$$= 1.56x10^{-5}$$



Video 17.4.1: Solution to exercise 17.4.1.

Determining K_{sp}

If a saturated solution of $La(IO_3)_3$ has an iodate concentration of 0.006M, what is K_{sp}?

$$La(IO_3)_3 \leftrightharpoons La^{+3} + 3IO_3^- \tag{17.4.9}$$

The lanthanum ion concentration = x and the iodate ion concentration = 3x=0.0060. So x=0.0020

$$K_{sp} = [La^{+3}][IO_3^{-3}]^3 = [0.0020]0.0060]^3 = 4.2x10^{-10} \tag{17.4.10}$$

Solubility and Common ion Effect

In section 17.1.3 solubility was introduced as an example of the common ion effect, and this problem was explained using ICE table and Le Chatelier's Principle.

What is the solubility of Calcium phosphate in a 0.100M sodium phosphate solution?

This is the same problem as above except that there is a common ion as the soluble sodium phosphate introduces phosphate that shifts the calcium phosphate to the left, reducing its solubility.

$$Ca_3PO_4(s) \leftharpoons 3Ca^{+2} + 2PO_4^{-3} \tag{17.4.11}$$

$$K_{sp}(Ca_3PO_4) = [Ca^{+2}]^3[PO_4^{-3}]^2 \tag{17.4.12}$$

noting that $[PO_4^{-3}] = 0.100M + 3x$ and ignoring the x (see section 17.1.3)

$$K_{sp}(Ca_3PO_4) = [3x]^3[.1]^2 = 0.27x^3 \tag{17.4.13}$$

$$x = \left(\frac{K_{sp}}{0.27}\right)^{\frac{1}{3}} = \left(\frac{2.07x10^{-33}}{0.27}\right)^{\frac{1}{3}} = 1.97x10^{-11} \tag{17.4.14}$$

Exercise 17.4.2

What is the lead concentration for a saturated solution of lead(II)bromide, and then mathematically demonstrate Le Chatlier's principle by determining the lead concentration when in the presence of a common ion by making the solution 1M in sodium bromide.

Answer

As the following video shows, the lead is 0.0118 in the absence of sodium bromide and is reduced to 6.6x10-6 in the presence of 1 M NaBr. This demonstrates Le Chatlier's principle as adding the bromide with the soluble sodium bromide salt pushed the equilbria of the insoluble lead(II)bromide salt to the left (consuming the bromide added), and thus removing the lead.



Video 17.4.2 Solution to exercise 17.4.2

Solubility Product Table

This values relate to 25°C.

table 17.4: Solubility Product Constants

Compound Name	Compound Formula	K_{sp}
Aluminum phosphate	$AlPO_4$	9.84×10^{-21}
Barium bromate	$Ba(BrO_3)_2$	2.43×10^{-4}
Barium carbonate	$BaCO_3$	2.58×10^{-9}
Barium chromate	$BaCrO_4$	1.17×10^{-10}
Barium fluoride	BaF_2	1.84×10^{-7}
Barium iodate	$Ba(IO_3)_2$	4.01×10^{-9}
Barium nitrate	$Ba(NO_3)_2$	4.64×10^{-3}
Barium sulfate	$BaSO_4$	1.08×10^{-10}
Barium sulfite	$BaSO_3$	5.0×10^{-10}
Beryllium hydroxide	$Be(OH)_2$	6.92×10^{-22}
Bismuth arsenate	$BiAsO_4$	4.43×10^{-10}
Bismuth iodide	BiI_3	7.71×10^{-19}
Cadmium carbonate	$CdCO_3$	1.0×10^{-12}
Cadmium fluoride	CdF_2	6.44×10^{-3}
Cadmium hydroxide	$Cd(OH)_2$	7.2×10^{-15}
Cadmium iodate	$Cd(IO_3)_2$	2.5×10^{-8}
Cadmium phosphate	$Cd_3(PO_4)_2$	2.53×10^{-33}
Cadmium sulfide	CdS	8.0×10^{-27}
Calcium carbonate	$CaCO_3$	3.36×10^{-9}
Calcium fluoride	CaF_2	3.45×10^{-11}
Calcium hydroxide	$Ca(OH)_2$	5.02×10^{-6}
Calcium iodate	$Ca(IO_3)_2$	6.47×10^{-6}
Calcium phosphate	$Ca_3(PO_4)_2$	2.07×10^{-33}
Calcium sulfate	$CaSO_4$	4.93×10^{-5}
Cesium perchlorate	$CsClO_4$	3.95×10^{-3}
Cesium periodate	$CsIO_4$	5.16×10^{-6}
Cobalt(II) arsenate	$Co_3(AsO_4)_2$	6.80×10^{-29}
Cobalt(II) hydroxide	$Co(OH)_2$	5.92×10^{-15}
Cobalt(II) phosphate	$Co_3(PO_4)_2$	2.05×10^{-35}
Copper(I) bromide	$CuBr$	6.27×10^{-9}
Copper(I) chloride	$CuCl$	1.72×10^{-7}
Copper(I) cyanide	$CuCN$	3.47×10^{-20}
Copper(I) iodide	CuI	1.27×10^{-12}
Copper(I) thiocyanate	$CuSCN$	1.77×10^{-13}

Compound Name	Compound Formula	K_{sp}
Copper(II) arsenate	$Cu_3(AsO_4)_2$	7.95×10^{-36}
Copper(II) oxalate	CuC_2O_4	4.43×10^{-10}
Copper(II) phosphate	$Cu_3(PO_4)_2$	1.40×10^{-37}
Copper(II) sulfide	CuS	6.3×10^{-36}
Europium(III) hydroxide	$Eu(OH)_3$	9.38×10^{-27}
Gallium(III) hydroxide	$Ga(OH)_3$	7.28×10^{-36}
Iron(II) carbonate	$FeCO_3$	3.13×10^{-11}
Iron(II) fluoride	FeF_2	2.36×10^{-6}
Iron(II) hydroxide	$Fe(OH)_2$	4.87×10^{-17}
Iron(III) hydroxide	$Fe(OH)_3$	2.79×10^{-39}
Iron(III) sulfide	FeS	6.3×10^{-18}
Lanthanum iodate	$La(IO_3)_3$	7.50×10^{-12}
Lead(II) bromide	$PbBr_2$	6.60×10^{-6}
Lead(II) carbonate	$PbCO_3$	7.40×10^{-14}
Lead(II) chloride	$PbCl_2$	1.70×10^{-5}
Lead(II) fluoride	PbF_2	3.3×10^{-8}
Lead(II) hydroxide	$Pb(OH)_2$	1.43×10^{-20}
Lead(II) iodate	$Pb(IO_3)_2$	3.69×10^{-13}
Lead(II) iodide	PbI_2	9.8×10^{-9}
Lead(II)selenite	$PbSeO_4$	1.37×10^{-7}
Lead(II) sulfate	$PbSO_4$	2.53×10^{-8}
Lead(II) sulfide	PbS	8.0×10^{-28}
Lithium carbonate	Li_2CO_3	8.15×10^{-4}
Lithium fluoride	LiF	1.84×10^{-3}
Lithium phosphate	Li_3PO_4	2.37×10^{-11}
Magnesium carbonate	$MgCO_3$	6.82×10^{-6}
Magnesium fluoride	MgF_2	5.16×10^{-11}
Magnesium hydroxide	$Mg(OH)_2$	5.61×10^{-12}
Magnesium phosphate	$Mg_3(PO_4)_2$	1.04×10^{-24}
Manganese(II) carbonate	$MnCO_3$	2.24×10^{-11}
Manganese(II) iodate	$Mn(IO_3)_2$	4.37×10^{-7}
Mercury(I) bromide	Hg_2Br_2	6.40×10^{-23}
Mercury(I) carbonate	Hg_2CO_3	3.6×10^{-17}
Mercury(I) chloride	Hg_2Cl_2	1.43×10^{-18}

Compound Name	Compound Formula	K_{sp}
Mercury(I) fluoride	Hg_2F_2	3.10×10^{-6}
Mercury(I) iodide	Hg_2I_2	5.2×10^{-29}
Mercury(I) oxalate	$Hg_2C_2O_4$	1.75×10^{-13}
Mercury(I) sulfate	Hg_2SO_4	6.5×10^{-7}
Mercury(I) thiocyanate	$Hg_2(SCN)_2$	3.2×10^{-20}
Mercury(II) bromide	$HgBr_2$	6.2×10^{-20}
Mercury (II) iodide	HgI_2	2.9×10^{-29}
Mercury(II) sulfide (red)	HgS	4×10^{-53}
Mercury(II) sulfide (black)	HgS	1.6×10^{-52}
Neodymium carbonate	$Nd_2(CO_3)_3$	1.08×10^{-33}
Nickel(II) carbonate	$NiCO_3$	1.42×10^{-7}
Nickel(II) hydroxide	$Ni(OH)_2$	5.48×10^{-16}
Nickel(II) iodate	$Ni(IO_3)_2$	4.71×10^{-5}
Nickel(II) phosphate	$Ni_3(PO_4)_2$	4.74×10^{-32}
Palladium(II) thiocyanate	$Pd(SCN)_2$	4.39×10^{-23}
Potassium hexachloroplatinate	K_2PtCl_6	7.48×10^{-6}
Potassium perchlorate	$KClO_4$	1.05×10^{-2}
Potassium periodate	KIO_4	3.71×10^{-4}
Praseodymium hydroxide	$Pr(OH)_3$	3.39×10^{-24}
Rubidium perchlorate	$RbClO_4$	3.00×10^{-3}
Scandium fluoride	ScF_3	5.81×10^{-24}
Scandium hydroxide	$Sc(OH)_3$	2.22×10^{-31}
Silver(I) acetate	$AgCH_3CO_2$	1.94×10^{-3}
Silver(I) arsenate	Ag_3AsO_4	1.03×10^{-22}
Silver(I) bromate	$AgBrO_3$	5.38×10^{-5}
Silver(I) bromide	AgBr	5.35×10^{-13}
Silver(I) carbonate	Ag_2CO_3	8.46×10^{-12}
Silver(I) chloride	AgCl	1.77×10^{-10}
Silver(I) chromate	Ag_2CrO_4	1.12×10^{-12}
Silver(I) cyanide	AgCN	5.97×10^{-17}
Silver(I) iodate	$AgIO_3$	3.17×10^{-8}
Silver(I) iodide	AgI	8.52×10^{-17}
Silver(I) oxalate	$Ag_2C_2O_4$	5.40×10^{-12}
Silver(I) phosphate	Ag_3PO_4	8.89×10^{-17}

Compound Name	Compound Formula	K_{sp}
Silver(I) sulfate	Ag_2SO_4	1.20×10^{-5}
Silver(I) sulfide	Ag_2S	6.3×10^{-50}
Silver(I) sulfite	Ag_2SO_3	1.50×10^{-14}
Silver(I) thiocyanate	AgSCN	1.03×10^{-12}
Strontium arsenate	$Sr_3(AsO_4)_2$	4.29×10^{-19}
Strontium carbonate	$SrCO_3$	5.60×10^{-10}
Strontium fluoride	SrF_2	4.33×10^{-9}
Strontium iodate	$Sr(IO_3)_2$	1.14×10^{-7}
Strontium sulfate	$SrSO_4$	3.44×10^{-7}
Thallium(I) bromate	$TlBrO_3$	1.10×10^{-4}
Thallium(I) bromide	TlBr	3.71×10^{-6}
Thallium(I) chloride	TlCl	1.86×10^{-4}
Thallium(I) chromate	Tl_2CrO_4	8.67×10^{-13}
Thallium(I) iodate	$TlIO_3$	3.12×10^{-6}
Thallium(I) iodide	TlI	5.54×10^{-8}
Thallium(I) thiocyanate	TlSCN	1.57×10^{-4}
Thallium(III) hydroxide	$Tl(OH)_3$	1.68×10^{-44}
Tin(II) hydroxide	$Sn(OH)_2$	5.45×10^{-27}
Tin(II) sulfide	SnS	1.0×10^{-25}
Yttrium carbonate	$Y_2(CO_3)_3$	1.03×10^{-31}
Yttrium fluoride	YF_3	8.62×10^{-21}
Yttrium hydroxide	$Y(OH)_3$	1.00×10^{-22}
Yttrium iodate	$Y(IO_3)_3$	1.12×10^{-10}
Zinc arsenate	$Zn_3(AsO_4)_2$	2.8×10^{-28}
Zinc carbonate	$ZnCO_3$	1.46×10^{-10}
Zinc fluoride	ZnF_2	3.04×10^{-2}
Zinc hydroxide	$Zn(OH)_2$	3×10^{-17}
Zinc selenide	ZnSe	3.6×10^{-26}
Zinc sulfide (wurtzite)	ZnS	1.6×10^{-24}
Zinc sulfide (sphalerite)	ZnS	2.5×10^{-22}

Source of data: *CRC Handbook of Chemistry and Physics*, 84th Edition (2004); sulfide data from *Lange's Handbook of Chemistry*, 15th Edition (1999).

Test Yourself

Homework: Section 17.4

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 17.4: Solubility of Salts is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

17.5: Precipitation Reactions

Introduction

Precipitation reactions

$$\underbrace{Ag^+(aq) + Cl^-(aq) \leftrightharpoons AgCl(s)}_{\text{Precipitation of silver chloride}} \tag{17.5.1}$$

are the opposite of solubility expressions.

$$\underbrace{AgCl(s) \leftrightharpoons Ag^+(aq) + Cl^-(aq)}_{\text{Dissolution of silver chloride}}, \quad K_{sp} = [Ag^+][Cl^-] \tag{17.5.2}$$

Therefore solubility constants can be used to determine if a precipitate will form. Although we could write these as precipitation reactions (in which case $K_{ppt} = 1/K_{sp}$), we will use solubility expressions and state that a precipitate will form for a "Product Loaded System," (when reactants are formed), that is, when the back reaction occurs. Review section 15.2.5, the Reaction Quotient.

K_{sp} and Q

Q, the reaction quotient is the equilibrium constant expression at any condition, and a review of 15.2.5, shows there are three possibilities.

- Q=K, No reaction, system is at equilibrium
- Q>K, Product loaded, reactants are produced until Q=K
- Q<K, Reactant loaded, products are produced until Q=K

A precipitate forms if Q>K_{sp} .

Exercise 17.5.1

The solubility product of calcium fluoride (CaF_2) is 3.45×10^{-11}. If 2.0 mL of a 0.10 M solution of NaF is added to 128 mL of a 2.0×10^{-5}M solution of $Ca(NO_3)_2$, will CaF_2 precipitate?

Answer

$Q = [Ca^{+2}][F^-]^2$

$$[Ca^{+2}] = \frac{n_{Ca^{+2}}}{V_T} = \frac{0.128L\left(2.0x10^{-5}M\right)}{0.128L + .002L} = 1.97x10^{-5}M \tag{17.5.3}$$

$$[F^-] = \frac{n_{F^-}}{V_T} = \frac{0.002L\left(0.10M\right)}{0.128L + .002L} = 1.54x10^{-3}M \tag{17.5.4}$$

$$Q = [1.97x10^{-5}][1.54x10^{-3}]^2 = 4.7x10^{-11} \tag{17.5.5}$$

Yes because Q>K_{sp} , but not much, as it is very close.

.

Fractional Precipitation

Two dissolved ions can be separated out if they form salts of different solubilities with the same counter ion. Consider the separation of Ag^+(aq) from Pb^{+2}(aq), both of which form insoluble salts with chloride

$$\begin{aligned} K_{sp}(PbCl_2) &= 1.6x10^{-5} \\ K_{sp}(AgCl) &= 1.8x10^{-10} \end{aligned} \tag{17.5.6}$$

There are three possibilities

1. Both are Product loaded (Q>K for both salts) and reactants are formed, making precipitates (remember, precipitates are the reactants not the products).

salt(s) -> cations(aq) + anions(aq)

$$AgCl(s) \leftrightharpoons Ag^{+}(aq) + Cl^{-}(aq) \qquad (17.5.7)$$
$$PbCl_2(s) \leftrightharpoons Pb^{+2}(aq) + 2Cl^{-}(aq)$$

2. Both are Reactant loaded (Q<K for both salts) and products are formed and both dissolve
3. One is product loaded (Q>K) and the other is reactant loaded (Q<K). The first forms a precipitate and the second dissolves.

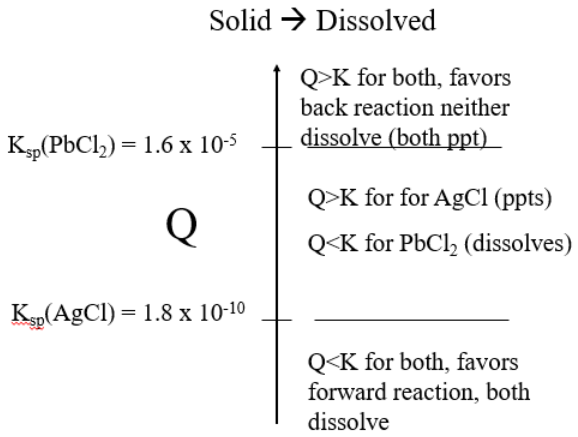


Figure 17.5.1: When Q>1.6x10^{-5} both silver and lead(II) chloride precipitate. When Q< 1.8x10^{-10} they both dissolve, and if Q is between those values only the silver chloride precipitates . (Copyright; Bob Belford CC.0)

Example 17.5.1

Consider a solution containing 0.1M silver nitrate and 0.1 M lead(II) nitrate that you wish to separate by adding chloride. Over what range of chloride will one precipitate and the other not, and which one will precipitate.

$$K_{sp}(PbCl_2 \; = \; 1.6x10^{-5} \qquad (17.5.8)$$
$$K_{sp}(AgCl \; = \; 1.8x10^{-10}$$

Solution

Step 1: Find the chloride concentration for each equilibria where Q=K

$$K_{PbCl_2} = [Pb^{+2}][Cl^{-}]^2 = 1.6x10^{-5} \quad \therefore \quad [Cl^{-}] = \sqrt{\frac{K_{PbCl_2}}{[Pb^{+2}]}} = \sqrt{\frac{1.6x10^{-5}}{0.1}} = 0.00158 \qquad (17.5.9)$$

$$K_{AgCl} = [Ag^{+}][Cl^{-}] \; = \; 1.8x10^{-10} \quad \therefore \quad [Cl^{-}] = \frac{K_{AgCl}}{[Ag^{+}]} = \frac{1.8x10^{-10}}{0.1} = 1.8x10^{-9}$$

Step 2: Find range where Q>K for only one reactant (anything above that they both precipitate) and for which Q<K for only one reactant (below which they both dissolve). So if [Cl^{-}]> 0.00158 than Q is greater than both Ks and a precipitate forms, if [Cl^{-}]< 1.8x10^{-9} than Q is less that both Ks and they both dissolve, and for the range

$$1.8x10^{-9} < [Cl^{-}] < 0.00158 \qquad (17.5.10)$$

only AgCl will precipitate

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

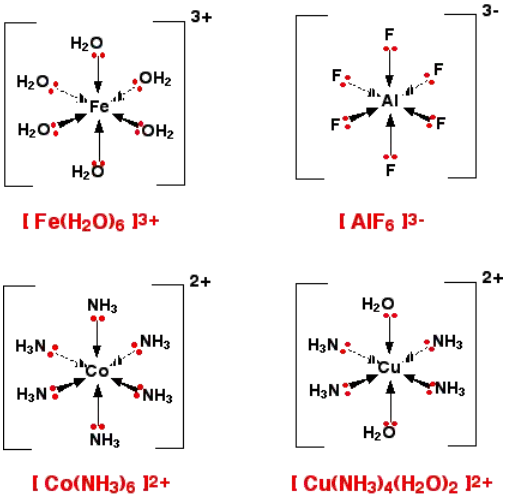
This page titled 17.5: Precipitation Reactions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

17.6: Equilibria Involving Complex Ions

Introduction

Metal cations can function as Lewis acids (review section 16.7.2.3) and form what are called coordination complexes. This is a type of Lewis acid/base reaction where the metal is the Lewis acid and the electron donor (lewis base) is called a ligand. Coordination complexes may be neutral or charged and if it is charged it is called a complex ion.

Figure 17.6.1 shows several complex ions and the formation of complexes can complicate other equilibria and influence the solubility of salts.





Video 17.6.1: Youtube video by Chemistry Channel visualizing how complex ions are formed (https://youtu.be/eLO0orGka8c)

Formation Constants

The following is a table of formation constants. An updated table (table E4) can always be found on LibreText by using the link at the header of each page, Reference Tales/Equilibrium Constants/E4: Complex Ion Formation Constants

Formation Constants for Complex Ions	
Equilibrium	K_f

https://chem.libretexts.org/@go/page/60766

$Al^{3+} + 6\,F^- \rightleftharpoons [AlF_6]^{3-}$	7×10^{19}
$Cd^{2+} + 4\,NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+}$	1.3×10^{7}
$Cd^{2+} + 4\,CN^- \rightleftharpoons [Cd(CN)_4]^{2-}$	3×10^{18}
$Co^{2+} + 6\,NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+}$	1.3×10^{5}
$Co^{3+} + 6\,NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+}$	2.3×10^{33}
$Cu^{+} + 2\,CN \rightleftharpoons [Cu(CN)_2]^{-}$	1.0×10^{16}
$Cu^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	1.7×10^{13}
$Fe^{2+} + 6\,CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$	1.5×10^{35}
$Fe^{3+} + 6\,CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	2×10^{43}
$Fe^{3+} + 6\,SCN^- \rightleftharpoons [Fe(SCN)_6]^{3-}$	3.2×10^{3}
$Hg^{2+} + 4\,Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.1×10^{16}
$Ni^{2+} + 6\,NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	2.0×10^{8}
$Ag^{+} + 2\,Cl^- \rightleftharpoons [AgCl_2]^{-}$	1.8×10^{5}
$Ag^{+} + 2\,CN^- \rightleftharpoons [Ag(CN)_2]^{-}$	1×10^{21}
$Ag^{+} + 2\,NH_3 \rightleftharpoons [Ag(NH_3)_2]^{+}$	1.7×10^{7}
$Zn^{2+} + 4\,CN^- \rightleftharpoons [Zn(CN)_4]^{2-}$	2.1×10^{19}
$Zn^{2+} + 4\,OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	2×10^{15}
$Fe^{3+} + SCN^- \rightleftharpoons [Fe(SCN)]^{2+}$	8.9×10^{2}
$Ag^{+} + 4\,SCN^- \rightleftharpoons [Ag(SCN)_4]^{3-}$	1.2×10^{10}
$Pb^{2+} + 4\,I^- \rightleftharpoons [PbI_4]^{2-}$	3.0×10^{4}
$Pt^{2+} + 4\,Cl^- \rightleftharpoons [PtCl_4]^{2-}$	1×10^{16}
$Cu^{2+} + 4\,CN \rightleftharpoons [Cu(CN)_4]^{2-}$	1.0×10^{25}
$Co^{2+} + 4\,SCN^- \rightleftharpoons [Co(SCN)_4]^{2-}$	1×10^{3}

Complex Ion Formation

This section is under construction

Consider the formation of the complex ion $[Cu(CN)_4]^{-2}$(aq),

Cu^{+2}(aq) + $4CN^-$(aq) $\leftrightharpoons$ $[Cu(CN)_4]^{-2}$(aq)

$K_f = \frac{[Cu(CN)_4]^{-2}}{[Cu^{+2}][CN^-]^4}$ K_f=1.0x10^{25}.

What is the copper(II) ion concentration for 0.10M $Cu(NO_3)_2$?

? Exercise 17.6.1

What is the copper(II) ion concentration for 0.10M $Cu(NO_3)_2$?

Answer

Since it is a soluble nitrate salt it all dissociates, and the concentration is 0.10M.

d

? Exercise 17.6.2

What is the copper(II) ion concentration for 0.10M $Cu(NO_3)_2$ if you add 1 mol of sodium cyanide to a liter of the 0.10M copper(II)nitrate solution? (K_f for $[Cu(CN)_4]^{-2}(aq) = 1.0x10^{25}$)

Answer

Since K_f=1x10^{25} >>1000 (very large) you assume the following equation goes to the right and all the cyanide becomes complexes

$$Cu^{+2}(aq) + 4CN^{-}(aq) \leftharpoons [Cu(CN)_4]^{-2}$$

20

$$Cu(CN)_4^{-2}(aq) = \frac{CN^-}{4} = \frac{1}{4} = 0.25M = f$$

$K_f=1x10^{25}$, which is very very large, so assume almost all the copper is converted to the complex, also note,

$$K_f = \frac{\left[Cu(CN)_4^{2+}\right]}{\left[Cu^{2+}\right]\left[CN^-\right]^4}$$

$$\left[Cu^{2+}\right] = \frac{\left[Cu(CN)_4^{2+}\right]}{K_f[CN^-]^4}$$

$$\left[Cu^{2+}\right] = \frac{[0.25]}{1*10^{25}[0.10]^4} = 1.2*10^{-8}$$

so \([Cu[CN]_4]^{-2}=\frac{CN^-}{4}=0.25M \)

d

and what is it if you add 1 mol of sodium cyanide to a liter of the 0.10M copper(II)nitrate solution? (K_f for $[Cu[CN)_4]^{-2}(aq) = 1.0x10^{25}$)

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 17.6: Equilibria Involving Complex Ions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

17.7: Solubility and Complex Ions

Introduction

Many cations form both precipitates and complex ions, and sometimes with the same ion. For example silver forms both a precipitate and a complex ion with chloride, and so the solubility product alone will lead to an incorrect estimate of its solubility.

Solubility Product for AgCl:

$$AgCl(s) \leftrightharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} = 1.8x10^{-10} \tag{17.7.1}$$

Complex ion formation for Silver and chloride:

$$Ag^+(aq) + 2Cl^-(aq) \leftrightharpoons [AgCl_2]^- \quad K_f = 1.1x10^5 \tag{17.7.2}$$

For pure silver chloride, K_{sp} gives the silver and chloride concentrations for a saturated solution because the ratio of silver to chloride is one-to-one. If an external source of chloride was introduced via another salt where chloride was a common ion the solubility of the silver does not go down as predicted by the common ion effect and Le Chatlier's Principle, but it actually goes up due to the formation of a complex ion. In the case where a second salt contributes chloride we need to add the above two equations, which means the total equilibrium constant is the product of the above two (review section 15.5, Balanced Equations and Equilibrium Constants).

$$\begin{aligned} AgCl(s) &\leftrightharpoons Ag^+(aq) + Cl^-(aq) \quad K = K_{sp} \\ \underline{Ag^+(aq) + 2Cl^-(aq) &\leftrightharpoons [AgCl_2]^-(aq) \quad K = K_f} \\ AgCl(s) + Cl^-(aq) &\leftrightharpoons [AgCl_2]^-(aq); \quad K = K_{sp}K_f = 2.0x10^{-5} \end{aligned} \tag{17.7.3}$$

Exercise 17.7.1

What is the $[AgCl_2]^-$ concentration in the presences of AgCl(s) for a solution that is 1.0M NaCl?

Answer

$$K = \frac{[AgCl_2^-]}{[Cl^-]} = \frac{x}{1.0 - x} \approx 2 \times 10^{-5} = x$$

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 17.7: Solubility and Complex Ions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

CHAPTER OVERVIEW

18: Entropy and Free Energy

18.1: Spontaneity and Energy Transfer
18.2: Dispersal of Energy- Entropy
18.3: Entropy - A Microscopic Understanding
18.4: Entropy Measurements and Values
18.5: Second Law and Gibbs Free Energy
18.6: Gibbs Free Energy

This page titled 18: Entropy and Free Energy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

18.1: Spontaneity and Energy Transfer

Introduction

This chapter builds upon chapter 5, Energy in Chemical Reactions, where we introduced two state functions, internal energy (U) and enthalpy (H), along with the First Law of Thermodynamics, which states that the energy change of the universe during a chemical process is zero. This allowed us to recognize that some reactions are exothermic and give heat to the surrounding, while others are endothermic and absorb heat from the surrounding. But it does not tell us if something will proceed spontaneously, and if so, in which directions and for how far? That is, in what direction will a chemical reaction proceed, and once completed, what will the equilibrium state look like? To answer these questions we will introduce in this chapter two new state functions, entropy (S) and Gibbs Free Energy (G), along with the second and third laws of thermodynamics. At the completion of this chapter you will be able to use thermodynamics to determine if a system is at equilibrium (Q=K), if it is product loaded (Q>K) or reactant loaded (Q<K), and what the composition of the system will look like when the reaction is over (K=?). That is, thermodynamics tells of if once the reaction is over you have lots of products (K>>1), lots of reactants (K<<1) or reactants and products coexisting in equilibrium (0.001<K<1000).

Thermodynamic Stability

Thermodynamics provides information on equilibrium conditions, but not how fast a state reaches equilibrium. This is important to understand as there are two different factors that influence the stability of a state, kinetics and thermodynamics. Consider the conversion of diamond to graphite. From the phase diagram of carbon, it can be seen that diamond is the thermodynamically favored allotrope under geological conditions of high pressure, but at ambient conditions, graphite is the more stable allotrope, and diamond spontaneously converts to graphite. Yet, diamonds are "stable" and this is because the activation energy for the process is so high that the rate becomes negligible, and to mortals, "diamonds last forever". The phase diagram is using the term "metastable diamond" to indicate that it is thermodynamically unstable, but kinetically stable, in the sense that the reaction rate is so slow that it is not observable on a normal timescale.

$$\mathrm{C}_{(s,\ \mathrm{diamond})} \longrightarrow \mathrm{C}_{(s,\ \mathrm{graphite})} \tag{18.1.1}$$

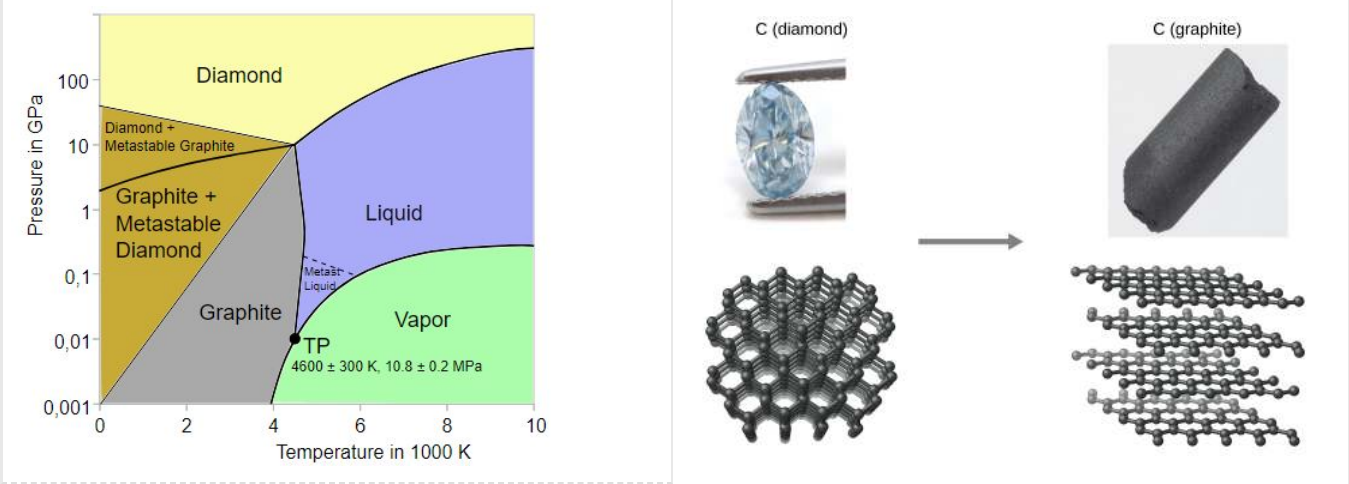


Figure18.1.1: Phase diagram showing graphite is the stable form of carbon at ambient conditions (note 1 GPa = 9,869 atm, and 1 atm = 0.000101 GPa). This indicates diamonds are not stable at atmospheric conditions, but "Diamonds Last Forever", right? Diamond is called "metastable" because it requires such a high activation energy that the rate is so slow that it does not occur at an observable rate, but it is thermodynamically unstable. It is important to understand that thermodynamics does not tell you how fast a reaction happens, but if a system is at equilibrium, and if not, in what direction it will go to reach equilibrium.

So it is important in the study of chemistry to realize that thermodynamic state functions give us information on the stability and reactivity of a system from the perspective of the current state of a system as it transforms to the final equilibrium state, but not the kinetics on how the transition between states is achieved. In this chapter we will focus on the thermodynamic meaning of spontaneous, which is a process that occurs without being driven by the addition of an external energy source.

Spontaneous and Nonspontaneous Processes

From a thermodynamic perspective many spontaneous processes are exothermic and release energy, like a ball rolling down a hill or a piece of paper combusting into carbon dioxide and water. This implies a reverse process in a nonspontaneous direction where you must add energy to the system to make a process occur, like pushing the ball up the hill, or forming plant matter from carbon dioxide and water through photosynthesis, which uses the energy of the sun to drive the process. This model is correct in the sense that there is a direction of spontaneity, and thus a direction of nonspontaneity, but it is incorrect in the sense that spontaneity is not necessarily related to exothermicity (release of energy). Yes, exothermic reactions tend to be spontaneous, but some endothermic reactions are also spontaneous. Consider the freezing of water or the melting of ice, which process is spontaneous?



Figure18.1.2 Does the ice melt or the water freeze? (image uploaded with permission of author).

Does the ice spontaneously melt (exothermic process) or the water spontaneously freeze (endothermic process)? Common sense tells us that it depends on the temperature; if the ambient temperature is above the freezing point the spontaneous process is the endothermic process of melting, while if the ambient temperature is below the freezing point it is the spontaneous exothermic process of freezing. So the direction of spontaneity is influenced by the temperature and can not be described by enthalpy and exothermicity alone. As we shall see, a new thermodynamic function called entropy can answer this question.

Dispersal of Matter and Energy

Expansion of Gas into Vacuum

Another spontaneous process is diffusion of a mobile substance from a region of high concentration to a region of lower concentration. Consider a gas in the left bulb of a container as in figure 18.1.3, where the right bulb is evacuated and contains no particles ($P_{right} = 0$, it is in a vacuum). If you open the stopcock the gas spontaneously flows from the left bulb to the right until the density is equal. Once this state is reached, the reverse process will not occur, where the gas completely leaves one bulb forming a vacuum.

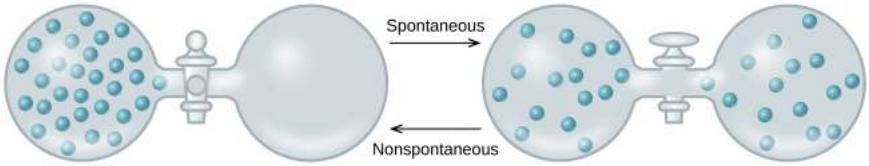


Figure18.1.3 The process of filling an evacuated container is spontaneous, while the reverse process of creating one is nonspontaneous.

If the above process occurs in an isolated system where no heat is transferred with the surroundings, the initial energy change of the right side is zero because P=0 (it is in a vacuum) and since the work of expansion is $-P\Delta V$, (review 5.4.1) there is no initial reduction in energy and so the process of a gas expanding into a vacuum is not being driven by a lowering of energy, and indeed is being driven by the dispersal of matter. That is, the equilibrium state is the state where the matter is the most dispersed. This is not to say the number of particles in the two bulbs are the same, as one bulb may be larger than the other. This is saying they move from an area of high density to low density until the density is the same.

Thermal Heat Transfer

If we look at heat transfer (figure 18.1.4) we see a similar process to that of figure 18.1.3 except that energy in the form of heat is being dispersed, as energy is flowing from the hot object to the cold object. This does not mean the energy is flowing from the

object with more energy to the object with less, as the cold object could be of greater mass, or be of a different type of material with a different heat capacitance (review section 5.2 heat capacitance, $q = mc\Delta T$. Initially the rate of heat transfer from the hot object to the cold object is faster than from the cold to the hot, and so there is a net transfer of heat from hot to cold until they reach the same temperature, at which time the rate of heat transfer between them is equal.



Figure18.1.4: Transfer of heat energy from high to low temperature.

Homework

section 18.1

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 18.1: Spontaneity and Energy Transfer is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

18.2: Dispersal of Energy- Entropy

Introduction

To understand the direction of spontaneity we need to introduce the concept of entropy and the **Second Law of Thermodynamics, which states that for a spontaneous process the entropy of the universe increases**. There are two definitions for entropy, the first is the thermodynamic definition developed by Clausius and is the operational definition we will be using in this class.

$$S = \frac{q_{reversible}}{T_{absolute}} \tag{18.2.1}$$

This definition is based on the work of Carnot, who studied steam heat engines and their efficiency as energy was transferred from the high temperature to the low temperature reservoirs.

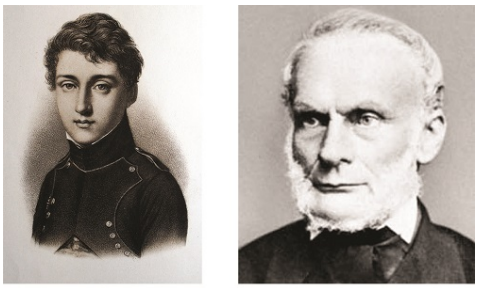


Figure18.2.1: *Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.*

The second definition is often called the configurational or statistical definition, as it is based on statistical thermodynamics and the ways a system can be configured.

$$S = K_B \ln W \tag{18.2.2}$$

Where K_B is the Boltzmann's constant (1.38065 × 10^{-23} J/K) and W (often labeled Ω) is the number of possible arrangements of the system. Boltzmann's work was actually on gases and K_B is the ideal gas constant (R) divided by Avogadro's number. Boltzmann's constant are now one of the "immutable" fundamental constants that is being used for the redefined SI base units.



Figure18.2.2: The Boltzmann equation is engraved on Ludwig Boltzmann's gravestone.

In this view, there are "microstates" that describe the various ways energy and matter can be configured, and the observable macroscopic state is a result of the probability of the available microstates. This will be briefly developed in the next section (18.3), with a focus on conceptual understanding.

Entropy is a State Function

Entropy is a state function like enthalpy or internal energy (review Section 5.4.4). This can be seen by rearranging Clausius's eq. for entropy as follows:

$$\Delta S = \frac{q_{rev}}{T} \rightarrow q_{rev} = T\Delta S \tag{18.2.3}$$

$$noting \;\; \Delta H = q_{rev,p} \;\; gives$$

$$\Delta H = T\Delta S$$

This means that like enthalpy, the entropy change between the final and initial state is independent of the path and only dependent of the values of the final and initial states.

Entropy as an Extensive Property

Extensive properties depend on the extent of the system (review section 1.6 Physical Properties) and properties like enthalpy, volume and mass are extensive (2 gallons of gasoline have twice the volume, mass and energy than one gallon), while intensive properties do not depend on the extent of the system (combining two one gallon containers of water at 25ºC does not result in two gallons at 50ºC, but two gallons at 25ºC).

If we take a closer look

$$\Delta H = T\Delta S \tag{18.2.4}$$

Since Enthalpy is an extensive property, and temperature is an intensive property, entropy must be extensive.

Second Law of Thermodynamics

The Second Law of Thermodynamics states that for a spontaneous process, the entropy of the Universe increases. This is often called times arrow, and the challenge is, how do we measure an increase in the entropy of the universe?

$$\Delta S_{Universe} > 0 \tag{18.2.5}$$

But also, as we shall see, the second law allows us to determine if a system is at equilibrium, and if it is not, in which way it will proceed (as it proceeds in the direction defined by the second law).

Third Law of Thermodynamics

The third law of thermodynamics states that the entropy of a pure crystal at the temperature of absolute zero is zero. A pure crystal is a crystal with a mono-isotopic constitution where there is only one possible microstate that represents its arrangement. If there was another isotope that would introduce entropy as there would be more than one microstate that could represent where the different isotopes are located.

At any temperature above absolute zero, the particle (atoms, molecules, or ions) that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure 18.2.1). The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy. A perfectly ordered system with only a single microstate available to it would have an entropy of zero. The only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), where each component atom, molecule, or ion is identical and fixed in place within a crystal lattice and exhibits no motion (ignoring quantum effects). Such a state of perfect order (or, conversely, zero disorder) corresponds to zero entropy. In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved. Nonetheless, the combination of these two ideals constitutes the basis for the third law of thermodynamics: the entropy of any perfectly ordered, crystalline substance at absolute zero is zero.

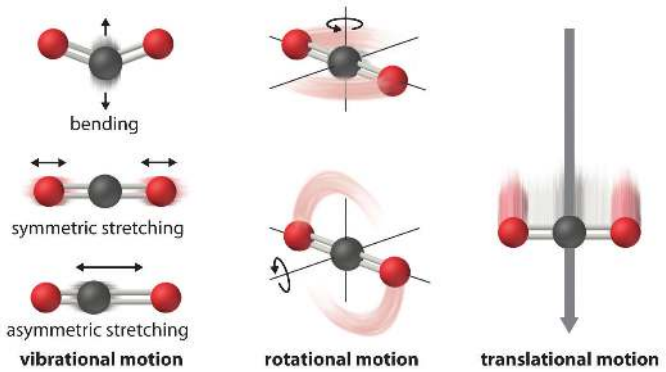


Figure 18.2.1: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion and have zero entropy. In practice, this is an unattainable ideal.

The third law of thermodynamics has two important consequences: it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature. In practice, chemists determine the absolute entropy of a substance by measuring the molar heat capacity (C_p) as a function of temperature and then plotting the quantity C_p/T versus T. The area under the curve between 0 K and any temperature T is the absolute entropy of the substance at T. In contrast, other thermodynamic properties, such as internal energy and enthalpy, can be evaluated in only relative terms, not absolute terms. In this section, we examine two different ways to calculate ΔS for a reaction or a physical change. The first, based on the definition of absolute entropy provided by the third law of thermodynamics, uses tabulated values of absolute entropies of substances. The second, based on the fact that entropy is a state function, uses a thermodynamic cycle similar to those discussed previously.

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 18.2: Dispersal of Energy- Entropy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

18.3: Entropy - A Microscopic Understanding

Introduction

Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the number of *microstates* possible for the system. A microstate (Ω) is a specific configuration of the locations and energies of the atoms or molecules that comprise a system like the following:

$$S = k \ln \Omega \quad (18.3.1)$$
$$or$$
$$S = k \ln W$$

Here k is the Boltzmann constant and has a value of 1.38×10^{-23} J/K.

In general chemistry 1 we calculated ground state electron distributions where electrons resided in specific orbitals, which if we followed the Aufbau principle, the lowest energy state as the ground state. But if we added energy to the system, excited states could be obtained. Each of these states is a type of microstate. The ground state of helium would be $1S^2$ with both electrons being in the ground state. As we add energy to the system the temperature goes up, and the electrons can exist in various excited states. Entropy is related to the number of available states, and increases as the number of states increases. In reality we are discussing the ways energy and particles can be distributed in a system, and there are microstates related to the various translational, vibrational, and rotational modes energy can be distributed in a system

Entropy is also a state function, and so the energy difference between its final (S_f) and initial (S_i) states is independent of the path:

$$\Delta S = S_f - S_i = k \ln \Omega_f - k \ln \Omega_i = k \ln \frac{\Omega_f}{\Omega_i} \quad (18.3.2)$$

For processes involving an increase in the number of microstates, $\Omega_f > \Omega_i$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $\Omega_f < \Omega_i$, yield a decrease in system entropy, $\Delta S < 0$.

Consider the general case of a system composed of N particles distributed among n boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in $2^4 = 16$ different microstates as illustrated in Figure 18.3.2 Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

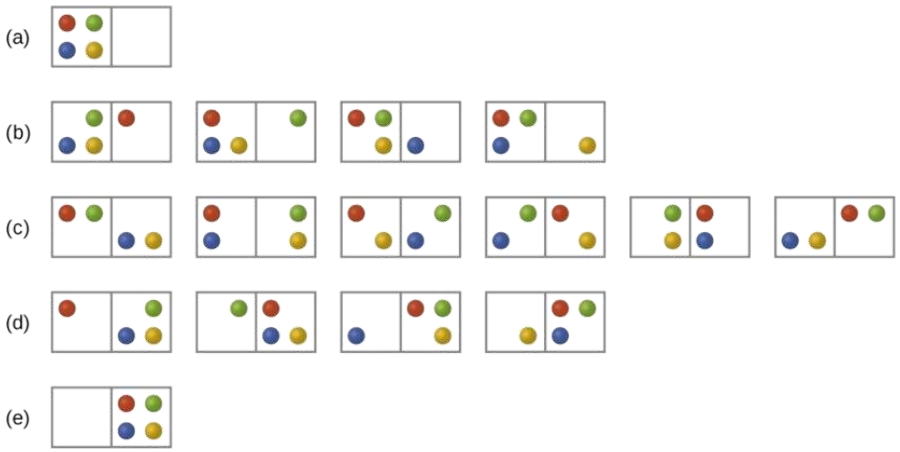


Figure 18.3.2: T*he sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.*

> *The most probable distribution is therefore the one of greatest entropy.*

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is

$$\frac{6}{16} = \frac{3}{8} \tag{18.3.3}$$

The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of

$$\frac{1}{16} \tag{18.3.4}$$

The probability of finding all particles in only one box (either the left box or right box) is then

$$\left(\frac{1}{16} + \frac{1}{16}\right) = \frac{2}{16} = \frac{1}{8} \tag{18.3.5}$$

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

In section 18.1.3 we looked at the expansion of a gas into a vacuum. We took a statistical thermodynamic approach, the least probable configuration would be for all the particles to be in one bulb and none in the other (analogous to (a) and (s) of figure 18.3.2 (above) and this state would have the lowest entropy. The state with the highest entropy would have an equivalent number of particles in both bulbs, analogous to (c) above, and so going from the initial state to the final state would represent an increase in entropy.

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

Some of this material was borrowed from OpenStax.,

This page titled 18.3: Entropy - A Microscopic Understanding is shared under a CC BY license and was authored, remixed, and/or curated by Robert Belford.

18.4: Entropy Measurements and Values

Introduction

So far we have introduced the Second Law of Thermodynamics, which states that for a spontaneous process the entropy of the universe increases, and we have introduced two definitions for entropy.

$$\underbrace{S = \frac{q_{rev}}{T_{abs}}}_{\text{thermodynamic definition of entropy}} \tag{18.4.1}$$

$$\underbrace{S = K_B ln W}_{\text{statistical thermodynamic definition of entropy}} \tag{18.4.2}$$

Predicting Entropy Changes

We will now look at some common processes where we can predict if entropy of the system will increase or decrease.

Phase Changes

Entropy changes across phases are typically easy to predict because some phases are clearly more dispersed than others.

$$S_{solid} < S_{liquid} < S_{gas} \tag{18.4.3}$$

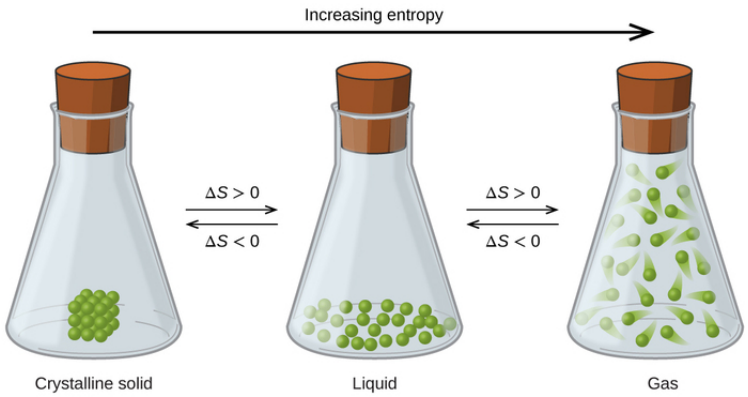


Figure18.4.1: Entropy increases as a substance transitions from a solid to a liquid to a gas.

This is pretty easy to see because the particulate material becomes far more dispersed as it transitions from a solid to a liquid to a gas. Not only are the locations of the particles more dispersed in going from left to right, but they also gain more energy, and so each particle has more energy microstates available to it, thereby increasing the entropy of the system.

Temperature Changes

As the temperature increases the entropy increases due to the increased number of available states. This can be seen by the energy profile on the left part of figure 18.4.2 where the different kinetic energy states could be visualized as a type of microstate. That is, at lower temperatures most of the molecules are in lower energy states, but as the temperature increases more and more molecules enter higher energy states, and so the entropy of the system increases.

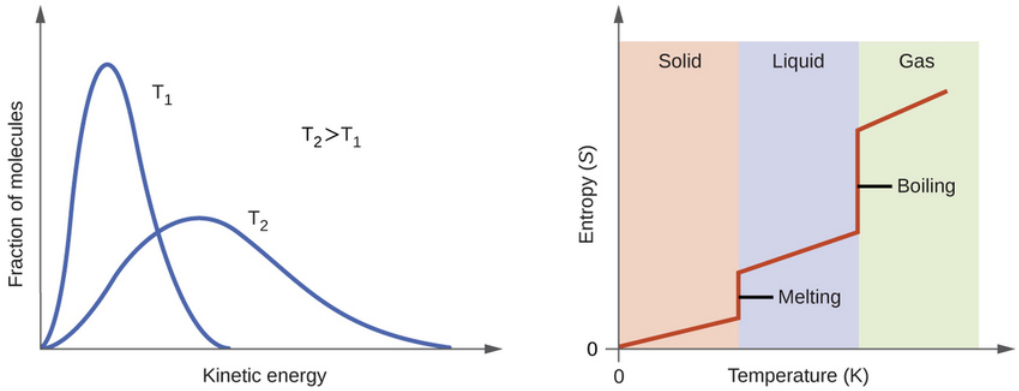


Figure18.4.1: The left side shows an energy diagram for a gas and that at higher temperatures there are more states available. The right side shows how entropy is a function of both phase changes and temperature changes.

Mixing (Dissolution)

Typically, dissolution process involves an increase in entropy because a solid becomes more dispersed as it dissolves, but this is not always the case, because sometimes the solute introduces order into the solvent. For example, the dissolution of calcium hydroxide has a negative not positive entropy change

$$Ca(OH)_2(s) \leftrightharpoons Ca(OH)_2(aq) \tag{18.4.4}$$

At first glance you would (incorrectly) think that the above equation represents an increase in entropy because $Ca(OH)_2(aq)$ is more dispersed than $Ca(OH)_2(s)$, which it is, but the water becomes more organized, and although water is not explicitly written in the above equation, it is the solvent of aqueous systems and the most common species. The water not only becomes oriented around the ions because of ion-dipole interactions, but in the case of many metal ions, form complex ions (see section 17.6). Hydroxide salts also have a common ion with the water and suppress its autodissociation (raising the pH) and so things can get real complex real quick. The important thing to note here is that the system is not just the solute, but the solute and the solvent, and sometimes a solute causes a decrease in the entropy of the solvent, and that effect is greater than the increase in entropy the solute itself undergoes. (In the case of calcium hydroxide, the solute (calcium hydroxide) did undergo an increase in entropy upon dissolution, but it induced a decrease in entropy of the solvent (water), so the net effect is a decrease in entropy.

Reactions that Change the Number of Particles

A reaction that increases the number of particles tends to increase the entropy because the greater the number of particles in a system, the greater the number of available microstates and thus the greater the entropy. But, if there is a phase change, that will have a larger effect. and so two gas particles becoming three solids would not have an increase in entropy.

Exercise 18.4.1

Consider the following reactions of the nature 2A + B --> 2C. Indicate if they would have an increase or decrease in entropy, and give major reason why.

$$\begin{aligned} &(a.)\ \ 2C(s) + O_2(g) \rightarrow 2CO(g) \\ &(b.)\ \ 2K(s) + Br_2(l) \rightarrow 2KBr(s) \\ &(c.)\ \ 2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \end{aligned} \tag{18.4.5}$$

Answer

(a.) Increase, even though the total number of particles decrease, the number of gas phase increases.
(b.) Decrease, because liquid becomes solid, and there are less particles
(c.) Decrease, phase is the same, but number of particles decreases.

Size (Complexity) of Molecules

If you consider each bond as having different ways to vibrate, and possibly rotate, then the more bonds and the more complex a molecule, the more ways it can distribute energy, and so the more microstates it has. This results in an increase in entropy. So one would expect a complex molecule to have a higher entropy than a simple molecule.

Standard State Entropies

Because entropy is a state function the entropy of a reaction can be calculated through standard state molar entropies of formation the same way they can be calculated for enthalpies of reaction (review section 5.7.3, Standard Enthalpies of Formation).

Molar Entropy

The standard molar entropy is the entropy contained in one mole of a substance at standard state. The standard state values used in this text are P=1 bar (0.983 atm), T=298K and the concentration of a solute equal to a one molar solution. Note, the standard temperature may change between tables, so you should always look at the table to see the referenced temperature. In this class that will be 298K. Also, prior to 1982 the standard state pressure was 1 atm, and so older data tables may reference that pressure.

The molar entropy is analogous to the molar enthalpy of formation, and represents the energy change associated with the formation of a compound from its elements in their standard state, except that it is calculated for the change in entropy from absolute zero, when the value equaled 0.

For liquid water the equation would be

$$H_2(g) + \frac{1}{2}O_2 \rightarrow H_2O(l) \quad S^o = 69.91 \frac{J}{mol \cdot K} \tag{18.4.6}$$

Table of Molar Entropies

The following table has the molar entropies for select substances. Table T1 is a more comprehensive table, that can be found from the header of any LibreText chemistry page using the links Reference_Tables/Thermodynamics_Tables/T1:_Standard_Thermodynamic_Quantities.

Open Table

Substance	S°_{298} (J mol−1 K−1)
carbon	
C(*s*, graphite)	5.740
C(*s*, diamond)	2.38
CO(*g*)	197.7
$CO_2(g)$	213.8
$CH_4(g)$	186.3
$C_2H_4(g)$	219.5
$C_2H_6(g)$	229.5
$CH_3OH(l)$	126.8
$C_2H_5OH(l)$	160.7
hydrogen	
$H_2(g)$	130.57
H(*g*)	114.6
$H_2O(g)$	188.71
$H_2O(l)$	69.91
HCI(*g*)	186.8
$H_2S(g)$	205.7
oxygen	
$O_2(g)$	205.03

There are several important differences to note between the standard state molar entropy and standard state molar enthalpy of formation, as can be seen in figure 18.4.2.

Substance	*State*	ΔH_f° $(\frac{\text{kJ}}{\text{mol}})$	S° $(\frac{\text{J}}{\text{mol·K}})$
Ag	s	0	42.6
Ag^+	aq	105.79	72.7
AgCl	s	−127.01	96.2
AgBr	s	−100.4	107.1
$AgNO_3$	s	−124.4	140.9
Al	s	0	28.3

Figure18.4.2: Comparison of standard entropies with standard molar enthalpies of formation.

Things to note in Figure 18.4.2:

1. ΔH_f^o represents the change in forming something from its constituent elements at standard state while the molar entropy is not a Δ and represents the actual value as compared to a value of zero at absolute zero. (see Molar Entropies: A Deeper Look)
2. Substances in the pure state (Ag(s) and Al(s)) have ΔH_f^o =0 as it represents the change in forming them from themselves, **but there is an entropy value,** which is the difference in entropy of the pure substance at 298K in contrast to the value of oK (which equals 0).
3. There are never negative S^o values, but there can be negative ΔH_f^o values.
4. The values of enthalpies are 1000 times larger, look at the units (kJ/mol, in contrast to J/mol-K).

deeper look at molar entropy as absolute value

Why does the standard molar entropy of formation for a pure substance not have a Δ, that is it is S_f^0 and has a value for a pure element in it's standard state, while standard enthalpies (and Free Energies) are expressed with a $Delta$, that is it is ΔH_f^0 or (ΔG_f^0), and their values of formation equal zero for elements in their standard state.

Deeper Look

Energy values, as you know, are all relative, and must be defined on a scale that is completely arbitrary; there is no such thing as the absolute energy of a substance, so we can arbitrarily define the enthalpy or internal energy of an element in its most stable form at 298K and 1 atm pressure as zero. The same is *not* true of the entropy; since entropy is a measure of the "dilution" of thermal energy, it follows that the less thermal energy available to spread through a system (that is, the lower the temperature), the smaller will be its entropy. In other words, as the absolute temperature of a substance approaches zero, so does its entropy. This principle is the basis of the *Third law of thermodynamics*, which states that the entropy of a perfectly-ordered solid at 0 K is zero.

The *absolute entropy* of a substance at any temperature above 0 K must be determined by calculating the increments of heat *q* required to bring the substance from 0 K to the temperature of interest, and then summing the ratios *q*/*T*. Two kinds of experimental measurements are needed:

The enthalpies associated with any **phase changes** the substance may undergo within the temperature range of interest. Melting of a solid and vaporization of a liquid correspond to sizeable increases in the number of microstates available to accept thermal energy, so as these processes occur, energy will flow into a system, filling these new microstates to the extent required to maintain a constant temperature (the freezing or boiling point); these inflows of thermal energy correspond to the heats of fusion and vaporization. The entropy increase associated with melting, for example, is just $\Delta H_{fusion}/T_m$. The **heat capacity** *C* of a phase expresses the quantity of heat required to change the temperature by a small amount ΔT , or more precisely, by an infinitesimal amount dT . Thus the entropy increase brought about by warming a substance over a range of temperatures that does not encompass a phase transition is given by the sum of the quantities $C\,dT/T$ for each increment of temperature dT . This is of course just the integral

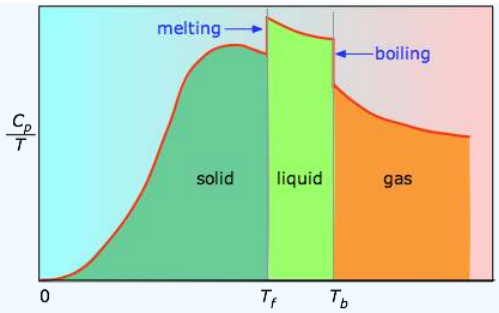


Figure 18.4.3: Heat capitity/temperature as a function of temperature

The area under each section of the plot represents the entropy change associated with heating the substance through an interval ΔT. To this must be added the enthalpies of melting, vaporization, and of any solid-solid phase changes. Values of C_p for temperatures near zero are not measured directly, but can be estimated from quantum theory.

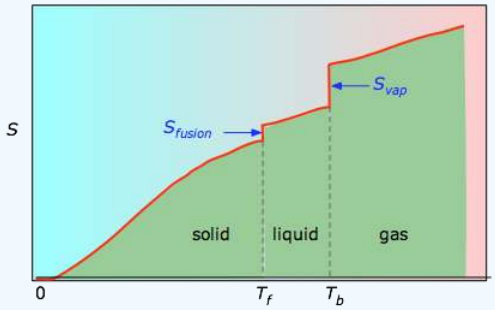


Figure 18.4.4: Molar entropy as a function of temperature

The cumulative areas from 0 K to any given temperature (taken from the experimental plot on the left) are then plotted as a function of T, and any phase-change entropies such as $S_{vap} = H_{vap} / T_b$ are added to obtain the absolute entropy at temperature T. As shown in Figure 18.4.4above, the entropy of a substance increases with temperature, and it does so for two reasons:

As the temperature rises, more microstates become accessible, allowing thermal energy to be more widely dispersed. This is reflected in the gradual increase of entropy with temperature. The molecules of solids, liquids, and gases have increasingly greater freedom to move around, facilitating the spreading and sharing of thermal energy. Phase changes are therefore accompanied by massive and discontinuous increase in the entropy.

$$S_{0^o \rightarrow T^o} = \int_{o^o}^{T^o} \frac{C_p}{T} dt \tag{18.4.7}$$

Because the heat capacity is itself slightly temperature dependent, the most precise determinations of absolute entropies require that the functional dependence of C on T be used in the above integral in place of a constant C.

$$S_{0^o \rightarrow T^o} = \int_{o^o}^{T^o} \frac{C_p(T)}{T} dt \tag{18.4.8}$$

When this is not known, one can take a series of heat capacity measurements over narrow temperature increments ΔT and measure the area under each section of the curve in Figure 18.4.3

Entropy of Reaction

One can calculate the standard state entropy of reaction from standard molar entropies the same way one can calculate the enthalpy of reaction from the standard state molar enthalpies of formation (review section 5.7.4, Calculating Enthalpy of Reaction From Standard Enthalpies of Formation).

$$\Delta S^\circ = \sum n S^\circ_{298}(\text{products}) - \sum m S^\circ_{298}(\text{reactants}) \tag{18.4.9}$$

https://chem.libretexts.org/@go/page/60791

Where n and m represents stoichiometric coefficients of individual products and reactants in the balanced equation representing the process. For example, $\Delta S°_{rxn}$ for the following reaction at room temperature

$$mA + nB \longrightarrow xC + yD \tag{18.4.10}$$

is computed as the following:

$$= [xS°_{298}(C) + yS°_{298}(D)] - [mS°_{298}(A) + nS°_{298}(B)] \tag{18.4.11}$$

Table 18.4.2lists some standard entropies at 298.15 K. You can find additional standard entropies in Tables T1 or T2.

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

Some of this material was borrowed from OpenStax.,

This page titled 18.4: Entropy Measurements and Values is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

18.5: Second Law and Gibbs Free Energy

Introduction

The Second Law of Thermodynamics states that a spontaneous process occurs when there is an increase in the entropy of the universe. Figure 18.5.1 shows a block diagram of the

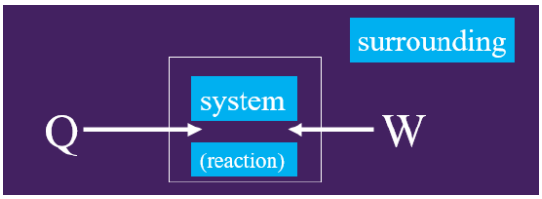


Figure 18.5.1: Block diagram of the universe consisting of the system (which is the reaction) and the surroundings.

Derivation of Gibbs Free Energy

According to the First Law of Thermodynamics, positive energy flow is when work is done on the system, or heat is added to it, and the total energy change of the universe is zero (the energy gained by the system is lost by the surroundings, and vice versa).

Writing the first law, and equating the entropy of the universe to that of the system plus the surroundings gives:

$$\begin{gathered} \Delta S_{Universe} > 0 \\ \Delta S_{Universe} = \Delta S_{System} + \Delta S_{Surroundings} \\ \therefore \\ \Delta S_{System} + \Delta S_{Surroundings} > 0 \end{gathered} \tag{18.5.1}$$

Noting that the system is the chemical reaction, and $\Delta S_{reaction}$ can be determined from the standard molar entropies (see section 18.4.3.2, Entropies of Reaction), gives the following expression of the second law:

$$\Delta S_{Reaction} + \Delta S_{Surroundings} > 0 \tag{18.5.2}$$

Noting from the Clausius definition of entropy

$$\begin{gathered} \Delta S_{Surroundings} = \frac{q_{surroundings}}{T} \\ so \\ \Delta S_{Reaction} + \frac{q_{Surroundings}}{T} > 0 \end{gathered} \tag{18.5.3}$$

and from the first law, that when the system loses heat, the surroundings gains heat,

$$\begin{gathered} q_{surroundings} = -q_{system} = -q_{reaction} \\ so \\ \Delta S_{reaction} + \frac{-q_{reaction}}{T} > 0 \end{gathered} \tag{18.5.4}$$

The above equation is very important because we now define entropy change of the universe in terms of the system, ie., the chemical reaction, where it is the change in entropy of the reaction, plus the changed induced to the surrounding by the heat transferred, that is $\frac{q}{T}$. Note, if the reaction is endothermic there is a reduction in entropy of the surroundings, and if it is exothermic, there is an increase.

Noting that the enthalpy of reaction is the heat transferred at constant pressure,

$$\Delta H_{reaction} = q_{p,reaction} \tag{18.5.5}$$

and substituting gives:

$$\Delta S_{Reaction} + \frac{-\Delta H_{Reaction}}{T} > 0 \tag{18.5.6}$$

Equation 18.5.6 is very important because it allows us to describe the Second Law of Thermodynamics in terms of the system (chemical reaction), and not the universe. This allows us to use standard state thermodynamic tables of molar entropy and enthalpies of formation to determine the entropies and enthalpies of reaction, and use that to determine the direction a reaction will spontaneously proceed in.

This relationship is so important that it has been rearranged into a new equation, Gibbs Free Energy (G).

First, multiply everything by T, giving:

$$T\Delta S_{reaction} - \Delta H_{reaction} > 0 \tag{18.5.7}$$

multiplying by negative 1 (-1) and rearranging (noting the sign of the inequality switches when you multiply by negative one).

$$\Delta H - T\Delta S < 0 \tag{18.5.8}$$

This is the definition of ΔG

$$\Delta G = \Delta H - T\Delta S \tag{18.5.9}$$

And for a spontaneous reaction

$$\underbrace{\Delta G = \Delta H - T\Delta S < 0}_{\text{for a spontaneous reaction}} \tag{18.5.10}$$

Gibbs Free Energy (G, sometimes given the symbol F), is also a state function, and all the things we learned with enthalpy in gen chem 1 apply. Its sign switches for the back reaction, it is an extensive property, and the values for a reaction can be determined from standard tables of free energies of formation.

Criteria for Spontaneity

Gibbs Free Energy quickly tells us if a system is at equilibrium $\Delta G = 0$, or if a reaction will occur ($\Delta G \neq 0$).

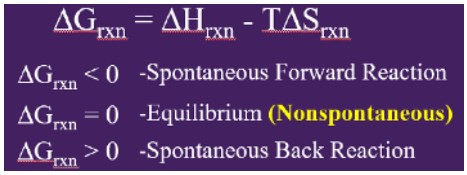


Figure18.5.2: Spontaneity is expressed in terms of Gibbs Free Energy. Note, for a system at equilibria $\Delta G = 0$, and if it is not at equilibria, either the forward or the reverse reaction will have a negative ΔG, and proceed spontaneously.

As pointed out in figure 18.5.3, Gibbs free energy has two terms that contribute to spontaneity, a temperature independent enthalpy term, and a temperature dependent entropy term.

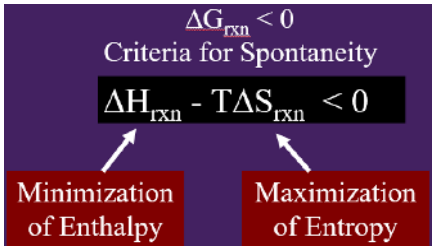


Figure18.5.3: Gibbs Free Energy can be viewed as the results of two energetic processes that are a function of the system, Enthalpy minimization and the temperature dependent entropy maximization.

One could say from Gibbs Free Energy expression that from the perspective of the system, there are two driving "forces" towards spontaneity, a decrease in energy (exothermic reactions contribute to a negative ΔG) and an increase in entropy (T is always positive, so only a [+] ΔS would contribute to a negative ΔG via the [-TΔS] term.)

Type	ΔH	ΔS	ΔG
1.	[+]	[-]	Always [+], never spontaneous

Type	ΔH	ΔS	ΔG
2.	[-]	[-]	[-] at low T, enthalpy driven process only spontaneous at low T
3.	[+]	[+]	[-] at high T, entropy driven process only spontaneous at high T
4.	[-]	[+]	Always [-], spontaneous at all T, both enthalpy and entropy driven

Table18.5.1, Temperature dependence of spontaneity as a function of the enthalpy and entropy changes of a reaction.

Phase Transitions

If a reaction is a phase change it fits the nature of types 3 & 4 in table 18.5.1. Melting is a type 3 process with a [+] ΔH and ΔS and is only spontaneous at a Temperature above the melting point. Freezing, the reverse process, is a type 2 process with a [-] ΔH and [-] ΔS, and is only spontaneous below the freezing point. The freezing or melting point is when the solid and liquid phases can coexist, and at that temperature $\Delta G = 0$. The standard state freezing point can be calculated from thermodynamic tables. At the boiling point ΔG=0 and the two phases can coexist in equilibrium.

$$\underbrace{\Delta G = \Delta H - T\Delta S = 0}_{\text{at the freezing point}} \tag{18.5.11}$$

If we consider ΔH and ΔS to be independent of temperature we can substitute the standard values into the above equation and get:

$$\underbrace{\Delta G = \Delta H^o - T\Delta S^o = 0}_{\text{at the freezing point}} \tag{18.5.12}$$

$$\therefore$$

$$T_{fp} = \frac{\Delta H^o_{s\rightarrow l}}{\Delta S^o_{s\rightarrow l}}$$

So the melting (or freezing) point is that temperature above which melting is spontaneous, below which freezing is spontaneous, and at which two phases can coexist in equilibrium. Thus you can use these tables to calculate phase transition temperatures like the melting or boiling point (next exercise).

Exercise 18.5.1

Using Table T1, Standard Thermodynamic Quantities, calculate the boiling point of ethanol, C_2H_5OH .

Answer

First calculate the entropy and enthalpy change associated with boiling from the standard state molar entropies and enthalpies of formation

$$\Delta H^o_{boiling} = \Delta H^o_f(gas) - \Delta H^o_f(liq) = -234.8 - (-277.6) = 42.8\frac{kJ}{mol}$$

$$\Delta S^o_{boiling} = \Delta S^o_f(gas) - \Delta S^o_f(liq) = 281.6 - 160.7 = 120.9\frac{J}{mol \cdot K}$$

Then noting that at the boiling point the two phases can coexist in equilibrium.

$$\Delta G^o = \Delta H^o - T\Delta S^o = 0$$

Rearranging and solving for T.

$$T = \frac{\Delta H^o_{boiling}}{\Delta S^o_{boiling}} = \frac{42.8 \frac{kJ}{mol}}{0.1209 \frac{kJ}{mol \cdot K}} = 354K = 80.9^oC$$

Driving Chemical Reactions

Gibbs Free Energy describes the spontaneity of a chemical reaction in terms of the entropy and enthalpy changes within the system, that is, of the chemical reaction itself. In section 15.2.5 the reaction quotient was introduced, which was the equilibrium constant expression at any conditions, and if \(Q \neq K), the system was not at equilibrium, and a reaction would spontaneously proceed in either the forward or reverse direction, depending on if Q is less than, or greater than K.

Q=K, **No reaction**, system is at equilibrium
Q>K, **Product loaded**, reactants are produced until Q=K
Q<K, **Reactant loaded**, products are produced until Q=K

This can be equated to the free energy through the following equation

$$\Delta G = \Delta G^o + RTlnQ \tag{18.5.13}$$

This is an important equation because it allows thermodynamics to relate spontaneity to reaction concentrations. That is, there are three possible conditions, the system is at equilibrium and no reaction occurs, it is Reactant Loaded and the Forward Reaction occurs, or it is Product Loaded, and the back reaction occurs.

Equilibrium Conditions

At equilibrium Q=K and ΔG_{rxn} = 0, so substituting these equilibrium conditions into eq. 18.5.11 gives

$$0 = \Delta G^o_{rxn} + RTlnK_{eq} \tag{18.5.14}$$

Rearranging gives two important equations:

$$\Delta G^o_{rxn} = -RTlnK \tag{18.5.15}$$

and

$$K = e^{\frac{-\Delta G^o_{rxn}}{RT}} \tag{18.5.16}$$

Equation 18.5.14 is very important because it allows us to calculate the equilibrium constant from standard state values. Note, if you are calculating K at 25° C you can calculate ΔG^o_{rxn} from ΔG^o_f in the standard thermodynamic tables.

$$\Delta G^o_{reaction} = \sum n\Delta G^o_{f_{products}} - \sum m\Delta G^o_{f_{reactants}} \tag{18.5.17}$$

(Where m and n are the respective stoichiometric coefficients of the reactant and product species.)

Reactant Loaded Systems

In a Reactant loaded system Q<K (review section 15.2.5) and the forward reaction occurs until Q=K. We will now show that when Q<K the value of ΔG *becomes* < 0 .

Starting with

$$\Delta G = \Delta G^o + RTlnQ \tag{18.5.18}$$

and substituting

$$\Delta G^o = -RTlnK \tag{18.5.19}$$

gives

$$\Delta G = -RTlnK + RTlnQ \tag{18.5.20}$$

Which can be rearranged to

$$\Delta G = RTln\frac{Q}{K} \tag{18.5.21}$$

If Q<K, then $\frac{Q}{K}$ is a fraction and its natural log is a negative number. Since R is a positive constant, and T is an absolute temperature (there are no negative degrees Kelvin), then $RTln\frac{Q}{K}$ must be negative, and thus ΔG is negative.

Product Loaded Systems

Here Q>K and the back reaction occurs until Q=K. We can use the exact same logic as above, and in eq. 18.5.20, except that $\frac{Q}{K}$ is a number bigger than one, which means its log is a positive value. This may be easier to see by rewriting eq. 18.5.20 into its exponential form

$$\frac{Q}{K} = e^{\frac{\Delta G}{RT}} \tag{18.5.22}$$

noting if $\Delta G = 0 \; then \; e^{\frac{\Delta G}{RT}} = e^{o} = 1$ and Q=K

if $\Delta G > 0 \; then \; e^{\frac{\Delta G}{RT}} = e^{[\text{positive number}]} > 1$ and Q>K , and the back reaction occurs until Q=K and $\Delta G = 0$

Likewise, for a Reactant loaded system (above)

$\Delta G < 0 \; then \; e^{\frac{\Delta G}{RT}} = e^{[\text{negative number}]} < 1$ (a fraction) and Q<K, and the forward reaction occurs until Q=K and $\Delta G = 0$

Contributors and Attributions

- Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 18.5: Second Law and Gibbs Free Energy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

18.6: Gibbs Free Energy

Introduction

In the previous section we derived Gibbs Free Energy from the Second Law of Thermodynamics and showed that a system will spontaneously react in the direction that lowers its Free Energy We showed that processes that reduced enthalpy (exothermic processes) or increased the entropy of the system contributed to spontaneity. We also showed that for a system at equilibrium, the change in free energy is zero.

Summary of Free Energy Equations

$$G = H - TS \tag{18.6.1}$$

$$\Delta G = \Delta H - T\Delta S \tag{18.6.2}$$

$$(\Delta G^o = \Delta H^o - T\Delta S^o) \tag{18.6.3}$$

$$\Delta G = \Delta G^o + RT \ln Q \tag{18.6.4}$$

$$\Delta G^o = -RT \ln K \tag{18.6.5}$$

$$K = e^{\frac{-\Delta G^o}{RT}} \tag{18.6.6}$$

Standard State Calculations

Equilibrium Constant at 298 K

Free energy values at standard state can be used to calculate equilibrium constants (using eq. 18.5.6).

Exercise 18.6.1

Using the table of standard state molar thermodynamic values (Table T.1), calculate the equilibrium constant K for the following reaction at 25° C.

$$2Ag_2O(s) \leftrightharpoons 4Ag(s) + O_2(g)$$

Answer

$$K = e^{\frac{-\Delta G^o}{RT}}$$

Noting, $\Delta G^o_{rxn} = 4(0) + 0 - [2(-11.2kJ/mol)] = 22.4kJ$, gives:

$$K = e^{\frac{-22.4kJ/mol}{\left(0.008314\frac{kJ}{mol \cdot K}\right)298K}} = 1.19 \times 10^{-4}$$

What does the above problem tell us about the stability of silver in the presence of oxygen? The positive ΔG^o tells us that at standard state conditions silver oxidide will not spontaneously form pure silver and oxygen. On the other hand, it says that silver will spontaneously react with oxygen and form the oxidized silver oxide. That is, silver sulfide is stable, and silver is thermodynamically reactive with oxygen. How fast the reaction occurs depends on the kinetics and specifically, the activation energy, but silver will spontaneously form silver oxide.

Equilibrium Constant at other Temperatures

In this class we will consider ΔH_{rxn} and ΔS_{rxn} to be independent of temperature. This is not a completely legitimate assumption, and is in fact really bad if the system undergoes a phase change.

Exercise 18.6.2

Consider the reaction

$$N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g)$$

Using Table T1, calculate ΔH^o_{rxn} and ΔS^o_{rxn} at 25 °C.

Answer

$$\Delta H^o_{rxn} = 2(-45.9\frac{kJ}{mol}) - [1(0) + 3(0)] = -91.8\frac{kJ}{mol}$$

.

$$\Delta S^o_{rxn} = 2(0.1928\frac{kJ}{mol \cdot K}) - [1(0.1916\frac{kJ}{mol \cdot K}) + 3(0.1307)\frac{kJ}{mol \cdot K}] = -0.1981\frac{kJ}{mol \cdot K}$$

.

from the previous exercise we get $\Delta H^o_{rxn} = -91.8\frac{kJ}{mol}$ and $\Delta S^o_{rxn} = -198.1\frac{J}{mol \cdot K}$

Let's compare these values to the values at 800 K and 1300 K

Temperature (K)	$\Delta H^o_{rxn}\frac{kJ}{mol}$	$\Delta S^o_{rxn}\frac{J}{mol \cdot K}$
298	-91.8	-198.1
800	-107.4	-225.4
1300	-112.4	-228.0

Exercise 18.6.3

Calculate ΔG^o_{rxn} and K at each temperature using thermodynamic values at that temperature.

Answer

$$\Delta G^o_{rxn}(298K) = -91.8\frac{kJ}{mol} - (298K)(-0.1981)\frac{kJ}{mol \cdot K} = -32.8\frac{kJ}{mol}$$

$$K_{eq} = e^{\frac{-\Delta G^o_{rxn}}{RT}} = e^{\frac{-(-32.8\frac{kJ}{mol})}{(0.008314\frac{kJ}{mol \cdot K})298K}} = 5.62 \times 10^5$$

$$\Delta G^o_{rxn}(800K) = -107.4\frac{kJ}{mol} - (800K)(-0.2254)\frac{kJ}{mol \cdot K} = 72.92\frac{kJ}{mol}$$

$$K_{eq} = e^{\frac{-\Delta G^o_{rxn}}{RT}} = e^{\frac{-(72.92\frac{kJ}{mol})}{(0.008314\frac{kJ}{mol \cdot K})800.K}} = 2 \times 10^{-5}$$

$$\Delta G^o_{rxn}(1300K) = -112.4\frac{kJ}{mol} - (1300K)(-0.2280)\frac{kJ}{mol \cdot K} = 184.0\frac{kJ}{mol}$$

$$K_{eq} = e^{\frac{-\Delta G^o_{rxn}}{RT}} = e^{\frac{-(184.0\frac{kJ}{mol})}{(0.008314\frac{kJ}{mol \cdot K})1300.K}} = 4.0 \times 10^{-8}$$

So from the above, we see that we have the following K values,

- $K(298K) = 5.62 \times 10^5$
- $K(800K) = 2 \times 10^{-5}$
- $K(1300K) = 4.0 \times 10^{-8}$.

This shows us several things. This is an enthalpy driven reaction and at low temperature it is favorable. But it is entropy impeded, and at high temperature becomes unfavorable.

Often times we do not have thermodynamic values outside of 298 K, and can still approximate ΔG^o_{rxn} by using the values of ΔH^o_{rxn} and ΔS^o_{rxn} at 25 °C, that is, we assume standard entropy and enthalpy are constant. Lets calculate K_{eq} at 800 K and 1300 K

using the ΔH^o_{rxn} and ΔS^o_{rxn} at 25 ºC (assuming they are constant over the temperature ranges).

Exercise 18.6.4

Calculate K_{eq} at 800 K and 1300 K using the ΔH^o_{rxn} and ΔS^o_{rxn} at 25 ºC .

Answer

$$\Delta G^o_{rxn}(800K) = -91.8\frac{kJ}{mol} - (800K)(-0.1981)\frac{kJ}{mol\cdot K} = 66.7\frac{kJ}{mol}$$

$$K_{eq} = e^{\frac{-\Delta G^o_{rxn}}{RT}} = e^{\frac{-(66.7\frac{kJ}{mol})}{(0.008314\frac{kJ}{mol\cdot K})800.K}} = 4.4\times10^{-5}$$

$$\Delta G^o_{rxn}(1300K) = -91.8\frac{kJ}{mol} - (1300K)(-0.1981)\frac{kJ}{mol\cdot K} = 165.7\frac{kJ}{mol}$$

$$K_{eq} = e^{\frac{-\Delta G^o_{rxn}}{RT}} = e^{\frac{-(165.7\frac{kJ}{mol})}{(0.008314\frac{kJ}{mol\cdot K})1300.K}} = 2.2\times10^{-7}$$

Note that now we get

- $K(800\ K) = 4\times10^{-5}$ (it is really 2×10^{-5})
- $K(1300\ K) = 2.2\times10^{-7}$ (it is really 4×10^{-8})

What we see here is that using standard entropy and enthalpy values at 298K gives us reasonably close K values at other temperatures, but the farther away we are from 298, the worse the results. Thus it is common to use the values of ΔH^o_{rxn} and ΔS^o_{rxn} at 25 degree C for other temperatures to calculate the free energy at the other temperature

$$\Delta G^o_{rxn} = \Delta H^o_{rxn} - T\Delta S^o_{rxn}$$

.

Two Meanings of Spontaneous

You will observe that there are two commonly used meanings for spontaneous. In the first context you are asking if a reaction is product favored, in the sense that once equilibrium is achieved, the reactants have converted to products. The second context is that of describing an actual mixture of reactants and products and asking in what direction (if any) will a reaction proceed, that is, is the system Reactant Loaded or Product Loaded.

Product/Reactant Favored Reactions

Here you are looking at the values of ΔG^o_{rxn} and K_{eq}, and asking do the equilibria favor reactants or products

Product Favored Reactions
ΔG^o_{rxn} <<0 (it is very negative) and $K \gg 1$ (it is a very large number).

Reactant Favored Reactions
ΔG^o_{rxn} >>0 (it is very large and positive) and $K \ll 1$ (it is a very small fraction).

Exercise 18.6.5

Does silver chloride dissolve in water?

Answer

Silver chloride has a very small K, K_{sp} = 1.8 x 10^{-10} .

$$\Delta G^o_{rxn} = -RTlnK = -(0.008314\frac{kJ}{mol\cdot K})298Kln(1.8\times10^{-10}) = 55.6kJ/mol \qquad (18.6.7)$$

Note, from Exercise 5 that for silver chloride, ΔG^o=55.6kJ/mol, which is a very large number and corresponds to a very small equilibrium constant, K_{sp} = 1.8 x 10^{-10}, and so we would say that silver chloride does not dissolve.

Product/Reactant Loaded Reactions

Here you are given concentrations of reactants and products and need to determine if ΔG is greater than, less than, or equal to Zero.

$$\Delta G_{rxn} = \Delta G^o_{rxn} + RT \ln Q \tag{18.6.8}$$

Where Q is the reaction quotient. If

$\Delta G_{rxn} < 0$ - Forward reaction is spontaneous
$\Delta G_{rxn} > 0$ - Reverse reaction is spontaneous
$\Delta G_{rxn} = 0$ - System is at Equilibrium

This meaning of spontaneous is different than the above meaning, and not stating whether an equilibrium is product or reactant favored, but if a reaction will occur. In the next example we will see that at very dilute (nanomolar) concentrations, even an insoluble salt will dissolve.

Exercise 18.6.6

Will 100 nmoles of silver chloride dissolve in one liter of water? (Can you make a 100. nM solution of AgCl?)

Answer

As we are given concentrations we need to look at ΔG_{rxn} and not ΔG^o_{rxn}, although we can use ΔG^o_{rxn} from the problem above that asked if silver chloride was a soluble salt.

$$\Delta G_{rxn} = \Delta G^o_{rxn} + RTlnQ \tag{18.6.9}$$

note, 100nM =100(10^{-9}M) =1\times 10^{-7}M, and Q=x^2.

$$\begin{aligned} \Delta G_{rxn} &= 55.6kJ/mol - (0.008314\frac{kJ}{mol \cdot K})298Kln(1.0 \times 10^{-7})^2 \\ &= 55.6kJ/mol + (-79.9kJ/mol) \\ &= -24.3kJ/mol \end{aligned} \tag{18.6.10}$$

What you notice in the above is that there are two terms contributing to ΔG, that which describes the equilibrium (ΔG^o), and that which describes the "loading" of the system, RTlnQ. As silver chloride is a very insoluble salt the first term is 55.6 kJ and positive. If the reaction quotient (Q) is a fraction (meaning few products and many reactants) its log is negative and it contributes towards spontaneity. If it is more negative than the first term is positive, the system is reactant loaded and will spontaneously make products. In the above exercise, the second term was -79.9kJ/mol and so the net ΔG is -23.4kJ/mol and the reaction proceeds, with the silver chloride spontaneously dissolving, even though we would call it an insoluble salt.

Driving NonSpontaneous Reactions

In General Chemistry 1, section 5.7.1, Hess's Law we noted that if we coupled two reactions the energy is additive, and this principle also holds for other state functions like Gibbs Free Energy. That is, Free Energies of Reactions are additive. What this means is that a nonspontaneous process ($\Delta G > O$) can become spontaneous if it is coupled to a second spontaneous process ($\Delta G < O$), if the second process is more negative than the first process is positive.

Consider the decomposition of chalcocite (Copper(i)sulfide).



Figure18.6.1: Chalcocite is a copper ore of Cu_2S, (image from Wikimedia)

Let's say we want to extract the copper from Chalcocite. The first question is, is it stable?

$$Cu_2S(s) \rightarrow 2Cu(s) + S(s) \tag{18.6.11}$$

From the table of standard molar Free Energies of formation (Table T1) the enthalpy of formation of chalcocite is -82.6kJ/mol.

$$2Cu(s) + S(s) \rightarrow 2Cu_2S(s) \quad \Delta G_f^o = -82.6kJ/mol \tag{18.6.12}$$

Noting in the above equation that copper and silver are in their standard states ($\Delta G_f^o = O$), means the free energy change for the first reaction (18.6.15) is the negative of its ΔG_f^o, or 86.2kJ. (Note the last value is written in units of kJ and not kJ/mol, as it is related to eq.18.6.15, and the per mole is implicit (per one mole of chalcocite consumed, and per two moles of copper and one mole sulfur produced). This tells us that chalcocite is stable and will not spontaneously form copper and sulfur.

Since we want to extract copper, we could find a reaction that consumes the sulfur, a byproduct, and whose (\Delta G^o_f <-82.6kJ\)) . From (Table T1) we see that $\Delta G_f^o(\text{sulfur dioxide})$ is -300kJ/mol

$$S(s) + O_2(g) \rightarrow SO_2(g) \quad \Delta G_f^o = -300.1kJ/mol \tag{18.6.13}$$

equation 1: $Cu_2S(s)$ --> 2Cu(s) + S(s) ΔH_1 =+82.6kJ (non spontaneous)
equation 2: S(s) + O_2 --> SO_2 ΔH_2 = -300.1kJ (spontaneous)

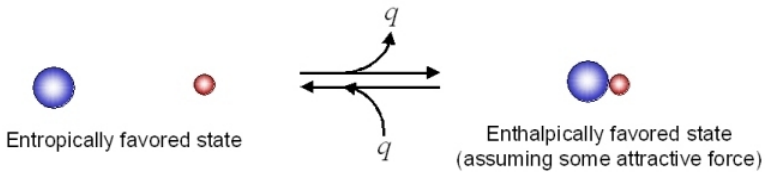
equation 3: $Cu_2S(s)$ + O_2 --> 2Cu(s) + SO_2 ΔH_3 = 82.6kJ +(-300.1kJ)=-217.5kJ (spontaneous)

Now that we have a thermodynamically feasible process the next step is to find the reaction conditions (temperature, catalysts...) that would allow it to proceed at a viable rate.

Enthalpically vs. Entropically Driving Reactions

Some textbooks and teachers say that the free energy, and thus the spontaneity of a reaction, depends on both the enthalpy and entropy changes of a reaction, and they sometimes even refer to reactions as "energy driven" or "entropy driven" depending on whether ΔH or the $T\Delta S$ term dominates. This is technically correct but misleading because it disguises the important fact that ΔS_{total}, which this equation expresses in an indirect way, is the *only* criterion of spontaneous change.

Consider the following possible states for two different types of molecules with some attractive force:

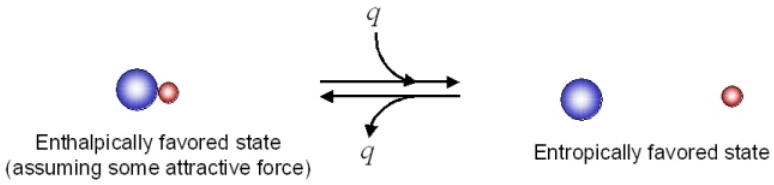


There would appear to be greater entropy on the left (state 1) than on the right (state 2). Thus the entropic change for the reaction as written (i.e. going to the right) would be (-) in magnitude, and the energetic contribution to the free energy change would be (+) (i.e. unfavorable) for the reaction as written.

In going to the right, there is an attractive force and the molecules adjacent to each other have a lower energy state (heat energy, q, is liberated). To go to the left, we have to overcome this attractive force (input heat energy) and the left direction is unfavorable with regard to heat energy q. The change in enthalpy is (-) in going to the right (q released), and this enthalpy change is negative (-)

in going to the right (and (+) in going to the left). This reaction as written, is therefore, **enthalpically favorable and entropically unfavorable**. Hence, it is **enthalpically driven**.

From Table 18.5.1, it would appear that **we might be able to get the reaction to go to the right at low temperatures** (lower temperature would minimize the energetic contribution of the entropic change). Looking at the same process from an opposite direction:



This reaction as written, is **entropically favorable, and enthalpically unfavorable**. It is **entropically driven**. From Table 18.5.1 , it would appear that **we might be able to get the reaction to go to the right at high temperatures** (high temperature would increase the energetic contribution of the entropic change).

Relationship between ΔG and Work

Gibbs Free Energy is the maximum available energy to do non PV work like mechanical or electrical work. Gibbs Free Energy is also very important to understand bioenergetics, and a foundation topic that will be used in upper level chemistry courses. Let's show how $\Delta G = W_{max}$ for systems at constant pressure and temperature.

$$\Delta G = \Delta H - T\Delta S \text{ at constant temperature} \tag{18.6.14}$$

$$\Delta H = \Delta U + P\Delta V \text{ at constant pressure} \tag{18.6.15}$$

Substituting the definition of enthalpy (18.6.19) into the definition of Free Energy (18.6.18) gives

$$\Delta G = \Delta U + P\Delta V - T\Delta S \text{ at constant temperature and pressure} \tag{18.6.16}$$

From the First Law of Thermodynamics we know

$$\Delta U = Q + W \tag{18.6.17}$$

substituting the First Law Internal Energy expression into the free energy equation gives

$$\Delta G = Q + W + P\Delta V - T\Delta S \text{ at constant temperature and pressure} \tag{18.6.18}$$

F**or maximum work, a process must be reversible**, and knowing the definition of entropy $\Delta S = \frac{Q_{rev}}{T}$ $gives$ $Q_{rev} = T\Delta S$, and substitution into the above eq. gives

$$\Delta G = \cancel{T\Delta S} + W_{rev} + P\Delta V \cancel{-T\Delta S} \text{ at constant temperature and pressure} \tag{18.6.19}$$
$$\Delta G = W_{rev} + P\Delta V \tag{18.6.20}$$

The reversible work **(W_{rev})** may be of expansion **($W_{rev,exp}$)** or non expansion (**$W_{rev,\ nonexp}$**), and noting from section 5.1.4.1, $W_{rev,exp} = -P\Delta V$ so $W_{rev} = W_{rev,nonexp} - P\Delta V$. Substituting for reversible work gives:

$$\Delta G = W_{rev} + P\Delta V \tag{18.6.21}$$
$$= W_{rev,nonexp} \cancel{-P\Delta V} + \cancel{P\Delta V} \tag{18.6.22}$$
$$= W_{rev,nonexp} \tag{18.6.23}$$

This is often written as

$$\Delta G = W_{max}\text{, the maximum amount of energy available to do work (at constant T \& P)} \tag{18.6.24}$$

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 18.6.2 the efficiencies of various energy-converting devices vary

widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table 18.6.2: Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30
fluorescent light	electrical → light	20
solar cell	light → electricity	10
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 18.6: Gibbs Free Energy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

CHAPTER OVERVIEW

19: Electron Transfer Reactions

19.1: Electrical Fundamentals
19.2: Oxidation-Reduction Reactions
19.3: Electrochemical Cells
19.4: Electrochemical Cell Fundamentals
19.5: Standard Electrochemical Potentials
19.6: Electrochemistry and Thermodynamics
19.7: Electrochemical Cells under Nonstandard Conditions
19.8: Corrosion
19.9: Electrolysis
19.10: Counting Electrons

This page titled 19: Electron Transfer Reactions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

19.1: Electrical Fundamentals

Introduction

In this chapter will introduce electrochemistry and be going over electrochemical cells, and so it seems prudent to introduce some of the fundamental concepts of electricity. This section does not have problem sets or activities, but will provide definitions you may want to refer back to as you are doing the other sections of this chapter. I am writing this section to help students who have not had physics and hope it will help make the other sections easier to understand.

Electricity refers to a number of phenomena associated with the presence and flow of electric charge. Electricity includes such diverse things as lightning, static electricity, the current generated by a battery as it discharges, and many other influences on our daily lives. The flow or movement of charge is an electric current (Figure 19.1.1). Electrons or ions may carry the charge through a conductor. Wires, electrodes are electronic conductors while electrolytes are ionic conductors, and the current must flow through a circuit.

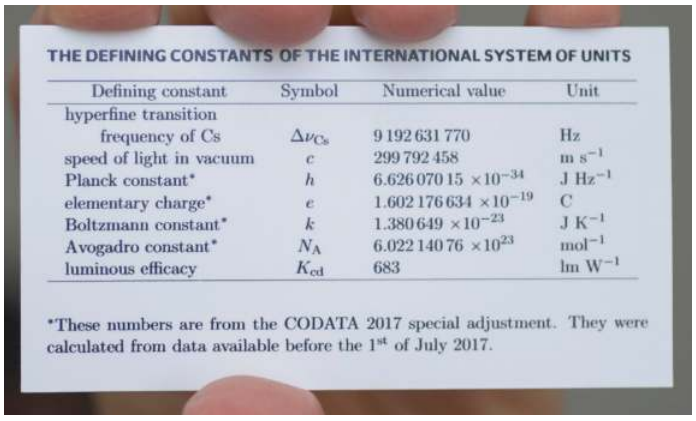


Figure 19.1.1: Electricity-related phenomena include lightning, accumulation of static electricity, and current produced by a battery. (credit left: modification of work by Thomas Bresson; credit middle: modification of work by Chris Darling; credit right: modification of work by Windell Oskay).

So what are the units that describe electricity? In section 1B.1.1 the 7 SI base units were introduced, and we learned that all measurable quantities can be quantified in terms of SI base units. So far in this class we have used 5 of the SI base units; mass (kg), time (s), length (m), temperature (K) and quantity (mol). We have not covered the SI units of electrical current, Ampere (A) or luminous intensity, candela (cd). This chapter uses the SI unit of the Ampere, which is a measure of electric current.

Units of Charge and Current

In May of 2019 the SI base unit definitions changed to depend on 7 immutable reference constants (defined numbers), and you should reference section 1B.1.3.1.2 of the first semester LibreText of this class. This change was initiated at the 26th meeting of Bureau International des Poids et Mesures, and the above 7 base units will be based on seven reference constants.



THE DEFINING CONSTANTS OF THE INTERNATIONAL SYSTEM OF UNITS

Defining constant	Symbol	Numerical value	Unit
hyperfine transition frequency of Cs	$\Delta\nu_{Cs}$	9 192 631 770	Hz
speed of light in vacuum	c	299 792 458	m s^{-1}
Planck constant*	h	6.626 070 15 $\times 10^{-34}$	J Hz^{-1}
elementary charge*	e	1.602 176 634 $\times 10^{-19}$	C
Boltzmann constant*	k	1.380 649 $\times 10^{-23}$	J K^{-1}
Avogadro constant*	N_A	6.022 140 76 $\times 10^{23}$	mol^{-1}
luminous efficacy	K_{cd}	683	lm W^{-1}

*These numbers are from the CODATA 2017 special adjustment. They were calculated from data available before the 1st of July 2017.

Figure 19.1.2: Card with SI defining constants, these values are considered as defined numbers. (Stoughton/NIST).

One of the 7 fundamental reference constants is the value of elementary charge, $e = 1.602176634 \times 10^{-19} Coulombs(C)$, which is the charge of an electron or proton: This constant is used in defining the SI base unit for charge, the ampere (A).

$$\text{Charge of Proton} = e = 1.602176634 \times 10^{-19} Coulombs(C) \tag{19.1.1}$$

$$\text{Charge of Electron} = e = -1.602176634 \times 10^{-19} Coulombs(C)$$

Rearranging, gives:

$$1 \text{ Coulomb} = \text{charge of } 6.241509074x10^{18} electrons \tag{19.1.2}$$

Although in this class we won't need so many significant figures (and the charge of the electron is negative).

Note, the 7 reference constants are immutable constants, which either define SI base units, or enable their derivation. The SI base unit associated with electric charge is the Ampere (A), which is a unit of current flow,

$$1\,A = \frac{1\,C}{s}. \tag{19.1.3}$$

The ampere base unit can be described by the reference constants of charge (e) and of time (s), the latter of which is based on the caesium-133 atomic clock frequency of 9,192,631,770 cycles/second (Hz).

In the early 1800s Michael Faraday pioneered electrochemical studies and noted that if a current flowed into a solution with metal ions, some of the ions could become attached to the electrode that provided the electrons (Figure 19.1.3). These cations migrated through the solution to the electrode and became "reduced", in that they gained electrons, and as we shall see, the electrode where reduction occurs is called the cathode. Such a technique could be used to plate silver onto a spoon as in Figure 19.1.3, but of interest, is that you can relate the mass gain of the spoon to the number of electrons transferred if you know the identity of the metal being plated onto the spoon.

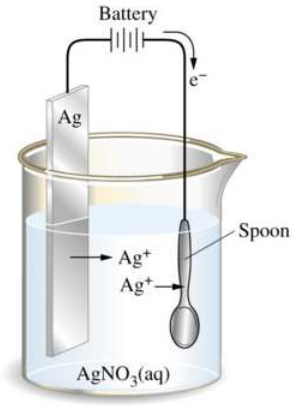


Figure 19.1.3: Electroplating silver onto a spoon

In the above reaction silver cations migrate to the spoon which acts as the cathode (where the ions become reduced by electrons provided through the external source, and this reduction reaction can be described by the following equation.

$$\text{Ag}^+ + e^- \rightarrow \text{Ag} \tag{19.1.4}$$

As the above equation relates one mol Ag^+ being converted to one mol Ag(s) as one mol e^- is transferred through the external circuit, the mass change can be related to the number of electrons transferred. Since the charge of an electron is defined through an SI constant (e= 1.602 176 634 × 10^{-19} Coulombs), the charge of a mole of electrons can be calculated, which is defined by a constant called *Faraday's constant*.

$$\begin{aligned} F &= |\text{charge of a mole of electrons}|^* \\ &= (\text{charge of one electron})(\text{Avogadro's number}) \\ &= \left(1.6022 \times 10^{-19} \frac{C}{electron}\right)\left(6.0221 \times 10^{23} \frac{electrons}{mol}\right) \\ &= 9.649 \times 10^4 \frac{C}{mol\ electrons} \end{aligned}$$

$$F = 96,500 \frac{C}{mol\ electrons} \tag{19.1.5}$$

*Note, Faraday's constant is thus the charge of a mole of protons or electrons.

Electrical Potential

Energy is the capacity to do work or transfer heat. Translational work results when an applied force moves an object distance (Δx) along the axis the force is applied.

$$W = F \cdot \Delta x \tag{19.1.6}$$

The Joule is the unit of energy that is defined in terms of translation, with one Joule being the energy associated when a force of 1 newton moves an object 1 meter in a straight line along the axis the force is applied.

Electric work is that associated with moving a charge (q) across an electric potential gradient (E), **Note: E is not energy but electric potential**.

$$W = q \cdot \Delta E \tag{19.1.7}$$

this is commonly written as

$$W = qE \tag{19.1.8}$$

where E is the electric potential difference between two points and has the units of volts. The electric work is a measure of the energy (Joules) required or released as a charged particle (q) moves across the potential (volts).

One joule of work is done when one coulomb of charge moves across a potential difference of 1 volt.

$$1\ Joule\ =\ 1\ Coulomb\,(1\ Volt) \tag{19.1.9}$$

So

$$1 Coulomb\ =\ \frac{1\ Joule}{1\ Volt} \tag{19.1.10}$$

Substituting for C in Faraday's constant gives

$$F = 96,500 \frac{Joules}{Volt \cdot mol\ electrons} \tag{19.1.11}$$

So Faraday's constant can also be expressed in terms of J/Volt mole -electrons

The SI unit for electrical current is the SI base unit called the ampere (A), which is a flow rate of 1 coulomb of charge per second (1 A = 1 C/s). An electric current flows in a path, called an electric circuit. In most chemical systems, it is necessary to maintain a closed path for current to flow. The flow of charge is generated by an electrical potential difference, or potential, between two points in the circuit. Electrical potential is the ability of the electric field to do work on the charge. The SI unit of electrical potential is the volt (V). When 1 coulomb of charge moves through a potential difference of 1 volt, it gains or loses 1 joule (J) of energy. Table 19.1.1 summarizes some of this information about electricity.

Table 19.1.1: Common Electrical Terms

Quantity	Definition	Measure or Unit
Electric charge	Charge of an electron Charge of mole electrons	1.602×10^{-19} C 1 F or 96,500 C
Electric current (A)	The movement of charge	ampere = A = 1 C/s
Electric potential (E or V)	The force trying to move the charge	volt = V = J/C

Sign Convention

Note that in electronics current flows from high potential to low potential, that is, it flows down the potential gradient. That is, the direction of flow is that of positive charge, but in reality, what flows for a conductive current are electrons, and those actually move towards the positive electrode.

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

19.1: Electrical Fundamentals is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

19.2: Oxidation-Reduction Reactions

Hypothes.is Tag = c1403c19 (case sensitive)
Group = UALRChem1403

Introduction

Oxidation-Reduction (Redox) reactions are a basic type of chemical reaction involving the transfer of electrons from one atom or chemical entity to another, or more accurately, from one type of orbital to another, that results in new bonds being formed. These were introduced in gen chem 1, section 3.6 Redox Reactions, and you may want to quickly review that material now, and be prepared to return to it if you need help in identifying the oxidation state of an atom. Note, the electron transfer may be between two different chemical species, or between atoms of the same species. This chapter introduces electrochemistry, which is the study of redox reactions.

Redox Review

Consider the reaction of elemental zinc and sulfur to form zinc sulfide.

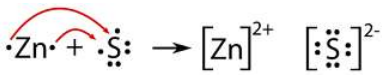


Figure 19.2.1: Reaction between zinc and sulfur.

Zinc is losing electrons in the reaction and is thus oxidized to the zinc cation, while sulfur is gaining electrons and is thus reduced to the sulfide anion.

$$\textbf{oxidation} = \text{loss of electrons} \tag{19.2.1}$$

$$\textbf{reduction} = \text{gain of electrons} \tag{19.2.2}$$

Note, we often use the term oxidant and reductant to introduce the species that cause oxidation and reduction, and thus zinc is the reducing agent (causes reduction, while being oxidized), and sulfur is the oxidizing agent (causes oxidation, while being reduced).

$$\textbf{Reductant (reducing agent)} = \text{species that is oxidized} \tag{19.2.3}$$

$$\textbf{Oxidant (oxidizing agent)} = \text{species that is reduced} \tag{19.2.4}$$

In the above example the electron(s) were being transferred from one chemical entity to another. When this happens we can split the chemical reaction into two half-reactions, one for the oxidation and one for the reduction. Note, these are coupled by the electrons transferred, and it is important to realize that the two half-reactions occur concurrently (the electrons leave the zinc and go to the sulfur). It should be noted that not all redox reactions can be broken into simple half-reactions, as sometimes the atoms being oxidized and those being reduced are different atoms on the same compound.

$$\underbrace{Zn \rightarrow Zn^{2+} + 2e^-}_{\text{Oxidation}} \tag{19.2.5}$$

$$\underbrace{S + 2e^- \rightarrow S^{2-}}_{\text{Reduction}} \tag{19.2.6}$$

However, not all redox reactions involve the transfer of electrons to produce ions. Consider, for example the standard formation reaction to form hydrogen sulfide from sulfur and hydrogen, which is similar to the above reaction for the production of zinc sulfide, but hydrogen sulfide is a covalent bond.

$$\mathrm{H_2 + S \rightarrow H_2S} \tag{19.2.7}$$

Because hydrogen sulfide is a covalent compound, electron transfer from the reductant to the oxidant does not occur in the explicit sense. But a look at the polarity of the covalent bond shows that the more electronegative sulfur has a higher density, and so electron density has been transferred. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called *oxidation number* has been defined. The oxidation number (or oxidation state) of an element in a compound is the charge its atoms would possess *if the compound was ionic*. Review the guidelines (3.6.2.1) from gen chem 1 on assigning oxidation numbers to each element in a molecule or ion.

Using the oxidation number provides a better and more universal definition of oxidation and reduction.

$$\textbf{oxidation} = \text{increase in oxidation number} \tag{19.2.8}$$
$$\textbf{reduction} = \text{decrease in oxidation number} \tag{19.2.9}$$

Balancing Redox Reactions

A balanced chemical equation must not only conserve mass and energy, but also charge. Consider the following equation for the formation of Iodine and ferrous ion from iodide and ferric ions, is it balanced?

$$Fe^{+3} + 2I^- \rightarrow Fe^{+2} + I_2 \tag{19.2.10}$$

.

Sure mass is balanced, but charge is not, as it is +1 on the reactant side and +2 on the product, which means an electron disappeared as products were being formed. Taking a closer look from the half-reaction perspective that two electrons were released but only one was transferred, and that an electron just disappeared.

$$\underbrace{2I^- \rightarrow I_2 + 2e^-}_{\text{Oxidation}} \tag{19.2.11}$$
$$\underbrace{Fe^{+3} + 1e^- \rightarrow Fe^{+2}}_{\text{Reduction}} \tag{19.2.12}$$

For the reaction to be balanced the number of electrons released in the oxidation half-reaction must equal the number gained in the reduction half-reaction, which means everything in the reduction half-reaction needs to be multiplied by two.

$$\underbrace{2I^- \rightarrow I_2 + 2e^-}_{\text{Oxidation}} \tag{19.2.13}$$
$$\underbrace{2Fe^{+3} + 2e^- \rightarrow 2Fe^{+2}}_{\text{Reduction}} \tag{19.2.14}$$

Note the two half-reactions are coupled by the electrons transferred, and the balanced equation would be the sum of the above two equations

$$2Fe^{+3} + 2I^- \rightarrow 2Fe^{+2} + I_2 \tag{19.2.15}$$

.

Note, charge is conserved in the above equation, which has a charge of +4 on both sides.

There are many techniques for balancing redox reactions and we will introduce two. The first is a half-reaction method that does not require you to calculate the oxidation number and can be used when the species being oxidized is a completely different chemical entity than the one being reduced. The second technique requires calculating the oxidation number and is needed for problems that can not be broken up into half-reactions, like ones where different atoms on the same species are getting oxidized and reduced, that is, electrons are being transferred across atoms within a molecule or compound.

Half-Reaction Method

If the chemical species being oxidized and reduced are different entities they can be separated into half-reactions, balanced for mass and charge, and then added in a way that balances the total charge. Many electrochemical systems are in aqueous solutions, with many also being in acidic or basic environments (an alkaline battery is a basic environment, and your car battery has battery acid, making it an acidic environment), So in this section we will learn how to balance reactions in acidic and basic environments.

Balancing Acidic Redox Reactions

The following steps allow you to balance a redox reaction and you often do not even have to identify the oxidation state of the various species.

1. Split Skeletal Eq. into 1/2 Reactions
2. For Each Half-Reaction
    1. Balance all Elements Except O and H
    2. Balance O by adding water
    3. Balance H by adding H^+.

4. Balance Charge by adding e^-.

3. Multiply 1/2 rxns by appropriate integer so electrons lost = electrons gained.
4. Add half-reactions, cancelling electrons lost and gained, and check work

Balancing Basic Redox Reactions

Balance as if it was acidic, and then add OH^- to both sides to neutralize H^+ (converting it to H_2O)

1. Split Skeletal Eq. into 1/2 Reactions
2. For Each Hal- Reaction
    1. Balance all Elements Except O and H
    2. Balance O by adding water
    3. Balance H by adding H^+.
    4. Balance Charge by adding e^-.
3. Multiply 1/2 rxns by appropriate integer so electrons lost = electrons gained.
4. Add half-reactions, cancelling electrons lost and gained, and check work
5. Add OH^- to both sides to neutralize H^+ (converting it to H_2O)

(only the last step is different from balancing acidic reactions)

Exercise 19.2.1

Balance the reaction of thiosulfate with iodine to produce sulfate and iodide in basic conditions.

$$\mathrm{S_2O_3^{-2} + I_2 \rightarrow SO_4^{-2} + I^-}$$

Video Tutorial Answer

The following video goes over the solution to this problem, which is:



Answer:

$$10OH^- + S_2O_3^{-2} + 4I_2 \leftarrow 2SO_4^{-2} + 5H_2O + 8I^- \tag{19.2.16}$$

Oxidation Method

This method can be used in reactions where one chemical has atoms being oxidized and other atoms being reduced, that is, the chemical is in both half-reactions.

1. Identify oxidation number of all atoms being oxidized or reduced.
    - Indicate oxidation state above the atom
    - **Review section 3.6.2.1 on oxidation numbers if needed**
2. Balance elements in "coupled" molecules
    - Balance elements other than oxygen or hydrogen.
3. Use a line to connect atoms undergoing a change in oxidation number:

- Above Eq. for atoms being oxidized
- Below Eq. for atoms being reduced

4. Balance Oxidizing and Reducing Equivalents
   - multiply by appropriate coefficients so total number on top equals total on bottom
5. If aqueous balance Oxygen by adding water
   1. If acidic balance hydrogen by adding H^+.
   2. If basic, treat as acidic and then add OH^- to remove H^+.
6. Double check work.

Test Yourself

Homework

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 19.2: Oxidation-Reduction Reactions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

19.3: Electrochemical Cells

Hypothes.is Tag = c1403c19 (case sensitive)
Group = UALRChem1403

Introduction

If a redox reaction can be split into half reactions it becomes possible to build a device, called an electrochemical cell, that has separate compartments (cells) for the oxidant and reductant. This physically prevents them from contacting each other and reacting, but allows for charge transfer in the form of electrons through an external circuit and in the form of counter ions in a salt bridge that connects the cells.

In general chemistry 1 we studied a type of reaction called a single displacement reaction (review section 3.2.1.3), where in a metal displacement reaction a pure metal could displace a the cation of an ionic compound. Let's look at the net ionic equations for the two possible single displacement reactions involved with zinc and copper.

$$Zn(s) + Cu^{+2} \rightarrow Cu(s) + Zn^{+2} \qquad (19.3.1)$$
$$or$$
$$Cu(s) + Zn^{+2} \rightarrow Zn(s) + Cu^{+2}$$

To identify which is spontaneous we used the activity series (review section 3.6.1.1) and from table 3.6a we see that zinc is more active than copper, meaning metallic zinc will spontaneously dissolve in a solution with Copper (II) ions. This means the top reaction above has a negative free energy (it is spontaneous) and could be used to do work, and the bottom reaction above has a positive free energy, which means nothing would happen, unless we added an external source of energy to drive it. In this section we will describe electrochemical cells, and focus on the above reaction to explain how they work. We will show that the spontaneous reactions above ($Zn(s) + Cu^{+2} \rightarrow Cu(s) + Zn^{+2}$) can be used to build a battery, which is commonly known as the Daniell cell, that was originally build by the British chemist John Frederic Daniell.

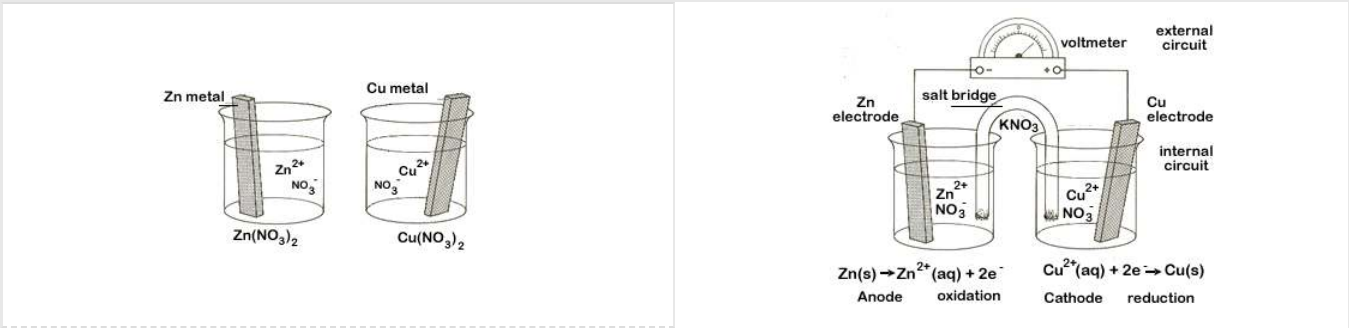
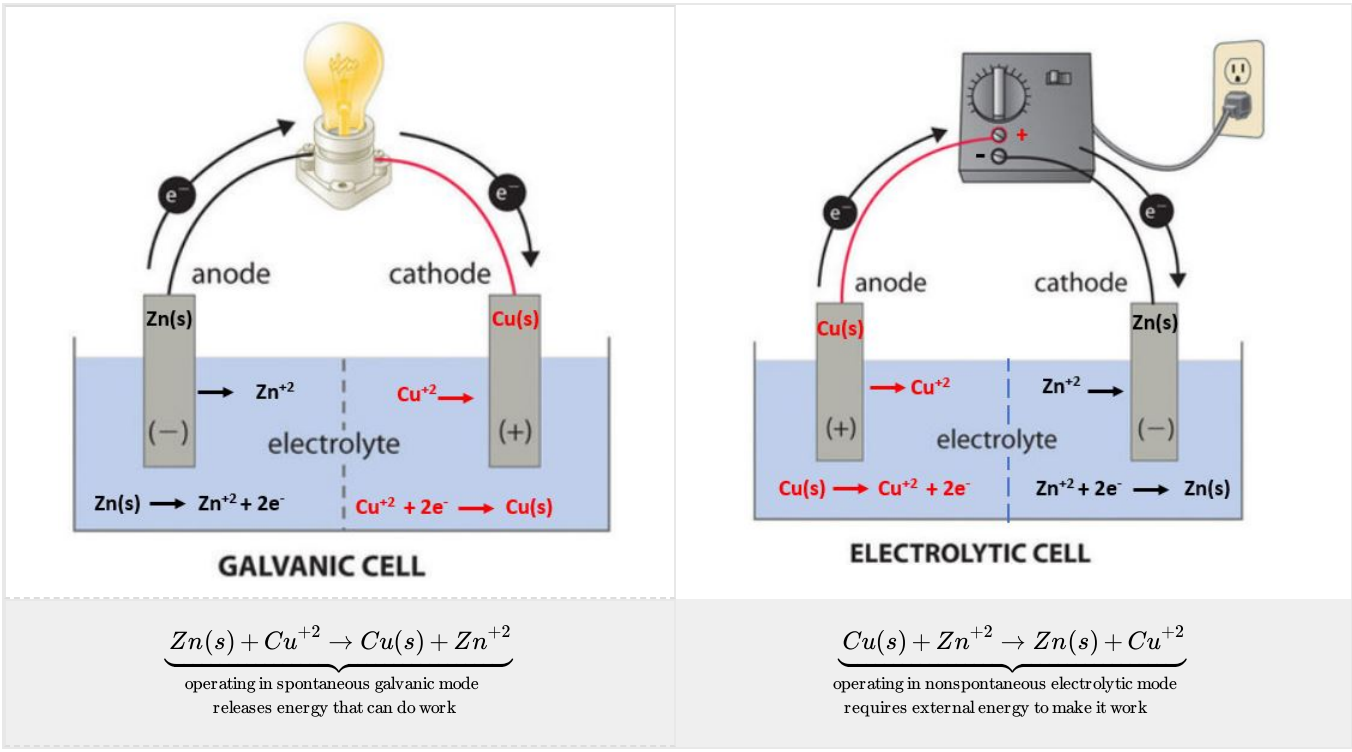


Figure 19.3.1: On the left are two isolated beakers with Zn(s)/Zn^{+2}(aq) and Cu(s)/Cu^{+2}(aq) and nothing happens. On the right is an electrochemical cell which allows electrons to flow from the reductant to the oxidant through an external circuit. In a spontaneous reaction electrons leave the zinc, go through the wire and are then taken up by the copper ions. The salt bridge prevents the copper ions from migrating to the zinc compartment.



Video:19.3.1: *This 2:54 minute video shows the spontaneous reaction between copper ions and zinc. Note, copper(II)sulfate is a blue solution and the kinetics are speeded up by using fine grained zinc particles (which increases the surface area) and with vigorous stirring it is broken into small pieces to increase the surface area. As the reaction proceeds the blue disappears and a copper colored solid appears on the bottom of the container.*

As the above video shows, placing zinc metal into the copper(II) solution results in a spontaneous redox reaction ($\Delta G < 0$), and if we placed the copper metal into the zinc solution no reaction would occur ($\Delta G > 0$). In an electrochemical cell, we allow electrons to be transferred, which will spontaneously occur in the direction of $\Delta G < 0$, and a cell operating in this fashion is called a galvanic or voltaic cell, which can be used to provide energy to do work, like the common "battery" we use in flashlights and electrical devices. Just as we could drive a nonspontaneous reaction by coupling it to a spontaneous reaction (review section 18.6.5), we could hook up an external supply of power with the opposite polarity and drive the reaction in the intrinsically nonspontaneous direction. In this case the electrochemical cell is operating in the electrolytic mode and being driven by an external source of energy.



$\underbrace{Zn(s) + Cu^{+2} \rightarrow Cu(s) + Zn^{+2}}$
operating in spontaneous galvanic mode releases energy that can do work

$\underbrace{Cu(s) + Zn^{+2} \rightarrow Zn(s) + Cu^{+2}}$
operating in nonspontaneous electrolytic mode requires external energy to make it work

Figure19.3.2: The two modes an electrochemical cell operates in. The left mode is the spontaneous redox reaction and can be used to provide energy to do work. The right mode is the electrolytic mode, which will not occur unless an external energy source is added to drive it. That is, the reaction on the electrolytic cell is not spontaneous unless it is driven by an external source

Sign Convention of Galvanic and Electrolytic Cells. Students are often confused that the sign convention of the anode and cathode switch for galvanic and electrolytic cells. What you need to realize is oxidation occurs at the anode and electrons leave the anode, and reduction occurs at the cathode, this is always true. In the Galvanic cell is is easy to see, and electrons flow from the Anodes through a load (light bulb) and to the cathode [+]. Now in an electrolytic cell the electrochemical cell sort of becomes like the load on the galvanic cell, and the sign of the electrodes are defined by the power supply. The copper electrode is hooked to the [+] electrode and there is no load between it and the electrode, so it is the [+] electrode, but it is the anode as electrons flow from it to the [+] electrode of the power supply, and then to the [-] anode. Simply speaking, the electrolytic cell must have an external power supply that drives the reaction, and the sign is based on the electrodes of the power supply

Components of Electrochemical Cells

An electrochemical cell splits the oxidant and reductant in a manner that allows electrons to flow through an external circuit from the reductant (which gets oxidized) to the oxidant (which causes reduction) while preventing them from physically touching each other. Figures 19.2.1, 19.2.2 and 19.2.3 represent electrochemical cells and you should look at those images while reading this section. The two compartments of an electrochemical cell where the half reactions occur are called the anode and the cathode, and they must have an electrode that you can connect the external circuit to.

- **Anode:** Oxidation occurs at the anode. This is always the case, but the sign of the anode switches between galvanic and electrolytic modes (see figure 19.2.2).
  - In a galvanic cell this is the negative electrode. This can be understood from two perspectives. From the reaction perspective, as the reductant (Zinc in the images on this page) lose electrons and enter the solution the electrode gains these electrons and thus acquires a negative charge, which can be transferred to something positive. The second is from the perspective of the external circuit, where the negative electrons flow to the positive terminal, which is the other electrode, making the anode the negative electrode
  - In an electrolytic cell this is the positive electrode. Here the electrode sign is not being determined by the cell reaction, but by the external power supply that is driving the reaction in the nonspontaneous direction. The right side of figure 19.2.2 shows the Daniel Cell being driven by an external power supply which has its [+] electrode connected to the cell with the copper. This causes the nonspontaneous reaction of electrons leaving the copper and moving towards the positive electrode. Since the wire connecting this to the power source has negligible resistance, this electrode is at roughly the same potential, and is thus the positive electrode. It must be emphasized that the reaction is being driven by the coupling of an external power supply that produces a negative free energy in the nonspontaneous direction, and this must be greater in magnitude than the spontaneous free energy that occurs in the galvanic cell, resulting in a net negative free energy that causes the intrinsically nonspontaneous reaction to occur. Because of this, the electrode sign is dictated by the external power supply. But the anode is still where oxidation occurs.
- **Cathode:** Reduction occurs at the cathode.
  - The cathode has the opposite signs of the anode, so it is [+] in a galvanic/voltaic cell, and [-] in an electrolytic cell.
- **Electrodes**: In order to hook up an external circuit you need have something to physically connect the wire to. There are two types of electrodes, active and inert.
  - **Active electrode**: This is an electrode that takes part of the half reaction, and thus must be a solid. In the Daniels (Zn^{+2}/Cu) cell both electrodes are active, and as the reaction proceeds the anode loses mass (as Zn converts to Zn^{+2} and enters the solution), while the cathode gains mass (as Cu^{+2} gains electrons from the external circuit and becomes Cu(s).
  - **Inert electrode**: This is an electrode that is made of a substance that does not undergo oxidation or reduction. Often times oxidants or reductants are not solids but gases or solutes, like in the hydrogen half reaction $2H^+(aq) + 2e^- \leftrightharpoons H_2(g)$, which has no solid material that can function as an electrode, and would thus require an additional substance like platinum or graphite, that would function as an inert electrode.
- **Electrolyte:** An electrolyte is a charged mobile ion that functions as a conducting medium and in the case of "wet cells" is typically an aqueous solution of ionic compounds. In the case of active electrodes this will often by a soluble salt that has a common ion that also makes a soluble salt with the metal of that half-cells electrode. For example, copper(II) sulfate is a soluble salt, so sodium sulfate would be a good electrolyte for that half cell. Sodium phosphate would not work because copper(II)phosphate would precipitate out.
- **External Circuit:** The external circuit allows electrons to flow from the anode to the cathode. In the case of a galvanic cell, this is a spontaneous flow and can be used to provide energy that can produce heat or do work. In the case of an electrolytic cell this requires an energy source to make it work.

- **Salt Bridge:** The salt bridge has two basic functions. First it completes the circuit and prevents charge buildup, which would stop the flow of electrons. That is, electrons flow towards a positive object and as they accumulate they reduce its "positiveness", and thus its ability to attract more electrons. The salt bridge prevents the buildup of negative charge by enabling an internal circuit that allows ions to complete the circuit and prevent charge buildup at the electrode.

  The second function of the salt bridge is to prevent the oxidant (Cu^{+2} in the Daniel cell) from migrating to the anode and being directly reduced by directly accepting electrons from the anode, and thus preventing the electrons from entering the external circuit. Thus it functions as a sort of "semipermeable membrane" allowing the electrolyte ions to freely migrate between half cells, but preventing the ions involved in the actual redox reaction from migrating. In reality some of the ions involved in the redox reaction do migrate through the salt bridge.

Cell Notation

Cell Notation is a shorthand way for describing an electrochemical cell. In cell notation you start with the anode on the left, and write down the reactants and products separated by a vertical line, which indicates a phase boundary (the salt bridge involves two phase boundaries). It should be noted that there needs to be a solid electrode at the very left of the anode and very right of the cathode. Finally, it is also important to note that these do not represent balanced equations, but identify what is being oxidized and what is being reduced.

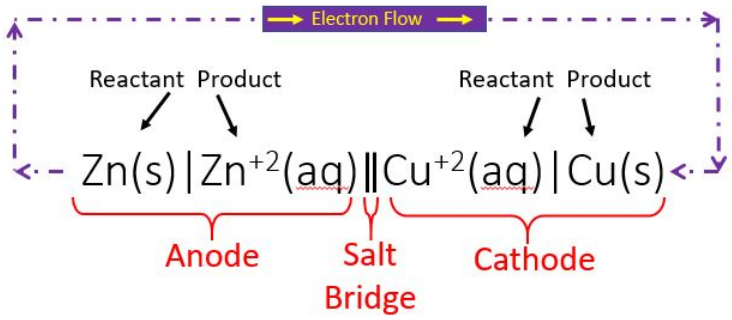


Figure19.3.3: Cell notation for zinc copper cell operating in galvanic mode. Note, the purple dotted line is not part of the cell notation, but shown here. That is, the above would be written as Zn(s)|Zn^{+2}(aq)||Cu^{+2}(aq)|Cu(s).

If the ion concentrations were known the (aq) would be changed with the molarity. So at standard one molar conditions the zinc copper cell would be written as

$$Zn(s)|Zn^{+2}(1M)||Cu^{+2}(1M)|Cu(s) \tag{19.3.2}$$

If the above cell was operating in electrolytic mode it would be written as

$$Cu(s)|Cu^{+2}(aq)||Zn^{+2}(aq)|Zn(s) \tag{19.3.3}$$

The half cell notation does not represent a balanced equation, and the ends must be solid, as they function as the electrode.

Example 19.3.1: Cell Notation

What is the cell notation for the redox reaction:

$$\mathrm{Cu(s) + 2\,Fe^{3+}(aq) \rightarrow Cu^{2+}(aq) + 2\,Fe^{2+}(aq)} \tag{19.3.4}$$

Solution

This can be broken into the following oxidation reactions

- Oxidation: $\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + 2}e^-$
- Reduction: $\mathrm{Fe^{3+}} + e^- \rightarrow \mathrm{Fe^{2+}}$

Which gives the cell of

$$\mathrm{Cu|Cu^{2+} \,||\, Fe^{3+}, Fe^{2+}|Pt} \tag{19.3.5}$$

There are three things to note in Equation 19.3.5.

1. First, the reduction half reaction involves two ions and so there is no solid, and an inert electrode had to be added (Pt) to the end of the cathode half reaction.
2. Second, the Fe^{+2} and Fe^{+3} are in the same phase and so you use a comma to separate them and not a vertical line (the vertical line represents a phase boundary).
3. And third, you are only identifying what is being oxidized (in the anode) and reduced (in the cathode), and so the cell notation does not represent a balanced chemical equation.

Voltaic (Galvanic) Cells

Galvanic cells are electrochemical cells that can be used to do work. Figure19.3.3 shows a typical galvanic cell that uses the spontaneous (Zn^{+2}/Cu) reaction (eq. 19.2.1 above). If the Zn^{+2} and Cu^{+2} ion concentrations in the two half cells is 1M a volt meter will read 1.10 volts. This is actually the open circuit potential that the voltmeter is reading, which correlates to no current flowing. The moment current flows [Zn^{+2}] increases while the [Cu^{+2}] decreases and this can be seen by the images in part (b) of figure 19.2.3 as the Zinc anode dissolves and copper ions attach themselves to the electrode and become reduced to neutral copper.

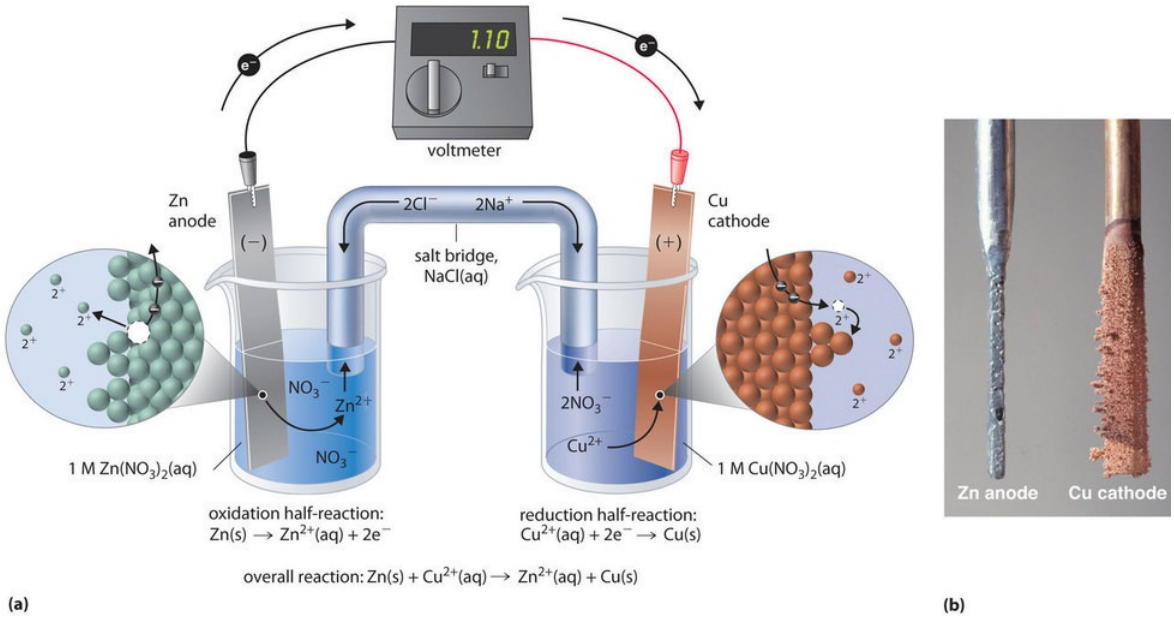


Figure19.3.3: Daniell Cell using the spontaneous (Zn^{+2}/Cu) reaction.

Exercise 19.3.1

Are the electrodes of the (Zn^{+2}/Cu) cell that is described in figure 19.2.3 active or passive electrodes?

Answer

Active electrodes because they take place in the Redox rection. This can be seen by the image on the right that shows the zinc anode losses mass as the copper cathode gains mass. In fact, if we measure the mass change of either the anode or cathode over time we could determine the number of electrons transferred, and calculate the average current over that time span that would have resulted in that mass change.



Note

We typically use the word "battery" to mean a galvanic (or voltaic) cell that can be used to power electrical devices, but that is technically incorrect and a battery can be galvanic or electrolytic. The term battery originally came from a series of cannons, and a battery of electrochemical cells represent a series of cells that are linked in series. Your 12 volt car battery is actually six 2 volt cells linked in series

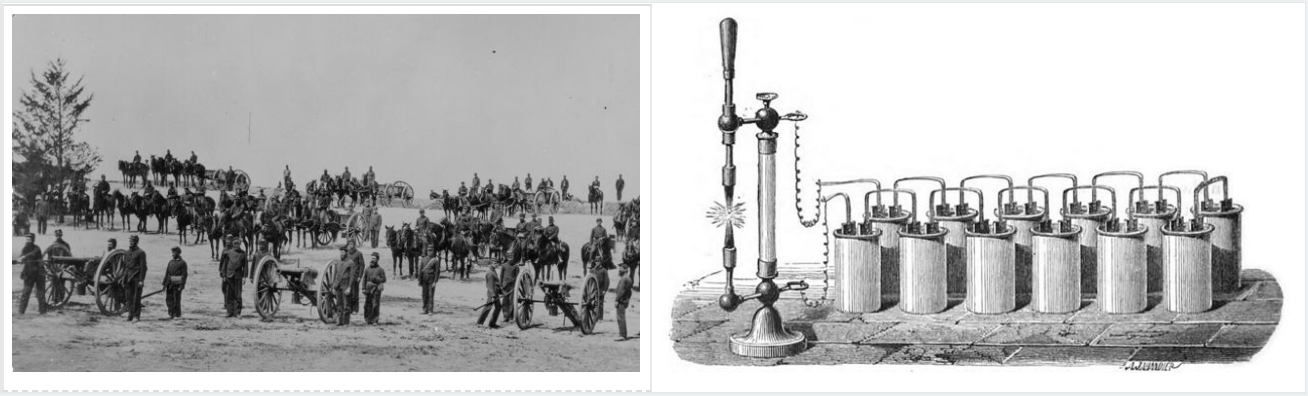


Figure19.3.3 Left is a Union Civil War artillery battery from the national archive, and to the left is an image of a carbon arc lamp being run by a battery of galvanic cells (wikicommons). Arc lamps predated incandescent lamps and were first demonstrated by Sir Humphry Davy in 1806, and by 1807 he had a high voltage battery of 3,000 cells that enabled him to discover sodium and potassium through the electrolysis of soda and potash. The following year he discovered magnesium, strontium and calcium.

Electronic Schematic Symbol of a battery implies cells connected in series

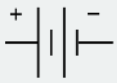


Figure19.3.3: The symbol used in circuit diagrams for a battery. The large vertical line is a cathode and the small is the anode, and this image implies two cells connected in series. In reality there can be many cells. Note, in electronics the convention of flow is the direction positive charge would flow, and this can cause confusion. That is, diagrams would show current flowing through an external circuit from the left electrode to the right electrode, while in reality, electrons are flowing from the right electrode (anode, where oxidation occurs) to the left electrode (cathode, where reduction occurs).

Test Yourself

Homework

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 19.3: Electrochemical Cells is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

19.4: Electrochemical Cell Fundamentals

Hypothes.is Tag = c1403c19 (case sensitive)
Group = UALRChem1403

Introduction

In the previous section (19.2) electrochemical cells were introduced, related to redox reactions that could be split into half reactions, and shown that a cell could be run in a galvanic (voltaic) or electrolytic mode. In this section we are going to apply some of the fundamentals of electricity that were introduced in section 19.0 to the operations of electrochemical cells.

Cell EMF and Free Energy

The cell EMF (ElectroMotive Force) or E_{cell}, which has units of Volts (V), is a measure of the spontaneous "force" that drives electrons through an external circuit from the anode to the cathode, and was introduced in section 19.03. It is a measure of the electric potential energy difference between the two electrodes. An analogy could be drawn between E_{cell} and the dependence of gravitational potential energy on the height of a waterfall.

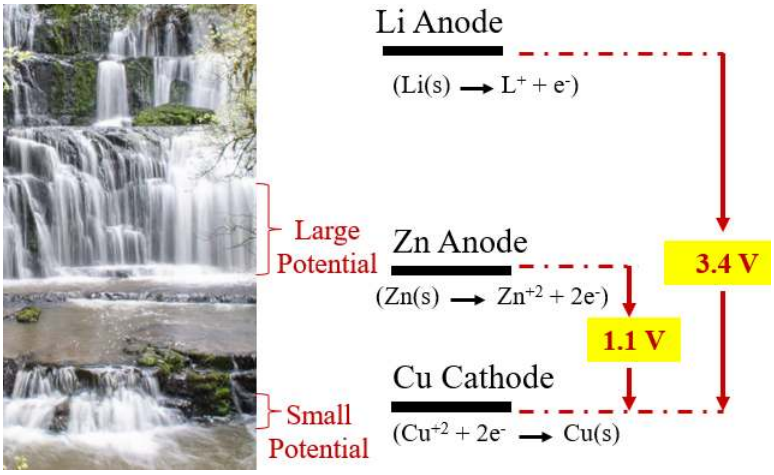


Figure 19.4.1: Just as water spontaneously flows down a waterfall, electrons spontaneously flow from anode to cathode. Here, cell potential is analogous to gravitational potential, and there are two factors relating the work that can be obtained from a waterfall, the height of the water, and the amount of water flowing over the Fall. Likewise, electric work is related to the potential difference and the amount of charge transferred across the potential drop.

Just as the amount of energy (work) that the water can do is dependent on both the quantity of water flowing over the waterfall and its height (mgh, see gravitational potential energy if interested), the electric potential energy is related to the charge transferred and the potential difference, which is related to the maximum possible work.

$$\text{Electric Work}_{max} = (\text{Charge}) \times (\text{Potential Difference})$$

$$W_e = qE_{Cell} \tag{19.4.1}$$

From section 19.0.2 we know that a Faraday is the charge of a mole of electrons

$$F = 96,500 \frac{C}{mol\ e^-} \tag{19.4.2}$$

and the charge "q" of "n" moles electrons is = nF

$$q = nF$$

$$q(C) = -N(\ \cancel{mol\ e^-})96,500(\frac{C}{\cancel{mol\ e^-}}) \tag{19.4.3}$$

(note: this equation is showing units in parenthesis).

Note, the minus sign comes from the fact that each electron has a negative charge. So

$$W_e = -nFE_{Cell} \tag{19.4.4}$$

From Section 18.6.7 we know that the maximum amount of work is related to ΔG, which can be related to the electric work

$$\Delta G = W_e = \Delta G \tag{19.4.5}$$

$$\Delta G = -nFE_{Cell} \tag{19.4.6}$$

The above makes sense as a spontaneous process has a positive cell potential ($E > 0$) and a negative Free Energy difference ($\Delta G < 0$).

Note, from the definition of the volt (Equation 19.6 of Section 19.0.3),

$$1\,C = 1\,\frac{J}{V} \tag{19.4.7}$$

and so Faraday's constant also has units of

$$F = 96,500\,\frac{J}{V \cdot mol\ e^-} \tag{19.4.8}$$

This can easily be seen by the dimensional analysis of Equation 19.4.4 or 19.4.6.

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

This page titled 19.4: Electrochemical Cell Fundamentals is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

19.5: Standard Electrochemical Potentials

Standard Cell Potential

In the last section we saw how the cell potential could be related to Gibbs Free Energy:

$$\Delta G = -nRE_{Cell} \tag{19.5.1}$$

If at standard state conditions we have:

$$\Delta G^o_{redox\ rxn} = -nRE^o_{Cell} \tag{19.5.2}$$

We know from chapter 19 that there are thermodynamic tables of standard state free energies of formation ΔG^o_f that can be used to calculate ΔG^o_{rxn}, and in this section we will learn how to create a table of standard state reduction potentials for half reactions, and use those to calculate E^o_{cell}. This table is similar to the activity series for oxidation half reactions (Section 3.6.1.1) we covered in general chemistry one, but is written as a reduction instead of an oxidation.

The challenge is how do we measure a potential, and what is zero potential? According to Coulomb's Law, zero potential would be when two charged particles are separated by infinity, which is not an attainable situation.

$$E = K\frac{q_1 q_2}{r} \tag{19.5.3}$$

For a redox reaction to occur one species must be reduced (gain electrons) and the other species must be oxidized (lose electrons), it is thus physically impossible to measure the potential of a single electrode. But you can measure the difference between the potentials of two electrodes. This means the value of the difference does not depend on the definition of zero potential. Consider the Zinc/Copper voltaic cell.

$$Zn_{(s)} \mid Zn^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s) \qquad E^\circ = 1.1\ V \tag{19.5.4}$$

The difference between the zinc anode of the copper cathode of the zinc/copper voltaic cell does not depend on what the true zero value is, along as both copper and zinc are measured against the same zero value. This is analogous to the difference between the boiling and freezing point of water being being the same in the kelvin (373.15-273.15) and Celsius (100 - 0), as they both have the same scale, just different zero points (0 Kelvin is absolute zero, 0 Celsius is the normal freezing point of water).

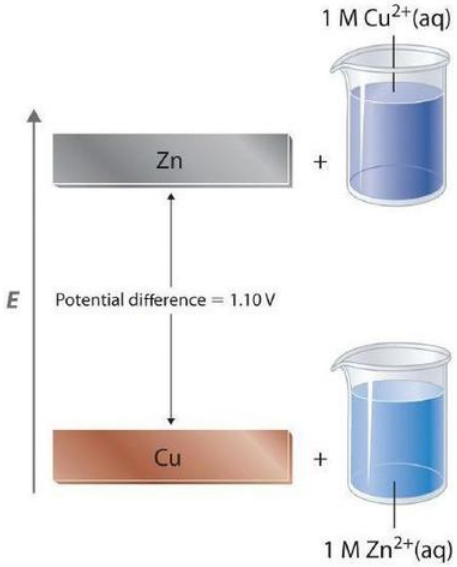


Figure 19.5.1: The potential difference between the species being oxidized and reduced is independent of the zero point as long as the same scale is used.

At standard state conditions the cell potential is the oxidation potential of the oxidation half reaction in the anode (because that species is being oxidized) and the reduction potential of the reduction half reaction in the cathode (because that species is getting reduced).

The potential of any half reaction can be written as either a reduction or oxidation potential (by simply writing the equation in the opposite direction and switching the sign). We will use a subscript to indicate the type of potential (oxidation or reduction potential) and parenthesis to indicate which half reaction is being described.

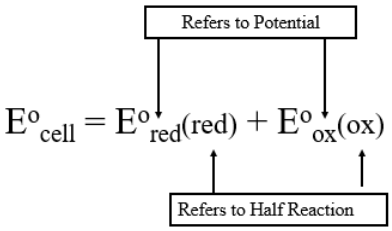


Figure 19.5.2: The subscript refers to the type of half potential and the parenthesis refers to which half reaction.

Since reduction is the opposite of oxidation, we can simply subtract the reduction potential of the oxidation half reaction.

> **Note:**
>
> Since $\Delta G_{redox\ rxn} = -nRE_{Cell}$ we can see that if you reverse a reaction, the sign of the cell potential is reversed. This means the reduction potential of a half reaction is the negative of its oxidation potential

$$\begin{aligned} E^o_{cell} &= E^o_{red}(red) + E^o_{ox}(ox) \\ &= E^o_{red}(red) - E^o_{red}(ox) \end{aligned} \tag{19.5.5}$$

Simply add the reduction potential of the species being reduced and subtract the reduction potential of the species being oxidized.

In this class we will use the standard hydrogen reference electrode (SHE) and define its reduction potential as zero. If you find a table with different values, it is probably using a different standard electrode. There are situations where the SHE will simply not work, like non aqueous systems or when measuring transient (short-lived) chemicals that disappear before the SHE electrode achieves equilibrium.

Standard Hydrogen Electrode (SHE)

The following figure shows the basic structure of the SHE (Standard Hydrogen Electrode). This electrode may act as a cathode (reduction) or as an anode (oxidation). Note, at standard conditions the gas pressure is 1 atm and the hydronium ion concentration is 1 M. The platinum electrode is an inert electrode that does not get oxidized or reduced, but allows electrons to transfer between the aqueous and gaseous phases within the cell.

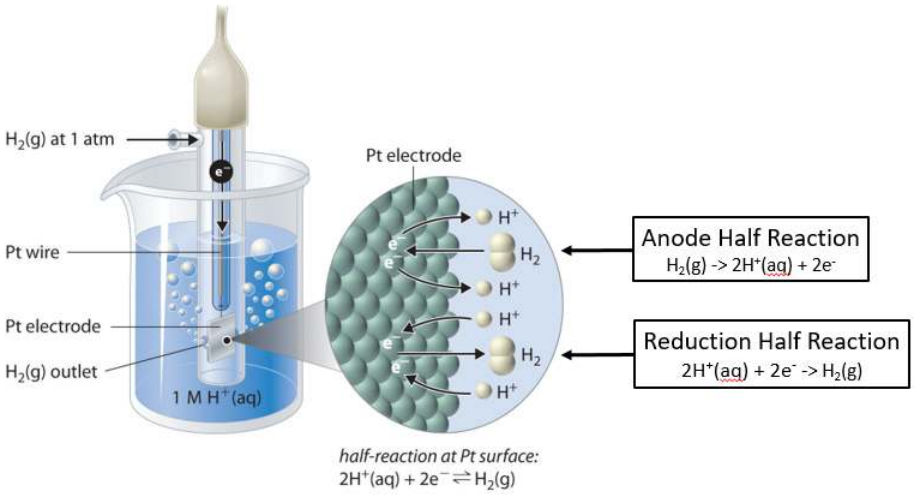


Figure 19.5.3: *he Standard Hydrogen Electrode. The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. Note, the SHE can act as either an Anode or Cathode.*

The standard potential of a reference electrode is 0 V, and we will write these as reduction potentials. So the standard reduction potential of the SHE is:

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \quad V = 0 \tag{19.5.6}$$

Because it is impossible to measure the potential of any electrode directly, defining a reference electrode like the **standard hydrogen electrode (SHE)** as having zero potential allows us to measure the reduction potential of any other substance by measuring it against the SHE. When the SHE half cell is connected to another half cell, it may be the anode or the cathode, depending on which process is spontaneous. At standard conditions, any substance that spontaneously oxidizes hydrogen in the SHE has a positive reduction potential (it gets reduced) and the SHE is functioning as an Anode. Any substance at standard state that gets oxidized by hydrogen in the SHE has a negative reduction potential and the SHE functions as a Cathode. These different processes are described in the next section.

SHE as Anode

A galvanic cell consisting of a SHE and Cu^{2+}/Cu half-cell can be used to determine the standard reduction potential for Cu^{2+} (Figure 19.5.1), which is shown to have a voltage of 0.337V at standard state conditions.

In cell notation, the reaction is

$$\mathrm{Pt}(s)\,|\,\mathrm{H_2}(g,\ 1\ \mathrm{atm})\,|\,\mathrm{H^+}(aq,\ 1\ M)\,\|\,\mathrm{Cu^{2+}}(aq,\ 1\ M)\,|\,\mathrm{Cu}(s) \tag{19.5.7}$$

Electrons flow from the anode to the cathode. The reactions, which are reversible, are

$$\begin{aligned}&\text{Anode (oxidation): } \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-}\\ &\text{Cathode (reduction): } \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cu}(s)\\ \hline &\text{Overall: } \mathrm{Cu^{2+}}(aq) + \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + \mathrm{Cu}(s)\end{aligned}$$

If a cell with the $\mathrm{Cu(s)|Cu^{+2}(aq)}$ half reaction at standard conditions is connected to the SHE, the open circuit potential is 0.337V (Figure 19.5.4).

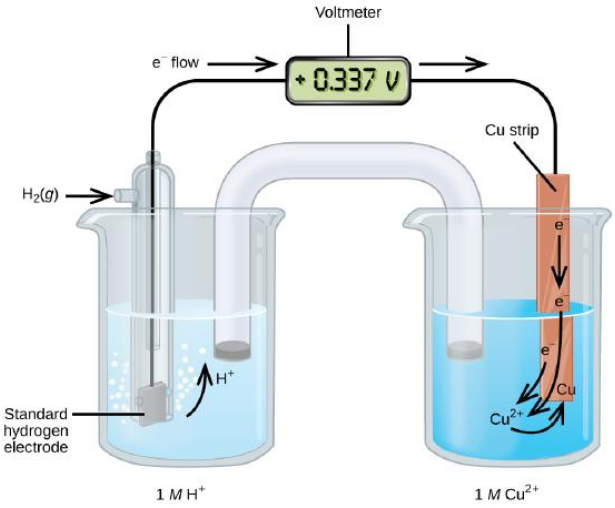


Figure 19.5.4: SHE acting as an anode. (Copyright; author via source)

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is necessary because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = \underbrace{E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}}_{\text{all potentials are reduction potentials}} \tag{19.5.8}$$

$$+0.34\ \text{V} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{H}^+/\text{H}_2} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - 0 = E^\circ_{\text{Cu}^{2+}/\text{Cu}} \tag{19.5.9}$$

Figure 19.5.2: *A galvanic cell can be used to determine the standard reduction potential of* Cu^{2+}.

Remember, Oxidation occurs at the Anode and Reduction occurs at the cathode. The Reduction Potential of Cu^{+2} is Positive because it is getting reduced (the SHE is getting oxidized in the anode, but by definition, its potential is zero, and so we are measuring the reduction potential of copper.)

SHE as Cathode

A galvanic cell consisting of a SHE and Cu^{2+}/Cu half-cell can be used to determine the standard reduction potential for Cu^{2+} (Figure 19.5.2), which is shown to have a voltage of 0.337V at standard state conditions.

In cell notation, the reaction is

$$\text{Zn}(s)\,|\,\text{Zn}^{2+}(aq,\ 1\ M)\,\|\,\text{H}^+(aq,\ 1\ M)\,|\,\text{H}_2(g,\ 1\ \text{atm})\,|\,\text{Pt}(s) \tag{19.5.10}$$

Electrons flow from the anode to the cathode. The reactions, which are reversible, are

$$\begin{aligned}&\text{Anode (oxidation): Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + 2\,\text{e}^-\\ &\text{Cathode (reduction): } 2\,\text{H}^+(aq) + 2\,\text{e}^- \longrightarrow \text{H}_2(g)\\ \hline &\text{Overall: Zn}(s) + 2\,\text{H}^+(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g)\end{aligned}$$

If a cell with the $\mathrm{Zn(s)|Zn^{+2}(aq)}$ half reaction at standard conditions is connected to the SHE, the open circuit potential is 0.76V (Figure 19.5.5).

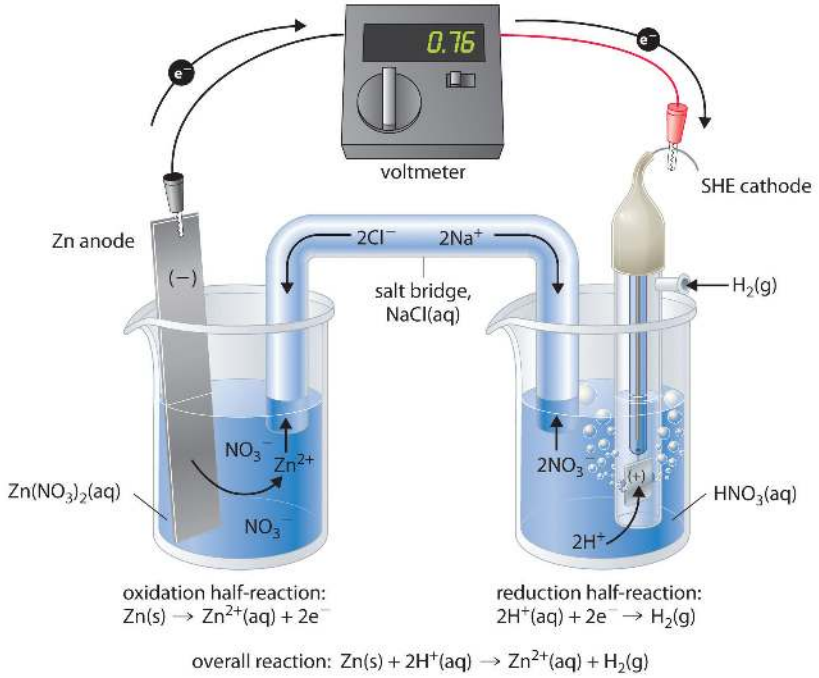


Figure 19.5.6: *The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn^{2+} couple is E°_{cell} = 0.76 V.*

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is necessary because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = \underbrace{E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}}_{\text{all potentials are reduction potentials}} \tag{19.5.11}$$

$$+0.76\ \text{V} = E^\circ_{\text{H}^+/\text{H}_2} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} = 0 - E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -E^\circ_{\text{Zn}^{2+}/\text{Zn}} \tag{19.5.12}$$

therefor the reduction potential of zinc is

$$E^\circ_{\text{Zn}^{2+}/\text{Cu}} = -0.76V \tag{19.5.13}$$

Remember, Oxidation occurs at the Anode and Reduction occurs at the cathode. The Reduction Potential of Zn^{+2} is Negative because it is getting oxidized (the SHE is getting reduced in the cathode, but by definition, its potential is zero, and so we are measuring the reduction potential of zinc.).

Standard Reduction Potential Tables

By selectively measuring different substance against the standard hydrogen electrode we can build a table of Reduction potentials that can then be used to calculate the standard state potential for any reaction from the standard reduction potential of the reductant and oxidant.

Note

LibreText gives you access to tables through the reference tab in the header of every webpage. There are two Standard reduction tables you can use: P1: Standard Reduction Potentials by Element and P2: Standard Reduction Potentials by Value

The following table is sorted by value.

Standard Potentials

Reduction 1/2 Reaction	E^o (V)
$F_2(g) + 2\ e^- \longrightarrow 2\ F^-(aq)$	+2.87
$Cl_2(g) + 2\ e^- \longrightarrow 2\ Cl^-(aq)$	+1.36
$Br_2(g) + 2\ e^- \longrightarrow 2\ Br^-(aq)$	+1.06
$Fe^{+3}(aq) + e^- \longrightarrow Fe^{+2}(aq)$	+0.54
$Cu^{+2}(aq) + 2e^- \longrightarrow Cu\,(s)$	+0.34
$2H^+(aq) + 2\ e^- \longrightarrow 2\ H_2(g)$	**0.000**
$Fe^{+2}(aq) + 2e^- \longrightarrow Fe\,(s)$	-0.44
$Zn^{+2}(aq) + 2e^- \longrightarrow Zn\,(s)$	- 0.76
$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71
$K^+(aq) + e^- \longrightarrow K(s)$	-2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.05

Figure 19.5.7: Select reduction potentials (use the Resources tab on the side to obtain a larger list

There are several things worth noting in Table 19.5.1. First, the highly electronegative fluorine has a very high reduction potential, meaning it tends to accept electrons, and likewise, its ion is very stable and does not want to lose electrons (fluoride's oxidation potential would b -2.87 V). Second, metals tend to lose electrons and so have very low oxidation potential, in fact many have negative reduction potentials, meaning they will give electrons to water).

Calculating Standard Reduction Potentials

With a table of reduction potentials you can calculate the Standard Reduction Potential for a chemical reaction. You note that in any redox reaction, one species must gain electrons (get reduced), while another loses electrons (gets oxidized). If you use the same standard state electrode (hydrogen in this class), the reduction potential for the reaction is the reduction potential of the cathode half reaction (where reduction occurs) minus that of the reduction potential of the anode half reaction (where oxidation occurs).

$$\mathrm{Zn}(s)\,|\,\mathrm{Zn}^{2+}(aq,\ 1\ M)\,\|\,\mathrm{Cu}^{2+}(aq,\ 1\ M)\,|\,\mathrm{Cu}(s) \tag{19.5.14}$$

The overall reaction is:

$$\mathrm{Zn}(s) + \mathrm{Cu}^{+2}(aq) \longrightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Cu(s)} \tag{19.5.15}$$

The cell potential is:

$$E^\circ_{\text{cell}} = \underbrace{E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}}_{\text{all potentials are reduction potentials}} \tag{19.5.16}$$

$$E^\circ{}_{cell} = .34V - .76V = 1.1V \tag{19.5.17}$$

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

-the great people at Open Stax

This page titled 19.5: Standard Electrochemical Potentials is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

19.6: Electrochemistry and Thermodynamics

Introduction

In section 19.3.2 we related free energy to cell potential with the following equation, which will allow us to relate thermodynamics to electrochemistry.

$$\Delta G = -nFE_{Cell} \tag{19.6.1}$$

We also know from section 18.6.3 where we discussed two meanings for "spontaneity".

- Spontaneous in the sense that it is product favored
  ΔG^o_{rxn}<<0 (it is very negative) and $K \gg 1$ (it is a very large number)
  (once equilibrium is reached there will be lots of products)
- Spontaneous in the sense that it is reactant loaded
  $\Delta G_{rxn} < 0$ (Forward reaction is spontaneous) and Q<K
  (the reaction will make products, even if not many)

We also know that from section 18.5.4.1 that at equilibrium Q=K and ΔG_{rxn} = 0, so substituting these equilibrium conditions into eq. 18.5.11 gives

$$\Delta G^o_{rxn} + RTlnK_{eq} = 0 \tag{19.6.2}$$

$$rearranging\ \ gives$$

$$\Delta G^o_{rxn} = -RTlnK$$

$$or$$

$$K = e^{\frac{-\Delta G^o_{rxn}}{RT}}$$

(note: the above are different forms of the same equation)

We will start by looking at systems that are at equilibrium, and see that we can determine K from standard state reduction potentials.

Equilibrium Constants and Standard Cell Potentials

We can get the equilibrium constant from a table of standard reduction potentials. Noting from

$$\Delta G^\circ = -RT\ln K \ \ and \ \ \Delta G^\circ = -nFE^\circ_{cell} \tag{19.6.3}$$

Gives the relationship between the standard free-energy change and the standard cell potential:

$$-nFE^\circ_{cell} = -RT\ln K \tag{19.6.4}$$

Rearranging this equation,

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right)\ln K \tag{19.6.5}$$

or in the exponential form

$$K = e^{\frac{nFE^o_{rxn}}{RT}} \tag{19.6.6}$$

Thus K is exponentially related to E°_{cell} and large equilibrium constants correspond to large positive values of E°_{cell}.

Example 19.6.2

Use the data in the References Table of Standard Potentials to calculate the equilibrium constant at standard conditions for the reaction of metallic lead with PbO_2 in the presence of sulfate ions to give $PbSO_4$ under standard conditions. (This reaction occurs when a car battery is discharged.) Report your answer to two significant figures.

Given: redox reaction

Asked for: K

Strategy:

A. Write the relevant half-reactions and potentials. From these, obtain the overall reaction and $E°_{cell}$.
B. Determine the number of electrons transferred in the overall reaction. Use Equation 19.5.6 to solve for K.

Solution:

A. The relevant half-reactions and potentials from Table P2 are as follows:

cathode:	$\mathrm{PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)}$	$E°_{\text{cathode}} = 1.69\ \text{V}$
anode:	$\mathrm{Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-}$	$E°_{\text{anode}} = -0.36\ \text{V}$
overall:	$\mathrm{Pb(s) + PbO_2(s) + 2SO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)}$	$E°_{\text{cell}} = 2.05\ \text{V}$

B. Two electrons are transferred in the overall reaction, so n = 2. Solving Equation ??? for log K and inserting the values of n and E°,

$$\begin{aligned} &= e^{\frac{nFE°_{rxn}}{RT}} \\ &= e^{\frac{2(96{,}500\ \frac{J}{V \cdot mol\ e^-})2.05V}{8.314\ \frac{J}{mol \cdot K}(298K)}} \\ &= 2.3 \times 10^{69} \end{aligned} \tag{19.6.7}$$

Thus the equilibrium lies far to the right, meaning the reaction will proceed towards products.

Exercise 19.6.3

Use the data in the Reference Table of Standard Potentials, calculate the equilibrium constant for the reaction of Sn^{2+}(aq) with oxygen to produce Sn^{4+}(aq) and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:

$$2Sn^{2+}_{(aq)} + O_{2(g)} + 4H^+_{(aq)} \rightleftharpoons 2Sn^{4+}_{(aq)} + 2H_2O_{(l)} \tag{19.6.8}$$

Answer

1.2×10^{73}

Figure \(\Pa

This page titled 19.6: Electrochemistry and Thermodynamics is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

19.7: Electrochemical Cells under Nonstandard Conditions

Skills to Develop

Make sure you thoroughly understand the following essential ideas. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- The Nernst equation relates the effective concentrations (*activities*) of the components of a cell reaction to the standard cell potential. For a simple reduction of the form $M^{n+} + ne^- \rightarrow M$, it tells us that a half-cell potential will change by 59/*n* mV per 10-fold change in the activity of the ion.
- Ionic concentrations can usually be used in place of activities when the total concentration of ions in the solution does not exceed about about 0.001*M*.
- In those reactions in which H^+ or OH^- ions take part, the cell potential will also depend on the pH. Plots of *E vs.* pH showing the stability regions of related species are very useful means of summarizing the redox chemistry of an element.

The *standard cell potentials* we discussed in a previous section refer to cells in which all dissolved substances are at unit *activity*, which essentially means an "effective concentration" of 1 M. Similarly, any gases that take part in an electrode reaction are at an effective pressure (known as the *fugacity*) of 1 atm. If these concentrations or pressures have other values, the cell potential will change in a manner that can be predicted from the principles you already know.

Cell Potentials Depend on Concentrations

Suppose, for example, that we reduce the concentration of Zn^{2+} in the Zn/Cu cell from its standard effective value of 1 M to an to a much smaller value:

$$Zn(s)|Zn^{2+}(aq, 0.001\ M)||Cu^{2+}(aq)|Cu(s) \tag{19.7.1}$$

This will reduce the value of Q for the cell reaction

$$Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s) \tag{19.7.2}$$

thus making it more spontaneous, or "driving it to the right" as the *Le Chatelier principle* would predict, and making its free energy change ΔG more negative than ΔG°, so that E would be more *positive* than E°. The relation between the actual cell potential E and the standard potential E° is developed in the following way. We begin with the equation derived previously which relates the standard free energy change (for the complete conversion of products into reactants) to the standard potential

$$\Delta G^\circ = -nFE^\circ \tag{19.7.3}$$

By analogy we can write the more general equation

$$\Delta G = -nFE \tag{19.7.4}$$

which expresses the change in free energy for any extent of reaction— that is, for any value of the reaction quotient Q. We now substitute these into the expression that relates ΔG and ΔG° which you will recall from the chapter on chemical equilibrium:

$$\Delta G = \Delta G^\circ + RT \ln Q \tag{19.7.5}$$

which gives

$$-nFE = -nFE^\circ + RT \ln Q \tag{19.7.6}$$

which can be rearranged to

$$\underbrace{E = E^\circ - \frac{RT}{nF} \ln Q}_{\text{applicable at all temperatures}} \tag{19.7.7}$$

This is the *Nernst equation* that relates the cell potential to the standard potential and to the activities of the electroactive species. Notice that the cell potential will be the same as E° only if Q is unity. The Nernst equation is more commonly written in base-10 log form and for 25 °C:

$$\underbrace{E = E^\circ - \frac{0.059}{n}\log_{10} Q}_{\text{Applicable at only 298K}} \tag{19.7.8}$$

Contributors

Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

This page titled 19.7: Electrochemical Cells under Nonstandard Conditions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

19.8: Corrosion

Skills to Develop

- To understand the process of corrosion.

Corrosion is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a patina. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion. Consequently, the development of methods for protecting metal surfaces from corrosion constitutes a very active area of industrial research. In this section, we describe some of the chemical and electrochemical processes responsible for corrosion. We also examine the chemical basis for some common methods for preventing corrosion and treating corroded metals.

Corrosion is a REDOX process.

Under ambient conditions, the oxidation of most metals is thermodynamically spontaneous, with the notable exception of gold and platinum. Hence it is actually somewhat surprising that any metals are useful at all in Earth's moist, oxygen-rich atmosphere. Some metals, however, are resistant to corrosion for kinetic reasons. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction. Aluminum cans also have a thin plastic layer to prevent reaction of the oxide with acid in the soft drink. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both.

In contrast to these metals, when iron corrodes, it forms a red-brown hydrated metal oxide ($Fe_2O_3 \cdot xH_2O$), commonly known as rust, that does not provide a tight protective film (Figure 19.8.1). Instead, the rust continually flakes off to expose a fresh metal surface vulnerable to reaction with oxygen and water. Because both oxygen and water are required for rust to form, an iron nail immersed in deoxygenated water will not rust—even over a period of several weeks. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil saturated with oxygen will not rust because of the absence of water.

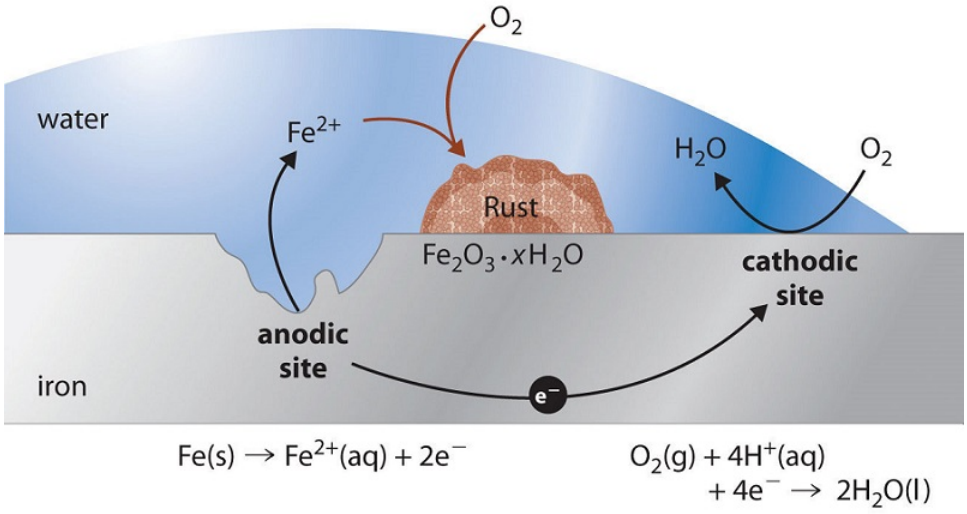


Figure 19.8.1: Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to Fe^{2+}(aq) at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust ($Fe_2O_3 \cdot xH_2O$) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen.

In the corrosion process, iron metal acts as the anode in a galvanic cell and is oxidized to Fe^{2+}; oxygen is reduced to water at the cathode. The relevant reactions are as follows:

- at cathode:

$$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)} \quad E^\circ = 1.23\ V \tag{19.8.1}$$

- at anode:

$$Fe(s) \rightarrow Fe^{2+}_{(aq)} + 2e^- \qquad E^\circ = -0.45\ V \tag{19.8.2}$$

- overall:

$$2Fe_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \qquad E^\circ = 1.68\ V \tag{19.8.3}$$

The Fe^{2+} ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing Fe^{3+}, as represented in the following equation:

$$4Fe^{2+}_{(aq)} + O_{2(g)} + (2+4x)H_2O \rightarrow 2Fe_2O_3 \cdot xH_2O + 4H^+_{(aq)} \tag{19.8.4}$$

The sign and magnitude of E° for the corrosion process (Equation 19.8.3) indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^+). Under neutral conditions, the driving force is somewhat less but still appreciable (E = 1.25 V at pH 7.0). Normally, the reaction of atmospheric CO_2 with water to form H^+ and HCO_3^- provides a low enough pH to enhance the reaction rate, as does acid rain. Automobile manufacturers spend a great deal of time and money developing paints that adhere tightly to the car's metal surface to prevent oxygenated water, acid, and salt from coming into contact with the underlying metal. Unfortunately, even the best paint is subject to scratching or denting, and the electrochemical nature of the corrosion process means that two scratches relatively remote from each other can operate together as anode and cathode, leading to sudden mechanical failure (Figure 19.8.2).

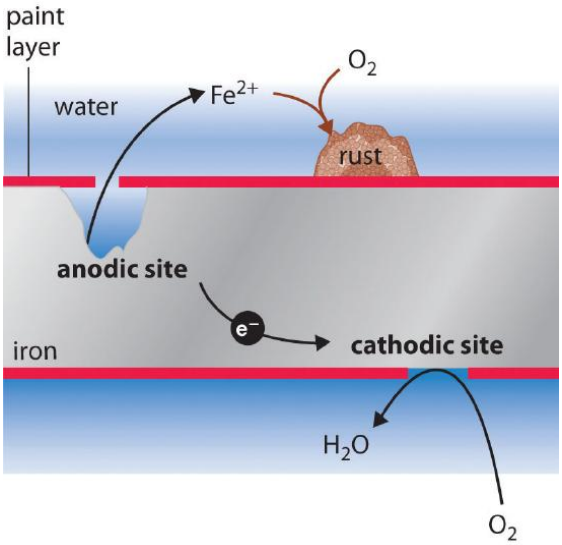


Figure 19.8.2: Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron. Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to Fe^{2+}(aq) at the less exposed site (the anode). Rust is formed when Fe^{2+}(aq) diffuses to a location where it can react with atmospheric oxygen, which is often remote from the anode. The electrochemical interaction between cathodic and anodic sites can cause a large pit to form under a painted surface, eventually resulting in sudden failure with little visible warning that corrosion has occurred.

Prophylactic Protection

One of the most common techniques used to prevent the corrosion of iron is applying a protective coating of another metal that is more difficult to oxidize. Faucets and some external parts of automobiles, for example, are often coated with a thin layer of chromium using an electrolytic process. With the increased use of polymeric materials in cars, however, the use of chrome-plated steel has diminished in recent years. Similarly, the "tin cans" that hold soups and other foods are actually made of steel coated with a thin layer of tin. Neither chromium nor tin is intrinsically resistant to corrosion, but both form protective oxide coatings.

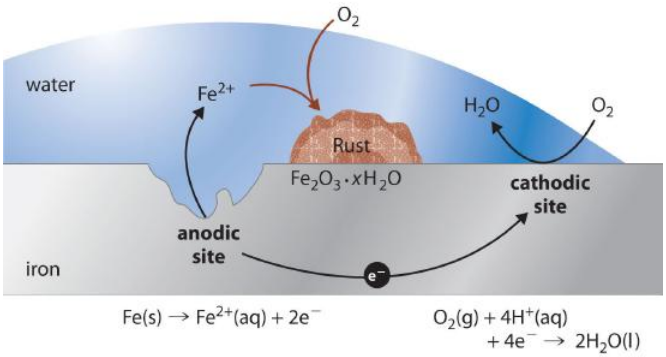


Figure 19.8.3: Galvanic Corrosion. If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can result in a dramatic increase in the rate at which iron is oxidized at the anode. Galvanic corrosion is likely to occur whenever two dissimilar metals are connected directly, allowing electrons to be transferred from one to the other.

As with a protective paint, scratching a protective metal coating will allow corrosion to occur. In this case, however, the presence of the second metal can actually increase the rate of corrosion. The values of the standard electrode potentials for Sn^{2+} ($E° = −0.14$ V) and Fe^{2+} ($E° = −0.45$ V) in Table P2 show that Fe is more easily oxidized than Sn. As a result, the more corrosion-resistant metal (in this case, tin) accelerates the corrosion of iron by acting as the cathode and providing a large surface area for the reduction of oxygen (Figure 19.8.3). This process is seen in some older homes where copper and iron pipes have been directly connected to each other. The less easily oxidized copper acts as the cathode, causing iron to dissolve rapidly near the connection and occasionally resulting in a catastrophic plumbing failure.

Cathodic Protection

One way to avoid these problems is to use a more easily oxidized metal to protect iron from corrosion. In this approach, called cathodic protection, a more reactive metal such as Zn ($E° = −0.76$ V for $Zn^{2+} + 2e^- \rightarrow Zn$) becomes the anode, and iron becomes the cathode. This prevents oxidation of the iron and protects the iron object from corrosion. The reactions that occur under these conditions are as follows:

$$\underbrace{O_{2(g)} + 4e^- + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}}_{\text{reduction at cathode}} \tag{19.8.5}$$

$$\underbrace{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}_{\text{oxidation at anode}} \tag{19.8.6}$$

$$\underbrace{2Zn_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Zn^{2+}_{(aq)} + 2H_2O_{(l)}}_{\text{overall}} \tag{19.8.7}$$

The more reactive metal reacts with oxygen and will eventually dissolve, “sacrificing” itself to protect the iron object. Cathodic protection is the principle underlying galvanized steel, which is steel protected by a thin layer of zinc. Galvanized steel is used in objects ranging from nails to garbage cans.



Crystalline surface of a hot-dip galvanized steel surface. This served both as prophylactic protection (protecting the underlying steel from the oxygen in the air) and cathodic protection (once exposed, the zinc will oxidize before the underlying steel).

In a similar strategy, **sacrificial electrodes** using magnesium, for example, are used to protect underground tanks or pipes (Figure 19.8.4). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

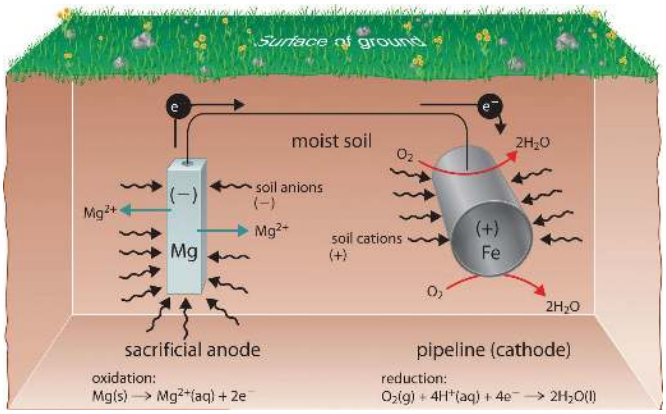


Figure 19.8.4: The Use of a Sacrificial Electrode to Protect Against Corrosion. Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium ($E° = -2.37$ V) is much more easily oxidized than iron ($E° = -0.45$ V), the Mg rod acts as the anode in a galvanic cell. The pipeline is therefore forced to act as the cathode at which oxygen is reduced. The soil between the anode and the cathode acts as a salt bridge that completes the electrical circuit and maintains electrical neutrality. As Mg(s) is oxidized to Mg^{2+} at the anode, anions in the soil, such as nitrate, diffuse toward the anode to neutralize the positive charge. Simultaneously, cations in the soil, such as H^+ or NH_4^+, diffuse toward the cathode, where they replenish the protons that are consumed as oxygen is reduced. A similar strategy uses many miles of somewhat less reactive zinc wire to protect the Alaska oil pipeline.

Example 19.8.1

Suppose an old wooden sailboat, held together with iron screws, has a bronze propeller (recall that bronze is an alloy of copper containing about 7%–10% tin).

a. If the boat is immersed in seawater, what corrosion reaction will occur? What is $E°_{cell}$?
b. How could you prevent this corrosion from occurring?

Given: identity of metals

Asked for: corrosion reaction, $E°_{cell}$, and preventive measures

Strategy:

A. Write the reactions that occur at the anode and the cathode. From these, write the overall cell reaction and calculate $E°_{cell}$.
B. Based on the relative redox activity of various substances, suggest possible preventive measures.

Solution:

a. **A** According to Table P2, both copper and tin are less active metals than iron (i.e., they have higher positive values of E° than iron). Thus if tin or copper is brought into electrical contact by seawater with iron in the presence of oxygen, corrosion will occur. We therefore anticipate that the bronze propeller will act as the cathode at which O_2 is reduced, and the iron screws will act as anodes at which iron dissolves:

$$\text{cathode:} \quad O_2(s) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \qquad E°_{cathode} = 1.23 \text{ V} \qquad (19.8.8)$$

$$\text{anode:} \quad Fe(s) \rightarrow Fe^{2+} + 2e^- \qquad E°_{anode} = -0.45 \text{ V} \qquad (19.8.9)$$

$$\text{overall:} \quad 2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l) \qquad E°_{overall} = 1.68 \text{ V} \qquad (19.8.10)$$

Over time, the iron screws will dissolve, and the boat will fall apart.

b. **B** Possible ways to prevent corrosion, in order of decreasing cost and inconvenience, are as follows: disassembling the boat and rebuilding it with bronze screws; removing the boat from the water and storing it in a dry place; or attaching an inexpensive piece of zinc metal to the propeller shaft to act as a sacrificial electrode and replacing it once or twice a year. Because zinc is a more active metal than iron, it will act as the sacrificial anode in the electrochemical cell and dissolve (Equation 19.8.7).



Zinc sacrificial anode (rounded object screwed to underside of hull) used to prevent corrosion on the screw in a boat via cathodic protection. Image by Rémi Kaupp and used with permission.

Exercise 19.8.1

Suppose the water pipes leading into your house are made of lead, while the rest of the plumbing in your house is iron. To eliminate the possibility of lead poisoning, you call a plumber to replace the lead pipes. He quotes you a very low price if he can use up his existing supply of copper pipe to do the job.

a. Do you accept his proposal?
b. What else should you have the plumber do while at your home?

Answer a

Not unless you plan to sell the house very soon because the Cu/Fe pipe joints will lead to rapid corrosion.

Answer a

Any existing Pb/Fe joints should be examined carefully for corrosion of the iron pipes due to the Pb–Fe junction; the less active Pb will have served as the cathode for the reduction of O_2, promoting oxidation of the more active Fe nearby.

Summary

Corrosion is a galvanic process that can be prevented using cathodic protection. The deterioration of metals through oxidation is a galvanic process called corrosion. Protective coatings consist of a second metal that is more difficult to oxidize than the metal being protected. Alternatively, a more easily oxidized metal can be applied to a metal surface, thus providing cathodic protection of the surface. A thin layer of zinc protects galvanized steel. Sacrificial electrodes can also be attached to an object to protect it.

19.8: Corrosion is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

19.9: Electrolysis

Skills to Develop

- To understand electrolysis and describe it quantitatively.

In this chapter, we have described various galvanic cells in which a spontaneous chemical reaction is used to generate electrical energy. In an electrolytic cell, however, the opposite process, called **electrolysis**, occurs: an external voltage is applied to drive a nonspontaneous reaction. In this section, we look at how electrolytic cells are constructed and explore some of their many commercial applications.

Electrolytic Cells

If we construct an electrochemical cell in which one electrode is copper metal immersed in a 1 M Cu^{2+} solution and the other electrode is cadmium metal immersed in a 1 $M\ Cd^{2+}$ solution and then close the circuit, the potential difference between the two compartments will be 0.74 V. The cadmium electrode will begin to dissolve (Cd is oxidized to Cd^{2+}) and is the anode, while metallic copper will be deposited on the copper electrode (Cu^{2+} is reduced to Cu), which is the cathode (Figure 19.9.1*a*).

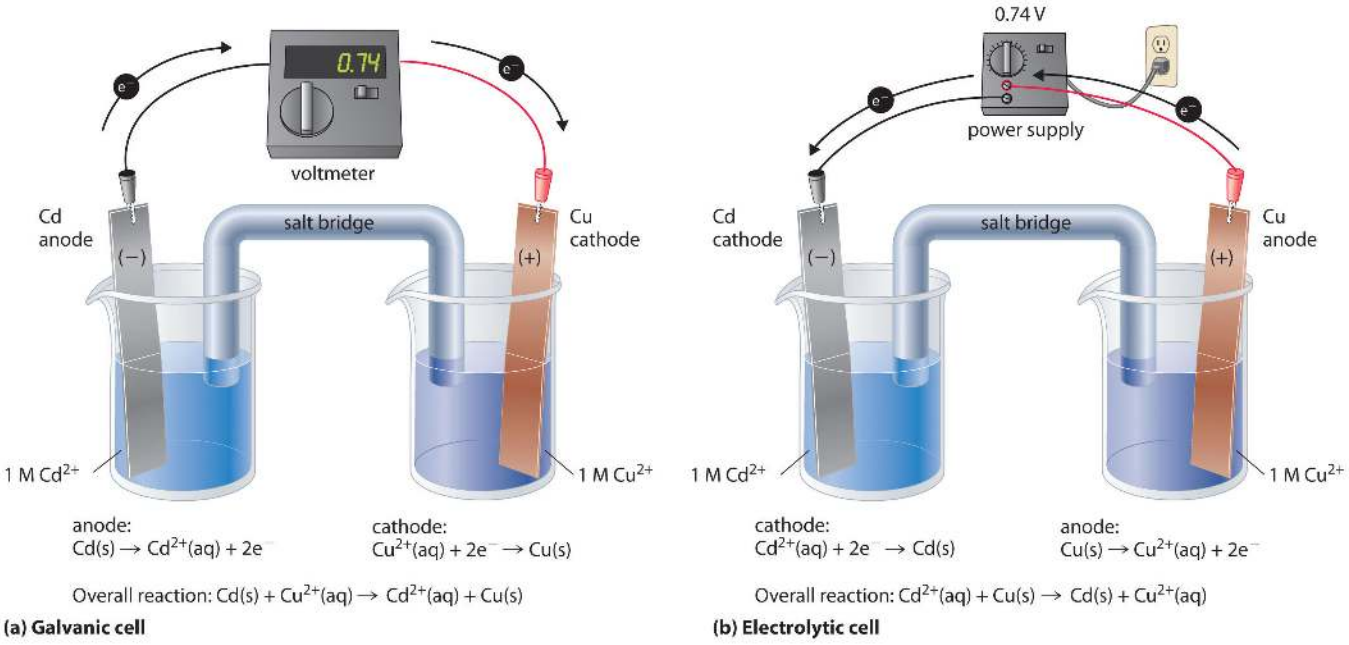


Figure 19.9.1: An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell. (a) When compartments that contain a Cd electrode immersed in 1 M Cd^{2+}(aq) and a Cu electrode immersed in 1 M Cu^{2+}(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to Cd^{2+}(aq) at the anode, and Cu^{2+}(aq) is spontaneously reduced to Cu(s) at the cathode. The potential of the galvanic cell is 0.74 V. (b) Applying an external potential greater than 0.74 V in the reverse direction forces electrons to flow from the Cu electrode [which is now the anode, at which metallic Cu(s) is oxidized to Cu^{2+}(aq)] and into the Cd electrode [which is now the cathode, at which Cd^{2+}(aq) is reduced to Cd(s)]. The anode in an electrolytic cell is positive because electrons are flowing from it, whereas the cathode is negative because electrons are flowing into it.

The overall reaction is as follows:

$$\mathrm{Cd(s) + Cu^{2+}(aq) \rightarrow Cd^{2+}(aq) + Cu(s)} \tag{19.9.1}$$

with $E^{\circ}_{cell} = 0.74\ V$

This reaction is thermodynamically spontaneous as written ($\Delta G^\circ < 0$):

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} \tag{19.9.2}$$

$$= -(2\ \text{mol e}^-)[96,486\ \text{J}/(\text{V}\cdot\text{mol})](0.74\ \text{V}) \tag{19.9.3}$$

$$= -140\ \text{kJ (per mole Cd)} \tag{19.9.4}$$

In this direction, the system is acting as a galvanic cell.

> *In an electrolytic cell, an external voltage is applied to drive a nonspontaneous reaction.*

The reverse reaction, the reduction of Cd^{2+} by Cu, is thermodynamically nonspontaneous and will occur only with an input of 140 kJ. We can force the reaction to proceed in the reverse direction by applying an electrical potential greater than 0.74 V from an external power supply. The applied voltage forces electrons through the circuit in the reverse direction, converting a galvanic cell to an electrolytic cell. Thus the copper electrode is now the anode (Cu is oxidized), and the cadmium electrode is now the cathode (Cd^{2+} is reduced) (Figure 19.9.1*b*). The signs of the cathode and the anode have switched to reflect the flow of electrons in the circuit. The half-reactions that occur at the cathode and the anode are as follows:

- cathode:

$$\mathrm{Cd^{2+}(aq) + 2\,e^- \rightarrow Cd(s)} \tag{19.9.5}$$

with $E^\circ_{cathode} = -0.40\,V$

- anode:

$$\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-} \tag{19.9.6}$$

with $E^\circ_{anode} = 0.34\,V$

- Overall:

$$\mathrm{Cd^{2+}(aq) + Cu(s) \rightarrow Cd(s) + Cu^{2+}(aq)} \tag{19.9.7}$$

with $E^\circ_{cell} = -0.74\,V$

Because $E^\circ_{cell} < 0$, the overall reaction—the reduction of Cd^{2+} by Cu—clearly **cannot** occur spontaneously and proceeds only when sufficient electrical energy is applied. The differences between galvanic and electrolytic cells are summarized in Table 19.9.1.

Table 19.9.1: Comparison of Galvanic and Electrolytic Cells

Property	Galvanic Cell	Electrolytic Cell
ΔG	< 0	> 0
E_{cell}	> 0	< 0
Electrode Process		
anode	oxidation	oxidation
cathode	reduction	reduction
Sign of Electrode		
anode	−	+
cathode	+	−

Electrolytic Reactions

At sufficiently high temperatures, ionic solids melt to form liquids that conduct electricity extremely well due to the high concentrations of ions. If two inert electrodes are inserted into molten $NaCl$, for example, and an electrical potential is applied, Cl^- is oxidized at the anode, and Na^+ is reduced at the cathode. The overall reaction is as follows:

$$\mathrm{2\,NaCl(l) \rightarrow 2\,Na(l) + Cl_2(g)} \tag{19.9.8}$$

This is the reverse of the formation of NaCl from its elements. The product of the reduction reaction is liquid sodium because the melting point of sodium metal is 97.8°C, well below that of $NaCl$ (801°C). Approximately 20,000 tons of sodium metal are produced commercially in the United States each year by the electrolysis of molten $NaCl$ in a Downs cell (Figure 19.9.2). In this specialized cell, $CaCl_2$ (melting point = 772°C) is first added to the $NaCl$ to lower the melting point of the mixture to about 600°C, thereby lowering operating costs.

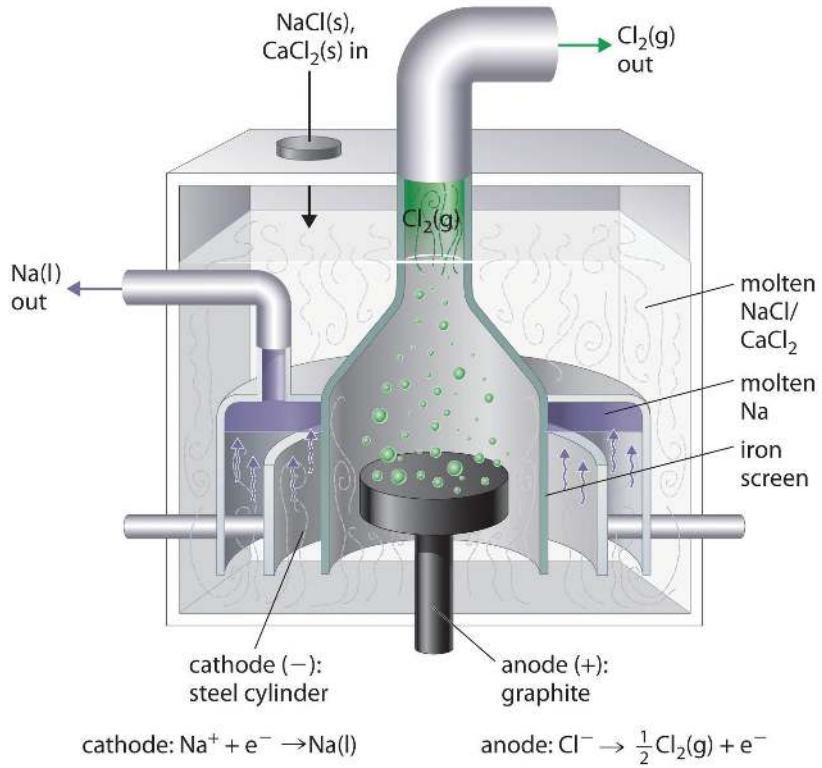


Figure 19.9.2: A Downs Cell for the Electrolysis of Molten NaCl. The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the sodium floats to the top of the melt and is collected in concentric capped iron cylinders surrounding the cathode. Gaseous chlorine collects in the inverted cone over the anode. An iron screen separating the cathode and anode compartments ensures that the molten sodium and gaseous chlorine do not come into contact.

Similarly, in the Hall–Heroult process used to produce aluminum commercially, a molten mixture of about 5% aluminum oxide (Al_2O_3; melting point = 2054°C) and 95% cryolite (Na_3AlF_6; melting point = 1012°C) is electrolyzed at about 1000°C, producing molten aluminum at the cathode and CO_2 gas at the carbon anode. The overall reaction is as follows:

$$2Al_2O_{3(l)} + 3C_{(s)} \rightarrow 4Al_{(l)} + 3CO_{2(g)} \tag{19.9.9}$$

Oxide ions react with oxidized carbon at the anode, producing CO_2(g).

There are two important points to make about these two commercial processes and about the electrolysis of molten salts in general.

1. The electrode potentials for molten salts are likely to be very different from the standard cell potentials listed in Table P2, which are compiled for the reduction of the hydrated ions in aqueous solutions under standard conditions.
2. Using a mixed salt system means there is a possibility of competition between different electrolytic reactions. When a mixture of NaCl and $CaCl_2$ is electrolyzed, Cl^- is oxidized because it is the only anion present, but either Na^+ or Ca^{2+} can be reduced. Conversely, in the Hall–Heroult process, only one cation is present that can be reduced (Al^{3+}), but there are three species that can be oxidized: C, O^{2-}, and F^-.

In the Hall–Heroult process, C is oxidized instead of O^{2-} or F^- because oxygen and fluorine are more electronegative than carbon, which means that C is a weaker oxidant than either O_2 or F_2. Similarly, in the Downs cell, we might expect electrolysis of a NaCl/$CaCl_2$ mixture to produce calcium rather than sodium because Na is slightly less electronegative than Ca (χ = 0.93 versus 1.00, respectively), making Na easier to oxidize and, conversely, Na^+ more difficult to reduce. In fact, the reduction of Na^+ to Na is the observed reaction. In cases where the electronegativities of two species are similar, other factors, such as the formation of complex ions, become important and may determine the outcome.

Example 19.9.1

If a molten mixture of $MgCl_2$ and KBr is electrolyzed, what products will form at the cathode and the anode, respectively?

Given: identity of salts

Asked for: electrolysis products

Strategy:

A. List all the possible reduction and oxidation products. Based on the electronegativity values shown in Figure 7.5, determine which species will be reduced and which species will be oxidized.
B. Identify the products that will form at each electrode.

Solution:

A The possible reduction products are Mg and K, and the possible oxidation products are Cl_2 and Br_2. Because Mg is more electronegative than K (χ = 1.31 versus 0.82), it is likely that Mg will be reduced rather than K. Because Cl is more electronegative than Br (3.16 versus 2.96), Cl_2 is a stronger oxidant than Br_2.

B Electrolysis will therefore produce Br_2 at the anode and Mg at the cathode.

Exercise 19.9.1

Predict the products if a molten mixture of $AlBr_3$ and LiF is electrolyzed.

Answer

Br_2 and Al

Electrolysis can also be used to drive the thermodynamically nonspontaneous decomposition of water into its constituent elements: H_2 and O_2. However, because pure water is a very poor electrical conductor, a small amount of an ionic solute (such as H_2SO_4 or Na_2SO_4) must first be added to increase its electrical conductivity. Inserting inert electrodes into the solution and applying a voltage between them will result in the rapid evolution of bubbles of H_2 and O_2 (Figure 19.9.3).

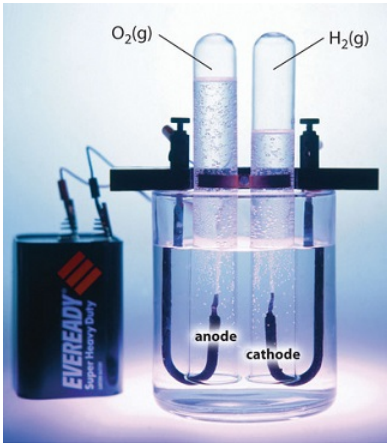


Figure 19.9.3: The Electrolysis of Water. Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode.

The reactions that occur are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ_{cathode} = 0V \tag{19.9.10}$$

- anode:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H +_{(aq)} + 4e^- \qquad E^\circ_{anode} = 1.23\ V \tag{19.9.11}$$

- overall:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \qquad E^\circ_{cell} = -1.23\ V \tag{19.9.12}$$

For a system that contains an electrolyte such as Na_2SO_4, which has a negligible effect on the ionization equilibrium of liquid water, the pH of the solution will be 7.00 and $[H^+] = [OH^-] = 1.0 \times 10^{-7}$. Assuming that $P_{O_2} = P_{H_2} = 1$ atm, we can use the

standard potentials to calculate E for the overall reaction:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log(P_{\text{O}_2} P^2_{\text{H}_2}) \tag{19.9.13}$$

$$E_{\text{cell}} = -1.23\ \text{V} - \left(\frac{0.0591\ \text{V}}{4}\right) \log(1) = -1.23\ \text{V} \tag{19.9.14}$$

Thus E_{cell} is −1.23 V, which is the value of $E°_{cell}$ if the reaction is carried out in the presence of 1 M H^+ rather than at pH 7.0.

In practice, a voltage about 0.4–0.6 V greater than the calculated value is needed to electrolyze water. This added voltage, called an **overvoltage**, represents the additional driving force required to overcome barriers such as the large activation energy for the formation of a gas at a metal surface. Overvoltages are needed in all electrolytic processes, which explain why, for example, approximately 14 V must be applied to recharge the 12 V battery in your car.

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation. The p-block metals and most of the transition metals are in this category, but metals in high oxidation states, which form oxoanions, cannot be reduced to the metal by simple electrolysis. Active metals, such as aluminum and those of groups 1 and 2, react so readily with water that they can be prepared only by the electrolysis of molten salts. Similarly, any nonmetallic element that does not readily oxidize water to O_2 can be prepared by the electrolytic oxidation of an aqueous solution that contains an appropriate anion. In practice, among the nonmetals, only F_2 cannot be prepared using this method. Oxoanions of nonmetals in their highest oxidation states, such as NO_3^-, SO_4^{2-}, PO_4^{3-}, are usually difficult to reduce electrochemically and usually behave like spectator ions that remain in solution during electrolysis.

> *In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation.*

Electroplating

In a process called **electroplating**, a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis. Electroplating is used to enhance the appearance of metal objects and protect them from corrosion. Examples of electroplating include the chromium layer found on many bathroom fixtures or (in earlier days) on the bumpers and hubcaps of cars, as well as the thin layer of precious metal that coats silver-plated dinnerware or jewelry. In all cases, the basic concept is the same. A schematic view of an apparatus for electroplating silverware and a photograph of a commercial electroplating cell are shown in Figure 19.9.4

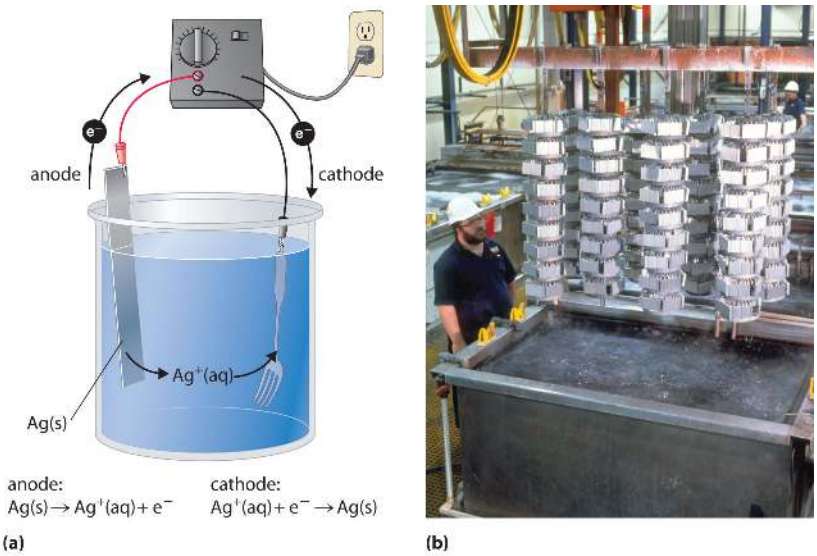


Figure 19.9.3: Electroplating. (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually consists of the metal that is being deposited (in this case, silver) that maintains the solution concentration as it dissolves. (b) In this commercial electroplating apparatus, a large number of objects can be plated simultaneously by lowering the rack into the Ag+ solution and applying the correct potential.

The half-reactions in electroplating a fork, for example, with silver are as follows:

- cathode (fork):

$$Ag^{+}_{(aq)} + e- \rightarrow Ag_{(s)} \qquad E^{\circ}{}_{cathode} = 0.80V \tag{19.9.15}$$

- anode (silver bar):

$$Ag_{(s)} \rightarrow Ag^{+}_{(aq)} \qquad E^{\circ}{}_{anode} = 0.80V \tag{19.9.16}$$

The overall reaction is the transfer of silver metal from one electrode (a silver bar acting as the anode) to another (a fork acting as the cathode). Because $E°_{cell}$ = 0 V, it takes only a small applied voltage to drive the electroplating process. In practice, various other substances may be added to the plating solution to control its electrical conductivity and regulate the concentration of free metal ions, thus ensuring a smooth, even coating.

This page titled 19.9: Electrolysis is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

19.10: Counting Electrons

Quantitative Considerations

If we know the stoichiometry of an electrolysis reaction, the amount of current passed, and the length of time, we can calculate the amount of material consumed or produced in a reaction. Conversely, we can use stoichiometry to determine the combination of current and time needed to produce a given amount of material.

The quantity of material that is oxidized or reduced at an electrode during an electrochemical reaction is determined by the stoichiometry of the reaction and the amount of charge that is transferred. For example, in the reaction $Ag^+(aq) + e^- \rightarrow Ag(s)$, 1 mol of electrons reduces 1 mol of Ag^+ to Ag metal. In contrast, in the reaction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$, 1 mol of electrons reduces only 0.5 mol of Cu^{2+} to Cu metal. Recall that the charge on 1 mol of electrons is 1 faraday (1 F), which is equal to 96,486 C. We can therefore calculate the number of moles of electrons transferred when a known current is passed through a cell for a given period of time. The total charge (C) transferred is the product of the current (A) and the time (t, in seconds):

$$C = A \times t \tag{19.10.1}$$

The stoichiometry of the reaction and the total charge transferred enable us to calculate the amount of product formed during an electrolysis reaction or the amount of metal deposited in an electroplating process.

For example, if a current of 0.60 A passes through an aqueous solution of $CuSO_4$ for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

$$\text{charge} = (0.60\ \text{A})(6.0\ \text{min})(60\ \text{s/min}) = 220\ \text{A} \cdot \text{s} = 220\ \text{C}$$

The number of moles of electrons transferred to Cu^{2+} is therefore

$$\text{moles e}^- = \frac{220\ \text{C}}{96{,}486\ \text{C/mol}} = 2.3 \times 10^{-3}\ \text{mol e}^-$$

Because two electrons are required to reduce a single Cu^{2+} ion, the total number of moles of Cu produced is half the number of moles of electrons transferred, or 1.2×10^{-3} mol. This corresponds to 76 mg of Cu. In commercial electrorefining processes, much higher currents (greater than or equal to 50,000 A) are used, corresponding to approximately 0.5 F/s, and reaction times are on the order of 3–4 weeks.

Example 19.10.2

A silver-plated spoon typically contains about 2.00 g of Ag. If 12.0 h are required to achieve the desired thickness of the Ag coating, what is the average current per spoon that must flow during the electroplating process, assuming an efficiency of 100%?

Given: mass of metal, time, and efficiency

Asked for: current required

Strategy:

A. Calculate the number of moles of metal corresponding to the given mass transferred.
B. Write the reaction and determine the number of moles of electrons required for the electroplating process.
C. Use the definition of the faraday to calculate the number of coulombs required. Then convert coulombs to current in amperes.

Solution:

A We must first determine the number of moles of Ag corresponding to 2.00 g of Ag:

$$\text{moles Ag} = \frac{2.00\ \text{g}}{107.868\ \text{g/mol}} = 1.85 \times 10^{-2}\ \text{mol Ag}$$

B The reduction reaction is $Ag^+(aq) + e^- \rightarrow Ag(s)$, so 1 mol of electrons produces 1 mol of silver.

C Using the definition of the faraday,

$$\text{coulombs} = (1.85 \times 10^{-2}\text{mol e}^-)(96{,}486\ \text{C/mol e}^-) = 1.78 \times 10^3\ \text{C / mole}$$

The current in amperes needed to deliver this amount of charge in 12.0 h is therefore

$$\text{amperes} = \frac{1.78 \times 10^3 \text{ C}}{(12.0 \text{ h})(60 \text{ min/h})(60 \text{ s/min})} \tag{19.10.2}$$

$$= 4.12 \times 10^{-2} \text{ C/s} = 4.12 \times 10^{-2} \text{ A} \tag{19.10.3}$$

Because the electroplating process is usually much less than 100% efficient (typical values are closer to 30%), the actual current necessary is greater than 0.1 A.

Exercise 19.10.2

A typical aluminum soft-drink can weighs about 29 g. How much time is needed to produce this amount of Al(s) in the Hall–Heroult process, using a current of 15 A to reduce a molten Al_2O_3/Na_3AlF_6 mixture?

Answer

5.8 h

This page titled 19.10: Counting Electrons is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Robert Belford.

CHAPTER OVERVIEW

20: Coordination Chemistry

Complexes or **coordination compounds** are molecules that posess a metal center that is bound to ligands (atoms, ions, or molecules that donate electrons to the metal). These complexes can be neutral or charged. When the complex is charged, it is stabilized by neighboring counter-ions.

20.1: Werner’s Theory of Coordination Compounds
20.2: Ligands
20.3: Nomenclature
20.4: Isomerism
20.5: Optical Isomerism in Metal Complexes
20.6: Stability Aspects of Complex-Ion Equilibria
20.7: Chelation
20.8: Bonding in Octahedral Complex Ions- Crystal Field Theory
20.9: Bonding in Non-Octahedral Complex Ions- Crystal Field Theory
20.10: Magnetic Behavior of Atoms, Molecules, and Materials
20.11: Magnetic Behavior of Complex Ions
20.12: Optical Properties of Coordination Compounds (Color)

20: Coordination Chemistry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

20.1: Werner's Theory of Coordination Compounds

Learning Objectives

- To know the most common structures observed for metal complexes.
- To predict the relative stabilities of metal complexes with different ligands

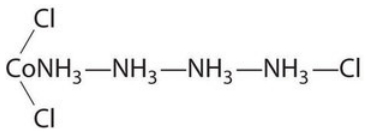
One of the most important properties of metallic elements is their ability to act as Lewis acids that form complexes with a variety of Lewis bases. A metal complex consists of a central metal atom or ion that is bonded to one or more ligands (from the Latin ligare, meaning "to bind"), which are ions or molecules that contain one or more pairs of electrons that can be shared with the metal. Metal complexes can be neutral, such as $Co(NH_3)_3Cl_3$; positively charged, such as $[Nd(H_2O)_9]^{3+}$; or negatively charged, such as $[UF_8]^{4-}$. Electrically charged metal complexes are sometimes called *complex ions*. A *coordination compound* contains one or more metal complexes.

Coordination compounds are important for at least three reasons. First, most of the elements in the periodic table are metals, and almost all metals form complexes, so metal complexes are a feature of the chemistry of more than half the elements. Second, many industrial catalysts are metal complexes, and such catalysts are steadily becoming more important as a way to control reactivity. For example, a mixture of a titanium complex and an organometallic compound of aluminum is the catalyst used to produce most of the polyethylene and polypropylene "plastic" items we use every day. Finally, transition-metal complexes are essential in biochemistry. Examples include hemoglobin, an iron complex that transports oxygen in our blood; cytochromes, iron complexes that transfer electrons in our cells; and complexes of Fe, Zn, Cu, and Mo that are crucial components of certain enzymes, the catalysts for all biological reactions.

History of the Coordination Compounds

Coordination compounds have been known and used since antiquity; probably the oldest is the deep blue pigment called Prussian blue: $KFe_2(CN)_6$. The chemical nature of these substances, however, was unclear for a number of reasons. For example, many compounds called "double salts" were known, such as $AlF_3 \cdot 3\,KF$, $Fe(CN)_2 \cdot 4\,KCN$, and $ZnCl_2 \cdot 2\,CsCl$, which were combinations of simple salts in fixed and apparently arbitrary ratios. Why should $AlF_3 \cdot 3\,KF$ exist but not $AlF_3 \cdot 4\,KF$ or $AlF_3 \cdot 2\,KF$? And why should a 3:1 KF:AlF3 mixture have different chemical and physical properties than either of its components? Similarly, adducts of metal salts with neutral molecules such as ammonia were also known—for example, $CoCl_3 \cdot 6\,NH_3$, which was first prepared sometime before 1798. Like the double salts, the compositions of these adducts exhibited fixed and apparently arbitrary ratios of the components. For example, $CoCl_3 \cdot 6\,NH_3$, $CoCl_3 \cdot 5\,NH_3$, $CoCl_3 \cdot 4\,NH_3$, and $CoCl_3 \cdot 3\,NH_3$ were all known and had very different properties, but despite all attempts, chemists could not prepare $CoCl_3 \cdot 2\,NH_3$ or $CoCl_3 \cdot NH_3$.

Although the chemical composition of such compounds was readily established by existing analytical methods, their chemical nature was puzzling and highly controversial. The major problem was that what we now call valence (i.e., the oxidation state) and coordination number were thought to be identical. As a result, highly implausible (to modern eyes at least) structures were proposed for such compounds, including the "Chattanooga choo-choo" model for $CoCl_3{\cdot}4NH_3$ shown here.



$CoCl_3 \cdot 4NH_3$

The modern theory of coordination chemistry is based largely on the work of Alfred Werner (1866–1919; Nobel Prize in Chemistry in 1913). In a series of careful experiments carried out in the late 1880s and early 1890s, he examined the properties of several series of metal halide complexes with ammonia. For example, five different "adducts" of ammonia with $PtCl_4$ were known at the time: $PtCl_4{\cdot}nNH_3$ (n = 2–6). Some of Werner's original data on these compounds are shown in Table 20.1.1. The electrical conductivity of aqueous solutions of these compounds was roughly proportional to the number of ions formed per mole, while the number of chloride ions that could be precipitated as AgCl after adding $Ag^+(aq)$ was a measure of the number of "free" chloride ions present. For example, Werner's data on $PtCl_4{\cdot}6NH_3$ in Table 20.1.1 showed that all the chloride ions were present as free chloride. In contrast, $PtCl_4{\cdot}2NH_3$ was a neutral molecule that contained no free chloride ions.

Alfred Werner (1866–1919)

Werner, the son of a factory worker, was born in Alsace. He developed an interest in chemistry at an early age, and he did his first independent research experiments at age 18. While doing his military service in southern Germany, he attended a series of chemistry lectures, and he subsequently received his PhD at the University of Zurich in Switzerland, where he was appointed professor of chemistry at age 29. He won the Nobel Prize in Chemistry in 1913 for his work on coordination compounds, which he performed as a graduate student and first presented at age 26. Apparently, Werner was so obsessed with solving the riddle of the structure of coordination compounds that his brain continued to work on the problem even while he was asleep. In 1891, when he was only 25, he woke up in the middle of the night and, in only a few hours, had laid the foundation for modern coordination chemistry.

Table 20.1.1: Werner's Data on Complexes of Ammonia with $PtCl_4$

Complex	Conductivity (ohm^{-1})	Number of Ions per Formula Unit	Number of Cl^- Ions Precipitated by Ag^+
$PtCl_4 \cdot 6NH_3$	523	5	4
$PtCl_4 \cdot 5NH_3$	404	4	3
$PtCl_4 \cdot 4NH_3$	299	3	2
$PtCl_4 \cdot 3NH_3$	97	2	1
$PtCl_4 \cdot 2NH_3$	0	0	0

These data led Werner to postulate that metal ions have two different kinds of valence: (1) a primary valence (**oxidation state**) that corresponds to the positive charge on the metal ion and (2) a secondary valence (**coordination number**) that is the total number of ligand-metal bonds bound to the metal ion. If Pt had a primary valence of 4 and a secondary valence of 6, Werner could explain the properties of the $PtCl_4 \cdot NH_3$ adducts by the following reactions, where the metal complex is enclosed in square brackets:

$$[Pt(NH_3)_6]Cl_4 \rightarrow [Pt(NH_3)_6]^{4+}(aq) + 4Cl^-(aq)$$
$$[Pt(NH_3)_5Cl]Cl_3 \rightarrow [Pt(NH_3)_5Cl]^{3+}(aq) + 3Cl^-(aq)$$
$$[Pt(NH_3)_4Cl_2]Cl_2 \rightarrow [Pt(NH_3)_4Cl_2]^{2+}(aq) + 2Cl^-(aq)$$
$$[Pt(NH_3)_3Cl_3]Cl \rightarrow [Pt(NH_3)_3Cl_3]^{+}(aq) + Cl^-(aq)$$
$$[Pt(NH_3)_2Cl_4] \rightarrow [Pt(NH_3)_2Cl_4]^{0}(aq)$$

Further work showed that the two missing members of the series—$[Pt(NH_3)Cl_5]^-$ and $[PtCl_6]^{2-}$—could be prepared as their mono- and dipotassium salts, respectively. Similar studies established coordination numbers of 6 for Co^{3+} and Cr^{3+} and 4 for Pt^{2+} and Pd^{2+}.

Werner's studies on the analogous Co^{3+} complexes also allowed him to propose a structural model for metal complexes with a coordination number of 6. Thus he found that $[Co(NH_3)_6]Cl_3$ (yellow) and $[Co(NH_3)_5Cl]Cl_2$ (purple) were 1:3 and 1:2 electrolytes. Unexpectedly, however, two different $[Co(NH_3)_4Cl_2]Cl$ compounds were known: one was red, and the other was green (Figure 20.1.1*a*). Because both compounds had the same chemical composition and the same number of groups of the same kind attached to the same metal, there had to be something different about the arrangement of the ligands around the metal ion. Werner's key insight was that the six ligands in $[Co(NH_3)_4Cl_2]Cl$ had to be arranged at the vertices of an octahedron because that was the only structure consistent with the existence of two, and only two, arrangements of ligands (Figure 20.1.1*b* His conclusion was corroborated by the existence of only two different forms of the next compound in the series: $Co(NH_3)_3Cl_3$.

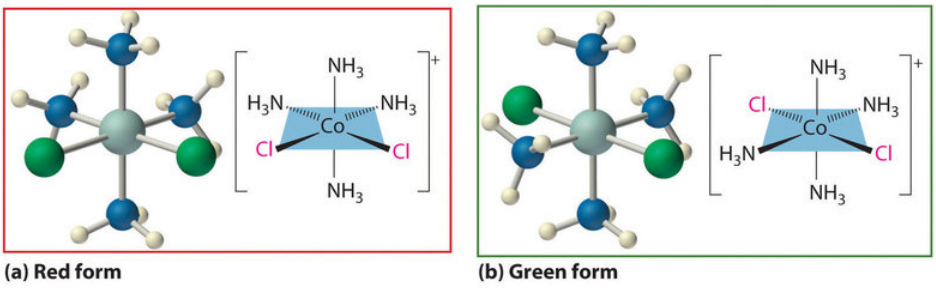


Figure 20.1.1: Complexes with Different Arrangements of the Same Ligands Have Different Properties. The $[Co(NH_3)_4Cl_2]^+$ ion can have two different arrangements of the ligands, which results in different colors: if the two Cl^- ligands are next to each other, the complex is red (a), but if they are opposite each other, the complex is green (b).

Example 20.1.1

In Werner's time, many complexes of the general formula MA_4B_2 were known, but no more than two different compounds with the same composition had been prepared for any metal. To confirm Werner's reasoning, calculate the maximum number of different structures that are possible for six-coordinate MA_4B_2 complexes with each of the three most symmetrical possible structures: a hexagon, a trigonal prism, and an octahedron. What does the fact that no more than two forms of any MA_4B_2 complex were known tell you about the three-dimensional structures of these complexes?

Given: three possible structures and the number of different forms known for MA_4B_2 complexes

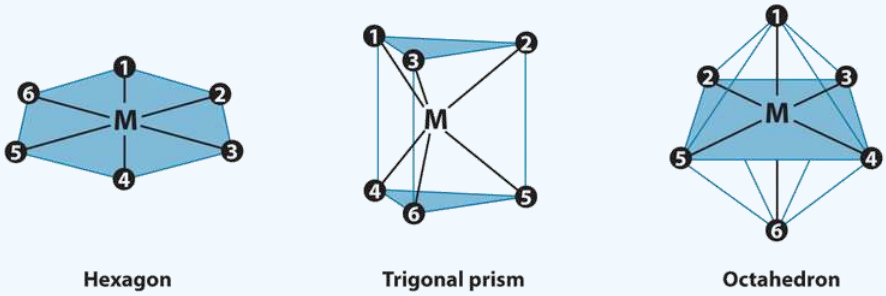
Asked for: number of different arrangements of ligands for MA_4B_2 complex for each structure

Strategy:

Sketch each structure, place a B ligand at one vertex, and see how many different positions are available for the second B ligand.

Solution

The three regular six-coordinate structures are shown here, with each coordination position numbered so that we can keep track of the different arrangements of ligands. For each structure, all vertices are equivalent. We begin with a symmetrical MA_6 complex and simply replace two of the A ligands in each structure to give an MA_4B_2 complex:



For the hexagon, we place the first B ligand at position 1. There are now three possible places for the second B ligand: at position 2 (or 6), position 3 (or 5), or position 4. These are the only possible arrangements. The (1, 2) and (1, 6) arrangements are chemically identical because the two B ligands are adjacent to each other. The (1, 3) and (1, 5) arrangements are also identical because in both cases the two B ligands are separated by an A ligand.

Turning to the trigonal prism, we place the first B ligand at position 1. Again, there are three possible choices for the second B ligand: at position 2 or 3 on the same triangular face, position 4 (on the other triangular face but adjacent to 1), or position 5 or 6 (on the other triangular face but not adjacent to 1). The (1, 2) and (1, 3) arrangements are chemically identical, as are the (1, 5) and (1, 6) arrangements.

In the octahedron, however, if we place the first B ligand at position 1, then we have only two choices for the second B ligand: at position 2 (or 3 or 4 or 5) or position 6. In the latter, the two B ligands are at opposite vertices of the octahedron, with the metal lying directly between them. Although there are four possible arrangements for the former, they are chemically identical because in all cases the two B ligands are adjacent to each other.

The number of possible MA_4B_2 arrangements for the three geometries is thus: hexagon, 3; trigonal prism, 3; and octahedron, 2. The fact that only two different forms were known for all MA_4B_2 complexes that had been prepared suggested that the correct structure was the octahedron but did not prove it. For some reason one of the three arrangements possible for the other two structures could have been less stable or harder to prepare and had simply not yet been synthesized. When combined with analogous results for other types of complexes (e.g., MA_3B_3), however, the data were best explained by an octahedral structure for six-coordinate metal complexes.

? Exercise 20.1.1

Determine the maximum number of structures that are possible for a four-coordinate MA_2B_2 complex with either a square planar or a tetrahedral symmetrical structure.

Answer

square planar, 2; tetrahedral, 1

Structures of Metal Complexes

The coordination numbers of metal ions in metal complexes can range from 2 to at least 9. In general, the differences in energy between different arrangements of ligands are greatest for complexes with low coordination numbers and decrease as the coordination number increases. Usually only one or two structures are possible for complexes with low coordination numbers, whereas several different energetically equivalent structures are possible for complexes with high coordination numbers ($n > 6$). The following presents the most commonly encountered structures for coordination numbers 2–9. Many of these structures should be familiar to you from our discussion of the valence-shell electron-pair repulsion (VSEPR) model because they correspond to the lowest-energy arrangements of n electron pairs around a central atom.

> *Compounds with low coordination numbers exhibit the greatest differences in energy between different arrangements of ligands.*

Coordination Number 2

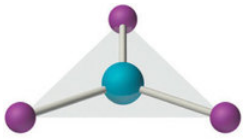
Although it is rare for most metals, this coordination number is surprisingly common for d^{10} metal ions, especially Cu^+, Ag^+, Au^+, and Hg^{2+}. An example is the $[Au(CN)_2]^-$ ion, which is used to extract gold from its ores. As expected based on VSEPR considerations, these complexes have the linear L–M–L structure shown here.



Linear ML_2

Coordination Number 3

Although it is also rare, this coordination number is encountered with d^{10} metal ions such as Cu^+ and Hg^{2+}. Among the few known examples is the HgI_3^- ion. Three-coordinate complexes almost always have the trigonal planar structure expected from the VSEPR model.

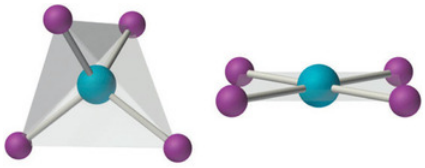


Trigonal planar ML_3

Coordination Number 4

Two common structures are observed for four-coordinate metal complexes: tetrahedral and square planar. The tetrahedral structure is observed for all four-coordinate complexes of nontransition metals, such as $[BeF_4]^{2-}$, and d^{10} ions, such as $[ZnCl_4]^{2-}$. It is also found for four-coordinate complexes of the first-row transition metals, especially those with halide ligands (e.g., $[FeCl_4]^-$ and $[FeCl_4]^{2-}$). In contrast, square planar structures are routinely observed for four-coordinate complexes of second- and third-row

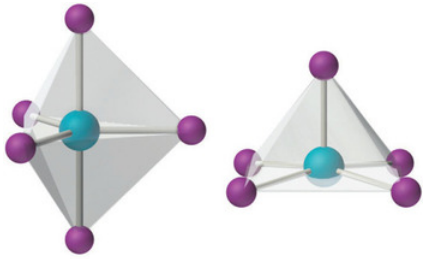
transition metals with d^8 electron configurations, such as Rh^+ and Pd^{2+}, and they are also encountered in some complexes of Ni^{2+} and Cu^{2+}.



Tetrahedral and square planar ML_4

Coordination Number 5

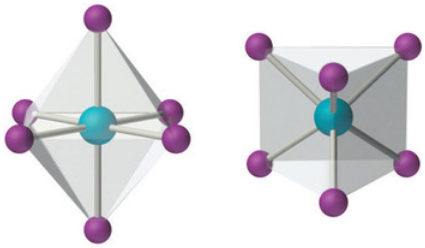
This coordination number is less common than 4 and 6, but it is still found frequently in two different structures: trigonal bipyramidal and square pyramidal. Because the energies of these structures are usually rather similar for most ligands, many five-coordinate complexes have distorted structures that lie somewhere between the two extremes.



Trigonal bipyramidal and square pyramidal ML_5

Coordination Number 6

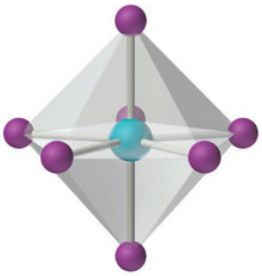
This coordination number is by far the most common. The six ligands are almost always at the vertices of an octahedron or a distorted octahedron. The only other six-coordinate structure is the trigonal prism, which is very uncommon in simple metal complexes.



Octahedral and trigonal prismatic ML_6

Coordination Number 7

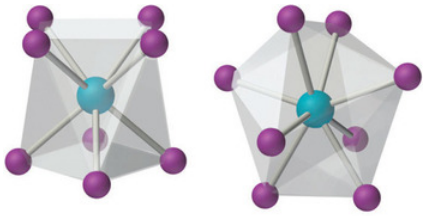
This relatively uncommon coordination number is generally encountered for only large metals (such as the second- and third-row transition metals, lanthanides, and actinides). At least three different structures are known, two of which are derived from an octahedron or a trigonal prism by adding a ligand to one face of the polyhedron to give a “capped” octahedron or trigonal prism. By far the most common, however, is the pentagonal bipyramid.



Pentagonal bipyramidal ML_7

Coordination Number 8

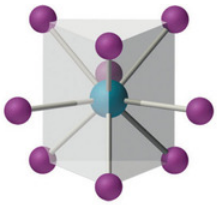
This coordination number is relatively common for larger metal ions. The simplest structure is the cube, which is rare because it does not minimize interligand repulsive interactions. Common structures are the square antiprism and the dodecahedron, both of which can be generated from the cube.



Square antiprismatic and trigonal dodecahedral ML_8

Coordination Number 9

This coordination number is found in larger metal ions, and the most common structure is the tricapped trigonal prism, as in $[Nd(H_2O)_9]^{3+}$.



Tricapped trigonal prismatic ML_9

Key Takeaways

- Coordination compounds are a major feature of the chemistry of over half the elements.
- Coordination compounds have important roles as industrial catalysts in controlling reactivity, and they are essential in biochemical processes.

Summary

Transition metals form metal complexes, polyatomic species in which a metal ion is bound to one or more ligands, which are groups bound to a metal ion. Complex ions are electrically charged metal complexes, and a coordination compound contains one or more metal complexes. Metal complexes with low coordination numbers generally have only one or two possible structures, whereas those with coordination numbers greater than six can have several different structures. Coordination numbers of two and three are common for d^{10} metal ions. Tetrahedral and square planar complexes have a coordination number of four; trigonal bipyramidal and square pyramidal complexes have a coordination number of five; and octahedral complexes have a coordination number of six. At least three structures are known for a coordination number of seven, which is generally found for only large metal ions. Coordination numbers of eight and nine are also found for larger metal ions.

20.1: Werner’s Theory of Coordination Compounds is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **24.1: Werner’s Theory of Coordination Compounds** by Anonymous is licensed CC BY-NC-SA 4.0.

20.2: Ligands

A metal ion in solution does not exist in isolation, but in combination with ligands (such as solvent molecules or simple ions) or chelating groups, giving rise to complex ions or coordination compounds. These complexes contain a central atom or ion, often a transition metal, and a cluster of ions or neutral molecules surrounding it. Ligands are ions or neutral molecules that bond to a central metal atom or ion. Ligands act as Lewis bases (electron pair donors), and the central atom acts as a Lewis acid (electron pair acceptor). Ligands have at least one donor atom with an electron pair used to form covalent bonds with the central atom.

The term ligand come from the latin word *ligare* (which meaning to bind) was first used by Alfred Stock in 1916 in relation to silicon chemistry. Ligands can be anions, cations, or neutral molecules. Ligands can be further characterized as monodentate, bidentate, tridentate etc. where the concept of teeth **(dent)** is introduced, hence the idea of bite angle etc. A monodentate ligand has only one donor atom used to bond to the central metal atom or ion.

Monodentate Ligands

The term "monodentate" can be translated as "one tooth," referring to the ligand binding to the center through only one atom. Some examples of monodentate ligands are: chloride ions (referred to as chloro when it is a ligand), water (referred to as aqua when it is a ligand), hydroxide ions (referred to as hydroxo when it is a ligand), and ammonia (referred to as ammine when it is a ligand).

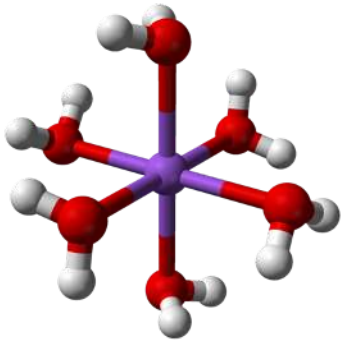


Figure 20.2.1: Central atom with six monodentate ligands attached. (Image courtesy of Wikimedia Commons.)

Bidentate Ligands

Bidentate ligands have two donor atoms which allow them to bind to a central metal atom or ion at two points. Common examples of bidentate ligands are ethylenediamine (en), and the oxalate ion (ox). Shown below is a diagram of ethylenediamine: the nitrogen (blue) atoms on the edges each have two free electrons that can be used to bond to a central metal atom or ion.

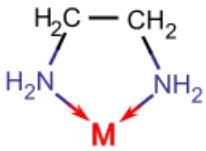


Figure 20.2.2: Ethylenediamine (en) is an example of a bidentate ligand. (Image courtesy of Wikimedia Commons.). Ethylenediamine (en) is a bidentate ligand that forms a five-membered ring in coordinating to a metal ion M

Polydentate Ligands

Polydentate ligands range in the number of atoms used to bond to a central metal atom or ion. EDTA, a hexadentate ligand, is an example of a polydentate ligand that has six donor atoms with electron pairs that can be used to bond to a central metal atom or ion.

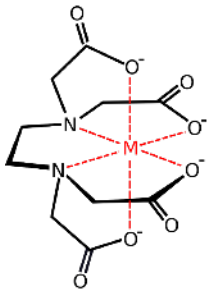
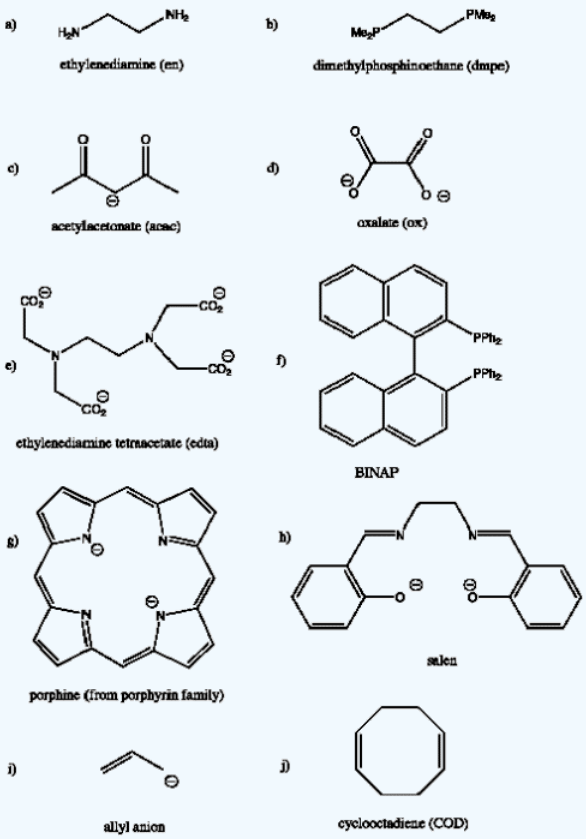


Figure 20.2.3: Ethylenediaminetetraaceticacid acid (EDTA) is a hexadentate ligand and can bind a Metal via multiple "teeth" (left) Unbound EDTA ion and (right) EDTA bound to a generic transition metal. (Images courtesy of Wikimedia Commons.)

Unlike polydentate ligands, ambidentate ligands can attach to the central atom in two places. A good example of this is thiocyanate, SCN^-, which can attach at either the sulfur atom or the nitrogen atom.

Example 20.2.1

Draw metal complexes using the ligands below and metal ions of your choice.



Chelation

Chelation is a process in which a polydentate ligand bonds to a metal ion, forming a ring. The complex produced by this process is called a chelate, and the polydentate ligand is referred to as a chelating agent. The term chelate was first applied in 1920 by Sir Gilbert T. Morgan and H.D.K. Drew, who stated: "The adjective chelate, derived from the great claw or chela (chely- Greek) of the lobster or other crustaceans, is suggested for the caliperlike groups which function as two associating units and fasten to the central atom so as to produce heterocyclic rings." As the name implies, chelating ligands have high affinity for metal ions relative to ligands with only one binding group (which are called monodentate = "single tooth") ligands. Both Ethylenediamine (Figure 20.2.2) and Ethylenediaminetetraaceticacid acid (Figure 20.2.3) are examples of chelating agents, but many others are commonly found in the inorganic laboratory.

The Chelate Effect

The chelate effect is the enhanced affinity of chelating ligands for a metal ion compared to the affinity of a collection of similar nonchelating (monodentate) ligands for the same metal.

The **macrocyclic effect** follows the same principle as the chelate effect, but the effect is further enhanced by the cyclic conformation of the ligand. Macrocyclic ligands are not only multi-dentate, but because they are covalently constrained to their cyclic form, they allow less conformational freedom. The ligand is said to be "pre-organized" for binding, and there is little entropy penalty for wrapping it around the metal ion. For example heme b is a tetradentate cyclic ligand that strongly complexes transition metal ions, including Fe^{+2} in hemogloben (Figure 20.2.4).

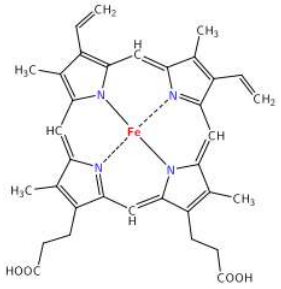
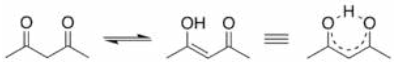


Figure 20.2.4: Heme b macrocyclic ligand that binds iron in hemoglobin

Some other common chelating and cyclic ligands are shown below:

- **Acetylacetonate** ($acac^-$, top) is an anionic bidentate ligand that coordinates metal ions through two oxygen atoms. $Acac^-$ is a hard base so it prefers hard acid cations. With divalent metal ions, $acac^-$forms neutral, volatile complexes such as $Cu(acac)_2$ and $Mo(acac)_2$ that are useful for chemical vapor deposition (CVD) of metal thin films.



- **2,2'-Bipyridine 2,2'-Bipyridine** (Figure 20.2.5: left) and related bidentate ligands such as 1,10-phenanthroline form propeller-shaped complexes with metals such as Ru^{2+}. The $[Ru(bpy)_3]^{2+}$ complex is photoluminescent and can also undergo photoredox reactions, making it an interesting compound for both photocatalysis and artificial photosynthesis.
- **Crown ethers** such as 18-crown-6 **2,2'-Bipyridine** (Figure 20.2.5: center) are cyclic hard bases that can complex alkali metal cations. Crowns can selectively bind Li^+, Na^+, or K^+ depending on the number of ethylene oxide units in the ring.
- The chelating properties of crown ethers are mimetic of the natural antibiotic **valinomycin** (**2,2'-Bipyridine** (Figure 20.2.5: right), which selectively transports K^+ ions across bacterial cell membranes, killing the bacterium by dissipating its membrane potential. Like crown ethers, valinomycin is a cyclic hard base.

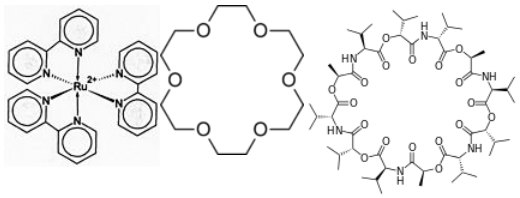


Figure 20.2.5: (let) 2,2'-Bipyridine, (center) 18-crown-6 2,2'-Bipyridine (right) valinomycin

References

1. Petrucci, Harwood, Herring, Madura. General Chemistry Principles & Modern Applications. Prentice Hall. New Jersey, 2007
2. Cox, Tony. (2004). Instant notes in inorganic chemistry. Oxford, UK: Taylor & Francis.
3. Libraries, Association, Robert Williams, and J. Silva. Bringing chemistry to life. Oxford University Press, USA, 1999. Print.
4. Moeller, Therald, Douville, Judith, & Libraries, Association. (1988). Inorganic Chemistry: A Modern Introduction. Amer Library Assn.
5. Bowker, R., Warmus, Mieczysław, Muzzy, Adrienne, LOCALIZADO, AUTOR, Hopkinson, Barbara, Saur, K, Izod, Irene, Hopkinson, Barbara, Saur, K, Books, K, & Company, K. (1994). Inorganic Chemistry Concepts. K G Saur Verlag Gmbh & Co.
6. Porterfield, William. (1984). Inorganic chemistry. Addison Wesley Publishing Company.

Contributors and Attributions

- Harjeet Bassi (UCD)
- Adapted from the Wikibook constructed by Chemistry 310 students at Penn State University.

20.2: Ligands is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **24.2: Ligands** is licensed CC BY-SA 4.0.

20.3: Nomenclature

Learning Objectives

- To learn the basis for complex ion and compound nomenclature

Coordination complexes have their own classes of isomers, different magnetic properties and colors, and various applications (photography, cancer treatment, etc), so it makes sense that they would have a naming system as well. Consisting of a metal and ligands, their formulas follow the pattern [Metal ligands]$^{\pm Charge}$, while names are written Prefix Ligands Metal (Oxidation State).

Introduction

According to the Lewis Acid-Base theory, ligands are Lewis bases since they can donate electrons to the central metal atom. The metals, in turn, are Lewis acids since they accept electrons. **Coordination complexes** consist of a ligand and a metal center cation and their charge can be positive, negative, or neutral. **Coordination compounds** are neutral compounds that contain at least one complex ions. Example of coordination complexes and compounds are:

- Complex Cation: $[Co(NH_3)_6]^{3+}$
- Complex Anion: $[CoCl_4(NH_3)_2]^-$
- Neutral Complex: $[CoCl_3(NH_3)_3]$
- Coordination Compound: $K_4[Fe(CN)_6]$

A ligand can be an anion or a neutral molecule that *donates an electron pair* to the complex (NH_3, H_2O, Cl^-). The number of ligands that attach to a metal depends on whether the ligand is **monodentate** or **polydentate**.

Rules to Complex Ion Nomenclature

To begin naming coordination complexes, here are some things to keep in mind.

1. Ligands are named first in alphabetical order.
2. The name of the metal comes next.
3. The oxidation state of the metal follows, noted by a Roman numeral in parentheses (II, IV).

Rule 1: Anionic Ligands

Ligands that act as anions which end in "-ide" are replaced with an ending "-o" (e.g., Chloride → Chloro). Anions ending with "-ite" and "-ate" are replaced with endings "-ito" and "-ato" respectively (e.g., Nitrite → Nitrito, Nitrate → Nitrato).

Table 20.3.1: Anionic Monodentate Ligands

Molecular Formula	Ligand Name	Molecular Formula	Ligand Name
F^-	Fluoro	OH^-	Hydroxo
Cl^-	Chloro	SO_4^{2-}	Sulfato
Br^-	Bromo	$S_2O_3^{2-}$	Thiosulfato
I^-	Iodo	NO_2^-	Nitrito-N-; Nitro
O^{2-}	Oxo	ONO^-	Nitrito-O-; Nitrito
CN^-	Cyano	SCN^-	Thiocyanato-S-; Thiocyanato
NC^-	Isocyano	NCS^-	Thiocyanato-N-; Isothiocyanato

Rule 2: Neutral Ligands

Most neutral molecules that are ligands carry their normal name. The few exceptions are the first four on the chart: ammine, aqua, carbonyl, and nitrosyl.

Table 20.3.2: Select Neutral Monodentate Ligands. Note: Ammine is spelled with two m's when referring to a ligand. Amines are a class of organic nitrogen-containing compounds.

Molecular Formula of Ligand	Ligand Name
NH_3	Ammine
H_2O	Aqua
CO	Carbonyl
NO	Nitrosyl
CH_3NH_2	Methylamine
C_5H_5N	Pyridine

Polydentate ligands follow the same rules for anions and neutral molecules.

Table 20.3.3: Select Polydentate ligands

Short name	Extended name
en	Ethylenediamine
ox^{2-}	Oxalato
$EDTA^{4-}$	Ethylenediaminetetraacetato

Rule 3: Ligand Multiplicity

The number of ligands present in the complex is indicated with the prefixes di, tri, etc. The exceptions are polydentates that have a prefix already in their name (en and $EDTA^{4-}$ are the most common). When indicating how many of these are present in a coordination complex, put the ligand's name in parentheses and use *bis* (for two ligands), *tris* (for three ligands), and *tetrakis* (for four ligands).

Table 20.3.4: Prefixes for indicating number of ligands in a complex.

Number of Ligands	Monodentate Ligands	Polydentate Ligands
1	mono	-
2	di	bis
3	tri	tris
4	tetra	tetrakis
5	penta	pentakis
6	hexa	hexakis

Prefixes always go before the ligand name; they are not taken into account when putting ligands in alphabetical order. Note that "mono" often is not used. For example, $[FeCl(CO)_2(NH_3)_3]^{2+}$ would be called triamminedicarbonylchloroiron(III) ion. Remember that ligands are always named first, before the metal is.

Example 20.3.1

What is the name of this complex ion: $[CrCl_2(H_2O)_4]^+$?

Solution

Let's start by identifying the ligands. The ligands here are Cl and H_2O. Therefore, we will use the monodentate ligand names of "chloro" and "aqua". Alphabetically, aqua comes before chloro, so this will be their order in the complex's name. There are 4 aqua's and 2 chloro's, so we will add the number prefixes before the names. Since both are monodentate ligands, we will say "tetra[aqua]di[chloro]".

Now that the ligands are named, we will name the metal itself. The metal is Cr, which is chromium. Therefore, this coordination complex is called tetraaquadichlorochromium(III) ion. See the next section for an explanation of the (III).

? Exercise 20.3.1

What is the name of this complex ion: $[CoCl_2(en)_2]^+$?

Answer

We take the same approach. There are two chloro and ethylenediamine ligands. The metal is Co, cobalt. We follow the same steps, except that *en* is a polydentate ligand with a prefix in its name (ethylene**di**amine), so "bis" is used instead of "di", and parentheses are added. Therefore, this coordination complex is called dichlorobis(ethylenediamine)cobalt(III) ion.

Rule 4: The Metals

When naming the metal center, you must know the formal metal name and the oxidation state. To show the oxidation state, we use Roman numerals inside parenthesis. For example, in the problems above, chromium and cobalt have the oxidation state of +3, so that is why they have (III) after them. Copper, with an oxidation state of +2, is denoted as copper(II). If the overall coordination complex is an anion, the ending "-ate" is attached to the metal center. Some metals also change to their Latin names in this situation. Copper +2 will change into cuprate(II). The following change to their Latin names when part of an anion complex:

Table 20.3.5: Latin terms for Select Metal Ion

Transition Metal	Latin
Iron	Ferrate
Copper	Cuprate
Tin	Stannate
Silver	Argentate
Lead	Plumbate
Gold	Aurate

The rest of the metals simply have -ate added to the end (cobaltate, nickelate, zincate, osmate, cadmate, platinate, mercurate, etc. Note that the -ate tends to replace -um or -ium, if present).

Finally, when a complex has an overall charge, "ion" is written after it. This is not necessary if it is neutral or part of a coordination compound (Example 20.3.3). Here are some examples with determining oxidation states, naming a metal in an anion complex, and naming coordination compounds.

✓ Example 20.3.2

What is the name of $[Cr(OH)_4]^-$?

Solution

Immediately we know that this complex is an anion. There is only one monodentate ligand, hydroxide. There are four of them, so we will use the name "tetrahydroxo". The metal is chromium, but since the complex is an anion, we will have to use the "-ate" ending, yielding "chromate". The oxidation state of the metal is 3 (x+(-1)4=-1). Write this with Roman numerals and parentheses (III) and place it after the metal to get tetrahydroxochromate(III) ion.

? Exercise 20.3.2

What is the name of $[CuCl_4]^{2-}$?

Answer

tetrachlorocuprate(II) ion

A last little side note: when naming a coordination compound, it is important that you name the cation first, then the anion. You base this on the charge of the ligand. Foe xample, for $NaCl$. The the positive Na cation comes first and the negative Cl^- anion follows.

Example 20.3.3

What is the name of $[Pt(NH_3)_4][Pt(Cl)_4]$?

Solution

NH_3 is neutral, making the first complex positively charged overall. Cl has a -1 charge, making the second complex the anion. Therefore, you will write the complex with NH_3 first, followed by the one with Cl (the same order as the formula). This coordination compound is called tetraammineplatinum(II) tetrachloroplatinate(II).

Exercise 20.3.3: The Nitro/Nitrito Ambidentate Ligand

What is the name of $[CoCl(NO_2)(NH_3)_4]^+$?

Answer

This coordination complex is called tetraamminechloronitrito-N-cobalt(III). N comes before the O in the symbol for the nitrite ligand, so it is called nitrito-N. If an O came first, as in $[CoCl(ONO)(NH_3)_4]^+$, the ligand would be called nitrito-O, yielding the name tetraamminechloronitrito-O-cobalt(III).

Nitro (for NO_2) and nitrito (for ONO) can also be used to describe the nitrite ligand, yielding the names tetraamminechloronitrocobalt(III) and tetraamminechloronitritocobalt(III).

Writing Formulas of Coordination Complexes

While chemistry typically follow the nomenclature rules for naming complexes and compounds, there is disagreement with the rules for constructing formulas of inorganic complexes. For example, the order of ligand names in their formula has been ambiguous with different conventions being used (charged vs neutral, number of each ligand, etc.). In 2005, IUPAC adopted the recommendation that all ligand names in formulas be listed **alphabetically** (in the same way as in the naming convention) irrespective of the charge or number of each ligand type.

However, this rule is not adhered to in many chemistry laboratories. For practice, the order of the ligands in chemical formulas does not matter as long as you write the transition metal first, which is the stance taken here.

Examples 20.3.4

Write the chemical formulas for:

a. Amminetetraaquachromium(II) ion
b. Amminesulfatochromium(II)

Solution

a. Amminetetraaquachromium(II) ion could be written as $[Cr(H_2O)_4(NH_3)]^{+2}$ or $[Cr(NH_3)(H_2O)_4]^{+2}$.
b. Amminesulfatochromium (II) could be written as $[Cr(SO_4)(NH_3)]$ or $[Cr(NH_3)(SO_4)]$.

Exercise 20.3.4

Write the chemical formulas for

a. Amminetetraaquachromium (II) sulfate
b. Potassium hexacyanoferrate (III)

Answer

a. Amminetetraaquachromium (II) sulfate can be written as $[Cr(H_2O)_4(NH_3)]SO_4$. Although $[Cr(NH_3)(H_2O)_4]SO_4$ is also acceptable.
b. Potassium hexacyanoferrate (III) is be written as $K_3[Fe(CN)_6]$

20.3: Nomenclature is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **23.3: Nomenclature of Coordination Chemistry** by Justin Hosung Lee, Sophia Muller is licensed CC BY-NC-SA 4.0.

20.4: Isomerism

Learning Objectives

- Explain the differences of Structural and Geometric isomerization in a coordination complexes or complex ions.
- Define Ionization, Linkage, and Coordination Isomerization (structural isomer classes)
- Define cis/tran and mer/fac isomerization (geometric isomer classes)

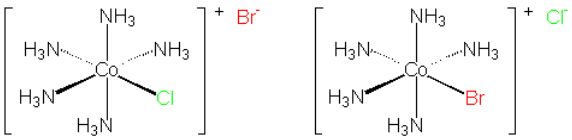
The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. 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. Isomers are compounds with the same molecular formula but different structural formulas and do not necessarily share similar properties. There are many different classes of isomers, like stereoisomers, enantiomers, and geometrical isomers. There are two main forms of isomerism: **structural isomerism** and **stereoisomerism** (spatial isomerism).

Class I: Structural Isomers

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*. Structural isomers, as their name implies, differ in their structure or bonding, which are separate from stereoisomers that differ in the spatial arrangement of the ligands are attached, but still have the bonding properties. The different chemical formulas in structural isomers are caused either by a difference in what ligands are bonded to the central atoms or how the individual ligands are bonded to the central atoms. When determining a structural isomer, you look at (1) the ligands that are bonded to the central metal and (2) which atom of the ligands attach to the central metal.

Ionization Isomerism

Ionization isomers occur when a ligand that is bound to the metal center exchanges places with an anion or neutral molecule that was originally outside the coordination complex. The geometry of the central metal ion and the identity of 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. A hydrate isomer is a specific kind of ionization isomer where a water molecule is one of the molecules that exchanges places.



[Co(NH$_3$)$_5$Cl]Br [Co(NH$_3$)$_5$Br]Cl

Figure 20.4.1: Ionization isomerism. The two isomers differ only in which ligands are bound to the center metal and which are counter ions in the second coordination sphere. (left) The chloride ion is bound to the cobalt as a chloro-ligand with the bromide ion as the counter ion. (right) In the other ionization isomer the bromide is acting as a bromo-ligand to the cobalt with the chloride acting as the counter ion. These two isomers are called pentaamminechlorocobalt(II) bromide (left) and pentaamminebromocobalt(II) chloride (right).

The difference between the ionization isomers can be view within the context of the ions generated when each are dissolved in solution. For example, when pentaamminebromocobalt(II) chloride is dissolved in water, Cl^- ions are generated:

$$CoBr(NH_3)_5Cl(s) \rightarrow CoBr(NH_3)_5^+(aq) + Cl^-(aq) \tag{20.4.1}$$

whereas when pentaamminechlorocobalt(II) bromide is dissolved, Br^- ions are generated:

$$CoCl(NH_3)_5Br(s) \rightarrow CoCl(NH_3)_5^+(aq) + Br^-(aq) \tag{20.4.2}$$

Notice that both anions are necessary to balance the charge of the complex, and that they differ in that one ion is directly attached to the central metal, but the other is not.

Solvate and Hydrate Isomerism: A special Type of Ionization 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 ($CrCl_3 \cdot 6\,H_2O$) 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. Alfred Werner's coordination theory 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 dots to signify "water molecules that are not bound to the central metal, but are part of the lattice:

- $[CrCl_2(H_2O)_4]Cl \cdot 2\,H_2O$: 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 waters of crystallization contribute to the total weight of water in a substance and are mostly present in a definite (stoichiometric) ratio.

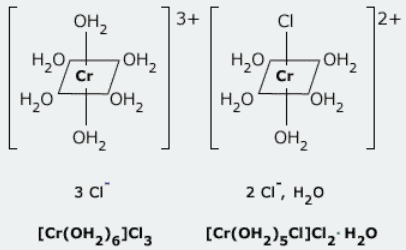


Figure 20.4.2: Hydrate iosomerisim. The $[Cr(H_2O)_6]Cl_3$ hydrate isomer (left) is violet colored and the $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ hydrate isomer is green-grey colored.

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 $NiCl_2 \cdot 6\,H_2O$ 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 (Figure 20.4.3).

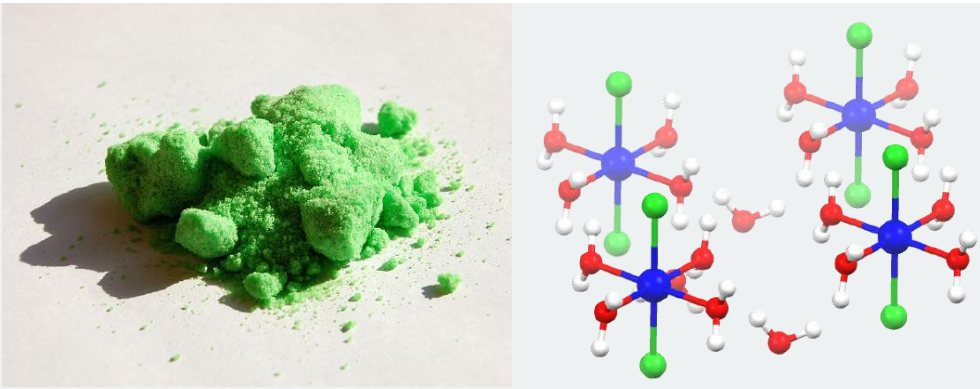


Figure 20.4.3: Water of hydration. (left) Image of $NiCl_2 \cdot 6\,H_2O$ salt (Public Domain; Benjah-bmm27 via Wikipedia). (right) Crystal Structure of $NiCl_2 \cdot 6\,H_2O$ with chlorine atoms (green), water molecules (red), and Ni metals (blue) indicated. Note that only four of the waters are bound as ligands to the nickel ions and two are outside of the coordination sphere. (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.

Coordination Isomerism

Coordination isomerism occurs in compounds containing complex anionic and complex cationic parts and can be viewed as an interchange of some ligands from the cation to the anion. Hence, there are two complex compounds bound together, one with a negative charge and the other with a positive charge. In coordination isomers, the anion and cation complexes of a coordination compound exchange one or more ligands. For example, the $[Zn(NH_3)_4][Cu(Cl_4)]$ and $[Cu(NH_3)_4][Zn(Cl_4)]$ compounds are coordination isomers (Figure 20.4.4).

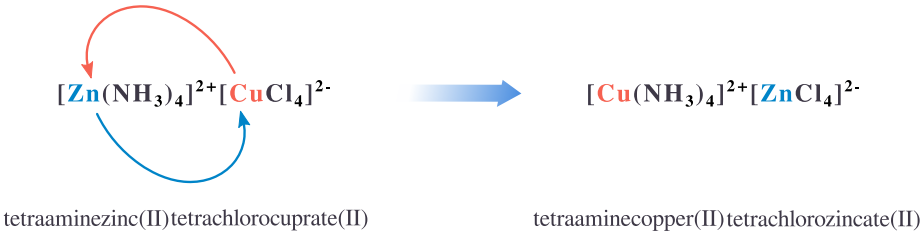


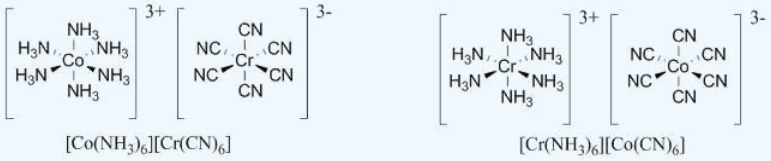
Figure 20.4.4: Coordination Isomerism. (CC BY-NC; Ümit Kaya)

Example 20.4.2: Coordination Isomers

What is the coordination isomer for the $[Co(NH_3)_6][Cr(CN)_6]$compound?

Solution

Coordination isomerism involves switching the metals between the cation and anion spheres.



Hence the $[Cr(NH_3)_6][Co(CN)_6]$compound is a coordination isomer of $[Co(NH_3)_6][Cr(CN)_6]$.

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 that 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 ligand** rather than an **ambidentate ligand**.

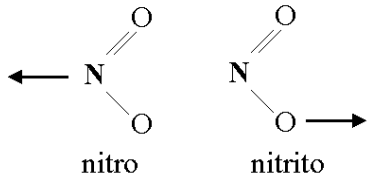


Figure 20.4.5: Linkage Isomerism in the NO_2 ligand. This occurs when a particular ligand is capable of coordinating to a metal in two different and distinct ways. from Angel C. de Dios.

As with all structural isomers, the formula of the complex is unchanged for each isomer, but the properties may differ. 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 20.4.3: Linkage Isomerization

The cationic cobalt complex $[Co(NH_3)_5(NO_2)]Cl_2$ exists in two separable linkage isomers of the complex ion: $(NH_3)_5(NO_2)]^{2+}$.

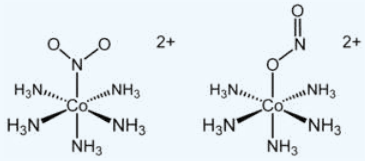


Figure 20.4.6: Linkage Isomerization. (left) The nitro isomer (Co-NO2) and (right) the nitrito isomer (Co-ONO)

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.

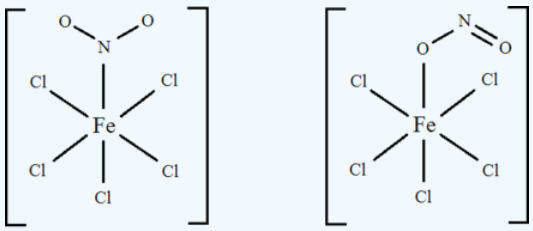
Another example of an ambidentate ligand is thiocyanate, SCN^-, which can attach to the transition metal at either the sulfur atom or the nitrogen atom. Such compounds give rise to linkage isomerism. Other ligands that give rise to linkage isomers include selenocyanate, $SeCN^-$ – isoselenocyanate, $NCSe^-$ and sulfite, SO_3^{2-}.

Exercise 20.4.3

Are $[FeCl_5(NO_2)]^{3-}$ and $[FeCl_5(ONO)]^{3-}$ complex ions linkage isomers of each other?

Answer

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:



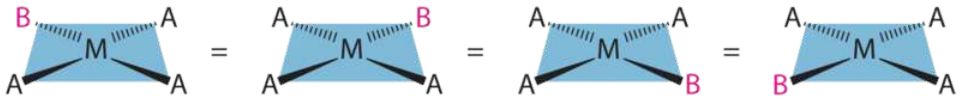
Class 2: Geometric Isomers

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

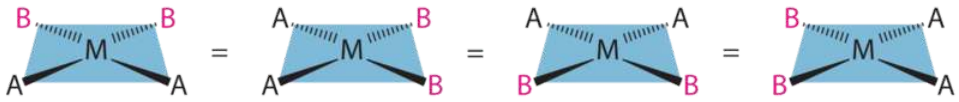
Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called geometrical isomers. They are most important for square planar and octahedral complexes.

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:

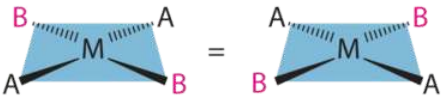


MA_3B square planar complex

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:

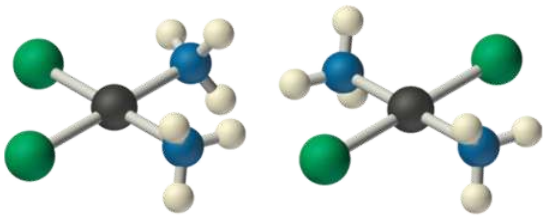


MA_2B_2 square planar complex, *cis* isomer



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.

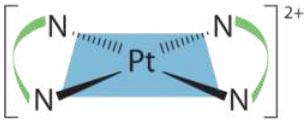


cis-$Pt(NH_3)_2Cl_2$ *trans*-$Pt(NH_3)_2Cl_2$

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:



$[Pt(en)_2]^{2+}$

? Exercise 20.4.4

Draw the cis and trans isomers of the following compounds:

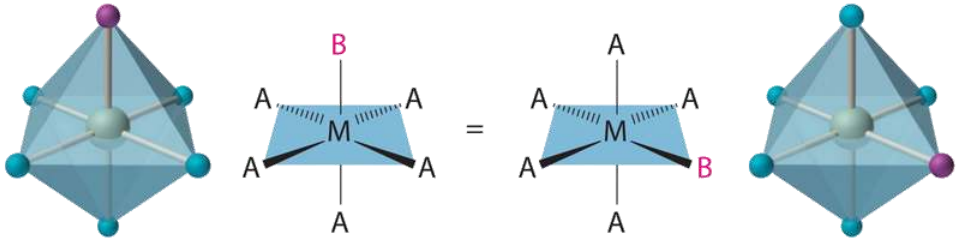
a. $(NH_3)_2IrCl(CO)$
b. $(H_3P)_2PtHBr$
c. $(AsH_3)_2PtH(CO)$

? Exercise 20.4.5

Only one isomer of $(tmeda)PtCl_2$ is possible [tmeda = $(CH_3)_2NCH_2CH_2N(CH_3)_2$; both nitrogens connect to the platinum]. Draw this isomer and explain why the other isomer is not possible.

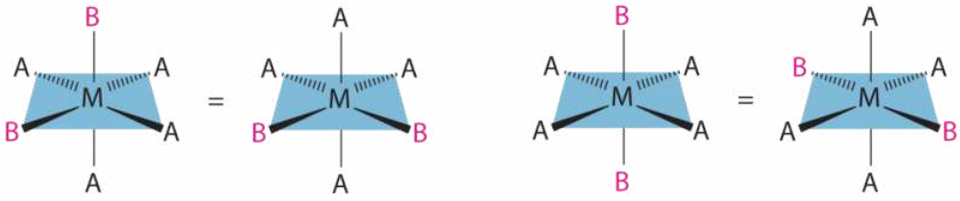
Octahedral Isomers

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

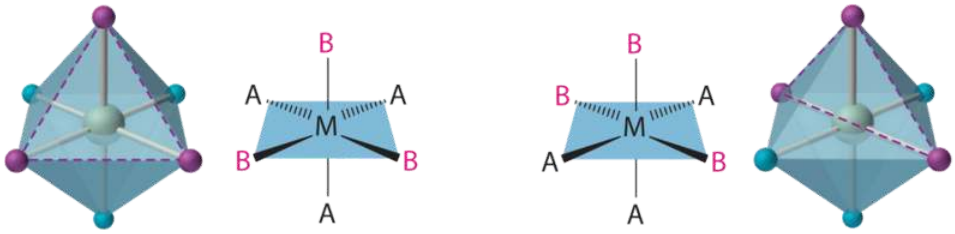
If two ligands in an octahedral complex are different from the other four, giving an MA_4B_2 complex, two isomers are possible. The two B ligands can be cis or trans. Cis- and trans-$[Co(NH_3)_4Cl_2]Cl$ are examples of this type of system:



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 20.4.4

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.

Solution

Given: formula of complex

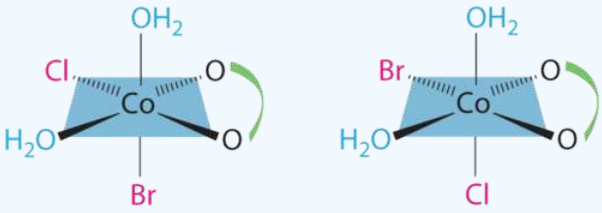
Asked for: structures of geometrical isomers

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***

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:



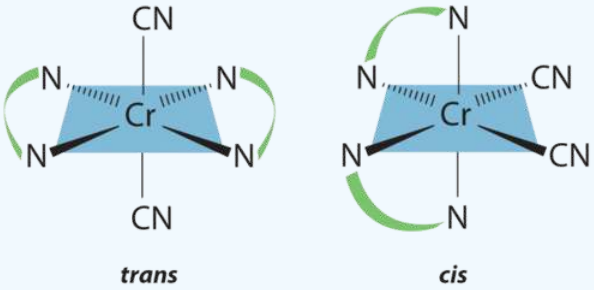
H_2O's *cis*; Br, Cl *cis*; Cl *trans* to O **H_2O's *cis*; Br, Cl *cis*; Br *trans* to O**

This complex can therefore exist as four different geometrical isomers.

Exercise 20.4.6

Draw all the possible geometrical isomers for the complex $[Cr(en)_2(CN)_2]^+$.

Answer



Two geometrical isomers are possible: *trans* and *cis*.

Summary

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**. 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.

Table 20.4.1 emphasizes the key differences of the three classes of structural isomers discussed below. The highlighted ions are the ions that switch or change somehow to make the type of structural isomer it is.

Table 20.4.1: Overview of Structural Isomer Classes

Structural Isomer	Examples
Ionization	$[CoBr(H_2O)_5]^+Cl^-$ and $[CoCl(H_2O)_5]^+Br^-$
Coordination	$[Zn(NH_3)_4]^+[CuCl_4]^{2-}$ and $[Cu(NH_3)_4]^+[ZnCl_4]^{2-}$
Linkage	$[Co(NO_2)_6]^{3-}$ and $[Co(ONO)_6]^{3-}$

References

1. Petrucci, Harwood, Herring, and Madura. General Chemistry: Principles and Modern Applications: Ninth Edition. New Jersey: Pearson, 2007.
2. Atkins, Peter, and Loretta Jones. Chemical Principles: The Quest for Insight: Fourth Edition. W. H. Freeman and Company, 2008. Print.

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)
- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

20.4: Isomerism is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **24.4: Isomerism in Coordination Complexes** is licensed CC BY-NC-SA 4.0.

20.5: Optical Isomerism in Metal Complexes

Optical isomers are stereoisomers that are related via non-superimposable mirror images of each other. They differ from geometric stereoisomers in that they rotate the polarization of plane-polarized light. These isomers are referred to as *enantiomers* or *chiral*.

Introduction

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 with a different polarization 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.

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 polarimeter is made up of a polarizer (#3 on Figure 20.5.1) and an analyzer (#7 on Figure 20.5.1). 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.

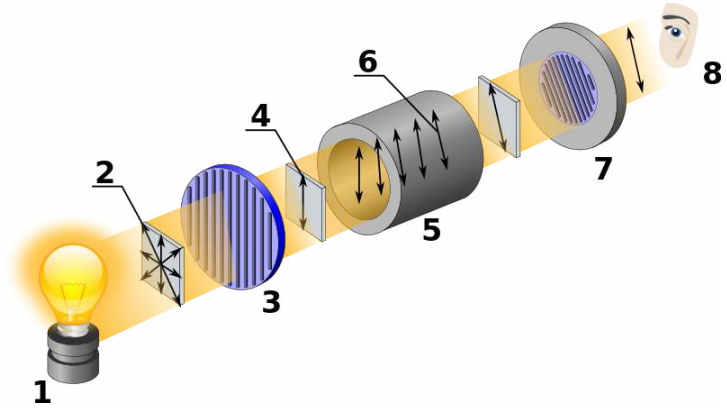


Figure 20.5.1: Schematic of a polarimeter showing the principles behind it's operation.The plane of polarization of plane polarised light (4) rotates (6) as it passes through an optically active sample (5). This angle is determined with a rotatable polarizing filter (7). (CC BY-SA 3.0; Kaidor via Wikipedia)

Chemists use polarimeters to investigate the influence of compounds (in the sample cell) on plane polarized light. Samples composed only of achiral molecules (e.g. water or hexane), have no effect on the polarized light beam. However, if a single enantiomer is examined (all sample molecules being right-handed, or all being left-handed), the plane of polarization is rotated in either a clockwise (positive) or counter-clockwise (negative) direction, and the analyzer must be turned an appropriate matching angle, **α**, if full light intensity is to reach the detector. In the above illustration, the sample has rotated the polarization plane clockwise by +90º, and the analyzer has been turned this amount to permit maximum light transmission.

The observed rotations (α) of enantiomers are opposite in direction. One enantiomer will rotate polarized light in a clockwise direction, termed **dextrorotatory** or (+), and its mirror-image partner in a counter-clockwise manner, termed **levorotatory** or (–). The prefixes dextro and levo come from the Latin *dexter*, meaning right, and *laevus*, for left, and are abbreviated *d* and *l* respectively. A 50:50 mixture of enantiomers has no observable optical activity. Such mixtures are called **racemates** or **racemic modifications**.

The "Mirror Image Method" to Determine Optical Isomers

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.

The **mirror image method** uses a mirror image of the molecule to determine 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.

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.

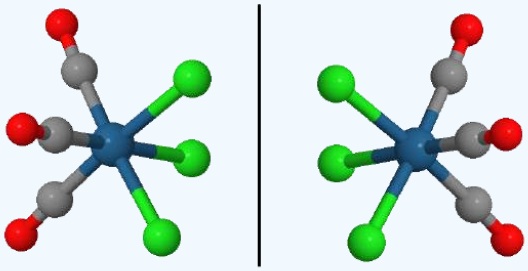
> *Non-superimposable means the structure cannot be rotated in a way that one can be put on top of another.*

Example 20.5.1: The $[OsCl_3(CO)_3]^-$ Ion

Are there enantiomers for the $fac-[OsCl_3(CO)_3]^-$ complex ion?

Solution

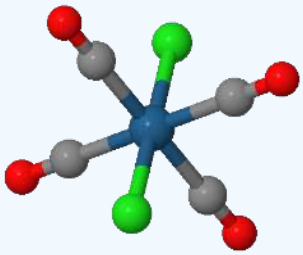
To use mirror image method, we draw the 3D structure for this geometric isomer (not the mer isomer) and then take a mirror image like below.



The left image can be rotated by 180° through a vertical axis to superimpose on the orginal. So the mer-$[OsCl_3(CO)_3]^-$ complex ion is not optically active or we can call it achiral.

Exercise 20.5.1

Use the mirror image method to determine if there are enantiomers for the $mer-[OsCl_3(CO)_3]^-$ complex ion.



Example 20.5.2

Consider the octahedral complex with six monodentate ligands $MA_2B_2C_2$ have both cis and trans isomers. However, the cis isomer will also have two optical isomers (Figure 20.5.2). No matter how one rotates one of the mirror images, they are are **not** superimposable.

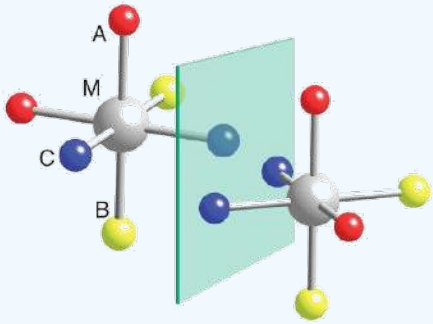


Figure 20.5.2: Two $MA_2B_2C_2$ enantiomers. (CC BY-SA-NC 4.0; ChemTube3D via Nick Greeves)

Exercise 20.5.1: $MA_2B_2C_2$

Confirm to yourself that if two like ligands in $MA_2B_2C_2$ are *trans* to each other, then the complex will not have an optical isomer.

Answer

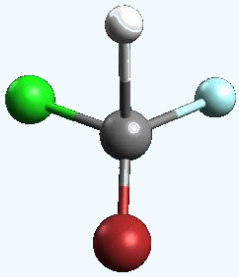
If two like ligands are *trans* then there will be a mirror plane of symmetry normal to the line connecting the ligands that are *trans* to each other. The presence of the mirror plane means this complex will not have an optical isomer.

The "Plane of Symmetry Method" to Determine Optical Isomers

The plane of symmetry method uses symmetry also 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 for that complex and it is called **achiral**.

Example 20.5.3: A Tetrahedral Complex

Consider the tetrahedral molecule, CHBrClF. Is this molecule optically active?

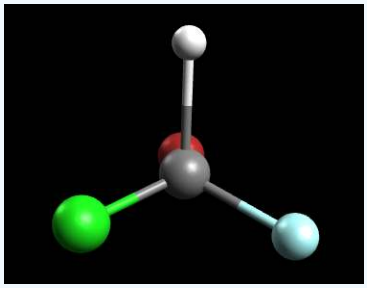


The CHBrClF molecule (note the color scheme: grey=carbon, white=hydrogen, green=chlorine, blue=fluorine, red=bromine)

Solution

- *Mirror-image method*

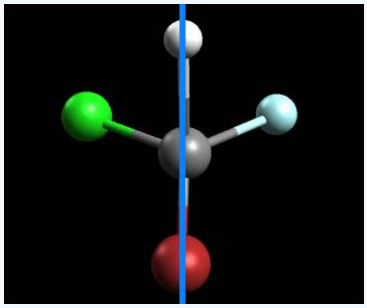
First take the Mirror-image method. The mirror image of the molecule is:



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.

- *Plane of Symmetry Method*

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:



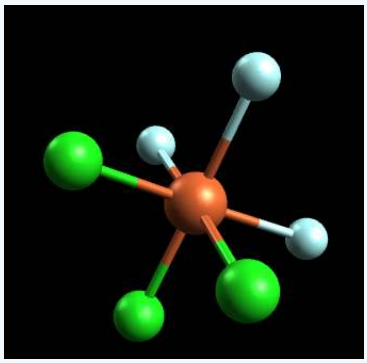
Since the left side is not identical to the right, this molecule does not have a symmetrical center and thus can be called chiral.Additionally, because it does not have a symmetrical center, we can conclude that this molecule has optical isomers. In general, when dealing with a tetrahedral molecule that 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 have no plane of symmetry. 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 20.5.4: An Octahedral Complex

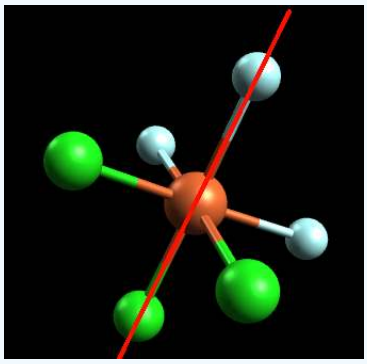
Is the octahedral compound $\mathrm{FeCl_3F_3}$ optically active?



(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.

Enantiomers in Octahedral Complexes with Bidentate Ligands

The examples you are most likely to need occur in octahedral complexes that contain bidentate ligands, e.g., complex ions like $\mathrm{[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}}$ or $\mathrm{[Cr(C_2O_4)_3]^{3-}}$. In bidentate complexes or chelating complexes, a ligand binds very tightly to the metal because it holds onto the metal via more than one atom. Ethylenediamine is one example of a bidentate ligand.

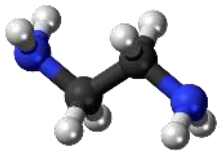
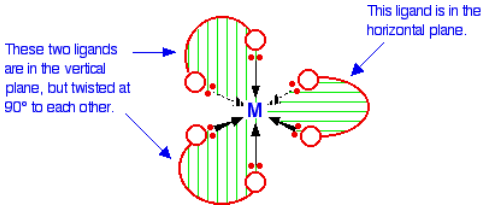


Figure 20.5.3: Ethylenediamine (sometimes abbreviated en) is an example of a bidentate ligand

As you may expect, bidentate ligands bind tightly to metals because they form two bonds with it, rather than just one. It is also important to recognize that in an octahedral complex, the two donor atoms in most bidentate ligand bind *cis* to each other and **cannot** reach all the way around the molecule to bind *trans* to each other (see below). The diagram below shows a simplified view of one of the complex ions with three oxalato ligands (also a bidentate ligand), however, 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 polarized light clockwise; the other rotates it counter-clockwise. In this case, the two isomers are:

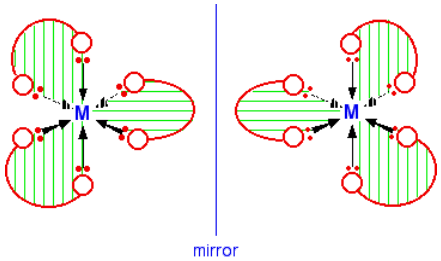
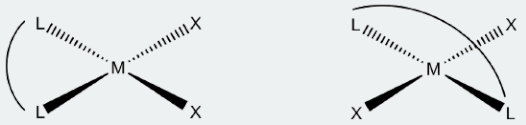


Figure 20.5.4: A left-handed propeller shape (left) is seen in one optical isomers of the $M(ox)_3^+$ octahedral complex. The other optical isomer is a right-handed propeller (right). These shapes are alternatively described as a left-handed screw and a right handed screw. If you can picture turning the shape so that it screws into the page behind it, which direction would you turn the screwdriver? If you would twist the screwdriver clockwise, then you have a right handed screw. If you would twist the screwdriver counter-clockwise, then you have a left handed screw.

Most, but not all, Bidentate Ligands Bind to Metals in the cis Orientation

A wide variety of bidentate ligands bind to metals in the cis fashion, but few can bind in the trans geometry. These are called trans-spanning ligands and required building a bridge between the bonding atoms (e.g. methylene brindges $-\mathrm{CH_2CH_2CH_2CH_2}-$).



Trans vs cis ligands in square planar complexes. (CC BY-SA 3.0; via Wikipedia)

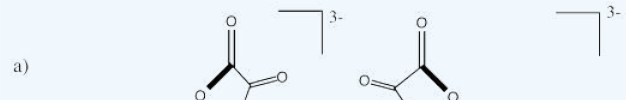
We will not consider any trans-spanning ligands in this text.

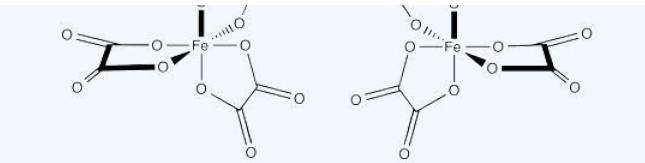
A complex containing three bidentate ligands can take on the shape of a left-handed propeller or a right-handed propeller. You may be able to see that there is no way of rotating the second isomer in space so that it looks exactly the same as the first one. As long as you draw the isomers carefully, with the second one a true reflection of the first, the two structures will be different.

These kinds of complexes were historically important in demonstrating how small molecules and ions bound to metal cations. By showing that some metal complexes were chiral and displayed optical activity, early 20th century workers such as Alfred Werner were able to rule out some competing ideas about the structures of metal compounds. Today, we know that metal complexes play important roles in enzymes in biology, and Werner's work on metal complexes laid the groundwork for how we think about these complexes. In addition, stereochemistry in metal complexes became very important in the late 20th century, especially as pharmaceutical companies looked for catalysts that could aid in the production of one enantiomer of a drug, and not the other, in order to maximize pharmaceutical effectiveness and minimize side effects.

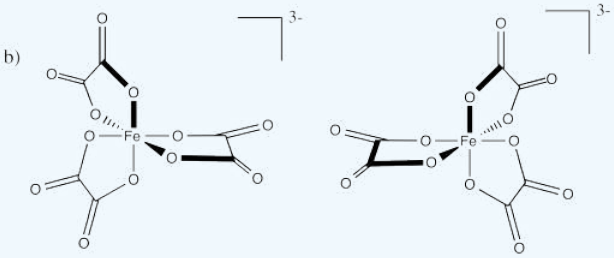
Exercise 20.5.1

Identify the relationships (types of isomers) between the following pairs of iron(III) oxalate ions.

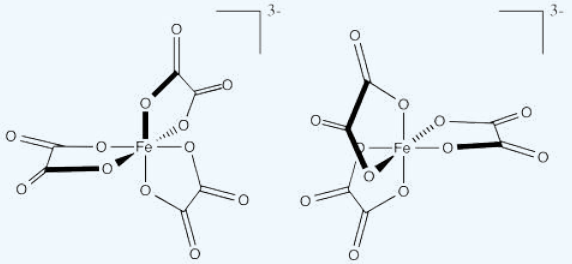




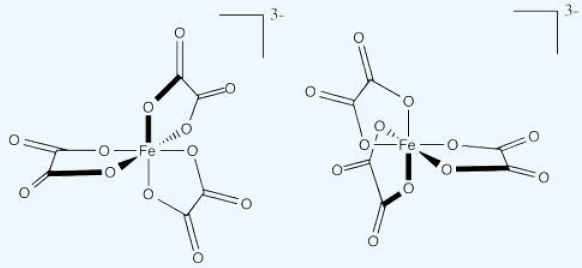
b)



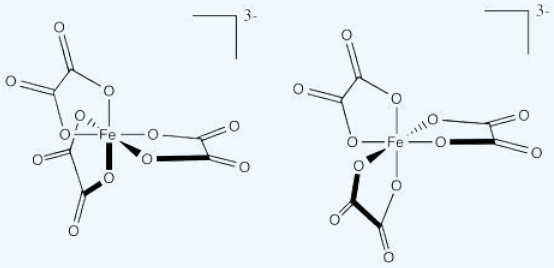
c)



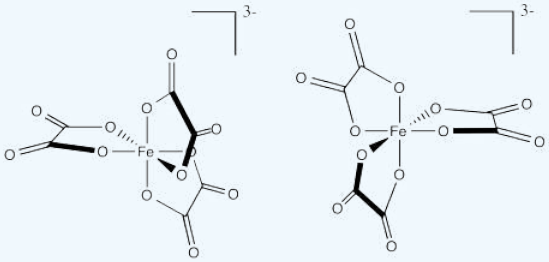
d)



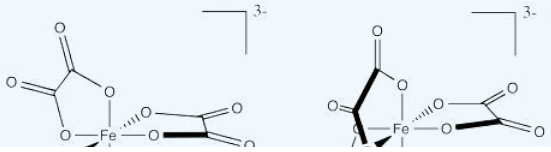
e)

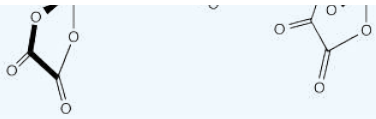


f)



g)





Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)
- Jim Clark (Chemguide.co.uk)
- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

20.5: Optical Isomerism in Metal Complexes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

20.6: Stability Aspects of Complex-Ion Equilibria

Learning Objectives

- To be introduced to complex ions, including ligands.

Previously, you learned that metal ions in aqueous solution are hydrated—that is, surrounded by a shell of usually four or six water molecules. A hydrated ion is one kind of a complex ion (or, simply, complex), a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons, such as the $[Al(H_2O)_6]^{3+}$ ion.

A complex ion forms from a metal ion and a ligand because of a Lewis acid–base interaction. The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base. Small, highly charged metal ions, such as Cu^{2+} or Ru^{3+}, have the greatest tendency to act as Lewis acids, and consequently, they have the greatest tendency to form complex ions.



Figure 20.6.1: The Formation of Complex Ions. An aqueous solution of $CuSO_4$ consists of hydrated Cu^{2+} ions in the form of pale blue $[Cu(H_2O)_6]^{2+}$ (left). The addition of aqueous ammonia to the solution results in the formation of the intensely blue-violet $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ions, usually written as $[Cu(NH_3)_4]^{2+}$ ion (right) because ammonia, a stronger base than H_2O, replaces water molecules from the hydrated Cu^{2+} ion. For a more complete description, see https://www.youtube.com/watch?v=IQNcLH6OZK0.

As an example of the formation of complex ions, consider the addition of ammonia to an aqueous solution of the hydrated Cu^{2+} ion $\{[Cu(H_2O)_6]^{2+}\}$. Because it is a stronger base than H_2O, ammonia replaces the water molecules in the hydrated ion to form the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion. Formation of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex is accompanied by a dramatic color change, as shown in Figure 20.6.1. The solution changes from the light blue of $[Cu(H_2O)_6]^{2+}$ to the blue-violet characteristic of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion.

The Formation Constant

The replacement of water molecules from $[Cu(H_2O)_6]^{2+}$ by ammonia occurs in sequential steps. Omitting the water molecules bound to Cu^{2+} for simplicity, we can write the equilibrium reactions as follows:

$$Cu^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)]^{2+}(aq) \quad \text{(step 1)}$$

with

$$K_1 = \frac{[Cu(NH_3)]^{2+}(aq)}{[Cu^{2+}(aq)][NH_3(aq)]}$$

$$[Cu(NH_3)]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)_2]^{2+}(aq) \quad \text{(step 2)}$$

with

$$K_2 = \frac{[Cu(NH_3)_2]^{2+}(aq)}{[[Cu(NH_3)]^{2+}(aq)][NH_3(aq)]}$$

$$[Cu(NH_3)_2]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)_3]^{2+}(aq) \quad \text{(step 3)}$$

with

$$K_3 = \frac{[Cu(NH_3)_3]^{2+}(aq)}{[[Cu(NH_3)_2]^{2+}(aq)][NH_3(aq)]}$$

$$[Cu(NH_3)_3]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) \quad \text{(step 4)}$$

with

$$K_4 = \frac{[Cu(NH_3)_4]^{2+}(aq)}{[[Cu(NH_3)_3]^{2+}(aq)][NH_3(aq)]}$$

The sum of the stepwise reactions is the overall equation for the formation of the complex ion: The hydrated Cu^{2+} ion contains six H_2O ligands, but the complex ion that is produced contains only four NH_3 ligands, not six.

$$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) \quad (20.6.1)$$

The equilibrium constant for the formation of the complex ion from the hydrated ion is called the **formation constant** (K_f). The equilibrium constant expression for K_f has the same general form as any other equilibrium constant expression. In this case, the expression is as follows:

$$\begin{aligned} K_f &= \frac{[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} \\ &= 2.1 \times 10^{13} \\ &= K_1 \times K_2 \times K_3 \times K_4 \end{aligned}$$

> *The formation constant (K_f) has the same general form as any other equilibrium constant expression.*

Water, a pure liquid, does not appear explicitly in the equilibrium constant expression, and the hydrated $Cu^{2+}(aq)$ ion is represented as Cu^{2+} for simplicity. As for any equilibrium, the larger the value of the equilibrium constant (in this case, K_f), the more stable the product. With $K_f = 2.1 \times 10^{13}$, the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is very stable. The formation constants for some common complex ions are listed in Table 20.6.1.

Table 20.6.1: Formation Constants for Selected Complex Ions in Aqueous Solution*

	Complex Ion	Equilibrium Equation	K_f
Ammonia Complexes	$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.1×10^7
	$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	2.1×10^{13}
	$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	5.5×10^8
Cyanide Complexes	$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$	1.1×10^{18}
	$[Ni(CN)_4]^{2-}$	$Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-}$	2.2×10^{31}
	$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	1×10^{42}
Hydroxide Complexes	$[Zn(OH)_4]^{2-}$	$Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	4.6×10^{17}
	$[Cr(OH)_4]^-$	$Cr^{3+} + 4OH^- \rightleftharpoons [Cr(OH)_4]^-$	8.0×10^{29}
Halide Complexes	$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.2×10^{15}
	$[CdI_4]^{2-}$	$Cd^{2+} + 4I \rightleftharpoons [CdI_4]^{2-}$	2.6×10^5
	$[AlF_6]^{3-}$	$Al^{3+} + 6F^- \rightleftharpoons [AlF_6]^{3-}$	6.9×10^{19}
Other Complexes	$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}

*Reported values are overall formation constants. Source: Data from *Lange's Handbook of Chemistry*, 15th ed. (1999).

	Complex Ion	Equilibrium Equation	K_f
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-}$	2.0×10^{20}

*Reported values are overall formation constants. Source: Data from *Lange's Handbook of Chemistry*, 15th ed. (1999).

Example 20.6.1

If 12.5 g of $Cu(NO_3)_2 \bullet 6\,H_2O$ is added to 500 mL of 1.00 M aqueous ammonia, what is the equilibrium concentration of $Cu^{2+}(aq)$?

Given: mass of Cu^{2+} salt and volume and concentration of ammonia solution

Asked for: equilibrium concentration of $Cu^{2+}(aq)$

Strategy:

A. Calculate the initial concentration of $Cu^{2+}(aq)$ due to the addition of copper(II) nitrate hexahydrate. Use the stoichiometry of the reaction shown in Equation 20.6.1 to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations of all species in solution.

B. Substitute the final concentrations into the expression for the formation constant (K_f) to calculate the equilibrium concentration of $Cu^{2+}(aq)$.

Solution

Adding an ionic compound that contains $Cu^{2+}(aq)$ to an aqueous ammonia solution will result in the formation of $[Cu(NH_3)_4]^{2+}(aq)$, as shown in Equation 20.6.1 We assume that the volume change caused by adding solid copper(II) nitrate to aqueous ammonia is negligible.

A The initial concentration of $Cu^{2+}(aq)$ from the amount of added copper nitrate prior to any reaction is as follows:

$$12.5\ \cancel{g}\ Cu(NO_3)_2 \cdot 6H_2O \left(\frac{1\ \text{mol}}{295.65\ \cancel{g}}\right)\left(\frac{1}{500\ \cancel{mL}}\right)\left(\frac{1000\ \cancel{mL}}{1\ \text{L}}\right) = 0.0846\ \text{M}$$

Because the stoichiometry of the reaction is four NH_3 to one Cu^{2+}, the amount of NH_3 required to react completely with the Cu^{2+} is 4(0.0846) = 0.338 M. The concentration of ammonia after complete reaction is 1.00 M − 0.338 M = 0.66 M. These results are summarized in the first two lines of the following table. Because the equilibrium constant for the reaction is large (2.1×10^{13}), the equilibrium will lie far to the right. Thus we will assume that the formation of $[Cu(NH_3)_4]^{2+}$ in the first step is complete and allow some of it to dissociate into Cu^{2+} and NH_3 until equilibrium has been reached. If we define *x* as the amount of Cu^{2+} produced by the dissociation reaction, then the stoichiometry of the reaction tells us that the change in the concentration of $[Cu(NH_3)_4]^{2+}$ is −*x*, and the change in the concentration of ammonia is +4*x*, as indicated in the table. The final concentrations of all species (in the bottom row of the table) are the sums of the concentrations after complete reaction and the changes in concentrations.

$$Cu^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

ICE	$[Cu^{2+}]$	$[NH_3]$	$[[Cu(NH_3)_4]^{2+}]$
initial	0.0846	1.00	0
after complete reaction	0	0.66	0.0846
change	+*x*	+4*x*	−*x*
final	*x*	0.66 + 4*x*	0.0846 − *x*

B Substituting the final concentrations into the expression for the formation constant (K_f) and assuming that $x \ll 0.0846$, which allows us to remove x from the sum and difference,

$$\begin{aligned} K_f &= \frac{\left[[\mathrm{Cu(NH_3)_4}]^{2+}\right]}{[\mathrm{Cu}^{2+}][\mathrm{NH_3}]^4} \\ &= \frac{0.0846 - x}{x(0.66 + 4x)^4} \\ &\approx \frac{0.0846}{x(0.66)^4} = 2.1 \times 10^{13} \\ x &= 2.1 \times 10^{-14} \end{aligned}$$

The value of *x* indicates that our assumption was justified. The equilibrium concentration of $Cu^{2+}(aq)$ in a 1.00 M ammonia solution is therefore 2.1×10^{-14} M.

? Exercise 20.6.1

The ferrocyanide ion ($[\mathrm{Fe(CN)_6}]^{4-}$) is very stable, with a K_f of 1×10^{35}. Calculate the concentration of cyanide ion in equilibrium with a 0.65 M solution of $\mathrm{K_4[Fe(CN)_6]}$.

Answer

2×10^{-6} M

The Effect of the Formation of Complex Ions on Solubility

What happens to the solubility of a sparingly soluble salt if a ligand that forms a stable complex ion is added to the solution? One such example occurs in conventional black-and-white photography. Recall that black-and-white photographic film contains light-sensitive microcrystals of AgBr, or mixtures of AgBr and other silver halides. AgBr is a sparingly soluble salt, with a K_{sp} of 5.35×10^{-13} at 25°C. When the shutter of the camera opens, the light from the object being photographed strikes some of the crystals on the film and initiates a photochemical reaction that converts AgBr to black Ag metal. Well-formed, stable negative images appear in tones of gray, corresponding to the number of grains of AgBr converted, with the areas exposed to the most light being darkest. To fix the image and prevent more AgBr crystals from being converted to Ag metal during processing of the film, the unreacted AgBr on the film is removed using a complexation reaction to dissolve the sparingly soluble salt.

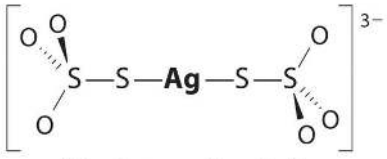
The reaction for the dissolution of silver bromide is as follows:

$$\mathrm{AgBr(s)} \rightleftharpoons \mathrm{Ag^+(aq) + Br^-(aq)} \tag{20.6.2}$$

with

$$K_{sp} = 5.35 \times 10^{-13} \text{ at } 25^\circ\mathrm{C} \tag{20.6.3}$$

The equilibrium lies far to the left, and the equilibrium concentrations of Ag^+ and Br^- ions are very low (7.31×10^{-7} M). As a result, removing unreacted AgBr from even a single roll of film using pure water would require tens of thousands of liters of water and a great deal of time. Le Chatelier's principle tells us, however, that we can drive the reaction to the right by removing one of the products, which will cause more AgBr to dissolve. Bromide ion is difficult to remove chemically, but silver ion forms a variety of stable two-coordinate complexes with neutral ligands, such as ammonia, or with anionic ligands, such as cyanide or thiosulfate ($S_2O_3^{2-}$). In photographic processing, excess AgBr is dissolved using a concentrated solution of sodium thiosulfate.



thiosulfate complex of Ag^+

The reaction of Ag^+ with thiosulfate is as follows:

$$Ag^{+}_{(aq)} + 2S_2O^{2-}_{3(aq)} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}_{(aq)} \tag{20.6.4}$$

with

$$K_f = 2.9 \times 10^{13} \tag{20.6.5}$$

The magnitude of the equilibrium constant indicates that almost all Ag^+ ions in solution will be immediately complexed by thiosulfate to form $[Ag(S_2O_3)_2]^{3-}$. We can see the effect of thiosulfate on the solubility of AgBr by writing the appropriate reactions and adding them together:

$$\begin{aligned} \mathrm{AgBr(s)} &\rightleftharpoons \mathrm{Ag^+(aq) + Br^-(aq)} \quad K_{\mathrm{sp}} = 5.35 \times 10^{-13} \\ \mathrm{Ag^+(aq) + 2S_2O_3^{2-}(aq)} &\rightleftharpoons \mathrm{[Ag(S_2O_3)_2]^{3-}(aq)} \quad K_{\mathrm{f}} = 2.9 \times 10^{13} \\ \mathrm{AgBr(s) + 2S_2O_3^{2-}(aq)} &\rightleftharpoons \mathrm{[Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)} \quad K = K_{\mathrm{sp}}K_{\mathrm{f}} = 15 \end{aligned}$$

Comparing K with K_{sp} shows that the formation of the complex ion increases the solubility of AgBr by approximately 3 × 10^{13}. The dramatic increase in solubility combined with the low cost and the low toxicity explains why sodium thiosulfate is almost universally used for developing black-and-white film. If desired, the silver can be recovered from the thiosulfate solution using any of several methods and recycled.

> *If a complex ion has a large K_f, the formation of a complex ion can dramatically increase the solubility of sparingly soluble salts.*

Example 20.6.2: Common Ion Effect in Complexation

Due to the common ion effect, we might expect a salt such as AgCl to be much less soluble in a concentrated solution of KCl than in water. Such an assumption would be incorrect, however, because it ignores the fact that silver ion tends to form a two-coordinate complex with chloride ions ($AgCl_2^-$). Calculate the solubility of AgCl in each situation:

a. in pure water
b. in 1.0 M KCl solution, ignoring the formation of any complex ions
c. the same solution as in part (b) except taking the formation of complex ions into account, assuming that $AgCl_2^-$ is the only Ag^+ complex that forms in significant concentrations

At 25°C, K_{sp} = 1.77 × 10^{-10} for AgCl and K_f = 1.1 × 10^5 for $AgCl_2^-$.

Given: K_{sp} of AgCl, K_f of $AgCl_2^-$, and KCl concentration

Asked for: solubility of AgCl in water and in KCl solution with and without the formation of complex ions

Strategy:

A. Write the solubility product expression for AgCl and calculate the concentration of Ag^+ and Cl^- in water.
B. Calculate the concentration of Ag^+ in the KCl solution.
C. Write balanced chemical equations for the dissolution of AgCl and for the formation of the $AgCl_2^-$ complex. Add the two equations and calculate the equilibrium constant for the overall equilibrium.
D. Write the equilibrium constant expression for the overall reaction. Solve for the concentration of the complex ion.

Solution

A. If we let *x* equal the solubility of AgCl, then at equilibrium

$$\mathrm{[Ag^+] = [Cl^-] = x\ M.}$$

Substituting this value into the solubility product expression,

$$\begin{aligned} K_{sp} &= [\mathrm{Ag^+}][\mathrm{Cl^-}] \\ &= (x)(x) \\ &= x^2 \\ &= 1.77 \times 10^{-10} \\ x &= 1.33 \times 10^{-5} \end{aligned}$$

Thus the solubility of AgCl in pure water at 25°C is 1.33 × 10^{-5} M.

B. If *x* equals the solubility of AgCl in the KCl solution, then at equilibrium [Ag^+] = *x* M and [Cl^-] = (1.0 + *x*) M. Substituting these values into the solubility product expression and assuming that $x \leq 1.0$:

$$\begin{aligned} K_{sp} &= [\mathrm{Ag^+}][\mathrm{Cl^-}] \\ &= (x)(1.0 + x) \\ &\approx x(1.0) \\ &= 1.77 \times 10^{-10} = x \end{aligned}$$

If the common ion effect were the only important factor, we would predict that AgCl is approximately five orders of magnitude less soluble in a 1.0 M KCl solution than in water.

C. To account for the effects of the formation of complex ions, we must first write the equilibrium equations for both the dissolution and the formation of complex ions. Adding the equations corresponding to K_{sp} and K_f gives us an equation that describes the dissolution of AgCl in a KCl solution. The equilibrium constant for the reaction is therefore the product of K_{sp} and K_f:

$$\begin{aligned} \mathrm{AgCl(s)} &\rightleftharpoons \mathrm{Ag^+(aq) + Cl^-(aq)} \quad K_{sp} = 1.77 \times 10^{-10} \\ \mathrm{Ag^+aq) + 2Cl^-} &\rightleftharpoons \mathrm{[AgCl_2]^-} \quad K_f = 1.1 \times 10^5 \\ \mathrm{AgCl(s) + Cl^-} &\rightleftharpoons \mathrm{[AgCl_2]^-} \quad K = K_{sp}K_f = 1.9 \times 10^{-5} \end{aligned}$$

D. If we let x equal the solubility of AgCl in the KCl solution, then at equilibrium [$AgCl_2^-$] = *x* and [Cl^-] = 1.0 − *x*. Substituting these quantities into the equilibrium constant expression for the net reaction and assuming that $x \leq 1.0$,

$$\begin{aligned} K &= \frac{[\mathrm{AgCl_2^-}]}{[\mathrm{Cl^-}]} \\ &= \frac{x}{1.0 - x} \approx 1.9 \times 10^{-5} \\ &= x \end{aligned}$$

That is, AgCl dissolves in 1.0 M KCl to produce a 1.9 × 10^{-5} M solution of the $AgCl_2^-$ complex ion. Thus we predict that AgCl has approximately the same solubility in a 1.0 M KCl solution as it does in pure water, which is 10^5 times greater than that predicted based on the common ion effect. (In fact, the measured solubility of AgCl in 1.0 M KCl is almost a factor of 10 greater than that in pure water, largely due to the formation of other chloride-containing complexes.)

? Exercise 20.6.2

Calculate the solubility of mercury(II) iodide (HgI_2) in each situation:

a. pure water
b. a 3.0 M solution of NaI, assuming $[HgI_4]^{2-}$ is the only Hg-containing species present in significant amounts

K_{sp} = 2.9 × 10^{-29} for HgI_2 and K_f = 6.8 × 10^{29} for $[HgI_4]^{2-}$.

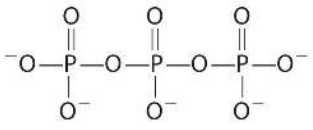
Answer a

1.9 × 10^{-10} M

Answer b

1.4 M

Complexing agents, molecules or ions that increase the solubility of metal salts by forming soluble metal complexes, are common components of laundry detergents. Long-chain carboxylic acids, the major components of soaps, form insoluble salts with Ca^{2+} and Mg^{2+}, which are present in high concentrations in "hard" water. The precipitation of these salts produces a bathtub ring and gives a gray tinge to clothing.



triphosphate

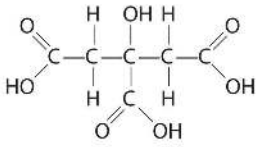
Adding a complexing agent such as pyrophosphate ($O_3POPO_3^{4-}$, or $P_2O_7^{4-}$) or triphosphate ($P_3O_{10}^{5-}$) to detergents prevents the magnesium and calcium salts from precipitating because the equilibrium constant for complex-ion formation is large:

$$Ca^{2+}(aq) + O_3POPO_4^{4-}(aq) \rightleftharpoons [Ca(O_3POPO_3)]^{2-}(aq)$$

with

$$K_f = 4 \times 10^4$$

However, phosphates can cause environmental damage by promoting eutrophication, the growth of excessive amounts of algae in a body of water, which can eventually lead to large decreases in levels of dissolved oxygen that kill fish and other aquatic organisms. Consequently, many states in the United States have banned the use of phosphate-containing detergents, and France has banned their use beginning in 2007. "Phosphate-free" detergents contain different kinds of complexing agents, such as derivatives of acetic acid or other carboxylic acids. The development of phosphate substitutes is an area of intense research.



Citric acid,
a hydroxy polycarboxylic acid

Commercial water softeners also use a complexing agent to treat hard water by passing the water over ion-exchange resins, which are complex sodium salts. When water flows over the resin, sodium ion is dissolved, and insoluble salts precipitate onto the resin surface. Water treated in this way has a saltier taste due to the presence of Na^+, but it contains fewer dissolved minerals.

Complexing Agents in MRIs

Another application of complexing agents is found in medicine. Unlike x-rays, magnetic resonance imaging (MRI) can give relatively good images of soft tissues such as internal organs. MRI is based on the magnetic properties of the ^1H nucleus of hydrogen atoms in water, which is a major component of soft tissues. Because the properties of water do not depend very much on whether it is inside a cell or in the blood, it is hard to get detailed images of these tissues that have good contrast. To solve this problem, scientists have developed a class of metal complexes known as "MRI contrast agents." Injecting an MRI contrast agent into a patient selectively affects the magnetic properties of water in cells of normal tissues, in tumors, or in blood vessels and allows doctors to "see" each of these separately (Figure 20.6.2). One of the most important metal ions for this application is Gd^{3+}, which with seven unpaired electrons is highly paramagnetic. Because $Gd^{3+}(aq)$ is quite toxic, it must be administered as a very stable complex that does not dissociate in the body and can be excreted intact by the kidneys. The complexing agents used for gadolinium are ligands such as $DTPA^{5-}$ (diethylene triamine pentaacetic acid), whose fully protonated form is shown in Figure 20.6.2

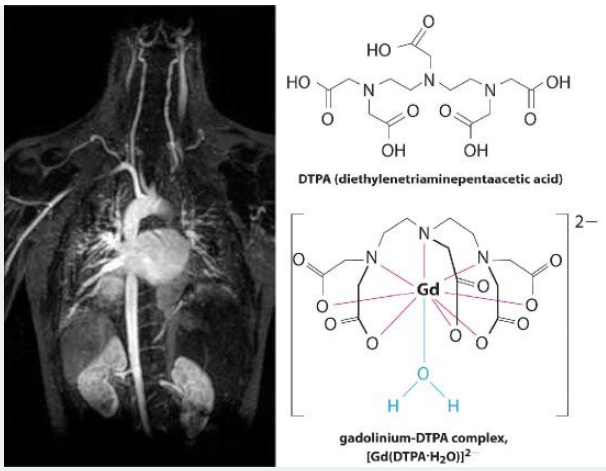


Figure 20.6.2: An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

Summary

The formation of complex ions can substantially increase the solubility of sparingly soluble salts if the complex ion has a large K_f. A complex ion is a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons. Small, highly charged metal ions have the greatest tendency to act as Lewis acids and form complex ions. The equilibrium constant for the formation of the complex ion is the formation constant (K_f). The formation of a complex ion by adding a complexing agent increases the solubility of a compound.

20.6: Stability Aspects of Complex-Ion Equilibria is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **24.8: Aspects of Complex-Ion Equilibria** is licensed CC BY-NC-SA 4.0.

20.7: Chelation

Ligands like chloride, water, and ammonia are said to be monodentate (one-toothed, from the Greek mono, meaning “one,” and the Latin dent-, meaning “tooth”): they are attached to the metal via only a single atom. Ligands can, however, be bidentate (two-toothed, from the Greek di, meaning “two”), tridentate (three-toothed, from the Greek tri, meaning “three”), or, in general, polydentate (many-toothed, from the Greek poly, meaning “many”), indicating that they are attached to the metal at two, three, or several sites, respectively. Ethylenediamine ($H_2NCH_2CH_2NH_2$, often abbreviated as en) and diethylenetriamine ($H_2NCH_2CH_2NHCH_2CH_2NH_2$, often abbreviated as dien) are examples of a bidentate and a tridentate ligand, respectively, because each nitrogen atom has a lone pair that can be shared with a metal ion. When a bidentate ligand such as ethylenediamine binds to a metal such as Ni^{2+}, a five-membered ring is formed. A metal-containing ring like that shown is called a chelate ring (from the Greek chele, meaning “claw”). Correspondingly, a polydentate ligand is a chelating agent, and complexes that contain polydentate ligands are called chelate complexes.



A chelate complex

Experimentally, it is observed that metal complexes of polydentate ligands are significantly more stable than the corresponding complexes of chemically similar monodentate ligands; this increase in stability is called the chelate effect. For example, the complex of Ni^{2+} with three ethylenediamine ligands, $[Ni(en)_3]^{2+}$, should be chemically similar to the Ni^{2+} complex with six ammonia ligands, $[Ni(NH_3)_6]^{2+}$. In fact, the equilibrium constant for the formation of $[Ni(en)_3]^{2+}$ is almost 10 orders of magnitude larger than the equilibrium constant for the formation of $[Ni(NH_3)_6]^{2+}$ (Table E4):

$$[Ni(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6H_2O(l) \quad K_f = 4 \times 10^8 \tag{20.7.1}$$

$$[Ni(H_2O)_6]^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O(l) \quad K_f = 2 \times 10^{18} \tag{20.7.2}$$

The formation constants are formulated as ligand exchange reactions with aqua ligands being displaced by new ligands (NH_3 or en) in the examples above.

> *Chelate complexes are more stable than the analogous complexes with monodentate ligands.*

The stability of a chelate complex depends on the size of the chelate rings. For ligands with a flexible organic backbone like ethylenediamine, complexes that contain five-membered chelate rings, which have almost no strain, are significantly more stable than complexes with six-membered chelate rings, which are in turn much more stable than complexes with four- or seven-membered rings. For example, the complex of nickel (II) with three ethylenediamine ligands is about 363,000 times more stable than the corresponding nickel (II) complex with trimethylenediamine ($H_2NCH_2CH_2CH_2NH_2$, abbreviated as tn):

$$[Ni(H_2O)_6]^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O(l) \quad K_f = 6.76 \times 10^{17} \tag{20.7.3}$$

$$[Ni(H_2O)_6]^{2+} + 3tn \rightleftharpoons [Ni(tn)_3]^{2+} + 6H_2O(l) \quad K_f = 1.86 \times 10^{12} \tag{20.7.4}$$

*The above measurements were done in a solution of ionic strength 0.15 at 25° C.

Example 20.7.1

Arrange $[Cr(en)_3]^{3+}$, $[CrCl_6]^{3-}$, $[CrF_6]^{3-}$, and $[Cr(NH_3)_6]^{3+}$ in order of increasing stability.

Given: four Cr(III) complexes

Asked for: relative stabilities

Strategy:

A Determine the relative basicity of the ligands to identify the most stable complexes.

B Decide whether any complexes are further stabilized by a chelate effect and arrange the complexes in order of increasing stability.

Solution

A The metal ion is the same in each case: Cr^{3+}. Consequently, we must focus on the properties of the ligands to determine the stabilities of the complexes. Because the stability of a metal complex increases as the basicity of the ligands increases, we need to determine the relative basicity of the four ligands. Our earlier discussion of acid–base properties suggests that ammonia and ethylenediamine, with nitrogen donor atoms, are the most basic ligands. The fluoride ion is a stronger base (it has a higher charge-to-radius ratio) than chloride, so the order of stability expected due to ligand basicity is

$$[CrCl_6]^{3-} < [CrF_6]^{3-} < [Cr(NH_3)_6]^{3+} \approx [Cr(en)_3]^{3+}.$$

B Because of the chelate effect, we expect ethylenediamine to form a stronger complex with Cr^{3+} than ammonia. Consequently, the likely order of increasing stability is

$$[CrCl_6]^{3-} < [CrF_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(en)_3]^{3+}.$$

? Exercise 20.7.1

Arrange $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$, and $[Co(en)_3]^{3+}$ in order of decreasing stability.

Answer: $[Co(en)_3]^{3+} > [Co(NH_3)_6]^{3+} > [CoF_6]^{3-}$

The Chelate Effect

The chelate effect can be seen by comparing the reaction of a chelating ligand and a metal ion with the corresponding reaction involving comparable monodentate ligands. For example, comparison of the binding of 2,2'-bipyridine with pyridine or 1,2-diaminoethane (ethylenediamine=en) with ammonia. It has been known for many years that a comparison of this type always shows that the complex resulting from coordination with the chelating ligand is **much more thermodynamically stable**. This can be seen by looking at the values for adding two monodentates compared with adding one bidentate, or adding four monodentates compared to two bidentates, or adding six monodentates compared to three bidentates.

> *The Chelate Effect is that complexes resulting from coordination with the chelating ligand is much more thermodynamically stable than complexes with non-chelating ligands.*

A number of points should be highlighted from the formation constants in Table E4. In Table 20.7.1, it can be seen that the ΔH° values for the formation steps are almost identical, that is, heat is evolved to about the same extent whether forming a complex involving monodentate ligands or bidentate ligands. What is seen to vary significantly is the ΔS° term which changes from negative (unfavorable) to positive (favorable). Note as well that there is a dramatic increase in the size of the ΔS° term for adding two compared to adding four monodentate ligands. (-5 to -35 $JK^{-1}mol^{-1}$). What does this imply, if we consider ΔS° to give a measure of disorder?

In the case of complex formation of Ni^{2+} with ammonia or 1,2-diaminoethane, by rewriting the equilibria, the following equations are produced.

$$\begin{array}{lcl} [Ni(H_2O)_6]^{2+} + 6\,NH_3 \overset{\beta_6}{\Leftrightarrow} [Ni(NH_3)_6]^{2+} & & \textbf{1f} \\ [Ni(NH_3)_6]^{2+} \Leftrightarrow [Ni(H_2O)_6]^{2+} + 6\,NH_3 & & \textbf{1d} \\ [Ni(H_2O)_6]^{2+} + 3\,en \overset{\beta_3}{\Leftrightarrow} [Ni(en)_3]^{2+} & & \textbf{2f} \\ \hline [Ni(NH_3)_6]^{2+} + 3\,en \Leftrightarrow [Ni(en)_3]^{2+} + 6NH_3 & & \textbf{3} \end{array}$$

Using the equilibrium constant for the reaction (3 above) where the *three* bidentate ligands replace the *six* monodentateligands, we find that at a temperature of 25° C:

$$\begin{aligned} \Delta G^\circ &= -2.303\,RT\,\log_{10} K \\ &= -2.303\,RT\,(18.28 - 8.61) \\ &= -54\ \text{kJ mol}^{-1} \end{aligned}$$

Based on measurements made over a range of temperatures, it is possible to break down the ΔG° term into the enthalpy and entropy components.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The result is that: $\Delta H^\circ = -29 kJ mol^{-1}$

$-T\Delta S^\circ = -25 \text{ kJ mol}^{-1}$
and at 25C (298K)
$\Delta S^\circ = +88 \text{ J K}^{-1} \text{ mol}^{-1}$

For many years, these numbers have been **incorrectly recorded** in textbooks. For example, the third edition of "Basic Inorganic Chemistry" by F.A. Cotton, G. Wilkinson and P.L. Gaus, John Wiley & Sons, Inc, 1995, on page 186 gives the values as:

$\Delta G^\circ = -67 \text{ kJ mol}^{-1}$
$\Delta H^\circ = -12 \text{ kJ mol}^{-1}$
$-T\Delta S^\circ = -55 \text{ kJ mol}^{-1}$

The conclusion they drew from these incorrect numbers was that the chelate effect was essentially an entropy effect, since the $T\Delta S^\circ$ contribution was nearly 5 times bigger than ΔH°.

In fact, the breakdown of the ΔG° into ΔH° and $T\Delta S^\circ$ shows that the two terms are nearly equal (-29 and -25 kJ mol^{-1}, respectively) with the ΔH° term a little bigger! The entropy term found is still much larger than for reactions involving a non-chelating ligand substitution at a metal ion. How can we explain this enhanced contribution from entropy? One explanation is to count the number of species on the left and right hand side of the equation above.

It will be seen that on the left-hand-side there are 4 species, whereas on the right-hand-side there are 7 species, that is a net gain of 3 species occurs as the reaction proceeds. This can account for the increase in entropy since it represents an increase in the disorder of the system. An alternative view comes from trying to understand how the reactions might proceed. To form a complex with 6 monodentates requires 6 separate favorable collisions between the metal ion and the ligand molecules. To form the tris-bidentate metal complex requires an initial collision for the first ligand to attach by one arm but remember that the other arm is always going to be nearby and only requires a rotation of the other end to enable the ligand to form the chelate ring.

If you consider dissociation steps, then when a monodentate group is displaced, it is lost into the bulk of the solution. On the other hand, if one end of a bidentate group is displaced the other arm is still attached and it is only a matter of the arm rotating around and it can be reattached again. **Both** conditions favor the formation of the complex with bidentate groups rather than monodentate groups.

20.7: Chelation is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Stability of Metal Complexes and Chelation** by Robert J. Lancashire is licensed CC BY-NC-SA 4.0.

20.8: Bonding in Octahedral Complex Ions- Crystal Field Theory

Learning Objectives

- To understand how crystal field theory explains the electronic structures and colors of metal complexes.

One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit. In this section, we describe crystal field theory (CFT), a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature. Even though this assumption is clearly not valid for many complexes, such as those that contain neutral ligands like CO, CFT enables chemists to explain many of the properties of transition-metal complexes with a reasonable degree of accuracy. The Learning Objective of this Module is to understand how crystal field theory explains the electronic structures and colors of metal complexes.

d-Orbital Splittings

CFT focuses on the interaction of the five (n − 1)d orbitals with ligands arranged in a regular array around a transition-metal ion. We will focus on the application of CFT to octahedral complexes, which are by far the most common and the easiest to visualize. Other common structures, such as square planar complexes, can be treated as a distortion of the octahedral model. According to CFT, an octahedral metal complex forms because of the electrostatic interaction of a positively charged metal ion with six negatively charged ligands or with the negative ends of dipoles associated with the six ligands. In addition, the ligands interact with one other electrostatically. As you learned in our discussion of the valence-shell electron-pair repulsion (VSEPR) model, the lowest-energy arrangement of six identical negative charges is an octahedron, which minimizes repulsive interactions between the ligands.

We begin by considering how the energies of the d orbitals of a transition-metal ion are affected by an octahedral arrangement of six negative charges. Recall that the five d orbitals are initially degenerate (have the same energy). If we distribute six negative charges uniformly over the surface of a sphere, the d orbitals remain degenerate, but their energy will be higher due to repulsive electrostatic interactions between the spherical shell of negative charge and electrons in the d orbitals (Figure $20.8.1a$). Placing the six negative charges at the vertices of an octahedron does not change the average energy of the d orbitals, but it does remove their degeneracy: the five d orbitals split into two groups whose energies depend on their orientations. As shown in Figure $20.8.1b$ the d_{z^2} and $d_{x^2-y^2}$ orbitals point directly at the six negative charges located on the x, y, and z axes. Consequently, the energy of an electron in these two orbitals (collectively labeled the e_g orbitals) will be greater than it will be for a spherical distribution of negative charge because of increased electrostatic repulsions. In contrast, the other three d orbitals (d_{xy}, d_{xz}, and d_{yz}, collectively called the t_{2g} orbitals) are all oriented at a 45° angle to the coordinate axes, so they point between the six negative charges. The energy of an electron in any of these three orbitals is lower than the energy for a spherical distribution of negative charge.

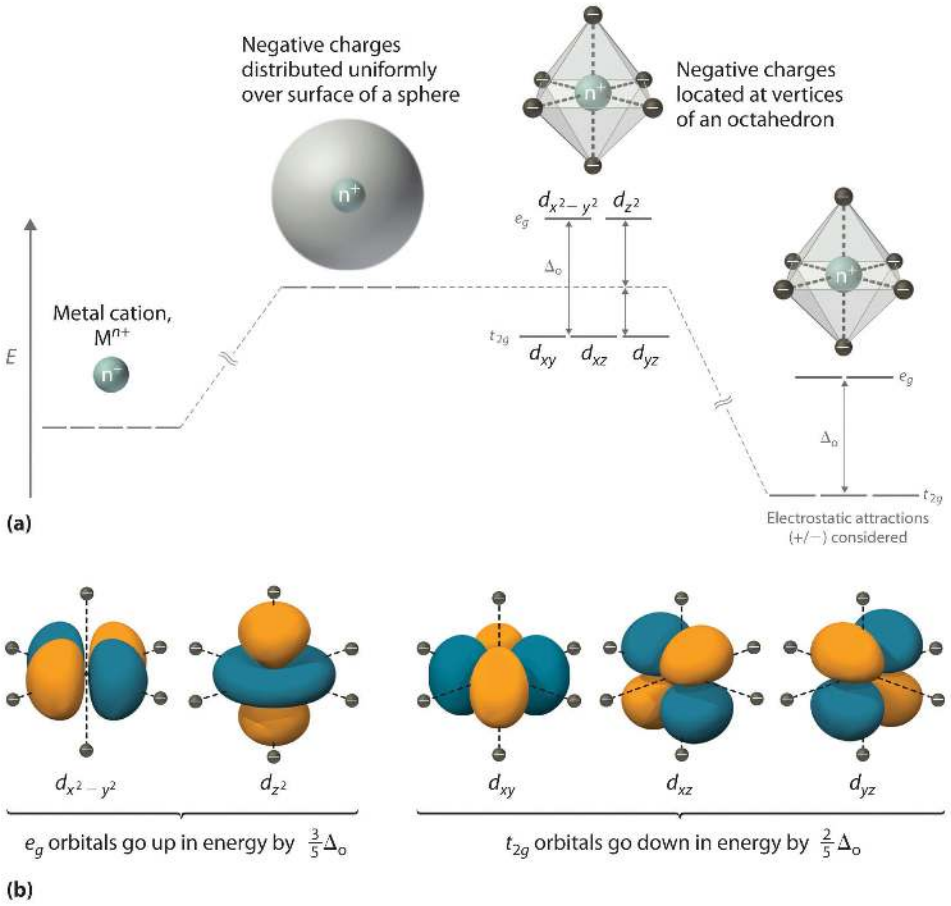


Figure 20.8.1: An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five d Orbitals to Split into Two Sets with Different Energies. (a) Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of −1 at each vertex of an octahedron causes the d orbitals to split into two groups with different energies: the $d_{x^2-y^2}$ and d_{z^2} orbitals increase in energy, while the d_{xy}, d_{xz}, and d_{yz} orbitals decrease in energy. The average energy of the five d orbitals is the same as for a spherical distribution of a −6 charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five d orbitals to decrease in energy but does not affect the splittings of the orbitals. (b) The two e_g orbitals (left) point directly at the six negatively charged ligands, which increases their energy compared with a spherical distribution of negative charge. In contrast, the three t_{2g} orbitals (right) point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge. (CC BY-SA-NC; anonymous by request)

The difference in energy between the two sets of d orbitals is called the crystal field splitting energy (Δ_o), where the subscript o stands for octahedral. As we shall see, the magnitude of the splitting depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. (Crystal field splitting energy also applies to tetrahedral complexes: Δ_t.) It is important to note that the splitting of the d orbitals in a crystal field does not change the total energy of the five d orbitals: the two e_g orbitals increase in energy by $0.6\Delta_o$, whereas the three t_{2g} orbitals decrease in energy by $0.4\Delta_o$. Thus the total change in energy is

$$2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0. \tag{20.8.1}$$

> *Crystal field splitting does not change the total energy of the d orbitals.*

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the d orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the d orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five d orbitals without affecting their splitting (as shown at the far right in Figure 20.8.1*a*).

Electronic Structures of Metal Complexes

We can use the d-orbital energy-level diagram in Figure 20.8.1 to predict electronic structures and some of the properties of transition-metal complexes. We start with the Ti^{3+} ion, which contains a single d electron, and proceed across the first row of the transition metals by adding a single electron at a time. We place additional electrons in the lowest-energy orbital available, while keeping their spins parallel as required by Hund's rule. As shown in Figure 20.8.2, for d^1–d^3 systems—such as $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, and $[Cr(H_2O)_6]^{3+}$, respectively—the electrons successively occupy the three degenerate t_{2g} orbitals with their spins parallel, giving one, two, and three unpaired electrons, respectively. We can summarize this for the complex $[Cr(H_2O)_6]^{3+}$, for example, by saying that the chromium ion has a d^3 electron configuration or, more succinctly, Cr^{3+} is a d^3 ion.

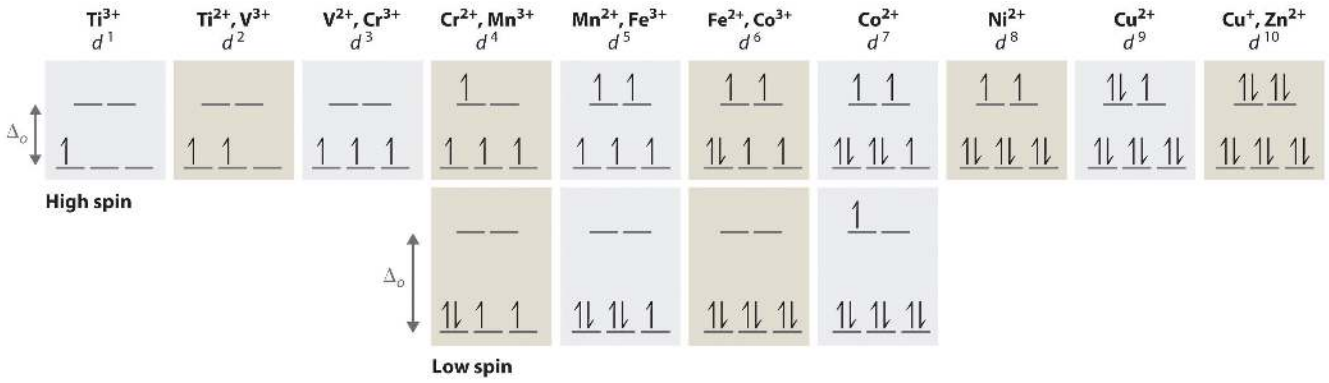


Figure 20.8.2: The Possible Electron Configurations for Octahedral d^n Transition-Metal Complexes (n = 1–10). Two different configurations are possible for octahedral complexes of metals with d^4, d^5, d^6, and d^7 configurations; the magnitude of Δ_o determines which configuration is observed. (CC BY-SA-NC; anonymous by request)

When we reach the d^4 configuration, there are two possible choices for the fourth electron: it can occupy either one of the empty e_g orbitals or one of the singly occupied t_{2g} orbitals. Recall that placing an electron in an already occupied orbital results in electrostatic repulsions that increase the energy of the system; this increase in energy is called the spin-pairing energy (P). If Δ_o is less than P, then the lowest-energy arrangement has the fourth electron in one of the empty e_g orbitals. Because this arrangement results in four unpaired electrons, it is called a high-spin configuration, and a complex with this electron configuration, such as the $[Cr(H_2O)_6]^{2+}$ ion, is called a high-spin complex. Conversely, if Δ_o is greater than P, then the lowest-energy arrangement has the fourth electron in one of the occupied t_{2g} orbitals. Because this arrangement results in only two unpaired electrons, it is called a low-spin configuration, and a complex with this electron configuration, such as the $[Mn(CN)_6]^{3-}$ ion, is called a low-spin complex. Similarly, metal ions with the d^5, d^6, or d^7 electron configurations can be either high spin or low spin, depending on the magnitude of Δ_o.

In contrast, only one arrangement of d electrons is possible for metal ions with d^8–d^{10} electron configurations. For example, the $[Ni(H_2O)_6]^{2+}$ ion is d^8 with two unpaired electrons, the $[Cu(H_2O)_6]^{2+}$ ion is d^9 with one unpaired electron, and the $[Zn(H_2O)_6]^{2+}$ ion is d^{10} with no unpaired electrons.

> *If Δ_o is less than the spin-pairing energy, a high-spin configuration results. Conversely, if Δ_o is greater, a low-spin configuration forms.*

Factors That Affect the Magnitude of Δ_o

The magnitude of Δ_o dictates whether a complex with four, five, six, or seven d electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of Δ_o (i.e., $\Delta_o > P$) yield a low-spin complex, whereas small values of Δ_o (i.e., $\Delta_o < P$) produce a high-spin complex. As we noted, the magnitude of Δ_o depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of Δ_o for some representative transition-metal complexes are given in Table 20.8.1.

Table 20.8.1: Crystal Field Splitting Energies for Some Octahedral (Δ_o)* and Tetrahedral (Δ_t) Transition-Metal Complexes

Octahedral Complexes	Δ_o (cm^{-1})	Octahedral Complexes	Δ_o (cm^{-1})	Tetrahedral Complexes	Δ_t (cm^{-1})

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.

Octahedral Complexes	Δ_o (cm^{-1})	Octahedral Complexes	Δ_o (cm^{-1})	Tetrahedral Complexes	Δ_t (cm^{-1})
$[Ti(H_2O)_6]^{3+}$	20,300	$[Fe(CN)_6]^{4-}$	32,800	VCl_4	9010
$[V(H_2O)_6]^{2+}$	12,600	$[Fe(CN)_6]^{3-}$	35,000	$[CoCl_4]^{2-}$	3300
$[V(H_2O)_6]^{3+}$	18,900	$[CoF_6]^{3-}$	13,000	$[CoBr_4]^{2-}$	2900
$[CrCl_6]^{3-}$	13,000	$[Co(H_2O)_6]^{2+}$	9300	$[CoI_4]^{2-}$	2700
$[Cr(H_2O)_6]^{2+}$	13,900	$[Co(H_2O)_6]^{3+}$	27,000		
$[Cr(H_2O)_6]^{3+}$	17,400	$[Co(NH_3)_6]^{3+}$	22,900		
$[Cr(NH_3)_6]^{3+}$	21,500	$[Co(CN)_6]^{3-}$	34,800		
$[Cr(CN)_6]^{3-}$	26,600	$[Ni(H_2O)_6]^{2+}$	8500		
$Cr(CO)_6$	34,150	$[Ni(NH_3)_6]^{2+}$	10,800		
$[MnCl_6]^{4-}$	7500	$[RhCl_6]^{3-}$	20,400		
$[Mn(H_2O)_6]^{2+}$	8500	$[Rh(H_2O)_6]^{3+}$	27,000		
$[MnCl_6]^{3-}$	20,000	$[Rh(NH_3)_6]^{3+}$	34,000		
$[Mn(H_2O)_6]^{3+}$	21,000	$[Rh(CN)_6]^{3-}$	45,500		
$[Fe(H_2O)_6]^{2+}$	10,400	$[IrCl_6]^{3-}$	25,000		
$[Fe(H_2O)_6]^{3+}$	14,300	$[Ir(NH_3)_6]^{3+}$	41,000		

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.

Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford, Inorganic Chemistry, 2nd ed. (New York: W. H. Freeman and Company, 1994).

Factor 1: Charge on the Metal Ion

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to it. Both factors decrease the metal–ligand distance, which in turn causes the negatively charged ligands to interact more strongly with the d orbitals. Consequently, the magnitude of Δ_o increases as the charge on the metal ion increases. Typically, Δ_o for a tripositive ion is about 50% greater than for the dipositive ion of the same metal; for example, for $[V(H_2O)_6]^{2+}$, Δ_o = 11,800 cm^{-1}; for $[V(H_2O)_6]^{3+}$, Δ_o = 17,850 cm^{-1}.

Factor 2: Principal Quantum Number of the Metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of Δ_o increases with increasing principal quantum number: Δ_o (3d) < Δ_o (4d) < Δ_o (5d). The data for hexaammine complexes of the trivalent Group 9 metals illustrate this point:

$$[Co(NH_3)_6]^{3+}: \Delta_o = 22{,}900\ cm^{-1}$$

$$[Rh(NH_3)_6]^{3+}: \Delta_o = 34{,}100\ cm^{-1}$$

$$[Ir(NH_3)_6]^{3+}: \Delta_o = 40{,}000\ cm^{-1}$$

The increase in Δ_o with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger d orbital–ligand interactions.

Factor 3: The Nature of the Ligands

Experimentally, it is found that the Δ_o observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of Δ_o decreases as the size of the donor atom increases. For example, Δ_o values for halide complexes generally decrease in the order $F^- > Cl^- > Br^- > I-$ because smaller, more localized charges, such as we see for F^-, interact more strongly with the d orbitals of the metal ion. In addition, a small neutral ligand with a highly localized lone pair, such as NH_3, results in significantly larger Δ_o values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as F^-. The experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series, shown here in order of decreasing Δ_o:

$$\underset{\text{strong-field ligands}}{CO \approx CN^- > NO_2^-} > en > NH_3 > \underset{\text{intermediate-field ligands}}{SCN^- > H_2O} > oxalate^{2-} > OH^- > F > acetate^- > \underset{\text{weak-field ligands}}{Cl^- > Br^- > I^-}$$

The values of Δ_o listed in Table 20.8.1 illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

> *The largest Δ_o splittings are found in complexes of metal ions from the third row of the transition metals with charges of at least +3 and ligands with localized lone pairs of electrons.*

Example 20.8.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[CoF_6]^{3-}$
b. $[Rh(CO)_2Cl_2]^-$

Given: complexes

Asked for: structure, high spin versus low spin, and the number of unpaired electrons

Strategy:

a. From the number of ligands, determine the coordination number of the compound.
b. Classify the ligands as either strong field or weak field and determine the electron configuration of the metal ion.
c. Predict the relative magnitude of Δ_o and decide whether the compound is high spin or low spin.
d. Place the appropriate number of electrons in the d orbitals and determine the number of unpaired electrons.

Solution

a. A With six ligands, we expect this complex to be octahedral.

B The fluoride ion is a small anion with a concentrated negative charge, but compared with ligands with localized lone pairs of electrons, it is weak field. The charge on the metal ion is +3, giving a d^6 electron configuration.

C Because of the weak-field ligands, we expect a relatively small Δ_o, making the compound high spin.

D In a high-spin octahedral d^6 complex, the first five electrons are placed individually in each of the d orbitals with their spins parallel, and the sixth electron is paired in one of the t_{2g} orbitals, giving four unpaired electrons.

b. A This complex has four ligands, so it is either square planar or tetrahedral.

B C Because rhodium is a second-row transition metal ion with a d^8 electron configuration and CO is a strong-field ligand, the complex is likely to be square planar with a large Δ_o, making it low spin. Because the strongest d-orbital interactions are along the x and y axes, the orbital energies increase in the order $d_{z^2}d_{yz}$, and d_{xz} (these are degenerate); d_{xy}; and $d_{x^2-y^2}$.

D The eight electrons occupy the first four of these orbitals, leaving the $d_{x^2-y^2}$. orbital empty. Thus there are no unpaired electrons.

Exercise 20.8.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[Mn(H_2O)_6]^{2+}$
b. $[PtCl_4]^{2-}$

Answer a

octahedral; high spin; five

Answer b

square planar; low spin; no unpaired electrons

Crystal Field Stabilization Energies

Recall that stable molecules contain more electrons in the lower-energy (bonding) molecular orbitals in a molecular orbital diagram than in the higher-energy (antibonding) molecular orbitals. If the lower-energy set of d orbitals (the t_{2g} orbitals) is selectively populated by electrons, then the stability of the complex increases. For example, the single d electron in a d^1 complex such as $[Ti(H_2O)_6]^{3+}$ is located in one of the t_{2g} orbitals. Consequently, this complex will be more stable than expected on purely electrostatic grounds by $0.4\Delta_o$. The additional stabilization of a metal complex by selective population of the lower-energy d orbitals is called its crystal field stabilization energy (CFSE). The CFSE of a complex can be calculated by multiplying the number of electrons in t_{2g} orbitals by the energy of those orbitals ($-0.4\Delta_o$), multiplying the number of electrons in e_g orbitals by the energy of those orbitals ($+0.6\Delta_o$), and summing the two. Table 20.8.2 gives CFSE values for octahedral complexes with different d electron configurations. The CFSE is highest for low-spin d^6 complexes, which accounts in part for the extraordinarily large number of Co(III) complexes known. The other low-spin configurations also have high CFSEs, as does the d^3 configuration.

Table 20.8.2: CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of Δo)

	High Spin		CFSE (Δ_o)	Low Spin		CFSE (Δ_o)
	t_{2g}	e_g		t_{2g}	e_g	
d^0			0			
d^1	↑		0.4			
d^2	↑ ↑		0.8			
d^3	↑ ↑ ↑		1.2			
d^4	↑ ↑ ↑	↑	0.6	↑↓ ↑ ↑		1.6
d^5	↑ ↑ ↑	↑ ↑	0.0	↑↓ ↑↓ ↑		2.0
d^6	↑↓ ↑ ↑	↑ ↑	0.4	↑↓ ↑↓ ↑↓		2.4
d^7	↑↓ ↑↓ ↑	↑ ↑	0.8	↑↓ ↑↓ ↑↓	↑	1.8
d^8	↑↓ ↑↓ ↑↓	↑ ↑	1.2			
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	0.6			
d^{10}	↑↓ ↑↓ ↑↓	↑↓ ↑↓	0.0			

CFSEs are important for two reasons. First, the existence of CFSE nicely accounts for the difference between experimentally measured values for bond energies in metal complexes and values calculated based solely on electrostatic interactions. Second, CFSEs represent relatively large amounts of energy (up to several hundred kilojoules per mole), which has important chemical consequences.

> *Octahedral d^3 and d^8 complexes and low-spin d^6, d^5, d^7, and d^4 complexes exhibit large CFSEs.*

Summary

Crystal field theory, which assumes that metal–ligand interactions are only electrostatic in nature, explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. Crystal field theory (CFT) is a bonding model that explains many properties of transition metals that cannot be explained using valence bond theory. In CFT, complex formation is assumed to be due to electrostatic interactions between a central metal ion and a set of negatively charged ligands or ligand dipoles arranged around the metal ion. Depending on the arrangement of the ligands, the d orbitals split into sets of orbitals with different energies. The difference between the energy levels in an octahedral complex is called the crystal field splitting energy (Δ_o), whose magnitude depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. The spin-pairing energy (P) is the increase in energy that occurs when an electron is added to an already occupied orbital. A high-spin configuration occurs when the Δ_o is less than P, which produces complexes with the maximum number of unpaired electrons possible. Conversely, a low-spin configuration occurs when the Δ_o is greater than P, which produces complexes with the minimum number of unpaired electrons possible. Strong-field ligands interact strongly with the d orbitals of the metal ions and give a large Δ_o, whereas weak-field ligands interact more weakly and give a smaller Δ_o. The colors of transition-metal complexes depend on the environment of the metal ion and can be explained by CFT.

20.8: Bonding in Octahedral Complex Ions- Crystal Field Theory is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **24.5: Bonding in Complex Ions: Crystal Field Theory** is licensed CC BY-NC-SA 4.0.

20.9: Bonding in Non-Octahedral Complex Ions- Crystal Field Theory

Learning Objectives

- Understand the d-orbital degeneracies of square planar and tetrahedral metal complexes.

Tetragonal and Square Planar Complexes

If two *trans*- ligands in an octahedral complex are either chemically different from the other four (as in *trans*-$[Co(NH_3)_4Cl_2]^+$), or at a different distance from the metal than the other four, the result is a tetragonally distorted octahedral complex. The electronic structures of such complexes are best viewed as the result of distorting an octahedral complex. Consider, for example, an octahedral complex such as $[Co(NH_3)_6]^{3+}$: two *trans*- NH_3 molecules are slowly removed from the metal along the ±z axes, as shown in the top half of Figure 20.9.1. As the two axial Co–N distances increase simultaneously, the d-orbitals that interact most strongly with the two axial ligands decrease in energy due to a decrease in electrostatic repulsions between the electrons in these orbitals and the negative ends of the ligand dipoles. The affected d orbitals are those with a component along the ±z axes—d_{z^2}, d_{xz}, and d_{yz}. These orbitals are not affected equally, however: because the d_{z^2} orbital points directly at the two ligands being removed, its energy will decrease much more rapidly than the degenerate energies of the d_{xz} and d_{yz}, as shown in the bottom half of Figure 20.9.1. In addition, the effective positive charge on the metal increases somewhat as the axial ligands are removed, increasing the attraction between the four remaining ligands and the metal. This increases the extent of their interactions with the other two d orbitals and increases their energies. Again, the two d orbitals are not affected equally: because the $d_{x^2-y^2}$ orbital points directly at the four in-plane ligands, its energy increases to a greater extent than the energy of the d_{xy} orbital, which points between the in-plane ligands. If the two axial ligands are moved infinitely far away from the metal, a square planar complex is formed. The energy of the d_{xy} orbital actually surpasses that of the d_{z^2} orbital in the process. The largest orbital splitting in a square planar complex, between the $d_{x^2-y^2}$ and d_{xy} energy levels, is identical in magnitude to Δ_o.

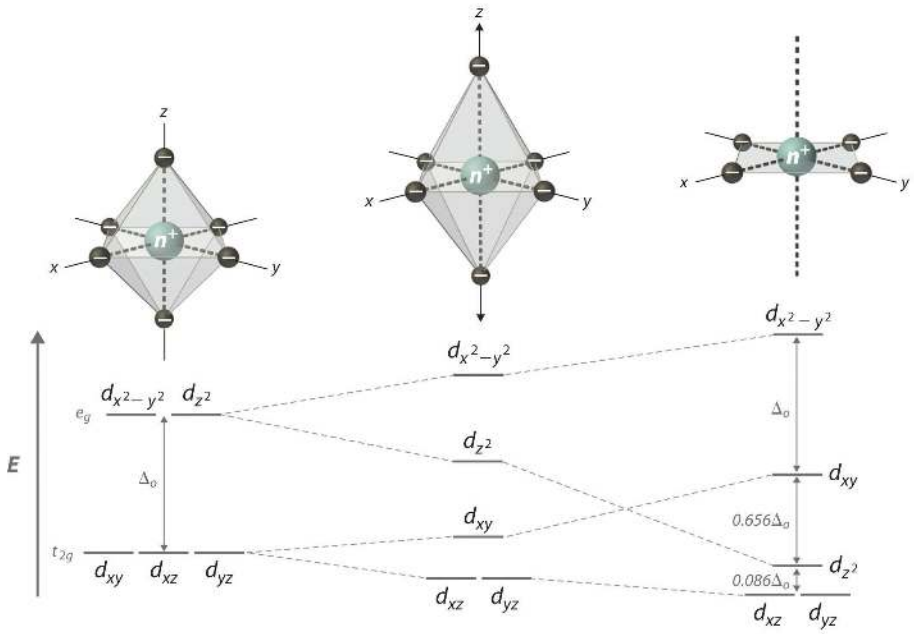


Figure 20.9.1 d-Orbital Splittings for Tetragonal and Square Planar Complexes. (CC BY-SA-NC; anonymous by request)

Moving the two axial ligands away from the metal ion along the z axis initially generates an elongated octahedral complex (the center compound of Figure 20.9.1) and eventually produces a square planar complex (right). As shown below the structures, an axial elongation causes the d_{z^2} d_{xz} and d_{yz} orbitals to decrease in energy and the $d_{x^2-y^2}$ and d_{xy} orbitals to increase in energy. The change in energy is not the same for all five d orbitals. The d_{z^2} orbital has a smaller xy component than does the d_{xy} orbital, so it reaches a lower energy level; thus, the order of these orbitals is reversed.

Tetrahedral Complexes

In a tetrahedral arrangement of four ligands around a metal ion, none of the ligands lies on any of the three coordinate axes (illustrated in part (a) in Figure 20.9.2); consequently, none of the five d orbitals points directly at the ligands. Nonetheless, the d_{xy}, d_{xz}, and d_{yz} orbitals interact more strongly with the ligands than do $d_{x^2-y^2}$ and d_{z^2}; this again results in a splitting of the five d orbitals into two groups. The splitting of the energies of the orbitals in a tetrahedral complex (Δ_t) is much smaller than that for an octahedral complex (Δ_o), however, for two reasons: first, the d orbitals interact less strongly with the ligands in a tetrahedral arrangement; second, there are only four negatively-charged regions rather than six, which decreases the electrostatic interactions by one-third if all other factors are equal. It can be shown that for complexes of the same metal ion with the same charge, the same ligands, and the same M–L distance, $\Delta_t = \frac{4}{9}\Delta_o$. The relationship between the splitting of the five d orbitals in octahedral and tetrahedral crystal fields imposed by the same ligands is shown schematically in part (b) in Figure 20.9.2

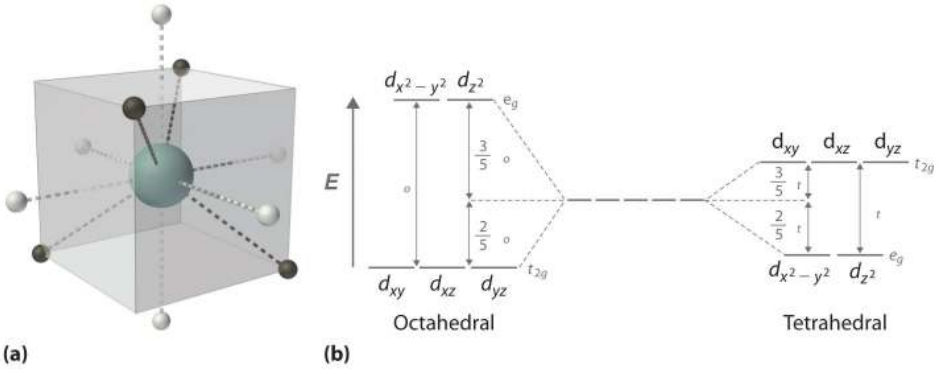


Figure 20.9.2: d-Orbital Splittings for a Tetrahedral Complex. (a) In a tetrahedral complex, none of the five d orbitals points directly at or between the ligands. (b) Because the d_{xy}, d_{xz}, and d_{yz}orbitals (the t_{2g} orbitals) interact more strongly with the ligands than do the $d_{x^2-y^2}$ and d_{z^2} orbitals (the e_g orbitals), the order of orbital energies in a tetrahedral complex is the opposite of the order in an octahedral complex. (CC BY-SA-NC; anonymous by request)

> *Δ_t < Δ_o because of weaker d-orbital–ligand interactions and decreased electrostatic interactions.*

Example 20.9.1: Predicting Structure

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

1. $[Cu(NH_3)_4]^{2+}$
2. $[Ni(CN)_4]^{2-}$

Solution

Because Δ_o is so large for the second- and third-row transition metals, all four-coordinate complexes of these metals are square planar due to the much higher crystal field stabilization energy (CFSE) for square planar versus tetrahedral structures. The only exception is for d^{10} metal ions such as Cd^{2+}, which have zero CFSE and are therefore tetrahedral as predicted by the VSEPR model. Four-coordinate complexes of the first-row transition metals can be either square planar or tetrahedral; the former is favored by strong-field ligands, whereas the latter is favored by weak-field ligands. For example, the $[Ni(CN)_4]^{2-}$ ion is square planar, while the $[NiCl_4]^{2-}$ ion is tetrahedral.

1.

The copper in this complex is a d^9 ion and it has a coordination number of 4. So it is probably either square planar or tetrahedral. To estimate which, we need to fill in the CFT splitting diagrams for each with 9 electrons and ask which has a lower energy. Comparing the square planer (Figure 20.9.1) splitting diagram with tetrahedral (Figure 20.9.2), suggests that 9 electrons will have a net lower total energy for square planar (since the $d_{x^2-y^2}$ orbital is high in energy, the others are lower).

For the square planar structure, neither high nor low spin states are possible (only one state) with a single unpaired electron.

2.

The nickle in this complex is a d^8 ion and it has a coordination number of 4. So it is probably either square planar or tetrahedral. To estimate which, we need to fill in the CFT splitting diagrams for each with 8 electrons and ask which has a

lower energy. Comparing the square planer (Figure 20.9.1) splitting diagram with tetrahedral (Figure 20.9.2), suggests that 8 electrons will have a net lower total energy for square planar (since the $d_{x^2-y^2}$ orbital is high in energy, the others are lower).

For the square planar structure, it is a low spin complex since a high spin requires a lot of energy to promote to the $d_{x^2-y^2}$ orbital. Hence, there are no unpaired electrons

? Exercise 20.9.1

What are the geometries of the following two complexes?

1. $[AlCl_4]^-$
2. $[Ag(NH_3)_2]^+$

Answer 1

tetrahedral

Answer 2

linear

Summary

Distorting an octahedral complex by moving opposite ligands away from the metal produces a tetragonal or square planar arrangement, in which interactions with equatorial ligands become stronger. Because none of the d orbitals points directly at the ligands in a tetrahedral complex, these complexes have smaller values of the crystal field splitting energy Δ_t. In tetrahedral molecular geometry, a central atom is located at the center of four substituents, which form the corners of a tetrahedron. Tetrahedral geometry is common for complexes where the metal has d^0 or d^{10} electron configuration. The CFT diagram for tetrahedral complexes has $d_{x^2-y^2}$ and d_{z^2} orbitals equally low in energy because they are between the ligand axis and experience little repulsion. In square planar molecular geometry, a central atom is surrounded by constituent atoms, which form the corners of a square on the same plane. The square planar geometry is prevalent for transition metal complexes with d^8 configuration. The CFT diagram for square planar complexes can be derived from octahedral complexes yet the $d_{x^2-y^2}$ level is the most destabilized and is left unfilled.

20.9: Bonding in Non-Octahedral Complex Ions- Crystal Field Theory is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Non-octahedral Complexes** by Anonymous is licensed CC BY-NC-SA 4.0.

20.10: Magnetic Behavior of Atoms, Molecules, and Materials

Learning Objectives

- To understand the difference between Ferromagnetism, paramagnetism and diamagnetism
- To identify if a chemical will be paramagnetic or diamagnetic when exposed to an external magnetic field

The magnetic moment of a system measures the strength and the direction of its magnetism. The term itself usually refers to the magnetic dipole moment. Anything that is magnetic, like a bar magnet or a loop of electric current, has a magnetic moment. A magnetic moment is a vector quantity, with a magnitude and a direction. An electron has an electron magnetic dipole moment, generated by the electron's intrinsic spin property, making it an electric charge in motion. There are many different magnetic behavior including paramagnetism, diamagnetism, and ferromagnetism.

An interesting characteristic of transition metals is their ability to form magnets. Metal complexes that have unpaired electrons are magnetic. Since the last electrons reside in the d orbitals, this magnetism must be due to having unpaired d electrons. The spin of a single electron is denoted by the quantum number m_s as +(1/2) or –(1/2). This spin is negated when the electron is paired with another, but creates a weak magnetic field when the electron is unpaired. More unpaired electrons increase the paramagnetic effects. The electron configuration of a transition metal (d-block) changes in a coordination compound; this is due to the repulsive forces between electrons in the ligands and electrons in the compound. Depending on the strength of the ligand, the compound may be paramagnetic or diamagnetic.

Ferromagnetism (Permanent Magnet)

Ferromagnetism is the basic mechanism by which certain materials (such as iron) form **permanent magnets**. This means the compound shows permanent magnetic properties rather than exhibiting them only in the presence of an external magnetic field (Figure 20.10.1). In a ferromagnetic element, electrons of atoms are grouped into domains in which each domain has the same charge. In the presence of a magnetic field, these domains line up so that charges are parallel throughout the entire compound. Whether a compound can be ferromagnetic or not depends on its number of unpaired electrons and on its atomic size.

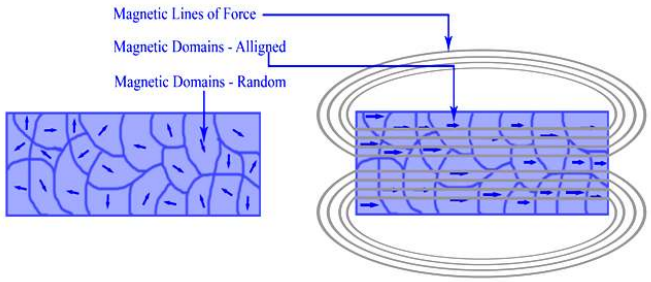


Figure 20.10.1: Ferromagnetism (a) nonmagnatized material and (2) Magnetized material with corresponding magnetic fields shown.

Ferromagnetism, the permanent magnetism associated with nickel, cobalt, and iron, is a common occurrence in everyday life. Examples of the knowledge and application of ferromagnetism include Aristotle's discussion in 625 BC, the use of the compass in 1187, and the modern-day refrigerator. Einstein demonstrated that electricity and magnetism are inextricably linked in his theory of special relativity.

Paramagnetism (Attracted to Magnetic Field)

Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. Hund's Rule states that electrons must occupy every orbital singly before any orbital is doubly occupied. This may leave the atom with many unpaired electrons. Because unpaired electrons can spin in either direction, they display magnetic moments in any direction. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen, O_2 is a good example of paramagnetism (described via molecular orbital theory). The following video shows liquid oxygen attracted into a magnetic field created by a strong magnet:



Video 20.10.1: Paramagnetism of Liquid Oxygen

Diamagnetism (Repelled by Magnetic Field)

As shown in the video, molecular oxygen (O_2) is paramagnetic and is attracted to the magnet. In contrast, molecular nitrogen (N_2) has no unpaired electrons and is diamagnetic; it is unaffected by the magnet. Diamagnetic substances are characterized by paired electrons, e.g., no unpaired electrons. According to the Pauli Exclusion Principle which states that no two electrons may occupy the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out; thus there is no net magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly ***repelled*** by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure 20.10.2

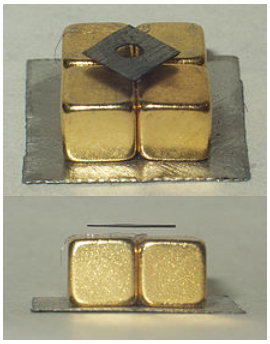


Figure 20.10.2: Levitating pyrolytic carbon: A small (~6 mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5 mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). (Public Domain; Splarka via Wikipedia).

How to Tell if a Substance is Paramagnetic or Diamagnetic

The magnetic properties of a substance can be determined by examining its electron configuration: If it has unpaired electrons, then the substance is paramagnetic and if all electrons are paired, the substance is then diamagnetic. This process can be broken into three steps:

1. Write down the electron configuration
2. Draw the valence orbitals
3. Identify if unpaired electrons exist
4. Determine whether the substance is paramagnetic or diamagnetic

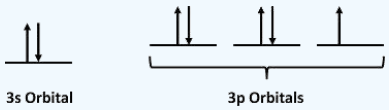
Example 20.10.1: Chlorine Atoms

Step 1: Find the electron configuration

For Cl atoms, the electron configuration is $3s^2 3p^5$

Step 2: Draw the valence orbitals

Ignore the core electrons and focus on the valence electrons only.



Step 3: Look for unpaired electrons

There is one unpaired electron.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

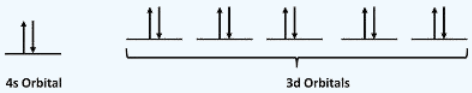
Since there is an unpaired electron, Cl atoms are paramagnetic (albeit, weakly).

Example 20.10.2: Zinc Atoms

Step 1: Find the electron configuration

For Zn atoms, the electron configuration is $4s^2 3d^{10}$

Step 2: Draw the valence orbitals



Step 3: Look for unpaired electrons

There are no unpaired electrons.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

Because there are no unpaired electrons, Zn atoms are diamagnetic.

Exercise 20.10.1

a. How many unpaired electrons are found in oxygen atoms ?
b. How many unpaired electrons are found in bromine atoms?
c. Indicate whether boron atoms are paramagnetic or diamagnetic.
d. Indicate whether F^- ions are paramagnetic or diamagnetic.
e. Indicate whether Fe^{2+} ions are paramagnetic or diamagnetic.

Answer a

The O atom has $2s^2 2p^4$ as the electron configuration. Therefore, O has 2 unpaired electrons.

Answer b

The Br atom has $4s^2 3d^{10} 4p^5$ as the electron configuration. Therefore, Br has 1 unpaired electron.

Answer c

The B atom has $2s^2 2p^1$ as the electron configuration. Because it has one unpaired electron, it is paramagnetic.

Answer d

The F^- ion has $2s^2 2p^6$ as the electron configuration. Because it has no unpaired electrons, it is diamagnetic.

Answer e

The Fe^{2+} ion has $3d^6$ as the electron configuration. Because it has 4 unpaired electrons, it is paramagnetic.

References

1. Pettrucci, Ralph H. General Chemistry: Principles and Modern Applications. 9th. Upper Saddle River: Pearson Prentice Hall, 2007
2. Sherman, Alan, Sharon J. Sherman, and Leonard Russikoff. Basic Concepts of Chemistry Fifth Edition. Boston, MA: Houghton Mifflin Company, 1992. Print.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)
- Dr. Richard Spinney (The Ohio State University)

20.10: Magnetic Behavior of Atoms, Molecules, and Materials is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

20.11: Magnetic Behavior of Complex Ions

Learning Objectives

- Discuss the correlation between the electronic structure of a coordination complex and its magnetic properties

Experimental evidence of magnetic measurements supports the theory of high- and low-spin complexes. Remember that molecules such as O_2 that contain unpaired electrons are paramagnetic. Paramagnetic substances are attracted to magnetic fields. Many transition metal complexes have unpaired electrons and hence are paramagnetic. Molecules such as N_2 and ions such as Na^+ and $[Fe(CN)_6]^{4-}$ that contain no unpaired electrons are **diamagnetic**. Diamagnetic substances have a slight tendency to be **repelled** by magnetic fields.

When an electron in an atom or ion is unpaired, the magnetic moment due to its spin makes the entire atom or ion **paramagnetic**. The size of the magnetic moment of a system containing unpaired electrons is related directly to the number of such electrons: the greater the number of unpaired electrons, the larger the magnetic moment. Magnetic susceptibility measures the force experienced by a substance in a magnetic field. When we compare the weight of a sample to the weight measured in a magnetic field (Figure 20.11.1), paramagnetic samples that are attracted to the magnet will appear heavier because of the force exerted by the magnetic field. We can calculate the number of unpaired electrons based on the increase in weight.

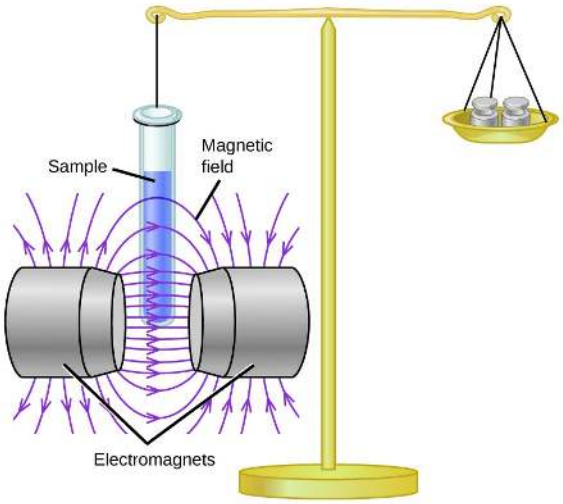


Figure 20.11.1: A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample. (CC BY-SA 3.0; OpenStax).

From this experiment, the measured magnetic moment of low-spin d^6 $[Fe(CN)_6]4-$ ion confirms that iron is diamagnetic, whereas the high-spin d^6 $[Fe(H_2O)_6]^{2+}$ complex has four unpaired electrons with a magnetic moment that confirms this arrangement. Therefore, the observed magnetic moment is used to determine the number of unpaired electrons present.

Magnetic Properties of Coordination Compounds

An interesting characteristic of transition metals is their ability to form magnets. Metal complexes that have unpaired electrons are magnetic. Since the last electrons reside in the d orbitals, this magnetism must be due to having unpaired d electrons. Considering only monometallic complexes, unpaired electrons arise because the complex has an odd number of electrons or because electron pairing is destabilized. For example, the Ti(III) ion has one d electron and must be (weakly) paramagnetic, regardless of the geometry or the nature of the ligands. However, the Ti(II) ion with two d-electrons, sometimes forms complexes with two unpaired electrons and sometimes forms complexes with no unpaired electrons.

As an example, Fe prefers to exist as Fe^{3+} and is known to have a coordination number of six. Since the configuration of Fe^{3+} has five d electrons, we would expect to see five unpaired spins in complexes with Fe. This is true for $[FeF_6]^{3-}$; however, $[Fe(CN)_6]^{3-}$ only has one unpaired electron, making it a weaker magnet. This trend can be explained based on the properties of the ligands. Based off the spectrochemical series, we expect CN^- ligands to have a stronger electric field than that of F^- ligands, so the energy differences in the d-orbitals should be greater for the cyanide complex.

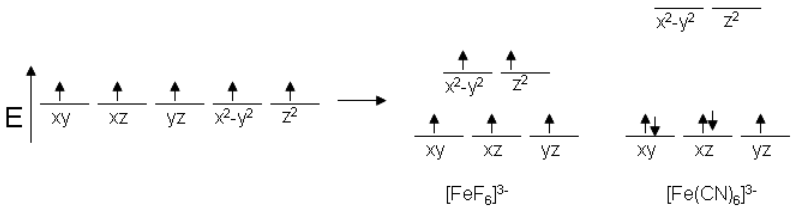


Figure 20.11.2: Crystal field theory splitting diagram. Example of influence of ligand electronic properties on d orbital splitting. This shows the comparison of low-spin versus high-spin electrons.

For this to make sense, there must be some sort of energy benefit to having paired spins for our cyanide complex (the spin pairing energy). That is, the energy level difference must be more than the repulsive energy of pairing electrons together. Since systems strive to achieve the lowest energy possible, the electrons will pair up before they will move to the higher orbitals. This is referred to as low spin, and an electron moving up before pairing is known as high spin.

Exercise 20.11.1

Which ligand is most likely to form a high-spin complexes when bound to transition metals: en, F^- , or CN^-?

Answer

F^- are more likely to form high spin complexes, since is a weak-field ligand on the spectrochemical series.

Tetrahedral complexes have naturally weaker splitting because none of the ligands lie within the plane of the orbitals. As a result, they have either have too many or too few d electrons to warrant consideration about high or low spin configurations. Square planar compounds, on the other hand, stem solely from transition metals with eight d electrons. For example, $[Ni(CN)_4]^{2-}$, $[Pt(NH_3)_3Cl]^+$, and $[PtCl_4]^{2-}$ are all diamagnetic. Since this encompasses the full spectrum of ligand strength, we can conclude that square planar compounds are always low spin and therefore are weakly magnetic.

Example 20.11.2

Which one of the following coordination compounds would you expect to be paramagnetic?

a. $[Zn(NH_3)_4]Cl_2$
b. $K[FeCl_4]$ (low spin, tetrahedral)
c. $[Cd(H_2O)_6]SO_4$

Solution

Let's consider each compound individually. Since each compound has only one complex ion, we only need to consider how the d electrons are distributed in the ligand field of that ion. We can ignore the other parts (the counter ions) of the compound.

a. The zinc ion in $[Zn(NH_3)_4]Cl_2$ has a +2 oxidation state, so it is a d^{10} ion since the zinc atom loses two 4s electrons and no 3d electrons to form the ion. We do not need to fill ion the electrons in the corresponding tetrahedral d-orbital diagram, since we know they will all be paired up. This is a diamagnetic compound.
b. The iron ion in $K[FeCl_4]$ (low spin, tetrahedral) has a 3+ oxidation state so it is a d^5 ion since the iron atom loses two 4s electrons and one 3d electron. Adding 5 electrons to the tetrahedral d-orbital diagram identifies that one electron will be unpaired. This compound will be paramagnetic (but weakly since only on electron is unpaired).
c. The cadmium ion in $[Cd(H_2O)_6]SO_4$ has a +2 oxidation state, so it is a d^{10} ion since the cadmium atom loses two 5s electrons and no 4d electrons to form the ion. We do not need to fill ion the electrons in the corresponding octahedral d-orbital diagram, since we know they will all be paired up. This is a diamagnetic compound.

Exercise 20.11.2

Predict the number of unpaired electrons for each of the following complex ions

a. $[Fe(CN)_6]^{4-}$
b. $[Ru(NH_3)_6]^{3+}$

c. $[Cr(NH_3)_6]^{2+}$
d. $[EuCl_6]^{4-}$

Answer a

Fe^{2+} is $3d^6$ ion and has 0 unpaired electron in low spin complexes

Answer b

Ru^{3+} is $4d^5$ ion and has 1 unpaired electron in low spin complexes

Answer c

Cr^{2+} is $4d^4$ ion and has 4 and 2 unpaired electrons in high spin and low spin complexes, respectively, depending on spin pairing energy

Answer d

Eu^{2+} is $4f^7$ ion and has 7 unpaired electrons in high spin complexes

In bi- and polymetallic complexes, in which the individual centers have an odd number of electrons or electrons are high-spin, the situation is more complicated. If there is interaction between the two (or more) metal centers, the electrons may couple, resulting in a weak magnet, or they may enhance each other. When there is no interaction, the two (or more) individual metal centers behave as if in two separate molecules.

Summary

- Unpaired electrons exist when the complex has an odd number of electrons or because electron pairing is destabilized.
- The more unpaired electrons, the stronger the magnetic property.
- Tetrahedral complexes have weaker splitting because none of the ligands lie within the plane of the orbitals.
- Square planar compounds are always low-spin and therefore are weakly magnetic.
- In bi- and polymetallic complexes, the electrons may couple through the ligands, resulting in a weak magnet, or they may enhance each other.

Contributors and Attributions

- Source: Boundless. "Magnetic Properties." *Boundless Chemistry* Boundless, 26 May. 2016. Retrieved 4 May. 2017 from www.boundless.com/chemistry/...ties-616-6882/.

20.11: Magnetic Behavior of Complex Ions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

20.12: Optical Properties of Coordination Compounds (Color)

The human eye perceives a mixture of all the colors, in the proportions present in sunlight, as white light. Complementary colors, those located across from each other on a color wheel, are also used in color vision. The eye perceives a mixture of two complementary colors, in the proper proportions, as white light. Likewise, when a color is missing from white light, the eye sees its complement. For example, when red photons are absorbed from white light, the eyes see the color green. When violet photons are removed from white light, the eyes see lemon yellow (Figure 20.12.1).

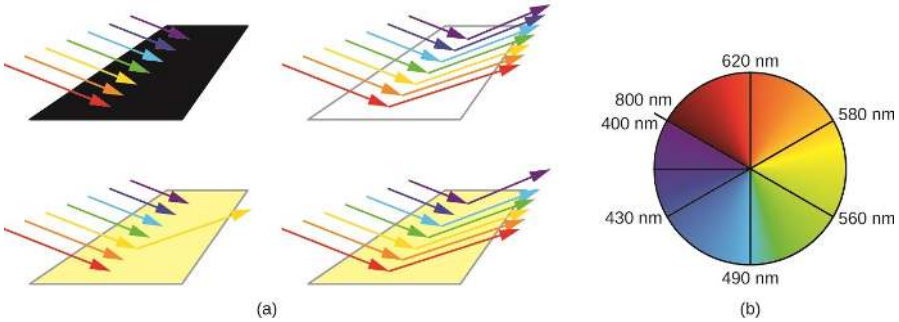


Figure 20.12.1: (a) An object is black if it absorbs all colors of light. If it reflects all colors of light, it is white. An object has a color if it absorbs all colors except one, such as this yellow strip. The strip also appears yellow if it absorbs the complementary color from white light (in this case, indigo). (b) Complementary colors are located directly across from one another on the color wheel. (CC BY 4.0; OpenStax)

The blue color of the $[Cu(NH_3)_4]^{2+}$ ion results because this ion absorbs orange and red light, leaving the complementary colors of blue and green (Figure 20.12.2). If white light (ordinary sunlight, for example) passes through $[Cu(NH_3)_4]SO_4$ solution, some wavelengths in the light are absorbed by the solution. The $[Cu(NH_3)_4]^{2+}$ ions in solution absorb light in the red region of the spectrum. The light which passes through the solution and out the other side will have all the colors in it except for the red. We see this mixture of wavelengths as pale blue (cyan). The diagram gives an impression of what happens if you pass white light through a $[Cu(NH_3)_4]SO_4$ solution.

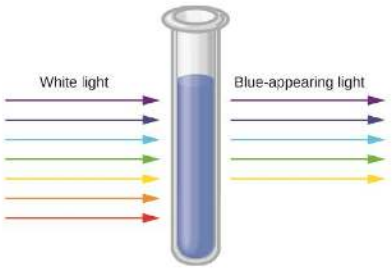


Figure 20.12.2: A solution of $[Cu(NH_3)_4]^{2+}$ ions absorbs red and orange light, so the transmitted light appears as the complementary color, blue. (CC BY 4.0; OpenStax)

Working out what color you will see is not easy if you try to do it by imagining "mixing up" the remaining colors. You would not have thought that all the other colors apart from some red would look cyan, for example. Sometimes what you actually see is quite unexpected. Mixing different wavelengths of light doesn't give you the same result as mixing paints or other pigments. You can, however, sometimes get some estimate of the color you would see using the idea of complementary colors.

Recall that the color we observe when we look at an object or a compound is due to light that is transmitted or reflected, not light that is absorbed, and that reflected or transmitted light is complementary in color to the light that is absorbed. Thus a green compound absorbs light in the red portion of the visible spectrum and vice versa, as indicated by the complementary color wheel.



Figure 20.12.3: The partially filled d orbitals of the stable ions $Cr^{3+}(aq)$, $Fe^{3+}(aq)$, and $Co^{2+}(aq)$ (left, center and right, respectively) give rise to various colors. (credit: Sahar Atwa)

The striking colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy d orbital to a higher-energy d orbital, which is called a **d–d transition** (Figure 20.12.4). For a photon to effect such a transition, its energy must be equal to the difference in energy between the two d orbitals, which depends on the magnitude of Δ_o.

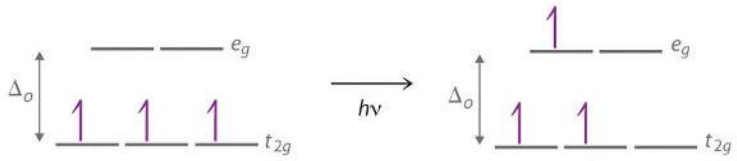


Figure 20.12.4: In a d–d transition of an octahedral complex, an electron in one of the t_{2g} orbitals of an octahedral complex such as the $[Cr(H_2O)_6]^{3+}$ ion absorbs a photon of light with energy equal to Δ_o, which causes the electron to move to an empty or singly occupied e_g orbital.

Example 20.12.1: Colors of Complexes

The octahedral complex $[Ti(H_2O)_6]^{3+}$ has a single *d* electron. To excite this electron from the ground state t_{2g} orbital to the e_g orbital, this complex absorbs light from 450 to 600 nm. The maximum absorbance corresponds to Δ_o and occurs at 499 nm. Calculate the value of Δ_o in Joules and predict what color the solution will appear.

Solution

We can convert wavelength to frequency:

$$\nu = \frac{c}{\lambda}$$

$$= \frac{3.00 \times 10^8\ m/s}{(499\ \cancel{nm}) \times \left(\frac{1\ m}{10^9\ \cancel{nm}}\right)}$$

$$= 6.01 \times 10^{14} s^{-1} = 6.01 \times 10^{14}\ Hz$$

And then using Planck's equation that related the frequency of light to energy

$$E = h\nu$$

so

$$E\ = (6.63 \times 10^{-34} \text{J·s}) \times (6.01 \times 10^{14}\ Hz)$$

$$= 3.99 \times 10^{-19}\ J$$

Because the complex absorbs 600 nm (orange) through 450 (blue), the indigo, violet, and red wavelengths will be transmitted, and the complex will appear purple.

Note: This is the energy for one transition (i.e., in one complex). If you want to calculate the energy in J/mol, then you have to multiply this by Avogadro's number (N_A).

Exercise 20.12.1

A complex that appears green, absorbs photons of what wavelengths?

Answer

red, 620–800 nm

Color Depends on Oxidation State

Small changes in the relative energies of the orbitals that electrons are transitioning between can lead to drastic shifts in the color of light absorbed. Therefore, the colors of coordination compounds depend on many factors. As shown in Figure 20.12.4, different aqueous metal ions can have different colors. In addition, different oxidation states of one metal can produce different colors, as shown for the vanadium complexes in the link below.



Watch this video of the reduction of vanadium complexes to observe the colorful effect of changing oxidation states.

Color Depends on Ligand Field

The specific ligands coordinated to the metal center also influence the color of coordination complexes. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of Δ_o, which depends on the structure of the complex. For example, the complex $[Cr(NH_3)_6]^{3+}$ has strong-field ligands and a relatively large Δ_o. Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color. A related complex with weak-field ligands, the $[Cr(H_2O)_6]^{3+}$ ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color. For example, the iron(II) complex $[Fe(H_2O)_6]SO_4$ appears blue-green because the high-spin complex absorbs photons in the red wavelengths (Figure 20.12.5). In contrast, the low-spin iron(II) complex $K_4[Fe(CN)_6]$ appears pale yellow because it absorbs higher-energy violet photons.



Figure 20.12.5: Both (a) hexaaquairon(II) sulfate and (b) potassium hexacyanoferrate(II) contain d^6 iron(II) octahedral metal centers, but they absorb photons in different ranges of the visible spectrum. (CC BY 4.0; OpenStax)

In general, strong-field ligands cause a large split in the energies of *d* orbitals of the central metal atom (large Δ_{oct}). Transition metal coordination compounds with these ligands are yellow, orange, or red because they absorb higher-energy violet or blue light. On the other hand, coordination compounds of transition metals with weak-field ligands are often blue-green, blue, or indigo because they absorb lower-energy yellow, orange, or red light.

> *Strong-field ligands cause a large split in the energies of d orbitals of the central metal atom and transition metal coordination compounds with these ligands are typically yellow, orange, or red because they absorb higher-energy violet or blue light. Coordination compounds of transition metals with weak-field ligands are often blue-green, blue, or indigo because they absorb lower-energy yellow, orange, or red light.*

Example 20.12.2: Matching Colors to Ligand Fields

Identify the color (either blue, green, yellow, or orange) for the following complex ions formed with Co^{3+}:

a. $[Co(CN)_6]_3^{-2}$
b. $[Co(NH_3)_6]_3^{3+}$

c. $[CoF_6]_3^{-4}$
d. $[Co(H_2O)_6]^{3+}$

Solution

Each of these complex ions has the same metal with the same oxidation state, so the ligand field is the relevant factors. Each of the complex ions also has an octahedral ligand field, so we only need to compare the strength of the ligands in determining Δ_o, which is determined by the spectrochemical series.

The ligands for each complex ions are: (a) CN^-, (b) NH_3, (c) F^- and (d) H_2O, which are ranked in increasing Δ_o magnitude:

$$F^- < H_2O < NH_3 < CN^- \tag{20.12.1}$$

The relationship between the Δ_o and the energy of the photons are absorbed in the d-d transition of Co^{3+} is given by equating Planck's equation to the crystal field splitting parameter:

$$E = h\nu = \frac{hc}{\lambda} = \Delta_o \tag{20.12.2}$$

Now, we need to get a relative correlation between observed color (to the eye) and the wavelength of the light that is absorbed. From the complementary color wheel in Figure 20.12.1we get the following relationships (arranged from highest energy absorbed to lowest):

- 400-nm Violet light absorbed → Green-yellow observed
- 430-nm Blue light absorbed → Orange observed
- 450-nm Blue light absorbed → Yellow observed
- 490-nm Blue-green light absorbed → Red observed
- 570-nm Yellow-green light absorbed → Violet observed
- 580-nm Yellow light absorbed → Dark blue observed
- 600-nm Orange light absorbed → Blue observed
- 650-nm Red light absorbed → Green observed

Of the four possible colors given in the problem (blue, green, yellow, and orange), the corresponding colors that are absorbed are (600 nm, 650 nm, 450 nm, and 430, respectively). From Equation 20.12.2, the smaller λ of absorbed light corresponds to the higher energy photons, so we would correlate the four wavelengths of absorbing photons in terms of increasing energy to observed color:

$$\underbrace{650\ nm}_{green} < \underbrace{600\ nm}_{blue} < \underbrace{450\ nm}_{yellow} < \underbrace{430\ nm}_{orange} \tag{20.12.3}$$

Now, just correlate the ranking in Equation 20.12.3to the ranking in Equation 20.12.1:

$$\underbrace{F^-}_{green} < \underbrace{H_2O}_{blue} < \underbrace{NH_3}_{yellow} < \underbrace{CN^-}_{orange}$$

and more specifically in terms of the original question

$$\underbrace{[CoF_6]_3^{-4}}_{green} < \underbrace{[Co(H_2O)_6]^{3+}}_{blue} < \underbrace{[Co(NH_3)_6]_3^{3+}}_{yellow} < \underbrace{[Co(CN)_6]_3^{-2}}_{orange}$$

? Exercise 20.12.1

If a complex ion $[M(NH_3)_6]^{2+}$ is red in solution, which of the following ligands, after a ligand exchange reaction to substitute for the ammine ligands, may shift the solution to be orange? More than one answer is possible.

$$Cl^-, CN^-, CO, F^- H_2O, I^-, en, NO_2^-, OH^-, SCN^-$$

Answer

Shifting from red to orange is an increase in Δ_o, so those ligands that are stronger field ligands than NH_3 in the list (deterimined via the spectrochemical series) are CN^-, CO, en, and NO_2^-.

A coordination compound of the Cu^+ ion has a d^{10} configuration, and all the e_g orbitals are filled. To excite an electron to a higher level, such as the 4*p* orbital, photons of very high energy are necessary. This energy corresponds to very short wavelengths in the ultraviolet region of the spectrum. No visible light is absorbed, so the eye sees no change, and the compound appears white or colorless. A solution containing $[Cu(CN)_2]^-$, for example, is colorless. On the other hand, octahedral Cu^{2+} complexes have a vacancy in the e_g orbitals, and electrons can be excited to this level. The wavelength (energy) of the light absorbed corresponds to the visible part of the spectrum, and Cu^{2+} complexes are almost always colored—blue, blue-green violet, or yellow (Figure 20.12.6). Although CFT successfully describes many properties of coordination complexes, molecular orbital explanations (beyond the introductory scope provided here) are required to understand fully the behavior of coordination complexes.



Figure 20.12.6: (a) Copper(I) complexes with d^{10} configurations such as CuI tend to be colorless, whereas (b) d^9 copper(II) complexes such as $Cu(NO_3)_2{\cdot}5H_2O$ are brightly colored. (CC BY 4.0; OpenStax)

Gems

A ruby is a pink to blood-red colored gemstone that consist of trace amounts of chromium in the mineral corundum Al_2O_3. In contrast, emeralds are colored green by trace amounts of chromium within a $Be_3Al_2Si_6O_{18}$ matrix. We can now understand why emeralds and rubies have such different colors, even though both contain Cr^{3+} in an octahedral environment provided by six oxide ions. Although the chemical identity of the six ligands is the same in both cases, the Cr–O distances are different because the compositions of the host lattices are different (Al_2O_3 in rubies and $Be_3Al_2Si_6O_{18}$ in emeralds). In ruby, the Cr–O distances are relatively short because of the constraints of the host lattice, which increases the d orbital–ligand interactions and makes Δ_o relatively large. Consequently, rubies absorb green light and the transmitted or reflected light is red, which gives the gem its characteristic color. In emerald, the Cr–O distances are longer due to relatively large $[Si_6O_{18}]^{12-}$ silicate rings; this results in decreased d orbital–ligand interactions and a smaller Δ_o. Consequently, emeralds absorb light of a longer wavelength (red), which gives the gem its characteristic green color. It is clear that the environment of the transition-metal ion, which is determined by the host lattice, dramatically affects the spectroscopic properties of a metal ion.



Gem-quality crystals of ruby and emerald. The colors of both minerals are due to the presence of small amounts of Cr^{3+} impurities in octahedral sites in an otherwise colorless metal oxide lattice.

The absorbance spectrum of a ruby is shown Figure $20.12.7; left$ The number and positions of the peaks in the spectrum is determined by the electronic structure of the compound, which in this case depends upon the identity of the metal and the identities, number, and geometry of the surrounding ions. Crystal field theory may be used to predict the electronic structure and thus the absorbance spectrum. If white light is shown on the gem, the absorbance spectrum indicates which wavelengths of light are removed. In this case, there are strong bands centered at 414 and 561 nm. These wavelengths correspond with blue and yellow-green light, respectively. For the most part, these colors are not present in the light reaching ones eyes. An alternative way to express this concept is to recognize that the spectrum of light reaching the eye is the product of the spectrum of the incident light (white light) and the **transmittance spectrum**. For this ruby, the transmittance spectrum has a peak at 481 nm and a broad plateau past 620 nm. (Note that there is significant attenuation of the light across the entire spectrum.) Thus only light with wavelengths near 481 nm (cyan) and greater than 620 nm (red) reach the eye.

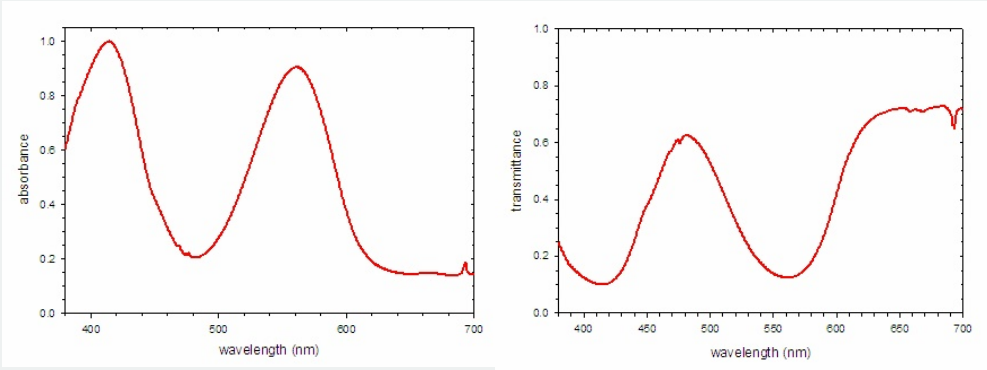
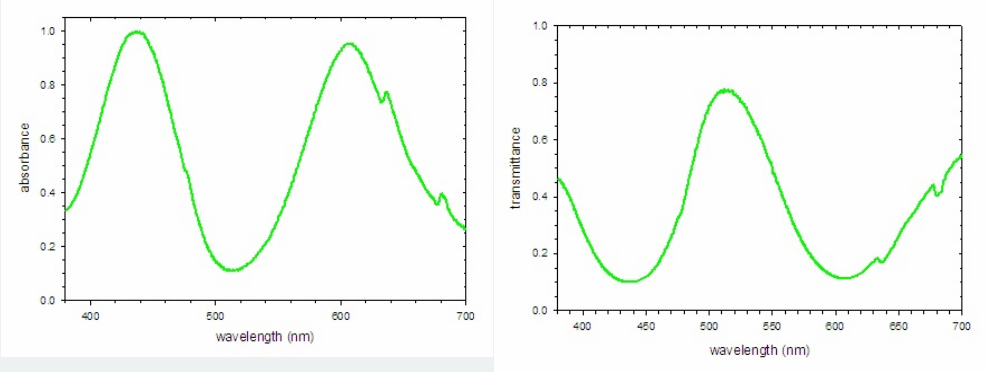


Figure 20.12.7: (left) Absorbance spectrum of a ruby from Chanthaburi, Thailand. (right) corresponding Transmittance spectrum of a ruby from Chanthaburi, Thailand. Data obtained from the Caltech Mineral Spectroscopy Server

A similar analysis of the spectrum of an emerald is possible. The absorbance spectrum (Figure $20.12.8; left$) shows strong bands at 438 and 606 nm, which remove blue and orange light, respectively. The light that is not absorbed is shown by the transmittance spectrum, which indicates the

dominant band of light reaching the eye is centered at 512 nm (green light) with smaller contributions from the far blue and red portions of the spectrum. This combination of wavelengths produces a deep green color.



(left) Absorbance spectrum of an emerald from Malyshevo, Ural, Russia. (right) Corresponding transmittance spectrum of the emerald from Malyshevo, Ural, Russia. Data obtained from the Caltech Mineral Spectroscopy Server

Summary

When atoms or molecules absorb light at the proper frequency, their electrons are excited to higher-energy orbitals. For many main group atoms and molecules, the absorbed photons are in the ultraviolet range of the electromagnetic spectrum, which cannot be detected by the human eye. For coordination compounds, the energy difference between the *d* orbitals often allows photons in the visible range to be absorbed.

Contributors and Attributions

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).
- Prof. David Blauch (Davidson College)

20.12: Optical Properties of Coordination Compounds (Color) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **24.7: Color and the Colors of Complexes** by OpenStax is licensed CC BY 4.0.

CHAPTER OVERVIEW

21: Nuclear Chemistry

UC Davis

Chemistry 2C

Nuclear reactions differ from other chemical processes in one critical way: in a nuclear reaction, the identities of the elements change. In addition, nuclear reactions are often accompanied by the release of enormous amounts of energy, as much as a billion times more than the energy released by chemical reactions. Moreover, the yields and rates of a nuclear reaction are generally unaffected by changes in temperature, pressure, or the presence of a catalyst.

21.1: Components of the Nucleus
21.2: Nuclear Reactions
21.3: Nuclear Radiation
21.4: Rates of Radioactive Decay
21.5: Stability of the Atomic Nucleus
21.6: The Origin of the Elements
21.7: Transmutation of the Elements
21.8: Nuclear Fission
21.9: Nuclear Fusion
21.E: Nuclear Chemistry (Exercises)

21: Nuclear Chemistry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

21.1: Components of the Nucleus

21.1: Components of the Nucleus is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

21.2: Nuclear Reactions

Learning Objectives

- To know the different kinds of radioactive decay.
- To balance a nuclear reaction.

The two general kinds of nuclear reactions are nuclear decay reactions and nuclear transmutation reactions**.** In a **nuclear decay reaction**, also called radioactive decay, an unstable nucleus emits radiation and is transformed into the nucleus of one or more other elements. The resulting daughter nuclei have a lower mass and are lower in energy (more stable) than the parent nucleus that decayed. In contrast, in a **nuclear transmutation reaction**, a nucleus reacts with a subatomic particle or another nucleus to form a product nucleus that is *more massive* than the starting material. As we shall see, nuclear decay reactions occur spontaneously under all conditions, but nuclear transmutation reactions occur only under very special conditions, such as the collision of a beam of highly energetic particles with a target nucleus or in the interior of stars. We begin this section by considering the different classes of radioactive nuclei, along with their characteristic nuclear decay reactions and the radiation they emit.

> *Nuclear decay reactions occur spontaneously under all conditions, whereas nuclear transmutation reactions are induced.*

Classes of Radioactive Nuclei

The three general classes of radioactive nuclei are characterized by a different decay process or set of processes:

1. **Neutron-rich nuclei.** The nuclei on the upper left side of the band of stable nuclei have a neutron-to-proton ratio that is too high to give a stable nucleus. These nuclei decay by a process that *converts a neutron to a proton*, thereby *decreasing* the neutron-to-proton ratio.
2. **Neutron-poor nuclei.** Nuclei on the lower right side of the band of stable nuclei have a neutron-to-proton ratio that is too low to give a stable nucleus. These nuclei decay by processes that have the net effect of *converting a proton to a neutron*, thereby *increasing* the neutron-to-proton ratio.
3. **Heavy nuclei.** With very few exceptions, heavy nuclei (those with $A \geq 200$) are intrinsically unstable regardless of the neutron-to-proton ratio, and all nuclei with $Z > 83$ are unstable. This is presumably due to the cumulative effects of electrostatic repulsions between the large number of positively charged protons, which cannot be totally overcome by the strong nuclear force, regardless of the number of neutrons present. Such nuclei tend to decay by emitting an α particle (a helium nucleus, ${}^{4}_{2}\text{He}$, which decreases the number of protons and neutrons in the original nucleus by 2. Because the neutron-to-proton ratio in an α particle is 1, the net result of alpha emission is an increase in the neutron-to-proton ratio.

> *Nuclear decay reactions always produce daughter nuclei that have a more favorable neutron-to- proton ratio and hence are more stable than the parent nucleus.*

Nuclear Decay Reactions

Just as we use the number and type of atoms present to balance a chemical equation, we can use the number and type of nucleons present to write a balanced nuclear equation for a nuclear decay reaction. This procedure also allows us to predict the identity of either the parent or the daughter nucleus if the identity of only one is known. Regardless of the mode of decay, the total number of nucleons is conserved in all nuclear reactions.

To describe nuclear decay reactions, chemists have extended the ${}^{A}_{Z}\text{X}$ notation for nuclides to include radioactive emissions. Table 21.2.1 lists the name and symbol for each type of emitted radiation. The most notable addition is the **positron**, a particle that has the same mass as an electron but a positive charge rather than a negative charge.

Table 21.2.1: Nuclear Decay Emissions and Their Symbols

Identity	Symbol	Charge	Mass (amu)
helium nucleus	${}^{4}_{2}\alpha$	+2	4.001506
electron	${}^{0}_{-1}\beta$ or β^{-}	−1	0.000549

Identity	Symbol	Charge	Mass (amu)
photon	${}^{0}_{0}\gamma$	—	—
neutron	${}^{1}_{0}\mathrm{n}$	0	1.008665
proton	${}^{1}_{1}\mathrm{p}$	+1	1.007276
positron	${}^{0}_{+1}\beta$ or β^{+}	+1	0.000549

Like the notation used to indicate isotopes, the upper left superscript in the symbol for a particle gives the mass number, which is the total number of protons and neutrons. For a proton or a neutron, $A = 1$. Because neither an electron nor a positron contains protons or neutrons, its mass number is 0. The numbers should not be taken literally, however, as meaning that these particles have zero mass; ejection of a beta particle (an electron) simply has a negligible effect on the mass of a nucleus.

Similarly, the lower left subscript gives the charge of the particle. Because protons carry a positive charge, $Z = +1$ for a proton. In contrast, a neutron contains no protons and is electrically neutral, so $Z = 0$. In the case of an electron, $Z = −1$, and for a positron, $Z = +1$. Because γ rays are high-energy photons, both A and Z are 0. In some cases, two different symbols are used for particles that are identical but produced in different ways. For example, the symbol ${}^{0}_{-1}\mathrm{e}$, which is usually simplified to e^{-}, represents a free electron or an electron associated with an atom, whereas the symbol ${}^{0}_{-1}\beta$, which is often simplified to β^{-}, denotes an electron that originates from within the nucleus, which is a β particle. Similarly, ${}^{4}_{2}\mathrm{He}^{2+}$ refers to the nucleus of a helium atom, and ${}^{4}_{2}\alpha$ denotes an identical particle that has been ejected from a heavier nucleus.

There are six fundamentally different kinds of nuclear decay reactions, and each releases a different kind of particle or energy. The essential features of each reaction are shown in Figure 21.2.1. The most common are alpha and beta decay and gamma emission, but the others are essential to an understanding of nuclear decay reactions.

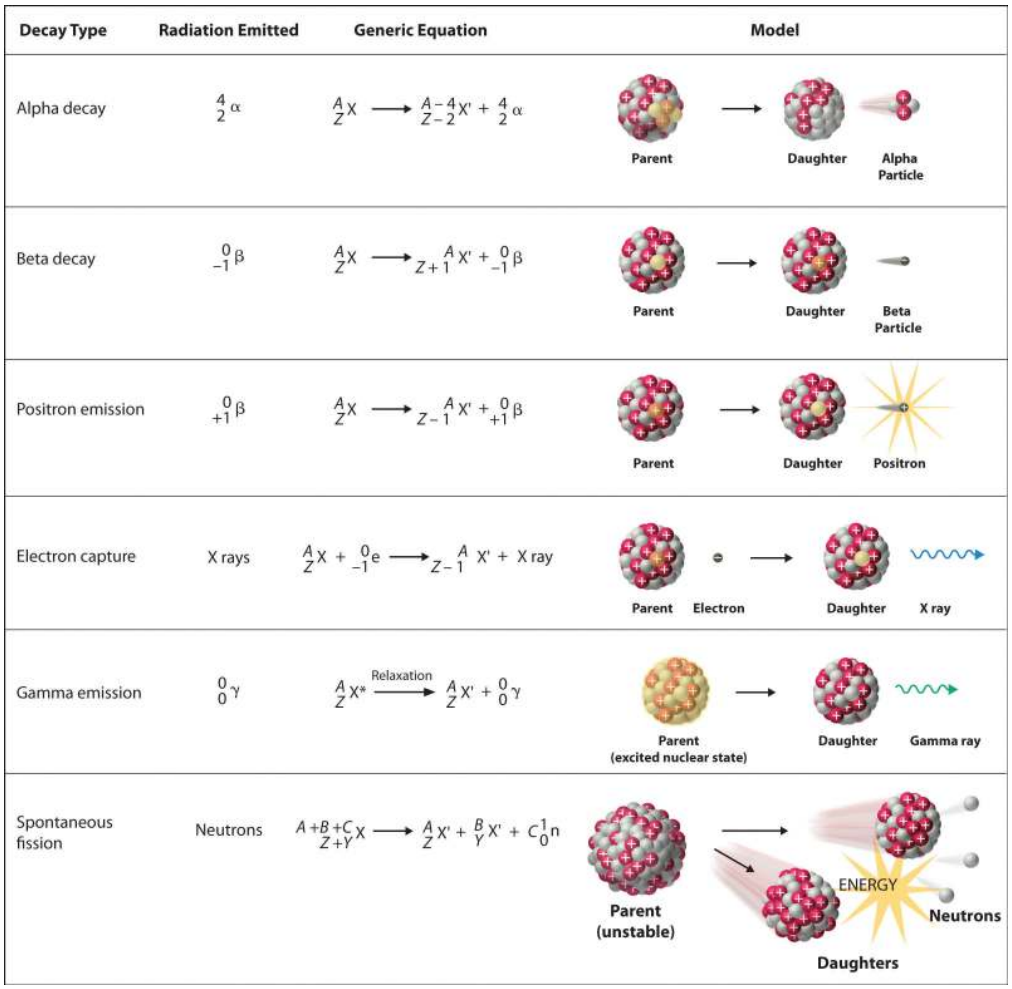


Figure 21.2.1: Common Modes of Nuclear Decay

Alpha Decay

Many nuclei with mass numbers greater than 200 undergo **alpha (α) decay**, which results in the emission of a helium-4 nucleus as an **alpha (α) particle**, $^4_2\alpha$. The general reaction is as follows:

$$\underset{\text{parent}}{^A_Z\text{X}} \rightarrow \underset{\text{daughter}}{^{A-4}_{Z-2}\text{X}'} + \underset{\substack{\text{alpha}\\\text{particle}}}{^4_2\alpha} \tag{21.2.1}$$

The daughter nuclide contains two fewer protons and two fewer neutrons than the parent. Thus α-particle emission produces a daughter nucleus with a mass number $A - 4$ and a nuclear charge $Z - 2$ compared to the parent nucleus. Radium-226, for example, undergoes alpha decay to form radon-222:

$$^{226}_{88}\text{Ra} \rightarrow ^{222}_{86}\text{Rn} + ^4_2\alpha \tag{21.2.2}$$

Because nucleons are conserved in this and all other nuclear reactions, the sum of the mass numbers of the products, 222 + 4 = 226, equals the mass number of the parent. Similarly, the sum of the atomic numbers of the products, 86 + 2 = 88, equals the atomic number of the parent. Thus the nuclear equation is balanced.

> Just as the total number of atoms is conserved in a chemical reaction, the total number of nucleons is conserved in a nuclear reaction.

Beta Decay

Nuclei that contain too many neutrons often undergo **beta (β) decay**, in which a neutron is converted to a proton and a high-energy electron that is ejected from the nucleus as a β particle:

$$\underset{\substack{\text{unstable}\\\text{neutron in}\\\text{nucleus}}}{{}^{1}_{0}\text{n}} \rightarrow \underset{\substack{\text{proton}\\\text{retained}\\\text{by nucleus}}}{{}^{1}_{1}\text{p}} + \underset{\substack{\text{beta particle}\\\text{emitted by}\\\text{nucleus}}}{{}^{0}_{-1}\beta} \tag{21.2.3}$$

The general reaction for beta decay is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z+1}\text{X}'} + \underset{\text{beta particle}}{{}^{0}_{-1}\beta} \tag{21.2.4}$$

Although beta decay does not change the mass number of the nucleus, it does result in an increase of +1 in the atomic number because of the addition of a proton in the daughter nucleus. Thus beta decay decreases the neutron-to-proton ratio, moving the nucleus toward the band of stable nuclei. For example, carbon-14 undergoes beta decay to form nitrogen-14:

$${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\beta \tag{21.2.5}$$

Once again, the number of nucleons is conserved, and the charges are balanced. The parent and the daughter nuclei have the same mass number, 14, and the sum of the atomic numbers of the products is 6, which is the same as the atomic number of the carbon-14 parent.

Positron Emission

Because a positron has the same mass as an electron but opposite charge, **positron emission** is the opposite of beta decay. Thus positron emission is characteristic of neutron-poor nuclei, which decay by transforming a proton to a neutron and emitting a high-energy positron:

$${}^{1}_{1}\text{p}^{+} \rightarrow {}^{1}_{0}\text{n} + {}^{0}_{+1}\beta^{+} \tag{21.2.6}$$

The general reaction for positron emission is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}\text{X}'} + \underset{\text{positron}}{{}^{0}_{+1}\beta^{+}} \tag{21.2.7}$$

Like beta decay, positron emission does not change the mass number of the nucleus. In this case, however, the atomic number of the daughter nucleus is lower by 1 than that of the parent. Thus the neutron-to-proton ratio has increased, again moving the nucleus closer to the band of stable nuclei. For example, carbon-11 undergoes positron emission to form boron-11:

$${}^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}\beta^{+} \tag{21.2.8}$$

Nucleons are conserved, and the charges balance. The mass number, 11, does not change, and the sum of the atomic numbers of the products is 6, the same as the atomic number of the parent carbon-11 nuclide.

Electron Capture

A neutron-poor nucleus can decay by either positron emission or **electron capture (EC)**, in which an electron in an inner shell reacts with a proton to produce a neutron:

$${}^{1}_{1}\text{p} + {}^{0}_{-1}\text{e} \rightarrow {}^{1}_{0}\text{n} \tag{21.2.9}$$

When a second electron moves from an outer shell to take the place of the lower-energy electron that was absorbed by the nucleus, an x-ray is emitted. The overall reaction for electron capture is thus

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} + \underset{\text{electron}}{{}^{0}_{-1}\text{e}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}\text{X}'} + \text{x-ray} \tag{21.2.10}$$

Electron capture does not change the mass number of the nucleus because both the proton that is lost and the neutron that is formed have a mass number of 1. As with positron emission, however, the atomic number of the daughter nucleus is lower by 1 than that of the parent. Once again, the neutron-to-proton ratio has increased, moving the nucleus toward the band of stable nuclei. For example, iron-55 decays by electron capture to form manganese-55, which is often written as follows:

$${}^{55}_{26}\text{Fe} \xrightarrow{\text{EC}} {}^{55}_{25}\text{Mn} + \text{x-ray} \tag{21.2.11}$$

The atomic numbers of the parent and daughter nuclides differ in Equation 20.2.11, although the mass numbers are the same. To write a balanced nuclear equation for this reaction, we must explicitly include the captured electron in the equation:

$$^{55}_{26}\mathrm{Fe} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{55}_{25}\mathrm{Mn} + \text{x-ray} \tag{21.2.12}$$

Both positron emission and electron capture are usually observed for nuclides with low neutron-to-proton ratios, but the decay rates for the two processes can be very different.

Gamma Emission

Many nuclear decay reactions produce daughter nuclei that are in a nuclear excited state, which is similar to an atom in which an electron has been excited to a higher-energy orbital to give an electronic excited state. Just as an electron in an electronic excited state emits energy in the form of a photon when it returns to the ground state, a nucleus in an excited state releases energy in the form of a photon when it returns to the ground state. These high-energy photons are γ rays. **Gamma** (γ) **emission** can occur virtually instantaneously, as it does in the alpha decay of uranium-238 to thorium-234, where the asterisk denotes an excited state:

$$^{238}_{92}\mathrm{U} \rightarrow \underset{\substack{\text{excited}\\ \text{nuclear}\\ \text{state}}}{^{234}_{90}\mathrm{Th}^{*}} + {}^{4}_{2}\alpha \xrightarrow{\text{relaxation}} {}^{234}_{90}\mathrm{Th} + {}^{0}_{0}\gamma \tag{21.2.13}$$

If we disregard the decay event that created the excited nucleus, then

$$^{234}_{88}\mathrm{Th}^{*} \rightarrow {}^{234}_{88}\mathrm{Th} + {}^{0}_{0}\gamma \tag{21.2.14}$$

or more generally,

$$^{A}_{Z}\mathrm{X}^{*} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{0}\gamma \tag{21.2.15}$$

Gamma emission can also occur after a significant delay. For example, technetium-99*m* has a half-life of about 6 hours before emitting a γ ray to form technetium-99 (the *m* is for metastable). Because γ rays are energy, their emission does not affect either the mass number or the atomic number of the daughter nuclide. Gamma-ray emission is therefore the only kind of radiation that does not necessarily involve the conversion of one element to another, although it is almost always observed in conjunction with some other nuclear decay reaction.

Spontaneous Fission

Only very massive nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that have different atomic numbers and atomic masses. This process is most important for the transactinide elements, with $Z \geq 104$. Spontaneous fission is invariably accompanied by the release of large amounts of energy, and it is usually accompanied by the emission of several neutrons as well. An example is the spontaneous fission of $^{254}_{98}\mathrm{Cf}$, which gives a distribution of fission products; one possible set of products is shown in the following equation:

$$^{254}_{98}\mathrm{Cf} \rightarrow {}^{118}_{46}\mathrm{Pd} + {}^{132}_{52}\mathrm{Te} + 4{}^{1}_{0}\mathrm{n} \tag{21.2.16}$$

Once again, the number of nucleons is conserved. Thus the sum of the mass numbers of the products (118 + 132 + 4 = 254) equals the mass number of the reactant. Similarly, the sum of the atomic numbers of the products [46 + 52 + (4 × 0) = 98] is the same as the atomic number of the parent nuclide.

✔ Example 21.2.1

Write a balanced nuclear equation to describe each reaction.

a. the beta decay of $^{35}_{16}\mathrm{S}$
b. the decay of $^{201}_{80}\mathrm{Hg}$ by electron capture
c. the decay of $^{30}_{15}\mathrm{P}$ by positron emission

Given: radioactive nuclide and mode of decay

Asked for: balanced nuclear equation

Strategy:

A Identify the reactants and the products from the information given.

B Use the values of *A* and *Z* to identify any missing components needed to balance the equation.

Solution

a.

A We know the identities of the reactant and one of the products (a β particle). We can therefore begin by writing an equation that shows the reactant and one of the products and indicates the unknown product as ${}^{A}_{Z}\mathrm{X}$:

$$ {}^{35}_{16}\mathrm{S} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\beta \tag{21.2.17} $$

B Because both protons and neutrons must be conserved in a nuclear reaction, the unknown product must have a mass number of *A* = 35 − 0 = 35 and an atomic number of *Z* = 16 − (−1) = 17. The element with *Z* = 17 is chlorine, so the balanced nuclear equation is as follows:

$$ {}^{35}_{16}\mathrm{S} \rightarrow {}^{35}_{17}\mathrm{Cl} + {}^{0}_{-1}\beta \tag{21.2.18} $$

b.

A We know the identities of both reactants: ${}^{201}_{80}\mathrm{Hg}$ and an inner electron, ${}^{0}_{-1}\mathrm{e}$. The reaction is as follows:

$$ {}^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{A}_{Z}\mathrm{X} $$

B Both protons and neutrons are conserved, so the mass number of the product must be *A* = 201 + 0 = 201, and the atomic number of the product must be *Z* = 80 + (−1) = 79, which corresponds to the element gold. The balanced nuclear equation is thus

$$ {}^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{201}_{79}\mathrm{Au} $$

c.

A As in part (a), we are given the identities of the reactant and one of the products—in this case, a positron. The unbalanced nuclear equation is therefore

$$ {}^{30}_{15}\mathrm{P} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{+1}\beta $$

B The mass number of the second product is *A* = 30 − 0 = 30, and its atomic number is *Z* = 15 − 1 = 14, which corresponds to silicon. The balanced nuclear equation for the reaction is as follows:

$$ {}^{30}_{15}\mathrm{P} \rightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{+1}\beta $$

? Exercise 21.2.1

Write a balanced nuclear equation to describe each reaction.

a. ${}^{11}_{6}\mathrm{C}$ by positron emission
b. the beta decay of molybdenum-99
c. the emission of an α particle followed by gamma emission from ${}^{185}_{74}\mathrm{W}$

Answer

a. ${}^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\beta$
b. ${}^{99}_{42}\mathrm{Mo} \rightarrow {}^{99m}_{43}\mathrm{Tc} + {}^{0}_{-1}\beta$
c. ${}^{185}_{74}\mathrm{W} \rightarrow {}^{181}_{72}\mathrm{Hf} + {}^{4}_{2}\alpha + {}^{0}_{0}\gamma$

✓ Example 21.2.2

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. ${}^{45}_{22}\mathrm{Ti}$
b. ${}^{242}_{94}\mathrm{Pu}$
c. ${}^{12}_{5}\mathrm{B}$
d. ${}^{256}_{100}\mathrm{Fm}$

Given: nuclide

Asked for: type of nuclear decay

Strategy:

Based on the neutron-to-proton ratio and the value of *Z*, predict the type of nuclear decay reaction that will produce a more stable nuclide.

Solution

a. This nuclide has a neutron-to-proton ratio of only 1.05, which is much less than the requirement for stability for an element with an atomic number in this range. Nuclei that have low neutron-to-proton ratios decay by converting a proton to a neutron. The two possibilities are positron emission, which converts a proton to a neutron and a positron, and electron capture, which converts a proton and a core electron to a neutron. In this case, both are observed, with positron emission occurring about 86% of the time and electron capture about 14% of the time.
b. Nuclei with $Z > 83$ are too heavy to be stable and usually undergo alpha decay, which decreases both the mass number and the atomic number. Thus $^{242}_{94}\mathrm{Pu}$ is expected to decay by alpha emission.
c. This nuclide has a neutron-to-proton ratio of 1.4, which is very high for a light element. Nuclei with high neutron-to-proton ratios decay by converting a neutron to a proton and an electron. The electron is emitted as a β particle, and the proton remains in the nucleus, causing an increase in the atomic number with no change in the mass number. We therefore predict that $^{12}_{5}\mathrm{B}$ will undergo beta decay.
d. This is a massive nuclide, with an atomic number of 100 and a mass number much greater than 200. Nuclides with $A \geq 200$ tend to decay by alpha emission, and even heavier nuclei tend to undergo spontaneous fission. We therefore predict that $^{256}_{100}\mathrm{Fm}$ will decay by either or both of these two processes. In fact, it decays by both spontaneous fission and alpha emission, in a 97:3 ratio.

? Exercise 21.2.2

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{32}_{14}\mathrm{Si}$
b. $^{43}_{21}\mathrm{Sc}$
c. $^{231}_{91}\mathrm{Pa}$

Answer

a. beta decay
b. positron emission or electron capture
c. alpha decay

Radioactive Decay Series

The nuclei of all elements with atomic numbers greater than 83 are unstable. Thus all isotopes of all elements beyond bismuth in the periodic table are radioactive. Because alpha decay decreases *Z* by only 2, and positron emission or electron capture decreases *Z* by only 1, it is impossible for any nuclide with $Z > 85$ to decay to a stable daughter nuclide in a single step, except via nuclear fission. Consequently, radioactive isotopes with $Z > 85$ usually decay to a daughter nucleus that is radiaoctive, which in turn decays to a second radioactive daughter nucleus, and so forth, until a stable nucleus finally results. This series of sequential alpha- and beta-decay reactions is called a **radioactive decay series**. The most common is the uranium-238 decay series, which produces lead-206 in a series of 14 sequential alpha- and beta-decay reactions (Figure 21.2.2). Although a radioactive decay series can be written for almost any isotope with $Z > 85$, only two others occur naturally: the decay of uranium-235 to lead-207 (in 11 steps) and thorium-232 to lead-208 (in 10 steps). A fourth series, the decay of neptunium-237 to bismuth-209 in 11 steps, is known to have occurred on the primitive Earth. With a half-life of “only” 2.14 million years, all the neptunium-237 present when Earth was formed decayed long ago, and today all the neptunium on Earth is synthetic.

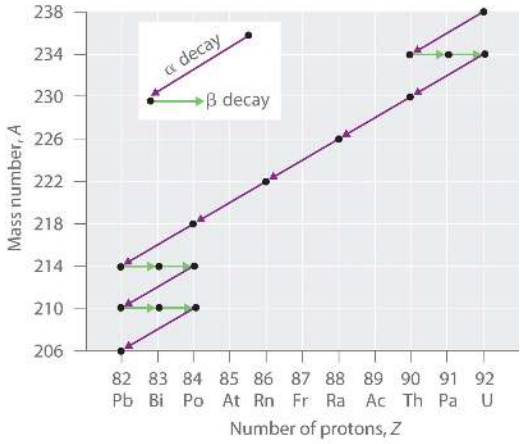


Figure 21.2.1: A Radioactive Decay Series. Three naturally occurring radioactive decay series are known to occur currently: the uranium-238 decay series, the decay of uranium-235 to lead-207, and the decay of thorium-232 to lead-208.

Due to these radioactive decay series, small amounts of very unstable isotopes are found in ores that contain uranium or thorium. These rare, unstable isotopes should have decayed long ago to stable nuclei with a lower atomic number, and they would no longer be found on Earth. Because they are generated continuously by the decay of uranium or thorium, however, their amounts have reached a steady state, in which their rate of formation is equal to their rate of decay. In some cases, the abundance of the daughter isotopes can be used to date a material or identify its origin.

Induced Nuclear Reactions

The discovery of radioactivity in the late 19th century showed that some nuclei spontaneously transform into nuclei with a different number of protons, thereby producing a different element. When scientists realized that these naturally occurring radioactive isotopes decayed by emitting subatomic particles, they realized that—in principle—it should be possible to carry out the reverse reaction, converting a stable nucleus to another more massive nucleus by bombarding it with subatomic particles in a nuclear transmutation reaction.

The first successful nuclear transmutation reaction was carried out in 1919 by Ernest Rutherford, who showed that α particles emitted by radium could react with nitrogen nuclei to form oxygen nuclei. As shown in the following equation, a proton is emitted in the process:

$$^{4}_{2}\alpha + {}^{14}_{7}\mathrm{N} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{p} \tag{21.2.19}$$

Rutherford's nuclear transmutation experiments led to the discovery of the neutron. He found that bombarding the nucleus of a light target element with an α particle usually converted the target nucleus to a product that had an atomic number higher by 1 and a mass number higher by 3 than the target nucleus. Such behavior is consistent with the emission of a proton after reaction with the α particle. Very light targets such as Li, Be, and B reacted differently, however, emitting a new kind of highly penetrating radiation rather than a proton. Because neither a magnetic field nor an electrical field could deflect these high-energy particles, Rutherford concluded that they were electrically neutral. Other observations suggested that the mass of the neutral particle was similar to the mass of the proton. In 1932, James Chadwick (Nobel Prize in Physics, 1935), who was a student of Rutherford's at the time, named these neutral particles neutrons and proposed that they were fundamental building blocks of the atom. The reaction that Chadwick initially used to explain the production of neutrons was as follows:

$$^{4}_{2}\alpha + {}^{9}_{4}\mathrm{Be} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} \tag{21.2.20}$$

Because α particles and atomic nuclei are both positively charged, electrostatic forces cause them to repel each other. Only α particles with very high kinetic energy can overcome this repulsion and collide with a nucleus (Figure 21.2.3). Neutrons have no electrical charge, however, so they are not repelled by the nucleus. Hence bombardment with neutrons is a much easier way to prepare new isotopes of the lighter elements. In fact, carbon-14 is formed naturally in the atmosphere by bombarding nitrogen-14 with neutrons generated by cosmic rays:

$$^{1}_{0}\mathrm{n} + {}^{14}_{7}\mathrm{N} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \tag{21.2.21}$$

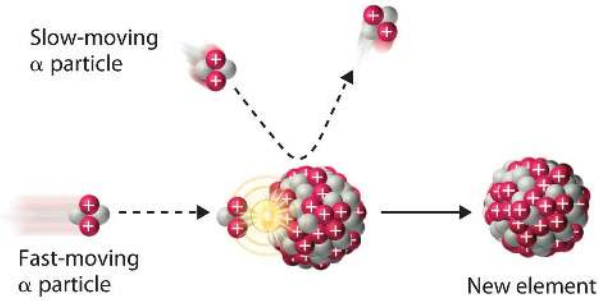


Figure 21.2.3: A Nuclear Transmutation Reaction. Bombarding a target of one element with high-energy nuclei or subatomic particles can create new elements. Electrostatic repulsions normally prevent a positively charged particle from colliding and reacting with a positively charged nucleus. If the positively charged particle is moving at a very high speed, however, its kinetic energy may be great enough to overcome the electrostatic repulsions, and it may collide with the target nucleus. Such collisions can result in a nuclear transmutation reaction.

Example 21.2.3

In 1933, Frédéric Joliot and Iréne Joliot-Curie (daughter of Marie and Pierre Curie) prepared the first artificial radioactive isotope by bombarding aluminum-27 with α particles. For each ^{27}Al that reacted, one neutron was released. Identify the product nuclide and write a balanced nuclear equation for this transmutation reaction.

Given: reactants in a nuclear transmutation reaction

Asked for: product nuclide and balanced nuclear equation

Strategy:

A Based on the reactants and one product, identify the other product of the reaction. Use conservation of mass and charge to determine the values of *Z* and *A* of the product nuclide and thus its identity.

B Write the balanced nuclear equation for the reaction.

Solution

A Bombarding an element with α particles usually produces an element with an atomic number that is 2 greater than the atomic number of the target nucleus. Thus we expect that aluminum (*Z* = 13) will be converted to phosphorus (*Z* = 15). With one neutron released, conservation of mass requires that the mass number of the other product be 3 greater than the mass number of the target. In this case, the mass number of the target is 27, so the mass number of the product will be 30. The second product is therefore phosphorus-30, $^{30}_{15}\mathrm{P}$.

B The balanced nuclear equation for the reaction is as follows:

$$^{27}_{13}\mathrm{Al} + {}^{4}_{2}\alpha \rightarrow {}^{30}_{15}\mathrm{P} + {}^{1}_{0}\mathrm{n} \tag{21.2.22}$$

Exercise 21.2.1

Because all isotopes of technetium are radioactive and have short half-lives, it does not exist in nature. Technetium can, however, be prepared by nuclear transmutation reactions. For example, bombarding a molybdenum-96 target with deuterium nuclei ($^{2}_{1}\mathrm{H}$) produces technetium-97. Identify the other product of the reaction and write a balanced nuclear equation for this transmutation reaction.

Answer

neutron, $^{1}_{0}\mathrm{n}$; $^{96}_{42}\mathrm{Mo} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{97}_{43}\mathrm{Tc} + {}^{1}_{0}\mathrm{n}$

We noted earlier in this section that very heavy nuclides, corresponding to $Z \geq 104$, tend to decay by spontaneous fission. Nuclides with slightly lower values of *Z*, such as the isotopes of uranium (*Z* = 92) and plutonium (*Z* = 94), do not undergo spontaneous fission at any significant rate. Some isotopes of these elements, however, such as $^{235}_{92}\mathrm{U}$ and $^{239}_{94}\mathrm{Pu}$ undergo induced nuclear fission when they are bombarded with relatively low-energy neutrons, as shown in the following equation for uranium-235 and in Figure 21.2.3:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{236}_{92}\mathrm{U} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} \tag{21.2.23}$$

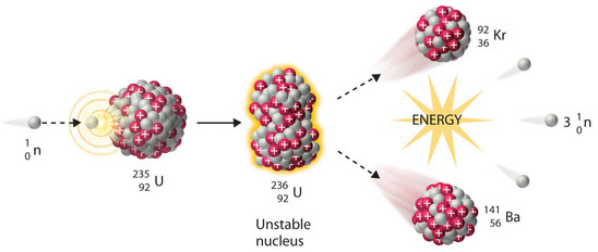


Figure 21.2.4: Neutron-Induced Nuclear Fission. Collision of a relatively slow-moving neutron with a fissile nucleus can split it into two smaller nuclei with the same or different masses. Neutrons are also released in the process, along with a great deal of energy.

Any isotope that can undergo a nuclear fission reaction when bombarded with neutrons is called a **fissile isotope**.

During nuclear fission, the nucleus usually divides asymmetrically rather than into two equal parts, as shown in Figure 21.2.4. Moreover, every fission event of a given nuclide does not give the same products; more than 50 different fission modes have been identified for uranium-235, for example. Consequently, nuclear fission of a fissile nuclide can never be described by a single equation. Instead, as shown in Figure 21.2.5, a distribution of many pairs of fission products with different yields is obtained, but the mass ratio of each pair of fission products produced by a single fission event is always roughly 3:2.

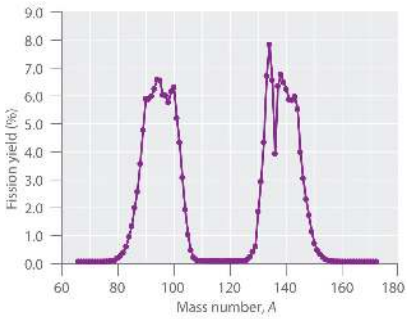


Figure 21.2.5: Mass Distribution of Nuclear Fission Products of ^{235}U. Nuclear fission usually produces a range of products with different masses and yields, although the mass ratio of each pair of fission products from a fission event is approximately 3:2. As shown in this plot, more than 50 different fission products are known for235U. Data source: T. R. England and B. F. Rider, Los Alamos National Laboratory, LA-UR-94-3106, ENDF-349 (1993).

Synthesis of Transuranium Elements

Uranium (Z = 92) is the heaviest naturally occurring element. Consequently, all the elements with Z > 92, the **transuranium elements**, are artificial and have been prepared by bombarding suitable target nuclei with smaller particles. The first of the transuranium elements to be prepared was neptunium (Z = 93), which was synthesized in 1940 by bombarding a ^{238}U target with neutrons. As shown in Equation 20.21, this reaction occurs in two steps. Initially, a neutron combines with a ^{238}U nucleus to form ^{239}U, which is unstable and undergoes beta decay to produce ^{239}Np:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\beta$$

Subsequent beta decay of ^{239}Np produces the second transuranium element, plutonium (Z = 94):

$$^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\beta$$

Bombarding the target with more massive nuclei creates elements that have atomic numbers significantly greater than that of the target nucleus (Table 21.2.2). Such techniques have resulted in the creation of the superheavy elements 114 and 116, both of which lie in or near the “island of stability."

Table 21.2.2: Some Reactions Used to Synthesize Transuranium Elements

$^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\alpha \rightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}\mathrm{n}$
$^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\alpha \rightarrow {}^{241}_{95}\mathrm{Am} + {}^{1}_{1}\mathrm{p} + {}^{1}_{0}\mathrm{n}$
$^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\alpha \rightarrow {}^{243}_{97}\mathrm{Bk} + {}^{1}_{1}\mathrm{p} + 2{}^{1}_{0}\mathrm{n}$

$^{253}_{99}\mathrm{Es} + {}^{4}_{2}\alpha \rightarrow {}^{256}_{101}\mathrm{Md} + {}^{1}_{0}\mathrm{n}$
$^{238}_{92}\mathrm{U} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{246}_{98}\mathrm{Cf} + 4{}^{1}_{0}\mathrm{n}$
$^{252}_{98}\mathrm{Cf} + {}^{10}_{5}\mathrm{B} \rightarrow {}^{256}_{103}\mathrm{Lr} + 6{}^{1}_{0}\mathrm{n}$

A device called a particle accelerator is used to accelerate positively charged particles to the speeds needed to overcome the electrostatic repulsions between them and the target nuclei by using electrical and magnetic fields. Operationally, the simplest particle accelerator is the linear accelerator (Figure 21.2.6), in which a beam of particles is injected at one end of a long evacuated tube. Rapid alternation of the polarity of the electrodes along the tube causes the particles to be alternately accelerated toward a region of opposite charge and repelled by a region with the same charge, resulting in a tremendous acceleration as the particle travels down the tube. A modern linear accelerator such as the Stanford Linear Accelerator (SLAC) at Stanford University is about 2 miles long.

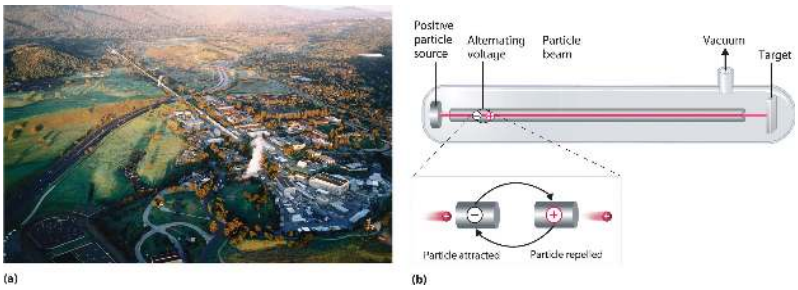


Figure 21.2.6: A Linear Particle Accelerator. (a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as they enter one section of the tube and repelled as they leave that section. As a result, the particles are continuously accelerated along the length of the tube.

To achieve the same outcome in less space, a particle accelerator called a cyclotron forces the charged particles to travel in a circular path rather than a linear one. The particles are injected into the center of a ring and accelerated by rapidly alternating the polarity of two large D-shaped electrodes above and below the ring, which accelerates the particles outward along a spiral path toward the target.

The length of a linear accelerator and the size of the D-shaped electrodes in a cyclotron severely limit the kinetic energy that particles can attain in these devices. These limitations can be overcome by using a synchrotron, a hybrid of the two designs. A synchrotron contains an evacuated tube similar to that of a linear accelerator, but the tube is circular and can be more than a mile in diameter. Charged particles are accelerated around the circle by a series of magnets whose polarities rapidly alternate.

Summary

In **nuclear decay reactions (or radioactive decay)**, the parent nucleus is converted to a more stable daughter nucleus. Nuclei with too many neutrons decay by converting a neutron to a proton, whereas nuclei with too few neutrons decay by converting a proton to a neutron. Very heavy nuclei (with $A \geq 200$ and $Z > 83$) are unstable and tend to decay by emitting an **α particle**. When an unstable nuclide undergoes radioactive decay, the total number of nucleons is conserved, as is the total positive charge. Six different kinds of nuclear decay reactions are known. *Alpha decay* results in the emission of an α particle, $^{4}_{2}\alpha$, and produces a daughter nucleus with a mass number that is lower by 4 and an atomic number that is lower by 2 than the parent nucleus. **Beta decay** converts a neutron to a proton and emits a high-energy electron, producing a daughter nucleus with the same mass number as the parent and an atomic number that is higher by 1. **Positron emission** is the opposite of beta decay and converts a proton to a neutron plus a positron. Positron emission does not change the mass number of the nucleus, but the atomic number of the daughter nucleus is lower by 1 than the parent. In **electron capture (EC)**, an electron in an inner shell reacts with a proton to produce a neutron, with emission of an x-ray. The mass number does not change, but the atomic number of the daughter is lower by 1 than the parent. In **gamma emission**, a daughter nucleus in a nuclear excited state undergoes a transition to a lower-energy state by emitting a γ ray. Very heavy nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that can have different atomic numbers and atomic masses with the release of neutrons. Many very heavy nuclei decay via a **radioactive decay series**—a succession of some combination of alpha- and beta-decay reactions. In **nuclear transmutation reactions**, a target nucleus is bombarded with energetic subatomic particles to give a product nucleus that is more massive than the original. All **transuranium elements**—elements with $Z > 92$—are artificial and must be prepared by nuclear transmutation reactions. These reactions are carried out in particle accelerators such as linear accelerators, cyclotrons, and synchrotrons.

Key Takeaway

Nuclear decay reactions occur spontaneously under all conditions and produce more stable daughter nuclei, whereas nuclear transmutation reactions are induced and form a product nucleus that is more massive than the starting material.

Key Equations

alpha decay

Equation 20.1: ${}^{A}_{Z}\mathrm{X} \rightarrow {}^{A-4}_{Z-2}\mathrm{X}' + {}^{4}_{2}\alpha$

beta decay

Equation 20.4: ${}^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z+1}\mathrm{X}' + {}^{0}_{-1}\beta$

positron emission

Equation 20.7: ${}^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z-1}\mathrm{X}' + {}^{0}_{+1}\beta$

electron capture

Equation 20.10: ${}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{A}_{Z-1}\mathrm{X}' + \text{x-ray}$

gamma emission

Equation 20.15: ${}^{A}_{Z}\mathrm{X}^{*} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{0}\gamma$

21.2: Nuclear Reactions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **24.3: Nuclear Reactions** by Anonymous is licensed CC BY-NC-SA 3.0.

21.3: Nuclear Radiation

Learning Objectives

- Write and balance nuclear equations
- To know the different kinds of radioactive decay.
- To balance a nuclear reaction.

Nuclear chemistry is the study of reactions that involve changes in nuclear structure. The chapter on atoms, molecules, and ions introduced the basic idea of nuclear structure, that the nucleus of an atom is composed of protons and, with the exception of ${}^{1}_{1}\mathrm{H}$, neutrons. Recall that the number of protons in the nucleus is called the atomic number (Z) of the element, and the sum of the number of protons and the number of neutrons is the mass number (A). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term nuclide and identify it by the notation:

$$ {}^{\mathrm{A}}_{\mathrm{Z}}\mathrm{X} \tag{21.3.1} $$

where

- X is the symbol for the element,
- A is the mass number, and
- Z is the atomic number.

Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example, ${}^{14}_{6}\mathrm{C}$ is called "carbon-14."

Protons and neutrons, collectively called nucleons, are packed together tightly in a nucleus. With a radius of about 10^{-15} meters, a nucleus is quite small compared to the radius of the entire atom, which is about 10^{-10} meters. Nuclei are extremely dense compared to bulk matter, averaging 1.8×10^{14} grams per cubic centimeter. For example, water has a density of 1 gram per cubic centimeter, and iridium, one of the densest elements known, has a density of 22.6 g/cm^3. If the earth's density were equal to the average nuclear density, the earth's radius would be only about 200 meters (earth's actual radius is approximately 6.4×10^6 meters, 30,000 times larger).

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are nuclear reactions. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

Nuclear Equations

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of subatomic particles rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that ${}^{17}_{8}\mathrm{O}$ is a product of the nuclear reaction of ${}^{14}_{7}\mathrm{N}$ and ${}^{4}_{2}\mathrm{He}$ if we knew that a proton, ${}^{1}_{1}\mathrm{H}$, was one of the two products. Example $21.3.1$ shows how we can identify a nuclide by balancing the nuclear reaction.

Example 21.3.1: Balancing Equations for Nuclear Reactions

The reaction of an α particle with magnesium-25 $\left({}^{25}_{12}\mathrm{Mg}\right)$ produces a proton and a nuclide of another element. Identify the new nuclide produced.

Solution

The nuclear reaction can be written as:

$$^{25}_{12}\text{Mg} + ^{4}_{2}\text{He} \rightarrow ^{1}_{1}\text{H} + ^{\text{A}}_{\text{Z}}\text{X}$$

where

- A is the mass number and
- Z is the atomic number of the new nuclide, X.

Because the sum of the mass numbers of the reactants must equal the sum of the mass numbers of the products:

$$25 + 4 = \text{A} + 1$$

so

$$\text{A} = 28$$

Similarly, the charges must balance, so:

$$12 + 2 = \text{Z} + 1$$

so

$$\text{Z} = 13$$

Check the periodic table: The element with nuclear charge = +13 is aluminum. Thus, the product is $^{28}_{13}\text{Al}$.

? Exercise 21.3.1

The nuclide $^{125}_{53}\text{I}$ combines with an electron and produces a new nucleus and no other massive particles. What is the equation for this reaction?

Answer

$$^{125}_{53}\text{I} + ^{0}_{-1}\text{e} \rightarrow ^{125}_{52}\text{Te}$$

The two general kinds of nuclear reactions are nuclear decay reactions and nuclear transmutation reactions**.** In a **nuclear decay reaction**, also called radioactive decay, an unstable nucleus emits radiation and is transformed into the nucleus of one or more other elements. The resulting daughter nuclei have a lower mass and are lower in energy (more stable) than the parent nucleus that decayed. In contrast, in a **nuclear transmutation reaction**, a nucleus reacts with a subatomic particle or another nucleus to form a product nucleus that is *more massive* than the starting material. As we shall see, nuclear decay reactions occur spontaneously under all conditions, but nuclear transmutation reactions occur only under very special conditions, such as the collision of a beam of highly energetic particles with a target nucleus or in the interior of stars. We begin this section by considering the different classes of radioactive nuclei, along with their characteristic nuclear decay reactions and the radiation they emit.

> *Nuclear decay reactions occur spontaneously under all conditions, whereas nuclear transmutation reactions are induced.*

Nuclear Decay Reactions

Just as we use the number and type of atoms present to balance a chemical equation, we can use the number and type of nucleons present to write a balanced nuclear equation for a nuclear decay reaction. This procedure also allows us to predict the identity of either the parent or the daughter nucleus if the identity of only one is known. Regardless of the mode of decay, the total number of nucleons is conserved in all nuclear reactions.

To describe nuclear decay reactions, chemists have extended the $^{A}_{Z}\text{X}$ notation for nuclides to include radioactive emissions. Table 21.3.1 lists the name and symbol for each type of emitted radiation. The most notable addition is the **positron**, a particle that has the same mass as an electron but a positive charge rather than a negative charge.

Table 21.3.1: Nuclear Decay Emissions and Their Symbols

Identity	Symbol	Charge	Mass (amu)
helium nucleus	${}^{4}_{2}\alpha$	+2	4.001506
electron	${}^{0}_{-1}\beta$ or β^{-}	−1	0.000549
photon	${}^{0}_{0}\gamma$	—	—
neutron	${}^{1}_{0}\mathrm{n}$	0	1.008665
proton	${}^{1}_{1}\mathrm{p}$	+1	1.007276
positron	${}^{0}_{+1}\beta$ or β^{+}	+1	0.000549

Like the notation used to indicate isotopes, the upper left superscript in the symbol for a particle gives the mass number, which is the total number of protons and neutrons. For a proton or a neutron, $A = 1$. Because neither an electron nor a positron contains protons or neutrons, its mass number is 0. The numbers should not be taken literally, however, as meaning that these particles have zero mass; ejection of a beta particle (an electron) simply has a negligible effect on the mass of a nucleus.

Similarly, the lower left subscript gives the charge of the particle. Because protons carry a positive charge, $Z = +1$ for a proton. In contrast, a neutron contains no protons and is electrically neutral, so $Z = 0$. In the case of an electron, $Z = −1$, and for a positron, $Z = +1$. Because γ rays are high-energy photons, both A and Z are 0. In some cases, two different symbols are used for particles that are identical but produced in different ways. For example, the symbol ${}^{0}_{-1}\mathrm{e}$, which is usually simplified to e^{-}, represents a free electron or an electron associated with an atom, whereas the symbol ${}^{0}_{-1}\beta$, which is often simplified to β^{-}, denotes an electron that originates from within the nucleus, which is a β particle. Similarly, ${}^{4}_{2}\mathrm{He}^{2+}$ refers to the nucleus of a helium atom, and ${}^{4}_{2}\alpha$ denotes an identical particle that has been ejected from a heavier nucleus.

There are six fundamentally different kinds of nuclear decay reactions, and each releases a different kind of particle or energy. The essential features of each reaction are shown in Figure 21.3.1. The most common are alpha and beta decay and gamma emission, but the others are essential to an understanding of nuclear decay reactions.

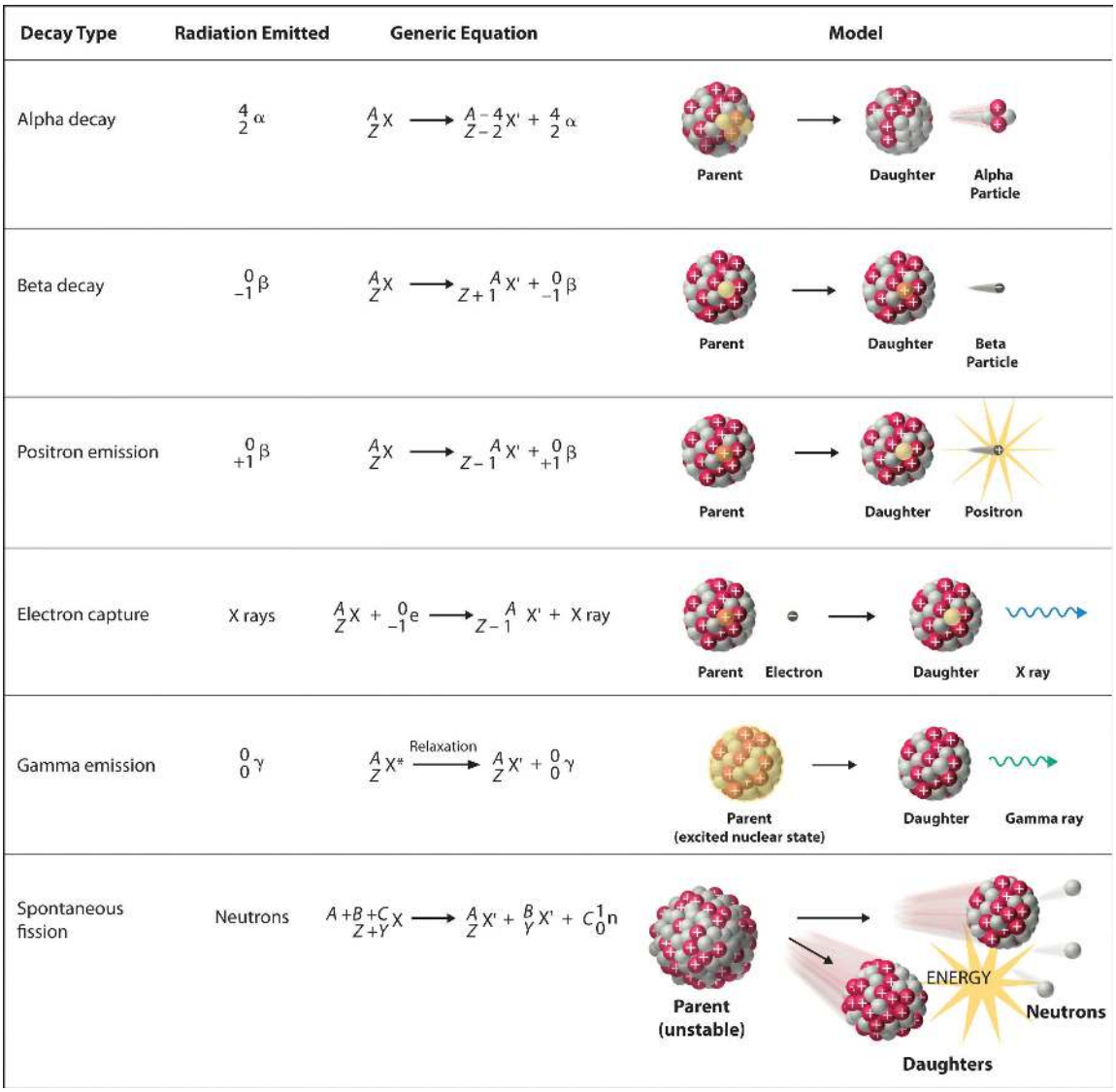


Figure 21.3.1: Common Modes of Nuclear Decay

The different types of decay are alpha, beta, positron emission, electron capture, gamma emission, and spontaneous fission.

Alpha α Decay

Many nuclei with mass numbers greater than 200 undergo **alpha (α) decay**, which results in the emission of a helium-4 nucleus as an **alpha (α) particle**, ${}^{4}_{2}\alpha$. The general reaction is as follows:

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A-4}_{Z-2}\text{X}'} + \underset{\substack{\text{alpha}\\ \text{particle}}}{{}^{4}_{2}\alpha} \tag{21.3.2}$$

The daughter nuclide contains two fewer protons and two fewer neutrons than the parent. Thus α-particle emission produces a daughter nucleus with a mass number $A - 4$ and a nuclear charge $Z - 2$ compared to the parent nucleus. Radium-226, for example, undergoes alpha decay to form radon-222:

$${}^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\alpha \tag{21.3.3}$$

Because nucleons are conserved in this and all other nuclear reactions, the sum of the mass numbers of the products, 222 + 4 = 226, equals the mass number of the parent. Similarly, the sum of the atomic numbers of the products, 86 + 2 = 88, equals the atomic number of the parent. Thus the nuclear equation is balanced.

> *Just as the total number of atoms is conserved in a chemical reaction, the total number of nucleons is conserved in a nuclear reaction.*

Beta β^- Decay

Nuclei that contain too many neutrons often undergo **beta (β) decay**, in which a neutron is converted to a proton and a high-energy electron that is ejected from the nucleus as a β particle:

$$\underset{\substack{\text{unstable}\\\text{neutron in}\\\text{nucleus}}}{{}^{1}_{0}\text{n}} \rightarrow \underset{\substack{\text{proton}\\\text{retained}\\\text{by nucleus}}}{{}^{1}_{1}\text{p}} + \underset{\substack{\text{beta particle}\\\text{emitted by}\\\text{nucleus}}}{{}^{0}_{-1}\beta} \tag{21.3.4}$$

The general reaction for beta decay is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z+1}\text{X}'} + \underset{\text{beta particle}}{{}^{0}_{-1}\beta} \tag{21.3.5}$$

Although beta decay does not change the mass number of the nucleus, it does result in an increase of +1 in the atomic number because of the addition of a proton in the daughter nucleus. Thus beta decay decreases the neutron-to-proton ratio, moving the nucleus toward the band of stable nuclei. For example, carbon-14 undergoes beta decay to form nitrogen-14:

$${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\beta$$

Once again, the number of nucleons is conserved, and the charges are balanced. The parent and the daughter nuclei have the same mass number, 14, and the sum of the atomic numbers of the products is 6, which is the same as the atomic number of the carbon-14 parent.

Positron β^+ Emission

Because a positron has the same mass as an electron but opposite charge, **positron emission** is the opposite of beta decay. Thus positron emission is characteristic of neutron-poor nuclei, which decay by transforming a proton to a neutron and emitting a high-energy positron:

$${}^{1}_{1}\text{p}^{+} \rightarrow {}^{1}_{0}\text{n} + {}^{0}_{+1}\beta^{+} \tag{21.3.6}$$

The general reaction for positron emission is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}\text{X}'} + \underset{\text{positron}}{{}^{0}_{+1}\beta^{+}}$$

Like beta decay, positron emission does not change the mass number of the nucleus. In this case, however, the atomic number of the daughter nucleus is lower by 1 than that of the parent. Thus the neutron-to-proton ratio has increased, again moving the nucleus closer to the band of stable nuclei. For example, carbon-11 undergoes positron emission to form boron-11:

$${}^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}\beta^{+}$$

Nucleons are conserved, and the charges balance. The mass number, 11, does not change, and the sum of the atomic numbers of the products is 6, the same as the atomic number of the parent carbon-11 nuclide.

Electron Capture

A neutron-poor nucleus can decay by either positron emission or **electron capture (EC)**, in which an electron in an inner shell reacts with a proton to produce a neutron:

$${}^{1}_{1}\text{p} + {}^{0}_{-1}\text{e} \rightarrow {}^{1}_{0}\text{n} \tag{21.3.7}$$

When a second electron moves from an outer shell to take the place of the lower-energy electron that was absorbed by the nucleus, an x-ray is emitted. The overall reaction for electron capture is thus

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} + \underset{\text{electron}}{{}^{0}_{-1}\text{e}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}\text{X}'} + \text{x-ray}$$

Electron capture does not change the mass number of the nucleus because both the proton that is lost and the neutron that is formed have a mass number of 1. As with positron emission, however, the atomic number of the daughter nucleus is lower by 1 than that of the parent. Once again, the neutron-to-proton ratio has increased, moving the nucleus toward the band of stable nuclei. For example, iron-55 decays by electron capture to form manganese-55, which is often written as follows:

$$^{55}_{26}\text{Fe} \xrightarrow{\text{EC}} {}^{55}_{25}\text{Mn} + \text{x-ray}$$

The atomic numbers of the parent and daughter nuclides differ in Equation 20.2.11, although the mass numbers are the same. To write a balanced nuclear equation for this reaction, we must explicitly include the captured electron in the equation:

$$^{55}_{26}\text{Fe} + {}^{0}_{-1}\text{e} \rightarrow {}^{55}_{25}\text{Mn} + \text{x-ray}$$

Both positron emission and electron capture are usually observed for nuclides with low neutron-to-proton ratios, but the decay rates for the two processes can be very different.

Gamma γ Emission

Many nuclear decay reactions produce daughter nuclei that are in a nuclear excited state, which is similar to an atom in which an electron has been excited to a higher-energy orbital to give an electronic excited state. Just as an electron in an electronic excited state emits energy in the form of a photon when it returns to the ground state, a nucleus in an excited state releases energy in the form of a photon when it returns to the ground state. These high-energy photons are γ rays. **Gamma** (γ) **emission** can occur virtually instantaneously, as it does in the alpha decay of uranium-238 to thorium-234, where the asterisk denotes an excited state:

$$^{238}_{92}\text{U} \rightarrow \underset{\substack{\text{excited}\\ \text{nuclear}\\ \text{state}}}{^{234}_{90}\text{Th}^*} + {}^{4}_{2}\alpha \xrightarrow{\text{relaxation}} {}^{234}_{90}\text{Th} + {}^{0}_{0}\gamma$$

If we disregard the decay event that created the excited nucleus, then

$$^{234}_{88}\text{Th}^* \rightarrow {}^{234}_{88}\text{Th} + {}^{0}_{0}\gamma$$

or more generally,

$$^{A}_{Z}\text{X}^* \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{0}\gamma$$

Gamma emission can also occur after a significant delay. For example, technetium-99*m* has a half-life of about 6 hours before emitting a γ ray to form technetium-99 (the *m* is for metastable). Because γ rays are energy, their emission does not affect either the mass number or the atomic number of the daughter nuclide. Gamma-ray emission is therefore the only kind of radiation that does not necessarily involve the conversion of one element to another, although it is almost always observed in conjunction with some other nuclear decay reaction.

Spontaneous Fission

Only very massive nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that have different atomic numbers and atomic masses. This process is most important for the transactinide elements, with $Z \geq 104$. Spontaneous fission is invariably accompanied by the release of large amounts of energy, and it is usually accompanied by the emission of several neutrons as well. An example is the spontaneous fission of $^{254}_{98}\text{Cf}$, which gives a distribution of fission products; one possible set of products is shown in the following equation:

$$^{254}_{98}\text{Cf} \rightarrow {}^{118}_{46}\text{Pd} + {}^{132}_{52}\text{Te} + 4{}^{1}_{0}\text{n}$$

Once again, the number of nucleons is conserved. Thus the sum of the mass numbers of the products (118 + 132 + 4 = 254) equals the mass number of the reactant. Similarly, the sum of the atomic numbers of the products [46 + 52 + (4 × 0) = 98] is the same as the atomic number of the parent nuclide.

✔ Example 21.3.2

Write a balanced nuclear equation to describe each reaction.

a. the beta decay of $^{35}_{16}\text{S}$

b. the decay of $^{201}_{80}\text{Hg}$ by electron capture
c. the decay of $^{30}_{15}\text{P}$ by positron emission

Given: radioactive nuclide and mode of decay

Asked for: balanced nuclear equation

Strategy:

A Identify the reactants and the products from the information given.

B Use the values of *A* and *Z* to identify any missing components needed to balance the equation.

Solution

a.

A We know the identities of the reactant and one of the products (a β particle). We can therefore begin by writing an equation that shows the reactant and one of the products and indicates the unknown product as $^{A}_{Z}\text{X}$:

$$^{35}_{16}\text{S} \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{-1}\beta$$

B Because both protons and neutrons must be conserved in a nuclear reaction, the unknown product must have a mass number of $A = 35 - 0 = 35$ and an atomic number of $Z = 16 - (-1) = 17$. The element with $Z = 17$ is chlorine, so the balanced nuclear equation is as follows:

$$^{35}_{16}\text{S} \rightarrow {}^{35}_{17}\text{Cl} + {}^{0}_{-1}\beta$$

b.

A We know the identities of both reactants: $^{201}_{80}\text{Hg}$ and an inner electron, $^{0}_{-1}\text{e}$. The reaction is as follows:

$$^{201}_{80}\text{Hg} + {}^{0}_{-1}\text{e} \rightarrow {}^{A}_{Z}\text{X}$$

B Both protons and neutrons are conserved, so the mass number of the product must be $A = 201 + 0 = 201$, and the atomic number of the product must be $Z = 80 + (-1) = 79$, which corresponds to the element gold. The balanced nuclear equation is thus

$$^{201}_{80}\text{Hg} + {}^{0}_{-1}\text{e} \rightarrow {}^{201}_{79}\text{Au}$$

c.

A As in part (a), we are given the identities of the reactant and one of the products—in this case, a positron. The unbalanced nuclear equation is therefore

$$^{30}_{15}\text{P} \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{+1}\beta$$

B The mass number of the second product is $A = 30 - 0 = 30$, and its atomic number is $Z = 15 - 1 = 14$, which corresponds to silicon. The balanced nuclear equation for the reaction is as follows:

$$^{30}_{15}\text{P} \rightarrow {}^{30}_{14}\text{Si} + {}^{0}_{+1}\beta$$

? Exercise 21.3.2

Write a balanced nuclear equation to describe each reaction.

a. $^{11}_{6}\text{C}$ by positron emission
b. the beta decay of molybdenum-99
c. the emission of an α particle followed by gamma emission from $^{185}_{74}\text{W}$

Answer a

$$^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}\beta$$

Answer d

$$^{99}_{42}\text{Mo} \rightarrow {}^{99m}_{43}\text{Tc} + {}^{0}_{-1}\beta$$

Answer c

$^{185}_{74}\mathrm{W} \rightarrow {}^{181}_{72}\mathrm{Hf} + {}^{4}_{2}\alpha + {}^{0}_{0}\gamma$

Example 21.3.3

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{45}_{22}\mathrm{Ti}$
b. $^{242}_{94}\mathrm{Pu}$
c. $^{12}_{5}\mathrm{B}$
d. $^{256}_{100}\mathrm{Fm}$

Given: nuclide

Asked for: type of nuclear decay

Strategy:

Based on the neutron-to-proton ratio and the value of *Z*, predict the type of nuclear decay reaction that will produce a more stable nuclide.

Solution

a. This nuclide has a neutron-to-proton ratio of only 1.05, which is much less than the requirement for stability for an element with an atomic number in this range. Nuclei that have low neutron-to-proton ratios decay by converting a proton to a neutron. The two possibilities are positron emission, which converts a proton to a neutron and a positron, and electron capture, which converts a proton and a core electron to a neutron. In this case, both are observed, with positron emission occurring about 86% of the time and electron capture about 14% of the time.
b. Nuclei with $Z > 83$ are too heavy to be stable and usually undergo alpha decay, which decreases both the mass number and the atomic number. Thus $^{242}_{94}\mathrm{Pu}$ is expected to decay by alpha emission.
c. This nuclide has a neutron-to-proton ratio of 1.4, which is very high for a light element. Nuclei with high neutron-to-proton ratios decay by converting a neutron to a proton and an electron. The electron is emitted as a β particle, and the proton remains in the nucleus, causing an increase in the atomic number with no change in the mass number. We therefore predict that $^{12}_{5}\mathrm{B}$ will undergo beta decay.
d. This is a massive nuclide, with an atomic number of 100 and a mass number much greater than 200. Nuclides with $A \geq 200$ tend to decay by alpha emission, and even heavier nuclei tend to undergo spontaneous fission. We therefore predict that $^{256}_{100}\mathrm{Fm}$ will decay by either or both of these two processes. In fact, it decays by both spontaneous fission and alpha emission, in a 97:3 ratio.

Exercise 21.3.3

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{32}_{14}\mathrm{Si}$
b. $^{43}_{21}\mathrm{Sc}$
c. $^{231}_{91}\mathrm{Pa}$

Answer a

beta decay

Answer d

positron emission or electron capture

Answer c

alpha decay

Radioactive Decay Series

The nuclei of all elements with atomic numbers greater than 83 are unstable. Thus all isotopes of all elements beyond bismuth in the periodic table are radioactive. Because alpha decay decreases Z by only 2, and positron emission or electron capture decreases Z by only 1, it is impossible for any nuclide with $Z > 85$ to decay to a stable daughter nuclide in a single step, except via nuclear fission. Consequently, radioactive isotopes with $Z > 85$ usually decay to a daughter nucleus that is radiaoctive, which in turn decays to a second radioactive daughter nucleus, and so forth, until a stable nucleus finally results. This series of sequential alpha- and beta-decay reactions is called a **radioactive decay series**. The most common is the uranium-238 decay series, which produces lead-206 in a series of 14 sequential alpha- and beta-decay reactions (Figure 21.3.2). Although a radioactive decay series can be written for almost any isotope with $Z > 85$, only two others occur naturally: the decay of uranium-235 to lead-207 (in 11 steps) and thorium-232 to lead-208 (in 10 steps). A fourth series, the decay of neptunium-237 to bismuth-209 in 11 steps, is known to have occurred on the primitive Earth. With a half-life of "only" 2.14 million years, all the neptunium-237 present when Earth was formed decayed long ago, and today all the neptunium on Earth is synthetic.

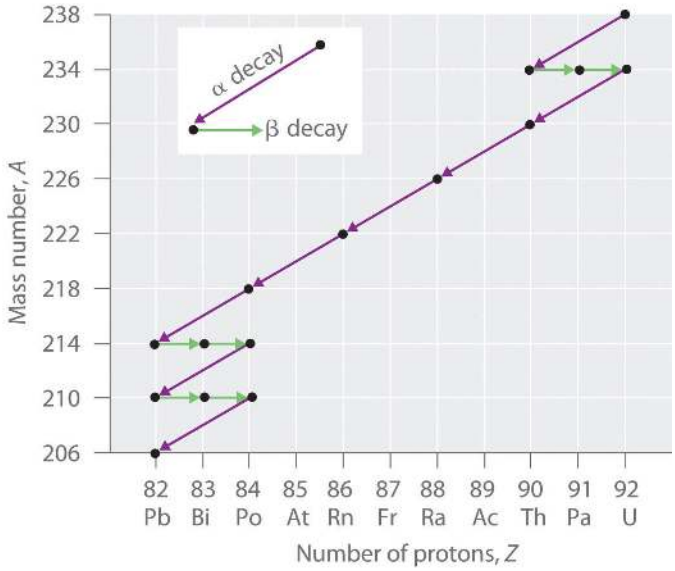


Figure 21.3.2 A Radioactive Decay Series. Three naturally occurring radioactive decay series are known to occur currently: the uranium-238 decay series, the decay of uranium-235 to lead-207, and the decay of thorium-232 to lead-208.

Graph of mass number against number of protons. The purple lines are alpha decay which are linear while the green lines are beta decay and are horizontal and parallel to the x axis.

Due to these radioactive decay series, small amounts of very unstable isotopes are found in ores that contain uranium or thorium. These rare, unstable isotopes should have decayed long ago to stable nuclei with a lower atomic number, and they would no longer be found on Earth. Because they are generated continuously by the decay of uranium or thorium, however, their amounts have reached a steady state, in which their rate of formation is equal to their rate of decay. In some cases, the abundance of the daughter isotopes can be used to date a material or identify its origin.

Induced Nuclear Reactions

The discovery of radioactivity in the late 19th century showed that some nuclei spontaneously transform into nuclei with a different number of protons, thereby producing a different element. When scientists realized that these naturally occurring radioactive isotopes decayed by emitting subatomic particles, they realized that—in principle—it should be possible to carry out the reverse reaction, converting a stable nucleus to another more massive nucleus by bombarding it with subatomic particles in a nuclear transmutation reaction.

The first successful nuclear transmutation reaction was carried out in 1919 by Ernest Rutherford, who showed that α particles emitted by radium could react with nitrogen nuclei to form oxygen nuclei. As shown in the following equation, a proton is emitted in the process:

$$ {}^{4}_{2}\alpha + {}^{14}_{7}\mathrm{N} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{p} $$

Rutherford's nuclear transmutation experiments led to the discovery of the neutron. He found that bombarding the nucleus of a light target element with an α particle usually converted the target nucleus to a product that had an atomic number higher by 1 and a mass number higher by 3 than the target nucleus. Such behavior is consistent with the emission of a proton after reaction with the α particle. Very light targets such as Li, Be, and B reacted differently, however, emitting a new kind of highly penetrating radiation rather than a proton. Because neither a magnetic field nor an electrical field could deflect these high-energy particles, Rutherford concluded that they were electrically neutral. Other observations suggested that the mass of the neutral particle was similar to the mass of the proton. In 1932, James Chadwick (Nobel Prize in Physics, 1935), who was a student of Rutherford's at the time, named these neutral particles neutrons and proposed that they were fundamental building blocks of the atom. The reaction that Chadwick initially used to explain the production of neutrons was as follows:

$$^{4}_{2}\alpha + {}^{9}_{4}\mathrm{Be} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} \tag{21.3.8}$$

Because α particles and atomic nuclei are both positively charged, electrostatic forces cause them to repel each other. Only α particles with very high kinetic energy can overcome this repulsion and collide with a nucleus (Figure 21.3.3). Neutrons have no electrical charge, however, so they are not repelled by the nucleus. Hence bombardment with neutrons is a much easier way to prepare new isotopes of the lighter elements. In fact, carbon-14 is formed naturally in the atmosphere by bombarding nitrogen-14 with neutrons generated by cosmic rays:

$$^{1}_{0}\mathrm{n} + {}^{14}_{7}\mathrm{N} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \tag{21.3.9}$$

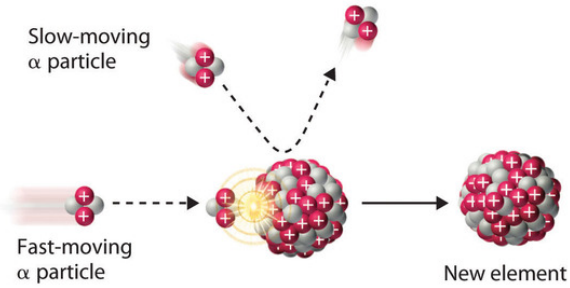


Figure 21.3.3: A Nuclear Transmutation Reaction. Bombarding a target of one element with high-energy nuclei or subatomic particles can create new elements. Electrostatic repulsions normally prevent a positively charged particle from colliding and reacting with a positively charged nucleus. If the positively charged particle is moving at a very high speed, however, its kinetic energy may be great enough to overcome the electrostatic repulsions, and it may collide with the target nucleus. Such collisions can result in a nuclear transmutation reaction.

Example 21.3.4

In 1933, Frédéric Joliot and Iréne Joliot-Curie (daughter of Marie and Pierre Curie) prepared the first artificial radioactive isotope by bombarding aluminum-27 with α particles. For each ^{27}Al that reacted, one neutron was released. Identify the product nuclide and write a balanced nuclear equation for this transmutation reaction.

Given: reactants in a nuclear transmutation reaction

Asked for: product nuclide and balanced nuclear equation

Strategy:

A Based on the reactants and one product, identify the other product of the reaction. Use conservation of mass and charge to determine the values of *Z* and *A* of the product nuclide and thus its identity.

B Write the balanced nuclear equation for the reaction.

Solution

A Bombarding an element with α particles usually produces an element with an atomic number that is 2 greater than the atomic number of the target nucleus. Thus we expect that aluminum (Z = 13) will be converted to phosphorus (Z = 15). With one neutron released, conservation of mass requires that the mass number of the other product be 3 greater than the mass number of the target. In this case, the mass number of the target is 27, so the mass number of the product will be 30. The second product is therefore phosphorus-30, $^{30}_{15}\mathrm{P}$.

B The balanced nuclear equation for the reaction is as follows:

$$^{27}_{13}\mathrm{Al} + {}^{4}_{2}\alpha \rightarrow {}^{30}_{15}\mathrm{P} + {}^{1}_{0}\mathrm{n}$$

? Exercise 21.3.4

Because all isotopes of technetium are radioactive and have short half-lives, it does not exist in nature. Technetium can, however, be prepared by nuclear transmutation reactions. For example, bombarding a molybdenum-96 target with deuterium nuclei ($^{2}_{1}\mathrm{H}$) produces technetium-97. Identify the other product of the reaction and write a balanced nuclear equation for this transmutation reaction.

Answer

neutron, $^{1}_{0}\mathrm{n}$; $^{96}_{42}\mathrm{Mo} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{97}_{43}\mathrm{Tc} + {}^{1}_{0}\mathrm{n}$:

We noted earlier in this section that very heavy nuclides, corresponding to $Z \geq 104$, tend to decay by spontaneous fission. Nuclides with slightly lower values of Z, such as the isotopes of uranium (Z = 92) and plutonium (Z = 94), do not undergo spontaneous fission at any significant rate. Some isotopes of these elements, however, such as $^{235}_{92}\mathrm{U}$ and $^{239}_{94}\mathrm{Pu}$ undergo induced nuclear fission when they are bombarded with relatively low-energy neutrons, as shown in the following equation for uranium-235 and in Figure 21.3.4:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{236}_{92}\mathrm{U} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} \tag{21.3.10}$$

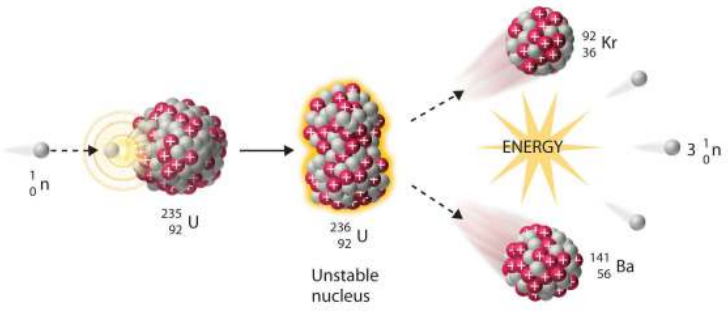


Figure 21.3.4 Neutron-Induced Nuclear Fission. Collision of a relatively slow-moving neutron with a fissile nucleus can split it into two smaller nuclei with the same or different masses. Neutrons are also released in the process, along with a great deal of energy.

Any isotope that can undergo a nuclear fission reaction when bombarded with neutrons is called a **fissile isotope**.

During nuclear fission, the nucleus usually divides asymmetrically rather than into two equal parts, as shown in Figure 21.3.4. Moreover, every fission event of a given nuclide does not give the same products; more than 50 different fission modes have been identified for uranium-235, for example. Consequently, nuclear fission of a fissile nuclide can never be described by a single equation. Instead, as shown in Figure 21.3.5, a distribution of many pairs of fission products with different yields is obtained, but the mass ratio of each pair of fission products produced by a single fission event is always roughly 3:2.

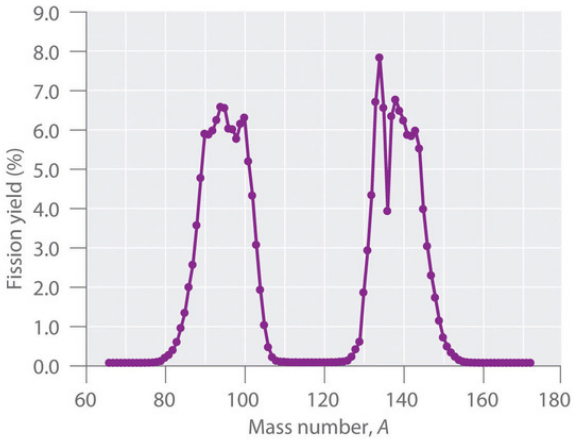


Figure 21.3.5: Mass Distribution of Nuclear Fission Products of ^{235}U. Nuclear fission usually produces a range of products with different masses and yields, although the mass ratio of each pair of fission products from a fission event is approximately 3:2. As shown in this plot, more than 50 different fission products are known for ^{235}U. Data source: T. R. England and B. F. Rider, Los Alamos National Laboratory, LA-UR-94-3106, ENDF-349 (1993).

Synthesis of Transuranium Elements

Uranium (Z = 92) is the heaviest naturally occurring element. Consequently, all the elements with Z > 92, the **transuranium elements**, are artificial and have been prepared by bombarding suitable target nuclei with smaller particles. The first of the transuranium elements to be prepared was neptunium (Z = 93), which was synthesized in 1940 by bombarding a ^{238}U target with neutrons. As shown in Equation 20.21, this reaction occurs in two steps. Initially, a neutron combines with a ^{238}U nucleus to form ^{239}U, which is unstable and undergoes beta decay to produce ^{239}Np:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\beta$$

Subsequent beta decay of ^{239}Np produces the second transuranium element, plutonium (Z = 94):

$$^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\beta$$

Bombarding the target with more massive nuclei creates elements that have atomic numbers significantly greater than that of the target nucleus (Table 21.3.2). Such techniques have resulted in the creation of the superheavy elements 114 and 116, both of which lie in or near the “island of stability."

Table 21.3.2: Some Reactions Used to Synthesize Transuranium Elements

$^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\alpha \rightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}\mathrm{n}$
$^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\alpha \rightarrow {}^{241}_{95}\mathrm{Am} + {}^{1}_{1}\mathrm{p} + {}^{1}_{0}\mathrm{n}$
$^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\alpha \rightarrow {}^{243}_{97}\mathrm{Bk} + {}^{1}_{1}\mathrm{p} + 2{}^{1}_{0}\mathrm{n}$
$^{253}_{99}\mathrm{Es} + {}^{4}_{2}\alpha \rightarrow {}^{256}_{101}\mathrm{Md} + {}^{1}_{0}\mathrm{n}$
$^{238}_{92}\mathrm{U} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{246}_{98}\mathrm{Cf} + 4{}^{1}_{0}\mathrm{n}$
$^{252}_{98}\mathrm{Cf} + {}^{10}_{5}\mathrm{B} \rightarrow {}^{256}_{103}\mathrm{Lr} + 6{}^{1}_{0}\mathrm{n}$

A device called a particle accelerator is used to accelerate positively charged particles to the speeds needed to overcome the electrostatic repulsions between them and the target nuclei by using electrical and magnetic fields. Operationally, the simplest particle accelerator is the linear accelerator (Figure 21.3.6), in which a beam of particles is injected at one end of a long evacuated tube. Rapid alternation of the polarity of the electrodes along the tube causes the particles to be alternately accelerated toward a region of opposite charge and repelled by a region with the same charge, resulting in a tremendous acceleration as the particle travels down the tube. A modern linear accelerator such as the Stanford Linear Accelerator (SLAC) at Stanford University is about 2 miles long.

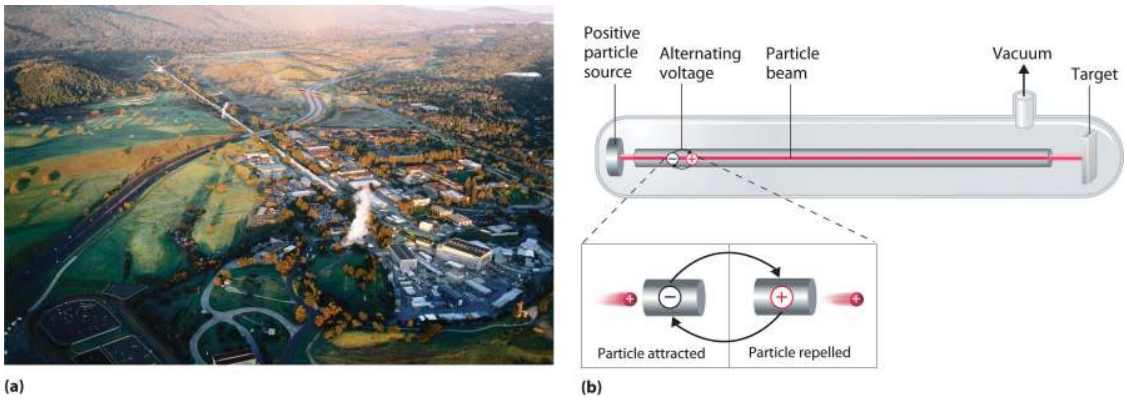


Figure 21.3.6: A Linear Particle Accelerator. (a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as they enter one section of the tube and repelled as they leave that section. As a result, the particles are continuously accelerated along the length of the tube.

To achieve the same outcome in less space, a particle accelerator called a cyclotron forces the charged particles to travel in a circular path rather than a linear one. The particles are injected into the center of a ring and accelerated by rapidly alternating the polarity of two large D-shaped electrodes above and below the ring, which accelerates the particles outward along a spiral path toward the target.

The length of a linear accelerator and the size of the D-shaped electrodes in a cyclotron severely limit the kinetic energy that particles can attain in these devices. These limitations can be overcome by using a synchrotron, a hybrid of the two designs. A synchrotron contains an evacuated tube similar to that of a linear accelerator, but the tube is circular and can be more than a mile in diameter. Charged particles are accelerated around the circle by a series of magnets whose polarities rapidly alternate.

Summary and Key Takeaway

- Nuclear decay reactions occur spontaneously under all conditions and produce more stable daughter nuclei, whereas nuclear transmutation reactions are induced and form a product nucleus that is more massive than the starting material.

In **nuclear decay reactions (or radioactive decay)**, the parent nucleus is converted to a more stable daughter nucleus. Nuclei with too many neutrons decay by converting a neutron to a proton, whereas nuclei with too few neutrons decay by converting a proton to a neutron. Very heavy nuclei (with $A \geq 200$ and $Z > 83$) are unstable and tend to decay by emitting an **α particle**. When an unstable nuclide undergoes radioactive decay, the total number of nucleons is conserved, as is the total positive charge. Six different kinds of nuclear decay reactions are known. *Alpha decay* results in the emission of an α particle, ${}^{4}_{2}\alpha$, and produces a daughter nucleus with a mass number that is lower by 4 and an atomic number that is lower by 2 than the parent nucleus. **Beta decay** converts a neutron to a proton and emits a high-energy electron, producing a daughter nucleus with the same mass number as the parent and an atomic number that is higher by 1. **Positron emission** is the opposite of beta decay and converts a proton to a neutron plus a positron. Positron emission does not change the mass number of the nucleus, but the atomic number of the daughter nucleus is lower by 1 than the parent. In **electron capture (EC)**, an electron in an inner shell reacts with a proton to produce a neutron, with emission of an x-ray. The mass number does not change, but the atomic number of the daughter is lower by 1 than the parent. In **gamma emission**, a daughter nucleus in a nuclear excited state undergoes a transition to a lower-energy state by emitting a γ ray. Very heavy nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that can have different atomic numbers and atomic masses with the release of neutrons. Many very heavy nuclei decay via a **radioactive decay series**—a succession of some combination of alpha- and beta-decay reactions. In **nuclear transmutation reactions**, a target nucleus is bombarded with energetic subatomic particles to give a product nucleus that is more massive than the original. All **transuranium elements**—elements with $Z > 92$—are artificial and must be prepared by nuclear transmutation reactions. These reactions are carried out in particle accelerators such as linear accelerators, cyclotrons, and synchrotrons.

Key Equations

alpha decay

$$ {}^{A}_{Z}\mathrm{X} \rightarrow {}^{A-4}_{Z-2}\mathrm{X}' + {}^{4}_{2}\alpha $$

beta decay

$$^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z+1}\mathrm{X}' + {}^{0}_{-1}\beta$$

positron emission

$$^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z-1}\mathrm{X}' + {}^{0}_{+1}\beta$$

electron capture

$$^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{A}_{Z-1}\mathrm{X}' + \text{x-ray}$$

gamma emission

$$^{A}_{Z}\mathrm{X}^{*} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{0}\gamma$$

21.3: Nuclear Radiation is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **21.1: Radioactivity** is licensed CC BY-NC-SA 3.0.

21.4: Rates of Radioactive Decay

Learning Objectives

- To know how to use half-lives to describe the rates of first-order reactions

The rate of radioactive decay is an intrinsic property of each radioactive isotope that is independent of the chemical and physical form of the radioactive isotope. The rate is also independent of temperature. In this section, we will describe radioactive decay rates and how half-lives can be used to monitor radioactive decay processes.

A Quick Primer from Chemical Kinetics

As discussed previously, the half-life of a first-order reaction is independent of the concentration of the reactants. This becomes evident when we rearrange the integrated rate law for a first-order reaction to produce the following equation:

$$\ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]} = kt \tag{21.4.1}$$

Substituting $[\mathrm{A}]_{0/2}$ for [A] and $t_{1/2}$ for t (to indicate a half-life) into Equation 21.4.1 gives

$$\ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]_0/2} = \ln 2 = kt_{1/2} \tag{21.4.2}$$

Substituting $\ln 2 \approx 0.693$ into the equation results in the expression for the half-life of a first-order reaction:

$$t_{1/2} = \frac{0.693}{k} \tag{21.4.3}$$

Thus, for a first-order reaction, each successive half-life is the same length of time. Since radioactivity follows first order decay kinetics, these equations are also applicable for this type of nuclear reactions.

In any sample of a given radioactive substance, the number of atoms of the radioactive isotope must decrease with time as their nuclei decay to nuclei of a more stable isotope. Using N to represent the number of atoms of the radioactive isotope, we can define the **rate of decay** of the sample, which is also called its **activity** (A) as the decrease in the number of the radioisotope's nuclei per unit time:

$$A = -\frac{\Delta N}{\Delta t} \tag{21.4.4}$$

Activity is usually measured in disintegrations per second (dps) or disintegrations per minute (dpm).

The activity of a sample is directly proportional to the number of atoms of the radioactive isotope in the sample:

$$A = kN \tag{21.4.5}$$

Here, the symbol k is the radioactive decay constant, which has units of inverse time (e.g., s^{-1}, yr^{-1}) and a characteristic value for each radioactive isotope. If we combine Equation 21.4.4 and Equation 21.4.5, we obtain the relationship between the number of decays per unit time and the number of atoms of the isotope in a sample:

$$-\frac{\Delta N}{\Delta t} = kN \tag{21.4.6}$$

Equation 21.4.6 is the same as the equation for the reaction rate of a first-order reaction, except that it uses numbers of atoms instead of concentrations. In fact, radioactive decay is a first-order process and can be described in terms of either the differential rate law (Equation 21.4.6) or the integrated rate law:

$$N = N_0 e^{-kt} \tag{21.4.7}$$

$$\ln \frac{N}{N_0} = -kt \tag{21.4.8}$$

Because radioactive decay is a first-order process, the time required for half of the nuclei in any sample of a radioactive isotope to decay is a constant, called the half-life of the isotope. The half-life tells us how radioactive an isotope is (the number of decays per unit time); thus it is the most commonly cited property of any radioisotope. For a given number of atoms, isotopes with shorter half-lives decay more rapidly, undergoing a greater number of radioactive decays per unit time than do isotopes with longer half-lives. The half-lives of several isotopes are listed in Table 21.4.1, along with some of their applications.

Table 21.4.1: Half-Lives and Applications of Some Radioactive Isotopes

Radioactive Isotope	Half-Life	Typical Uses
hydrogen-3 (tritium)	12.32 yr	biochemical tracer
carbon-11	20.33 min	positron emission tomography (biomedical imaging)
carbon-14	5.70×10^3 yr	dating of artifacts
sodium-24	14.951 h	cardiovascular system tracer
phosphorus-32	14.26 days	biochemical tracer
potassium-40	1.248×10^9 yr	dating of rocks
iron-59	44.495 days	red blood cell lifetime tracer
cobalt-60	5.2712 yr	radiation therapy for cancer
technetium-99*m**	6.006 h	biomedical imaging
iodine-131	8.0207 days	thyroid studies tracer
radium-226	1.600×10^3 yr	radiation therapy for cancer
uranium-238	4.468×10^9 yr	dating of rocks and Earth's crust
americium-241	432.2 yr	smoke detectors

*The *m* denotes metastable, where an excited state nucleus decays to the ground state of the same isotope.

Radioisotope Dating Techniques

In our earlier discussion, we used the half-life of a first-order reaction to calculate how long the reaction had been occurring. Because nuclear decay reactions follow first-order kinetics and have a rate constant that is independent of temperature and the chemical or physical environment, we can perform similar calculations using the half-lives of isotopes to estimate the ages of geological and archaeological artifacts. The techniques that have been developed for this application are known as radioisotope dating techniques.

The most common method for measuring the age of ancient objects is carbon-14 dating. The carbon-14 isotope, created continuously in the upper regions of Earth's atmosphere, reacts with atmospheric oxygen or ozone to form $^{14}CO_2$. As a result, the CO_2 that plants use as a carbon source for synthesizing organic compounds always includes a certain proportion of $^{14}CO_2$ molecules as well as nonradioactive $^{12}CO_2$ and $^{13}CO_2$. Any animal that eats a plant ingests a mixture of organic compounds that contains approximately the same proportions of carbon isotopes as those in the atmosphere. When the animal or plant dies, the carbon-14 nuclei in its tissues decay to nitrogen-14 nuclei by a radioactive process known as beta decay, which releases low-energy electrons (β particles) that can be detected and measured:

$$^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + \beta^- \tag{21.4.9}$$

The half-life for this reaction is 5700 ± 30 yr.

The $^{14}C/^{12}C$ ratio in living organisms is 1.3×10^{-12}, with a decay rate of 15 dpm/g of carbon (Figure 21.4.1). Comparing the disintegrations per minute per gram of carbon from an archaeological sample with those from a recently living sample enables scientists to estimate the age of the artifact, illustrated below. Using this method implicitly assumes that the $^{14}CO_2/^{12}CO_2$ ratio in the atmosphere is constant, which is not strictly correct. Other methods, such as tree-ring dating, have been used to calibrate the

dates obtained by radiocarbon dating, and all radiocarbon dates reported are now corrected for minor changes in the $^{14}CO_2/^{12}CO_2$ ratio over time.

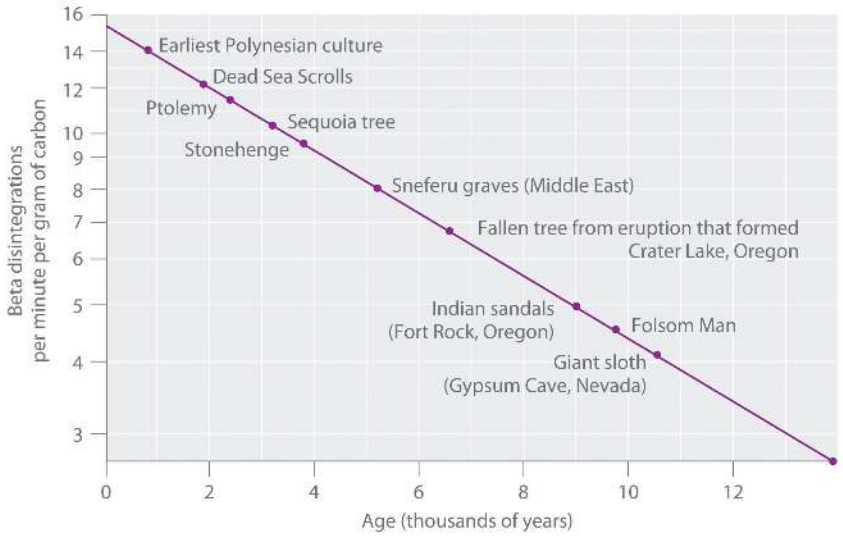


Figure 21.4.1: Radiocarbon Dating. A plot of the specific activity of ^{14}C versus age for a number of archaeological samples shows an inverse linear relationship between ^{14}C content (a log scale) and age (a linear scale).

Example 21.4.1

In 1990, the remains of an apparently prehistoric man were found in a melting glacier in the Italian Alps. Analysis of the ^{14}C content of samples of wood from his tools gave a decay rate of 8.0 dpm/g carbon. How long ago did the man die?

Given: isotope and final activity

Asked for: elapsed time

Strategy:

A Use Equation 21.4.5 to calculate N_0/N. Then substitute the value for the half-life of ^{14}C into Equation 21.4.3 to find the rate constant for the reaction.

B Using the values obtained for N_0/N and the rate constant, solve Equation 21.4.8 to obtain the elapsed time.

Solution

We know the initial activity from the isotope's identity (15 dpm/g), the final activity (8.0 dpm/g), and the half-life, so we can use the integrated rate law for a first-order nuclear reaction (Equation 21.4.8) to calculate the elapsed time (the amount of time elapsed since the wood for the tools was cut and began to decay).

$$\ln \frac{N}{N_0} = -kt$$

$$\frac{\ln(N/N_0)}{k} = t$$

A From Equation 21.4.5, we know that $A = kN$. We can therefore use the initial and final activities (A_0 = 15 dpm and A = 8.0 dpm) to calculate N_0/N:

$$dfracA_0A = \frac{kN_0}{kN} = \frac{N_0}{N} = \frac{15}{8.0}$$

Now we need only calculate the rate constant for the reaction from its half-life (5730 yr) using Equation 21.4.3:

$$t_{1/2} = \frac{0.693}{k}$$

This equation can be rearranged as follows:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730\ \text{yr}} = 1.22 \times 10^{-4}\ \text{yr}^{-1}$$

B Substituting into the equation for *t*,

$$t = \frac{\ln(N_0/N)}{k} = \frac{\ln(15/8.0)}{1.22 \times 10^{-4}\ \text{yr}^{-1}} = 5.2 \times 10^{3}\ \text{yr}$$

From our calculations, the man died 5200 yr ago.

Exercise 21.4.1

It is believed that humans first arrived in the Western Hemisphere during the last Ice Age, presumably by traveling over an exposed land bridge between Siberia and Alaska. Archaeologists have estimated that this occurred about 11,000 yr ago, but some argue that recent discoveries in several sites in North and South America suggest a much earlier arrival. Analysis of a sample of charcoal from a fire in one such site gave a ^{14}C decay rate of 0.4 dpm/g of carbon. What is the approximate age of the sample?

Answer

30,000 yr

Summary

- The half-life of a first-order reaction is independent of the concentration of the reactants.
- The half-lives of radioactive isotopes can be used to date objects.

The half-life of a reaction is the time required for the reactant concentration to decrease to one-half its initial value. The half-life of a first-order reaction is a constant that is related to the rate constant for the reaction: $t_{1/2} = 0.693/k$. Radioactive decay reactions are first-order reactions. The rate of decay, or activity, of a sample of a radioactive substance is the decrease in the number of radioactive nuclei per unit time.

21.4: Rates of Radioactive Decay is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

21.5: Stability of the Atomic Nucleus

Learning Objectives

- To calculate a mass-energy balance and a nuclear binding energy.
- To understand the differences between nuclear fission and fusion.

Nuclear reactions, like chemical reactions, are accompanied by changes in energy. The energy changes in nuclear reactions, however, are enormous compared with those of even the most energetic chemical reactions. In fact, the energy changes in a typical nuclear reaction are so large that they result in a measurable change of mass. In this section, we describe the relationship between mass and energy in nuclear reactions and show how the seemingly small changes in mass that accompany nuclear reactions result in the release of enormous amounts of energy.

Mass–Energy Balance

The relationship between mass (m) and energy (E) is expressed in the following equation:

$$E = mc^2 \tag{21.5.1}$$

where c is the speed of light (2.998×10^8 m/s), and E and m are expressed in units of joules and kilograms, respectively. Albert Einstein first derived this relationship in 1905 as part of his special theory of relativity: the mass of a particle is directly proportional to its energy. Thus according to Equation 20.27, every mass has an associated energy, and similarly, any reaction that involves a change in energy must be accompanied by a change in mass. This implies that all exothermic reactions should be accompanied by a decrease in mass, and all endothermic reactions should be accompanied by an increase in mass. Given the law of conservation of mass, how can this be true? The solution to this apparent contradiction is that chemical reactions are indeed accompanied by changes in mass, but these changes are simply too small to be detected. As you may recall, all particles exhibit wavelike behavior, but the wavelength is inversely proportional to the mass of the particle (actually, to its momentum, the product of its mass and velocity). Consequently, wavelike behavior is detectable only for particles with very small masses, such as electrons. For example, the chemical equation for the combustion of graphite to produce carbon dioxide is as follows:

$$\mathrm{C(graphite)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \quad \Delta H^\circ = -393.5\ \mathrm{kJ/mol} \tag{21.5.2}$$

Combustion reactions are typically carried out at constant pressure, and under these conditions, the heat released or absorbed is equal to ΔH. When a reaction is carried out at constant volume, the heat released or absorbed is equal to ΔE. For most chemical reactions, however, ΔE ≈ ΔH. If we rewrite Einstein's equation as

$$\Delta E = (\Delta m)c^2 \tag{21.5.3}$$

we can rearrange the equation to obtain the following relationship between the change in mass and the change in energy:

$$\Delta m = \frac{\Delta E}{c^2} \tag{21.5.4}$$

Because 1 J = 1 (kg·m^2)/s^2, the change in mass is as follows:

$$\Delta m = \frac{-393.5\ \mathrm{kJ/mol}}{(2.998 \times 10^8\ \mathrm{m/s})^2} = \frac{-3.935 \times 10^5 (\mathrm{kg \cdot m^2})/(\mathrm{s^2 \cdot mol})}{(2.998 \times 10^8\ \mathrm{m/s})^2} = -4.38 \times 10^{-12}\ \mathrm{kg/mol} \tag{21.5.5}$$

This is a mass change of about 3.6×10^{-10} g/g carbon that is burned, or about 100-millionths of the mass of an electron per atom of carbon. In practice, this mass change is much too small to be measured experimentally and is negligible.

In contrast, for a typical nuclear reaction, such as the radioactive decay of ^{14}C to ^{14}N and an electron (a β particle), there is a much larger change in mass:

$$^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + {}^{0}_{-1}\beta \tag{21.5.6}$$

We can use the experimentally measured masses of subatomic particles and common isotopes to calculate the change in mass directly. The reaction involves the conversion of a neutral ^{14}C atom to a positively charged ^{14}N ion (with six, not seven, electrons) and a negatively charged β particle (an electron), so the mass of the products is identical to the mass of a neutral ^{14}N atom. The

total change in mass during the reaction is therefore the difference between the mass of a neutral ^{14}N atom (14.003074 amu) and the mass of a ^{14}C atom (14.003242 amu):

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} \tag{21.5.7}$$

$$= 14.003074 \text{ amu} - 14.003242 \text{ amu} = -0.000168 \text{ amu} \tag{21.5.8}$$

The difference in mass, which has been released as energy, corresponds to almost one-third of an electron. The change in mass for the decay of 1 mol of ^{14}C is −0.000168 g = -1.68×10^{-4} g = -1.68×10^{-7} kg. Although a mass change of this magnitude may seem small, it is about 1000 times larger than the mass change for the combustion of graphite. The energy change is as follows:

$$\Delta E = (\Delta m)c^2 = (-1.68 \times 10^{-7} \text{ kg})(2.998 \times 10^8 \text{ m/s})^2 \tag{21.5.9}$$

$$= -1.51 \times 10^{10} (\text{kg} \cdot \text{m}^2)/\text{s}^2 = -1.51 \times 10^{10} \text{ J} = -1.51 \times 10^7 \text{ kJ} \tag{21.5.10}$$

The energy released in this nuclear reaction is more than 100,000 times greater than that of a typical chemical reaction, even though the decay of ^{14}C is a relatively low-energy nuclear reaction.

Because the energy changes in nuclear reactions are so large, they are often expressed in kiloelectronvolts (1 keV = 10^3 eV), megaelectronvolts (1 MeV = 10^6 eV), and even gigaelectronvolts (1 GeV = 10^9 eV) per atom or particle. The change in energy that accompanies a nuclear reaction can be calculated from the change in mass using the relationship 1 amu = 931 MeV. The energy released by the decay of one atom of ^{14}C is thus

$$(-1.68 \times 10^{-4} \text{ amu}) \left(\frac{931 \text{ MeV}}{\text{amu}} \right) = -0.156 \text{ MeV} = -156 \text{ keV} \tag{21.5.11}$$

Example 21.5.1

Calculate the changes in mass (in atomic mass units) and energy (in joules per mole and electronvolts per atom) that accompany the radioactive decay of ^{238}U to ^{234}Th and an α particle. The α particle absorbs two electrons from the surrounding matter to form a helium atom.

Given: nuclear decay reaction

Asked for: changes in mass and energy

Strategy:

A Use the mass values in Table 20.1 to calculate the change in mass for the decay reaction in atomic mass units.

B Use Equation 20.30 to calculate the change in energy in joules per mole.

C Use the relationship between atomic mass units and megaelectronvolts to calculate the change in energy in electronvolts per atom.

Solution

A Using particle and isotope masses from Table 20.1, we can calculate the change in mass as follows:

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} = (\text{mass } ^{234}\text{Th} + \text{mass } ^4_2\text{He}) - \text{mass } ^{238}\text{U} \tag{21.5.12}$$

$$= (234.043601 \text{ amu} + 4.002603 \text{ amu}) - 238.050788 \text{ amu} = -0.004584 \text{ amu} \tag{21.5.13}$$

B Thus the change in mass for 1 mol of ^{238}U is −0.004584 g or -4.584×10^{-6} kg. The change in energy in joules per mole is as follows:

$$\Delta E = (\Delta m)c^2 = (-4.584 \times 10^{-6} \text{ kg})(2.998 \times 10^8 \text{ m/s})^2 = -4.120 \times 10^{11} \text{ J/mol}$$

C The change in energy in electronvolts per atom is as follows:

$$\Delta E = -4.584 \times 10^{-3} \text{ amu} \times \frac{931 \text{ MeV}}{\text{amu}} \times \frac{1 \times 10^6 \text{ eV}}{1 \text{ MeV}} = -4.27 \times 10^6 \text{ eV/atom}$$

? Exercise 21.5.1

Calculate the changes in mass (in atomic mass units) and energy (in kilojoules per mole and kiloelectronvolts per atom) that accompany the radioactive decay of tritium (^{3}H) to ^{3}He and a β particle.

Answer

$\Delta m = -2.0 \times 10^{-5}$ amu; $\Delta E = -1.9 \times 10^6$ kJ/mol = −19 keV/atom

Nuclear Binding Energies

We have seen that energy changes in both chemical and nuclear reactions are accompanied by changes in mass. Einstein's equation, which allows us to interconvert mass and energy, has another interesting consequence: The mass of an atom is always less than the sum of the masses of its component particles. The only exception to this rule is hydrogen-1 (^{1}H), whose measured mass of 1.007825 amu is identical to the sum of the masses of a proton and an electron. In contrast, the experimentally measured mass of an atom of deuterium (^{2}H) is 2.014102 amu, although its calculated mass is 2.016490 amu:

$$m_{^2\mathrm{H}} = m_{\text{neutron}} + m_{\text{proton}} + m_{\text{electron}} \tag{21.5.14}$$

$$= 1.008665 \text{ amu} + 1.007276 \text{ amu} + 0.000549 \text{ amu} = 2.016490 \text{ amu} \tag{21.5.15}$$

The difference between the sum of the masses of the components and the measured atomic mass is called the **mass defect** of the nucleus. Just as a molecule is more stable than its isolated atoms, a nucleus is more stable (lower in energy) than its isolated components. Consequently, when isolated nucleons assemble into a stable nucleus, energy is released. According to Equation 21.5.4, this release of energy must be accompanied by a decrease in the mass of the nucleus.

The amount of energy released when a nucleus forms from its component nucleons is the **nuclear binding energy** (Figure 21.2.1). In the case of deuterium, the mass defect is 0.002388 amu, which corresponds to a nuclear binding energy of 2.22 MeV for the deuterium nucleus. Because the magnitude of the mass defect is proportional to the nuclear binding energy, both values indicate the stability of the nucleus.

> Just as a molecule is more stable (lower in energy) than its isolated atoms, a nucleus is more stable than its isolated components.

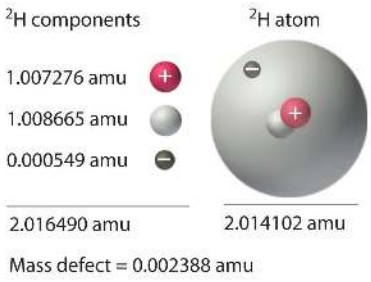


Figure 21.5.1: Nuclear Binding Energy in Deuterium. *The mass of a ^{2}H atom is less than the sum of the masses of a proton, a neutron, and an electron by 0.002388 amu; the difference in mass corresponds to the nuclear binding energy. The larger the value of the mass defect, the greater the nuclear binding energy and the more stable the nucleus.*

Not all nuclei are equally stable. Chemists describe the relative stability of different nuclei by comparing the binding energy per nucleon, which is obtained by dividing the nuclear binding energy by the mass number (A) of the nucleus. As shown in Figure 21.5.2, the binding energy per nucleon increases rapidly with increasing atomic number until about Z = 26, where it levels off to about 8–9 MeV per nucleon and then decreases slowly. The initial increase in binding energy is not a smooth curve but exhibits sharp peaks corresponding to the light nuclei that have equal numbers of protons and neutrons (e.g., ^{4}He, ^{12}C, and ^{16}O). As mentioned earlier, these are particularly stable combinations.

Because the maximum binding energy per nucleon is reached at ^{56}Fe, all other nuclei are thermodynamically unstable with regard to the formation of ^{56}Fe. Consequently, heavier nuclei (toward the right in 21.5.2) should spontaneously undergo reactions such as alpha decay, which result in a decrease in atomic number. Conversely, lighter elements (on the left in Figure 21.5.2) should spontaneously undergo reactions that result in an increase in atomic number. This is indeed the observed pattern.

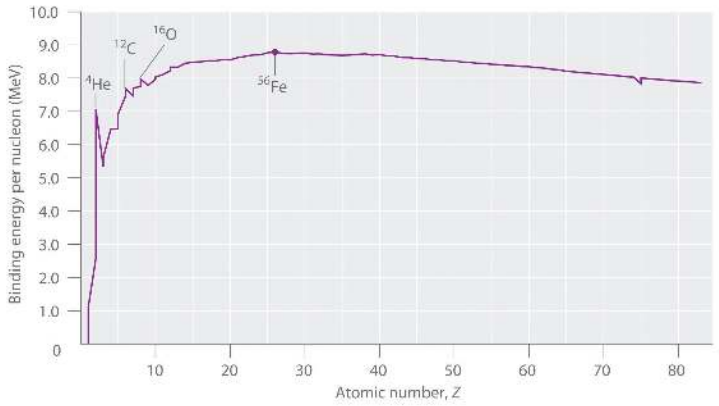


Figure 21.5.3: The Curve of Nuclear Binding Energy. This plot of the average binding energy per nucleon as a function of atomic number shows that the binding energy per nucleon increases with increasing atomic number until about Z = 26, levels off, and then decreases. The sharp peaks correspond to light nuclei that have equal numbers of protons and neutrons.

Heavier nuclei spontaneously undergo nuclear reactions that *decrease* their atomic number. Lighter nuclei spontaneously undergo nuclear reactions that *increase* their atomic number.

Example 21.5.2

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{56}Fe. The experimental mass of the nuclide is given in Table A4.

Given: nuclide and mass

Asked for: nuclear binding energy and binding energy per nucleon

Strategy:

A Sum the masses of the protons, electrons, and neutrons or, alternatively, use the mass of the appropriate number of ^{1}H atoms (because its mass is the same as the mass of one electron and one proton).

B Calculate the mass defect by subtracting the experimental mass from the calculated mass.

C Determine the nuclear binding energy by multiplying the mass defect by the change in energy in electronvolts per atom. Divide this value by the number of nucleons to obtain the binding energy per nucleon.

Solution

A An iron-56 atom has 26 protons, 26 electrons, and 30 neutrons. We could add the masses of these three sets of particles; however, noting that 26 protons and 26 electrons are equivalent to 26 ^{1}H atoms, we can calculate the sum of the masses more quickly as follows:

$$\text{calculated mass} = 26(\text{mass } {}^{1}_{1}\text{H}) + 30(\text{mass } {}^{1}_{0}\text{n}) \tag{21.5.16}$$

$$= 26(1.007825)\text{amu} + 30(1.008665)\text{amu} = 56.463400 \text{ amu} \tag{21.5.17}$$

$$\text{experimental mass} = 55.934938 \tag{21.5.18}$$

B We subtract to find the mass defect:

$$\text{mass defect} = \text{calculated mass} - \text{experimental mass} \tag{21.5.19}$$

$$= 56.463400 \text{ amu} - 55.934938 \text{ amu} = 0.528462 \text{ amu} \tag{21.5.20}$$

C The nuclear binding energy is thus 0.528462 amu × 931 MeV/amu = 492 MeV. The binding energy per nucleon is 492 MeV/56 nucleons = 8.79 MeV/nucleon.

? Exercise 21.5.2

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{238}U.

Answer 1800 MeV/^{238}U; 7.57 MeV/nucleon

Nuclear Fission and Fusion

N**uclear fission** is the splitting of a heavy nucleus into two lighter ones. Fission was discovered in 1938 by the German scientists Otto Hahn, Lise Meitner, and Fritz Strassmann, who bombarded a sample of uranium with neutrons in an attempt to produce new elements with Z > 92. They observed that lighter elements such as barium (Z = 56) were formed during the reaction, and they realized that such products had to originate from the neutron-induced fission of uranium-235:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} \tag{21.5.21}$$

This hypothesis was confirmed by detecting the krypton-92 fission product. The nucleus usually divides asymmetrically rather than into two equal parts, and the fission of a given nuclide does not give the same products every time.

In a typical nuclear fission reaction, more than one neutron is released by each dividing nucleus. When these neutrons collide with and induce fission in other neighboring nuclei, a self-sustaining series of nuclear fission reactions known as a **nuclear chain reaction** can result (Figure 21.5.3). For example, the fission of ^{235}U releases two to three neutrons per fission event. If absorbed by other ^{235}U nuclei, those neutrons induce additional fission events, and the rate of the fission reaction increases geometrically. Each series of events is called a generation. Experimentally, it is found that some minimum mass of a fissile isotope is required to sustain a nuclear chain reaction; if the mass is too low, too many neutrons are able to escape without being captured and inducing a fission reaction. The minimum mass capable of supporting sustained fission is called the **critical mass**. This amount depends on the purity of the material and the shape of the mass, which corresponds to the amount of surface area available from which neutrons can escape, and on the identity of the isotope. If the mass of the fissile isotope is greater than the critical mass, then under the right conditions, the resulting supercritical mass can release energy explosively. The enormous energy released from nuclear chain reactions is responsible for the massive destruction caused by the detonation of nuclear weapons such as fission bombs, but it also forms the basis of the nuclear power industry.

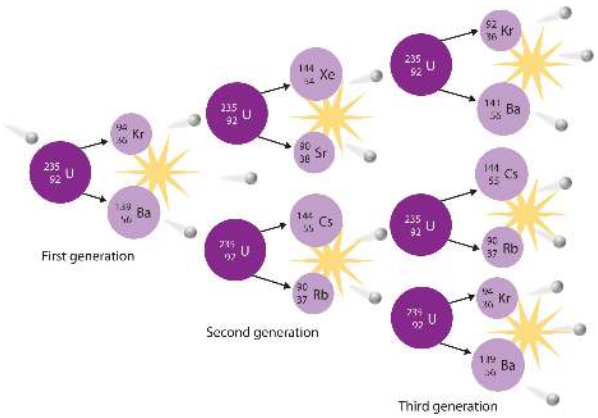


Figure 21.5.3: A Nuclear Chain Reaction. The process is initiated by the collision of a single neutron with a ^{235}U nucleus, which undergoes fission, as shown in Figure 20.6. Because each neutron released can cause the fission of another ^{235}U nucleus, the rate of a fission reaction accelerates geometrically. Each series of events is a generation.

Nuclear fusion, in which two light nuclei combine to produce a heavier, more stable nucleus, is the opposite of nuclear fission. As in the nuclear transmutation reactions discussed in Section 20.2, the positive charge on both nuclei results in a large electrostatic energy barrier to fusion. This barrier can be overcome if one or both particles have sufficient kinetic energy to overcome the electrostatic repulsions, allowing the two nuclei to approach close enough for a fusion reaction to occur. The principle is similar to adding heat to increase the rate of a chemical reaction. As shown in the plot of nuclear binding energy per nucleon versus atomic number in Figure 21.2.3, fusion reactions are most exothermic for the lightest element. For example, in a typical fusion reaction, two deuterium atoms combine to produce helium-3, a process known as deuterium–deuterium fusion (D–D fusion):

$$2{}^{2}_{1}\mathrm{H} \rightarrow {}^{3}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} \tag{21.5.22}$$

In another reaction, a deuterium atom and a tritium atom fuse to produce helium-4 (Figure 21.5.4), a process known as deuterium–tritium fusion (D–T fusion):

$$^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} \tag{21.5.23}$$

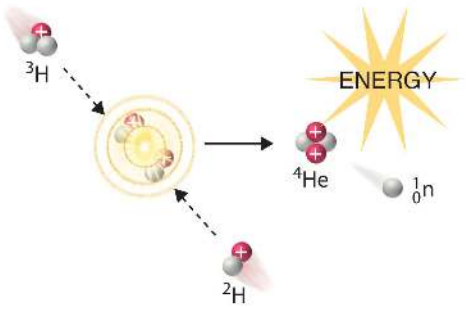


Figure 21.5.4: Nuclear Fusion. In a nuclear fusion reaction, lighter nuclei combine to produce a heavier nucleus. As shown, fusion of ^{3}H and ^{2}H to give ^{4}He and a neutron releases an enormous amount of energy. In principle, nuclear fusion can produce much more energy than fission, but very high kinetic energy is required to overcome electrostatic repulsions between the positively charged nuclei and initiate the fusion reaction.

Initiating these reactions, however, requires a temperature comparable to that in the interior of the sun (approximately 1.5×10^7 K). Currently, the only method available on Earth to achieve such a temperature is the detonation of a fission bomb. For example, the so-called hydrogen bomb (or H bomb) is actually a deuterium–tritium bomb (a D–T bomb), which uses a nuclear fission reaction to create the very high temperatures needed to initiate fusion of solid lithium deuteride (^{6}LiD), which releases neutrons that then react with ^{6}Li, producing tritium. The deuterium-tritium reaction releases energy explosively. Example 9 and its corresponding exercise demonstrate the enormous amounts of energy produced by nuclear fission and fusion reactions. In fact, fusion reactions are the power sources for all stars, including our sun.

Example 21.5.3

Calculate the amount of energy (in electronvolts per atom and kilojoules per mole) released when the neutron-induced fission of ^{235}U produces ^{144}Cs, ^{90}Rb, and two neutrons:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{144}_{55}\mathrm{Cs} + {}^{90}_{37}\mathrm{Rb} + 2{}^{1}_{0}\mathrm{n}$$

Given: balanced nuclear reaction

Asked for: energy released in electronvolts per atom and kilojoules per mole

Strategy:

A Following the method used in Example 21.5.1, calculate the change in mass that accompanies the reaction. Convert this value to the change in energy in electronvolts per atom.

B Calculate the change in mass per mole of ^{235}U. Then use Equation 21.5.3 to calculate the change in energy in kilojoules per mole.

Solution

A The change in mass that accompanies the reaction is as follows:

$$\Delta m = \mathrm{mass}_{\mathrm{products}} - \mathrm{mass}_{\mathrm{reactants}} = \mathrm{mass}(^{144}_{55}\mathrm{Cs} + {}^{90}_{37}\mathrm{Rb} + {}^{1}_{0}\mathrm{n}) - \mathrm{mass}\ {}^{235}_{92}\mathrm{U} \tag{21.5.24}$$

$$= (143.932077\ \mathrm{amu} + 89.914802\ \mathrm{amu} + 1.008665\ \mathrm{amu}) - 235.043930\ \mathrm{amu} \tag{21.5.25}$$

$$= -0.188386\ \mathrm{amu} \tag{21.5.26}$$

The change in energy in electronvolts per atom is as follows:

$$\Delta E = (-0.188386\ \mathrm{amu})(931\ \mathrm{MeV/amu}) = -175\ \mathrm{MeV}$$

B The change in mass per mole of $^{235}_{92}$U is −0.188386 g = -1.88386×10^{-4} kg, so the change in energy in kilojoules per mole is as follows:

$$\Delta E = (\Delta m)c^2 = (-1.88386 \times 10^{-4}\ \mathrm{kg})(2.998 \times 10^8\ \mathrm{m/s})^2 \tag{21.5.27}$$

$$= -1.693 \times 10^{13}\ \mathrm{J/mol} = -1.693 \times 10^{10}\ \mathrm{kJ/mol} \tag{21.5.28}$$

Exercise 21.5.3

Calculate the amount of energy (in electronvolts per atom and kilojoules per mole) released when deuterium and tritium fuse to give helium-4 and a neutron:

$$^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n}$$

Answer

$\Delta E = -17.6 \text{ MeV/atom} = -1.697 \times 10^{9} \text{ kJ/mol}$

Summary

Unlike a chemical reaction, a nuclear reaction results in a significant change in mass and an associated change of energy, as described by Einstein's equation. Nuclear reactions are accompanied by large changes in energy, which result in detectable changes in mass. The change in mass is related to the change in energy according to Einstein's equation: $\Delta E = (\Delta m)c^2$. Large changes in energy are usually reported in kiloelectronvolts or megaelectronvolts (thousands or millions of electronvolts). With the exception of $^{1}\mathrm{H}$, the experimentally determined mass of an atom is always less than the sum of the masses of the component particles (protons, neutrons, and electrons) by an amount called the mass defect of the nucleus. The energy corresponding to the mass defect is the nuclear binding energy, the amount of energy released when a nucleus forms from its component particles. In nuclear fission, nuclei split into lighter nuclei with an accompanying release of multiple neutrons and large amounts of energy. The critical mass is the minimum mass required to support a self-sustaining nuclear chain reaction. Nuclear fusion is a process in which two light nuclei combine to produce a heavier nucleus plus a great deal of energy.

21.5: Stability of the Atomic Nucleus is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **24.5: Thermodynamic Stability of the Atomic Nucleus** by Anonymous is licensed CC BY-NC-SA 4.0.

21.6: The Origin of the Elements

Learning Objectives

- To understand how nuclear transmutation reactions lead to the formation of the elements in stars and how they can be used to synthesize transuranium elements.

The relative abundances of the elements in the known universe vary by more than 12 orders of magnitude. For the most part, these differences in abundance cannot be explained by differences in nuclear stability. Although the ^{56}Fe nucleus is the most stable nucleus known, the most abundant element in the known universe is not iron, but hydrogen (^{1}H), which accounts for about 90% of all atoms. In fact, ^{1}H is the raw material from which all other elements are formed. In this section, we explain why ^{1}H and ^{2}He together account for at least 99% of all the atoms in the known universe. We also describe the nuclear reactions that take place in stars, which transform one nucleus into another and create all the naturally occurring elements.

Relative Abundances of the Elements on Earth and in the Known Universe

The relative abundances of the elements in the known universe and on Earth relative to silicon are shown in Figure 21.6.1. The data are estimates based on the characteristic emission spectra of the elements in stars, the absorption spectra of matter in clouds of interstellar dust, and the approximate composition of Earth as measured by geologists. The data in Figure 21.6.1 illustrate two important points. First, except for hydrogen, the most abundant elements have even atomic numbers. Not only is this consistent with the known trends in nuclear stability, but it also suggests that heavier elements are formed by combining helium nuclei (Z = 2). Second, the relative abundances of the elements in the known universe and on Earth are often very different, as indicated by the data in Table 21.6.1 for some common elements.

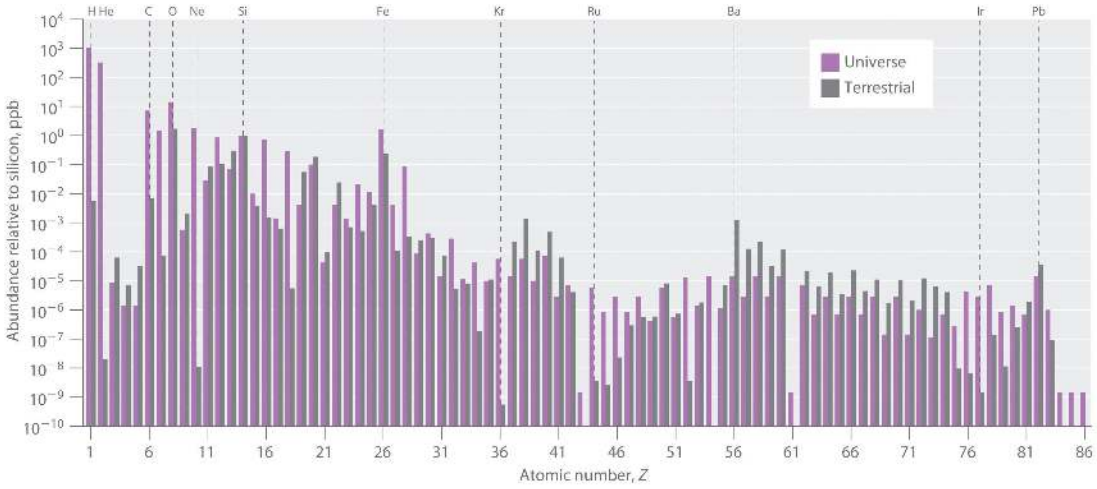


Figure 21.6.1: The Relative Abundances of the Elements in the Universe and on Earth. In this logarithmic plot, the relative abundances of the elements relative to that of silicon (arbitrarily set equal to 1) in the universe (green bars) and on Earth (purple bars) are shown as a function of atomic number. Elements with even atomic numbers are generally more abundant in the universe than elements with odd atomic numbers. Also, the relative abundances of many elements in the universe are very different from their relative abundances on Earth. (CC BY-NC-SA 3.0; anonymous)

Bar graph of abundance realtive to silicon in pbb against atomic number. The purple bars are universe elements while the gray bars are terrestrial elements.

Some of these differences are easily explained. For example, nonmetals such as H, He, C, N, O, Ne, and Kr are much less abundant relative to silicon on Earth than they are in the rest of the universe. These elements are either noble gases (He, Ne, and Kr) or elements that form volatile hydrides, such as NH_3, CH_4, and H_2O. Because Earth's gravity is not strong enough to hold such light substances in the atmosphere, these elements have been slowly diffusing into outer space ever since our planet was formed. Argon is an exception; it is relatively abundant on Earth compared with the other noble gases because it is continuously produced in rocks by the radioactive decay of isotopes such as ^{40}K. In contrast, many metals, such as Al, Na, Fe, Ca, Mg, K, and Ti, are relatively abundant on Earth because they form nonvolatile compounds, such as oxides, that cannot escape into space. Other metals, however, are much less abundant on Earth than in the universe; some examples are Ru and Ir. This section explains some of the reasons for the great differences in abundances of the metallic elements.

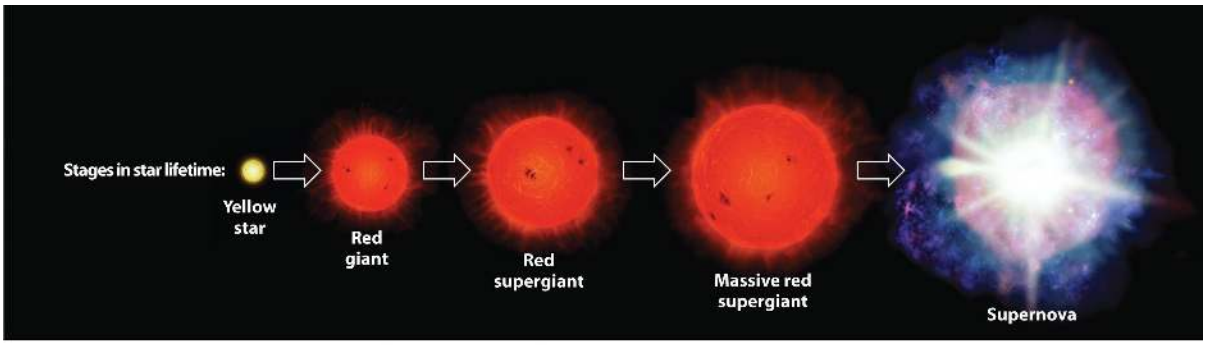
Table 21.6.1: Relative Abundances of Elements on Earth and in the Known Universe

Terrestrial/Universal Element	Abundance Ratio
H	0.0020
He	2.4×10^{-8}
C	0.36
N	0.02
O	46
Ne	1.9×10^{-6}
Na	1200
Mg	48
Al	1600
Si	390
S	0.84
K	5000
Ca	710
Ti	2200
Fe	57

All the elements originally present on Earth (and on other planets) were synthesized from hydrogen and helium nuclei in the interiors of stars that have long since exploded and disappeared. Six of the most abundant elements in the universe (C, O, Ne, Mg, Si, and Fe) have nuclei that are integral multiples of the helium-4 nucleus, which suggests that helium-4 is the primary building block for heavier nuclei.

Synthesis of the Elements in Stars

Elements are synthesized in discrete stages during the lifetime of a star, and some steps occur only in the most massive stars known (Figure 21.6.2). Initially, all stars are formed by the aggregation of interstellar "dust," which is mostly hydrogen. As the cloud of dust slowly contracts due to gravitational attraction, its density eventually reaches about 100 g/cm^3, and the temperature increases to about 1.5×10^7 K, forming a dense plasma of ionized hydrogen nuclei. At this point, self-sustaining nuclear reactions begin, and the star "ignites," creating a yellow star like our sun.



Core Temperature:	1.5×10^7 K	2×10^8 K	7×10^8 K	3×10^9 K	1×10^{11} K
Primary Nuclear Reaction:	^{1}H fusion	^{4}He fusion	$^4\text{He} + {}^{12}\text{C}$ $^{12}\text{C} + {}^{12}\text{C}$ $^{12}\text{C} + {}^{16}\text{O}$	Proton–neutron exchange reactions	Multiple neutron captures
Elements Formed:	He	C, O, Ne, Mg	Na, Si, S, Ar, Ca	Fe, Ni	Elements with $Z > 28$

Figure 21.6.2: Nuclear Reactions during the Life Cycle of a Massive Star. At each stage in the lifetime of a star, a different fuel is used for nuclear fusion, resulting in the formation of different elements. Fusion of hydrogen to give helium is the primary fusion reaction in young stars. As the star ages, helium accumulates and begins to "burn," undergoing fusion to form heavier elements such as carbon and oxygen. As the adolescent star matures, significant amounts of iron and nickel are formed by fusion of the heavier elements formed previously. The heaviest elements are formed only during the final death throes of the star—the formation of a nova or supernova.

The stages in a stare lifetime are yellow star, red giant, red supergiant, massive red supergiant and finally supernova.

In the first stage of its life, the star is powered by a series of nuclear fusion reactions that convert hydrogen to helium:

$$\begin{aligned} {}^1_1\text{H} + {}^1_1\text{H} &\rightarrow {}^2_1\text{H} + {}^0_{+1}\beta \\ {}^2_1\text{H} + {}^1_1\text{H} &\rightarrow {}^3_2\text{He} + {}^0_0\gamma \\ {}^3_2\text{He} + {}^3_2\text{He} &\rightarrow {}^4_2\text{He} + 2{}^1_1\text{H} \end{aligned} \tag{21.6.1}$$

The overall reaction is the conversion of four hydrogen nuclei to a helium-4 nucleus, which is accompanied by the release of two positrons, two γ rays, and a great deal of energy:

$$4{}^1_1\text{H} \rightarrow {}^4_2\text{He} + 2{}^0_{+1}\beta + 2{}^0_0\gamma \tag{21.6.2}$$

These reactions are responsible for most of the enormous amount of energy that is released as sunlight and solar heat. It takes several billion years, depending on the size of the star, to convert about 10% of the hydrogen to helium.

Once large amounts of helium-4 have been formed, they become concentrated in the core of the star, which slowly becomes denser and hotter. At a temperature of about 2×10^8 K, the helium-4 nuclei begin to fuse, producing beryllium-8:

$$2{}^4_2\text{He} \rightarrow {}^8_4\text{Be} \tag{21.6.3}$$

Although beryllium-8 has both an even mass number and an even atomic number, its also has a low neutron-to-proton ratio (and other factors beyond the scope of this text) that makes it unstable; it decomposes in only about 10^{-16} s. Nonetheless, this is long enough for it to react with a third helium-4 nucleus to form carbon-12, which is very stable. Sequential reactions of carbon-12 with helium-4 produce the elements with even numbers of protons and neutrons up to magnesium-24:

$${}^8_4\text{Be} \xrightarrow{{}^4_2\text{He}} {}^{12}_6\text{C} \xrightarrow{{}^4_2\text{He}} {}^{16}_8\text{O} \xrightarrow{{}^4_2\text{He}} {}^{20}_{10}\text{Ne} \xrightarrow{{}^4_2\text{He}} {}^{24}_{12}\text{Mg} \tag{21.6.4}$$

So much energy is released by these reactions that it causes the surrounding mass of hydrogen to expand, producing a red giant that is about 100 times larger than the original yellow star.

As the star expands, heavier nuclei accumulate in its core, which contracts further to a density of about 50,000 g/cm3, so the core becomes even hotter. At a temperature of about 7×10^8 K, carbon and oxygen nuclei undergo nuclear fusion reactions to produce sodium and silicon nuclei:

$${}^{12}_6\text{C} + {}^{12}_6\text{C} \rightarrow {}^{23}_{11}\text{Na} + {}^1_1\text{H} \tag{21.6.5}$$

$${}^{12}_6\text{C} + {}^{16}_8\text{O} \rightarrow {}^{28}_{14}\text{Si} + {}^0_0\gamma \tag{21.6.6}$$

At these temperatures, carbon-12 reacts with helium-4 to initiate a series of reactions that produce more oxygen-16, neon-20, magnesium-24, and silicon-28, as well as heavier nuclides such as sulfur-32, argon-36, and calcium-40:

$$^{12}_{6}\text{C} \xrightarrow{^{4}_{2}\text{He}} {}^{16}_{8}\text{O} \xrightarrow{^{4}_{2}\text{He}} {}^{20}_{10}\text{Ne} \xrightarrow{^{4}_{2}\text{He}} {}^{24}_{12}\text{Mg} \xrightarrow{^{4}_{2}\text{He}} {}^{28}_{14}\text{Si} \xrightarrow{^{4}_{2}\text{He}} {}^{32}_{16}\text{S} \xrightarrow{^{4}_{2}\text{He}} {}^{36}_{18}\text{Ar} \xrightarrow{^{4}_{2}\text{He}} {}^{40}_{20}\text{Ca} \tag{21.6.7}$$

The energy released by these reactions causes a further expansion of the star to form a red supergiant, and the core temperature increases steadily. At a temperature of about 3×10^9 K, the nuclei that have been formed exchange protons and neutrons freely. This equilibration process forms heavier elements up to iron-56 and nickel-58, which have the most stable nuclei known.

The Formation of Heavier Elements in Supernovas

None of the processes described so far produces nuclei with Z > 28. All naturally occurring elements heavier than nickel are formed in the rare but spectacular cataclysmic explosions called supernovas (Figure 21.6.2). When the fuel in the core of a very massive star has been consumed, its gravity causes it to collapse in about 1 s. As the core is compressed, the iron and nickel nuclei within it disintegrate to protons and neutrons, and many of the protons capture electrons to form neutrons. The resulting neutron star is a dark object that is so dense that atoms no longer exist. Simultaneously, the energy released by the collapse of the core causes the supernova to explode in what is arguably the single most violent event in the universe. The force of the explosion blows most of the star's matter into space, creating a gigantic and rapidly expanding dust cloud, or nebula (Figure 21.6.3). During the extraordinarily short duration of this event, the concentration of neutrons is so great that multiple neutron-capture events occur, leading to the production of the heaviest elements and many of the less stable nuclides. Under these conditions, for example, an iron-56 nucleus can absorb as many as 64 neutrons, briefly forming an extraordinarily unstable iron isotope that can then undergo multiple rapid β-decay processes to produce tin-120:

$$^{56}_{26}\text{Fe} + 64\,^{1}_{0}\text{n} \rightarrow {}^{120}_{26}\text{Fe} \rightarrow {}^{120}_{50}\text{Sn} + 24\,^{0}_{-1}\beta \tag{21.6.8}$$

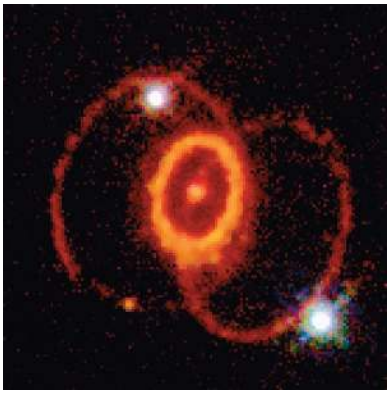


Figure 21.6.3: A Supernova. A view of the remains of Supernova 1987A, located in the Large Magellanic Cloud, showing the circular halo of expanding debris produced by the explosion. Multiple neutron-capture events occur during a supernova explosion, forming both the heaviest elements and many of the less stable nuclides.

Although a supernova occurs only every few hundred years in a galaxy such as the Milky Way, these rare explosions provide the only conditions under which elements heavier than nickel can be formed. The force of the explosions distributes these elements throughout the galaxy surrounding the supernova, and eventually they are captured in the dust that condenses to form new stars. Based on its elemental composition, our sun is thought to be a second- or third-generation star. It contains a considerable amount of cosmic debris from the explosion of supernovas in the remote past.

Example 21.6.1: Carbon Burning Stars

The reaction of two carbon-12 nuclei in a carbon-burning star can produce elements other than sodium. Write a balanced nuclear equation for the formation of

a. magnesium-24.
b. neon-20 from two carbon-12 nuclei.

Given: reactant and product nuclides

Asked for: balanced nuclear equation

Strategy:

Use conservation of mass and charge to determine the type of nuclear reaction that will convert the reactant to the indicated product. Write the balanced nuclear equation for the reaction.

Solution

a. A magnesium-24 nucleus (Z = 12, A = 24) has the same nucleons as two carbon-12 nuclei (Z = 6, A = 12). The reaction is therefore a fusion of two carbon-12 nuclei, and no other particles are produced: ${}^{12}_{6}\mathrm{C} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{24}_{12}\mathrm{Mg}$.

b. The neon-20 product has Z = 10 and A = 20. The conservation of mass requires that the other product have A = (2 × 12) − 20 = 4; because of conservation of charge, it must have Z = (2 × 6) − 10 = 2. These are the characteristics of an α particle. The reaction is therefore ${}^{12}_{6}\mathrm{C} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{20}_{10}\mathrm{Ne} + {}^{4}_{2}\alpha$.

? Exercise 21.6.1

How many neutrons must an iron-56 nucleus absorb during a supernova explosion to produce an arsenic-75 nucleus? Write a balanced nuclear equation for the reaction.

Answer

19 neutrons; ${}^{56}_{26}\mathrm{Fe} + 19{}^{1}_{0}\mathrm{n} \rightarrow {}^{75}_{26}\mathrm{Fe} \rightarrow {}^{75}_{33}\mathrm{As} + 7{}^{0}_{-1}\beta$

Summary

Hydrogen and helium are the most abundant elements in the universe. Heavier elements are formed in the interior of stars via multiple neutron-capture events. By far the most abundant element in the universe is hydrogen. The fusion of hydrogen nuclei to form helium nuclei is the major process that fuels young stars such as the sun. Elements heavier than helium are formed from hydrogen and helium in the interiors of stars. Successive fusion reactions of helium nuclei at higher temperatures create elements with even numbers of protons and neutrons up to magnesium and then up to calcium. Eventually, the elements up to iron-56 and nickel-58 are formed by exchange processes at even higher temperatures. Heavier elements can only be made by a process that involves multiple neutron-capture events, which can occur only during the explosion of a supernova.

21.6: The Origin of the Elements is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **21.3: Nuclear Transmutations** by Anonymous is licensed CC BY-NC-SA 3.0.

21.7: Transmutation of the Elements

Although the conversion of one element to another is the basis of natural radioactive decay, it is also possible to convert one element to another experimentally. The conversion of one element to another is the process of transmutation. In 1919 Rutherford converted a stable isotope to an unstable one. By bombarding ^{14}N with α particles he created ^{17}O, which is an unstable isotope of oxygen. Transmutation may also be accomplished by bombardment with neutrons.

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H} \tag{21.7.1}$$

Historically, part of Alchemy was the study of methods of creating gold from base metals, such lead. Where the Alchemists failed in this quest, we can now succeed. Thus, bombardment of platinum-198 with a neutron creates an unstable isotope of platinum that undergoes beta decay to gold-199. Unfortunately, while we may succeed in making gold, the platinum we make it from is actually worth more than the gold making this particular transmutation economically non-viable!

$$^{198}_{78}\mathrm{Pt} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{199}_{78}\mathrm{Pt} \rightarrow {}^{199}_{79}\mathrm{Au} + {}^{0}_{-1}\beta \tag{21.7.2}$$

Transuranium Elements

Uranium (Z = 92) is the heaviest naturally occurring element. Consequently, all the elements with Z > 92, the **transuranium elements**, are artificial and have been prepared by bombarding suitable target nuclei with smaller particles. The first of the transuranium elements to be prepared was neptunium (Z = 93), which was synthesized in 1940 by bombarding a ^{238}U target with neutrons. As shown in Equation \(\ref{20.41}\) this reaction occurs in two steps. Initially, a neutron combines with a ^{238}U nucleus to form ^{239}U, which is unstable and undergoes beta decay to produce ^{239}Np:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\beta \tag{21.7.3}$$

Subsequent beta decay of ^{239}Np produces the second transuranium element, plutonium (Z = 94):

$$^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\beta \tag{21.7.4}$$

Bombarding the target with more massive nuclei creates elements that have atomic numbers significantly greater than that of the target nucleus (Table 21.7.1). Such techniques have resulted in the creation of the superheavy elements 114 and 116, both of which lie in or near the “island of stability." As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval.

Table 21.7.1: Preparation of Some of the Transuranium Elements

	Name		Symbol	Atomic Number	Reaction
americium	Am	95	$^{239}_{94}\mathrm{Pu} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{240}_{95}\mathrm{Am} + {}^{0}_{-1}\mathrm{e}$		
curium	Cm	96	$^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}\mathrm{n}$		
californium	Cf	98	$^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{243}_{97}\mathrm{Bk} + 2\,{}^{1}_{0}\mathrm{n}$		
einsteinium	Es	99	$^{238}_{92}\mathrm{U} + 15\,{}^{1}_{0}\mathrm{n} \longrightarrow {}^{253}_{99}\mathrm{Es} + 7\,{}^{0}_{-1}\mathrm{e}$		
mendelevium	Md	101	$^{253}_{99}\mathrm{Es} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{256}_{101}\mathrm{Md} + {}^{1}_{0}\mathrm{n}$		
nobelium	No	102	$^{246}_{96}\mathrm{Cm} + {}^{12}_{6}\mathrm{C} \longrightarrow {}^{254}_{102}\mathrm{No} + 4\,{}^{1}_{0}\mathrm{n}$		
rutherfordium	Rf	104	$^{249}_{98}\mathrm{Cf} + {}^{12}_{6}\mathrm{C} \longrightarrow {}^{257}_{104}\mathrm{Rf} + 4\,{}^{1}_{0}\mathrm{n}$		
seaborgium	Sg	106	$^{206}_{82}\mathrm{Pb} + {}^{54}_{24}\mathrm{Cr} \longrightarrow {}^{257}_{106}\mathrm{Sg} + 3\,{}^{1}_{0}\mathrm{n}$ $^{249}_{98}\mathrm{Cf} + {}^{18}_{8}\mathrm{O} \longrightarrow {}^{263}_{106}\mathrm{Sg} + 4\,{}^{1}_{0}\mathrm{n}$		

	Name			Symbol			Atomic Number			Reaction
meitnerium	Mt	107	$^{209}_{83}\mathrm{Bi} + {}^{58}_{26}\mathrm{Fe} \longrightarrow {}^{266}_{109}\mathrm{Mt} + {}^{1}_{0}\mathrm{n}$							

Particle Accelerators

A device called a particle accelerator is used to accelerate positively charged particles to the speeds needed to overcome the electrostatic repulsions between them and the target nuclei by using electrical and magnetic fields. Operationally, the simplest particle accelerator is the linear accelerator (Figure 21.7.2), in which a beam of particles is injected at one end of a long evacuated tube. Rapid alternation of the polarity of the electrodes along the tube causes the particles to be alternately accelerated toward a region of opposite charge and repelled by a region with the same charge, resulting in a tremendous acceleration as the particle travels down the tube. A modern linear accelerator such as the Stanford Linear Accelerator (SLAC) at Stanford University is about 2 miles long.

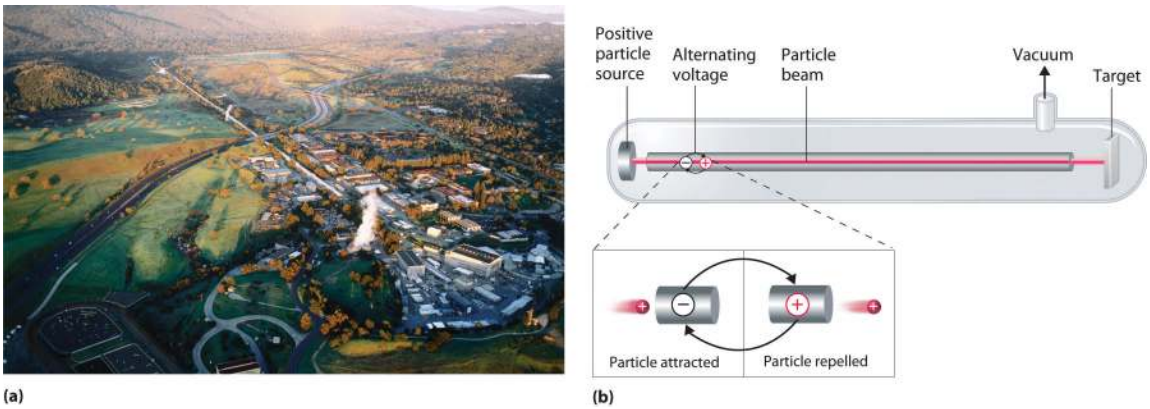


Figure 21.7.2: A Linear Particle Accelerator. (a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as they enter one section of the tube and repelled as they leave that section. As a result, the particles are continuously accelerated along the length of the tube.

To achieve the same outcome in less space, a particle accelerator called a cyclotron forces the charged particles to travel in a circular path rather than a linear one. The particles are injected into the center of a ring and accelerated by rapidly alternating the polarity of two large D-shaped electrodes above and below the ring, which accelerates the particles outward along a spiral path toward the target.

The length of a linear accelerator and the size of the D-shaped electrodes in a cyclotron severely limit the kinetic energy that particles can attain in these devices. These limitations can be overcome by using a synchrotron, a hybrid of the two designs. A synchrotron contains an evacuated tube similar to that of a linear accelerator, but the tube is circular and can be more than a mile in diameter. Charged particles are accelerated around the circle by a series of magnets whose polarities rapidly alternate.

Contributors and Attributions

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).
- Hans Lohninger (Epina eBook Team)

  Template:HideTOC
- Andrew R. Barron

21.7: Transmutation of the Elements is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

21.8: Nuclear Fission

Skills to Develop

- Explain nuclear fission
- Relate the concepts of critical mass and nuclear chain reactions
- Summarize basic requirements for nuclear fission

Many heavier elements with smaller binding energies per nucleon can decompose into more stable elements that have intermediate mass numbers and larger binding energies per nucleon—that is, mass numbers and binding energies per nucleon that are closer to the "peak" of the binding energy graph near 56. Sometimes neutrons are also produced. This decomposition is called fission, the breaking of a large nucleus into smaller pieces. The breaking is rather random with the formation of a large number of different products. Fission usually does not occur naturally, but is induced by bombardment with neutrons. The first reported nuclear fission occurred in 1939 when three German scientists, Lise Meitner, Otto Hahn, and Fritz Strassman, bombarded uranium-235 atoms with slow-moving neutrons that split the U-238 nuclei into smaller fragments that consisted of several neutrons and elements near the middle of the periodic table. Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in Figure 21.8.1.

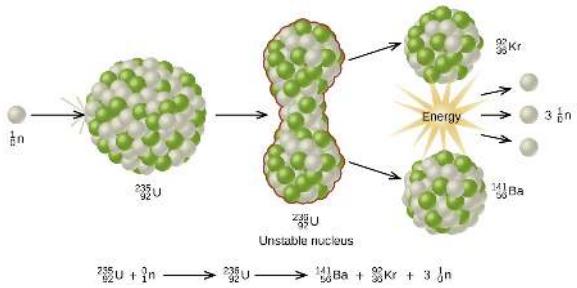


Figure 21.8.1: When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

Among the products of Meitner, Hahn, and Strassman's fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances. A few of the many reactions that occur for U-235, and a graph showing the distribution of its fission products and their yields, are shown in Figure 21.8.2. Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

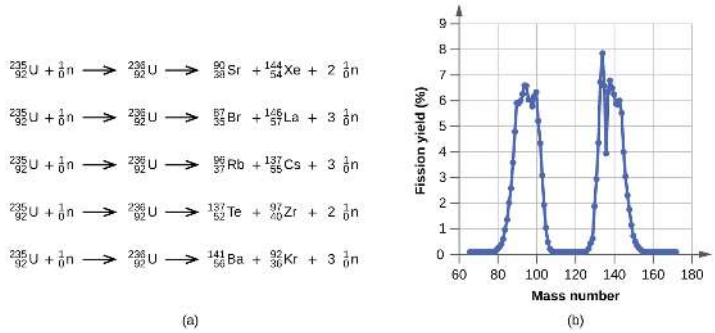


Figure 21.8.2: (a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this "lost" mass is converted into a very large amount of energy, about 1.8×10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

As described earlier, when undergoing fission U-235 produces two "medium-sized" nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear chain reaction (Figure 21.8.3). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

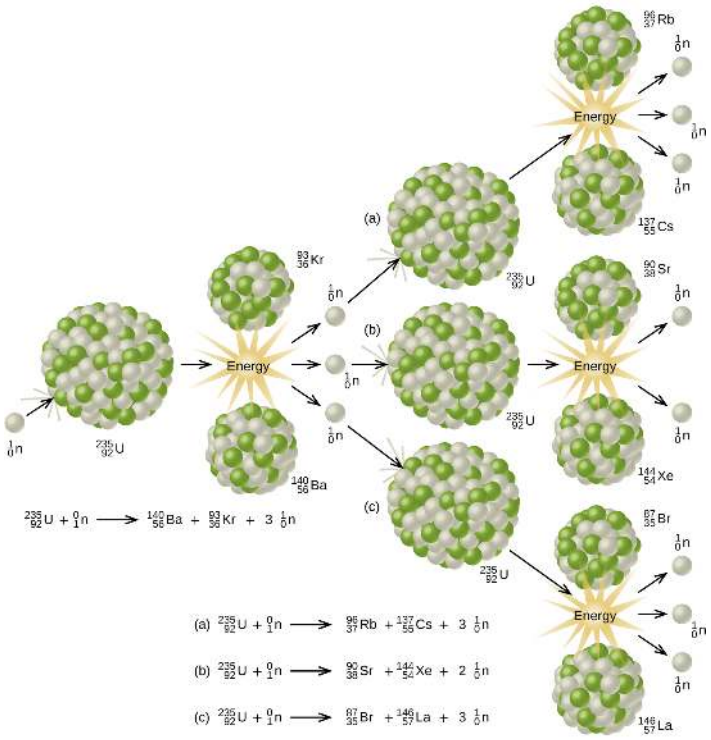


Figure 21.8.3: The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

Material that can sustain a nuclear fission chain reaction is said to be fissile or fissionable. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a critical mass. An amount of fissionable material that cannot sustain a chain reaction is a subcritical mass. An amount of material in which there is an increasing rate of fission is known as a supercritical mass. The critical mass depends on the type of material: its purity, the temperature, the shape of the sample, and how the neutron reactions are controlled (Figure 21.8.4).

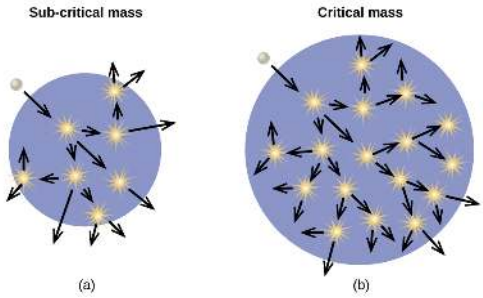


Figure 21.8.4: (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

An atomic bomb (Figure 21.8.5) contains several pounds of fissionable material, $^{235}_{92}U$ or $^{239}_{94}Pu$, a source of neutrons, and an explosive device for compressing it quickly into a small volume. When fissionable material is in small pieces, the proportion of neutrons that escape through the relatively large surface area is great, and a chain reaction does not take place. When the small pieces of fissionable material are brought together quickly to form a body with a mass larger than the critical mass, the relative number of escaping neutrons decreases, and a chain reaction and explosion result.

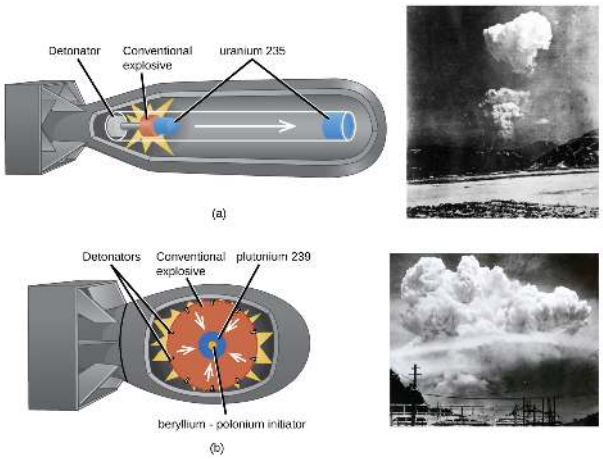


Figure 21.8.5: (a) The nuclear fission bomb that destroyed Hiroshima on August 6, 1945, consisted of two subcritical masses of U-235, where conventional explosives were used to fire one of the subcritical masses into the other, creating the critical mass for the nuclear explosion. (b) The plutonium bomb that destroyed Nagasaki on August 12, 1945, consisted of a hollow sphere of plutonium that was rapidly compressed by conventional explosives. This led to a concentration of plutonium in the center that was greater than the critical mass necessary for the nuclear explosion.

Fission Reactors

Chain reactions of fissionable materials can be controlled and sustained without an explosion in a nuclear reactor (Figure 21.8.6). Any nuclear reactor that produces power via the fission of uranium or plutonium by bombardment with neutrons must have at least five components: nuclear fuel consisting of fissionable material, a nuclear moderator, reactor coolant, control rods, and a shield and containment system. We will discuss these components in greater detail later in the section. The reactor works by separating the fissionable nuclear material such that a critical mass cannot be formed, controlling both the flux and absorption of neutrons to allow shutting down the fission reactions. In a nuclear reactor used for the production of electricity, the energy released by fission reactions is trapped as thermal energy and used to boil water and produce steam. The steam is used to turn a turbine, which powers a generator for the production of electricity.

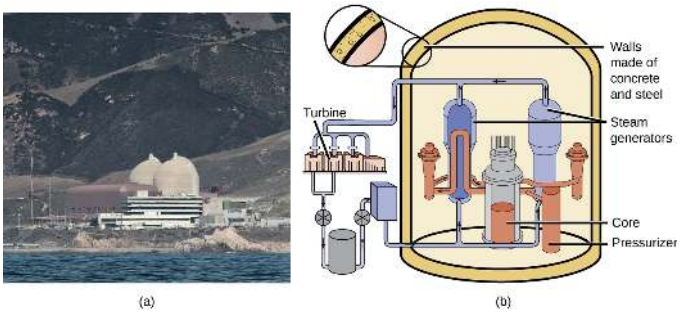


Figure 21.8.6: (a) The Diablo Canyon Nuclear Power Plant near San Luis Obispo is the only nuclear power plant currently in operation in California. The domes are the containment structures for the nuclear reactors, and the brown building houses the turbine where electricity is generated. Ocean water is used for cooling. (b) The Diablo Canyon uses a pressurized water reactor, one of a few different fission reactor designs in use around the world, to produce electricity. Energy from the nuclear fission reactions in the core heats water in a closed, pressurized system. Heat from this system produces steam that drives a turbine, which in turn produces electricity. (credit a: modification of work by “Mike” Michael L. Baird; credit b: modification of work by the Nuclear Regulatory Commission)

Nuclear Fuels

Nuclear fuel consists of a fissionable isotope, such as uranium-235, which must be present in sufficient quantity to provide a self-sustaining chain reaction. In the United States, uranium ores contain from 0.05–0.3% of the uranium oxide U_3O_8; the uranium in the ore is about 99.3% nonfissionable U-238 with only 0.7% fissionable U-235. Nuclear reactors require a fuel with a higher concentration of U-235 than is found in nature; it is normally enriched to have about 5% of uranium mass as U-235. At this concentration, it is not possible to achieve the supercritical mass necessary for a nuclear explosion. Uranium can be enriched by gaseous diffusion (the only method currently used in the US), using a gas centrifuge, or by laser separation.

In the gaseous diffusion enrichment plant where U-235 fuel is prepared, UF_6 (uranium hexafluoride) gas at low pressure moves through barriers that have holes just barely large enough for UF_6 to pass through. The slightly lighter $^{235}UF_6$ molecules diffuse through the barrier slightly faster than the heavier $^{238}UF_6$ molecules. This process is repeated through hundreds of barriers, gradually increasing the concentration of $^{235}UF_6$ to the level needed by the nuclear reactor. The basis for this process, Graham’s law, is described in the chapter on gases. The enriched UF_6 gas is collected, cooled until it solidifies, and then taken to a fabrication facility where it is made into fuel assemblies. Each fuel assembly consists of fuel rods that contain many thimble-sized, ceramic-encased, enriched uranium (usually UO_2) fuel pellets. Modern nuclear reactors may contain as many as 10 million fuel pellets. The amount of energy in each of these pellets is equal to that in almost a ton of coal or 150 gallons of oil.

Nuclear Moderators

Neutrons produced by nuclear reactions move too fast to cause fission (Figure 21.8.4). They must first be slowed to be absorbed by the fuel and produce additional nuclear reactions. A nuclear moderator is a substance that slows the neutrons to a speed that is low enough to cause fission. Early reactors used high-purity graphite as a moderator. Modern reactors in the US exclusively use heavy water ($^2_1H_2O$) or light water (ordinary H_2O), whereas some reactors in other countries use other materials, such as carbon dioxide, beryllium, or graphite.

Reactor Coolants

A nuclear reactor coolant is used to carry the heat produced by the fission reaction to an external boiler and turbine, where it is transformed into electricity. Two overlapping coolant loops are often used; this counteracts the transfer of radioactivity from the reactor to the primary coolant loop. All nuclear power plants in the US use water as a coolant. Other coolants include molten sodium, lead, a lead-bismuth mixture, or molten salts.

Control Rods

Nuclear reactors use control rods (Figure 21.8.8) to control the fission rate of the nuclear fuel by adjusting the number of slow neutrons present to keep the rate of the chain reaction at a safe level. Control rods are made of boron, cadmium, hafnium, or other elements that are able to absorb neutrons. Boron-10, for example, absorbs neutrons by a reaction that produces lithium-7 and alpha particles:

$$^{10}_5B + ^1_0n \longrightarrow ^7_3Li + ^4_2He \tag{21.8.1}$$

When control rod assemblies are inserted into the fuel element in the reactor core, they absorb a larger fraction of the slow neutrons, thereby slowing the rate of the fission reaction and decreasing the power produced. Conversely, if the control rods are removed, fewer neutrons are absorbed, and the fission rate and energy production increase. In an emergency, the chain reaction can be shut down by fully inserting all of the control rods into the nuclear core between the fuel rods.

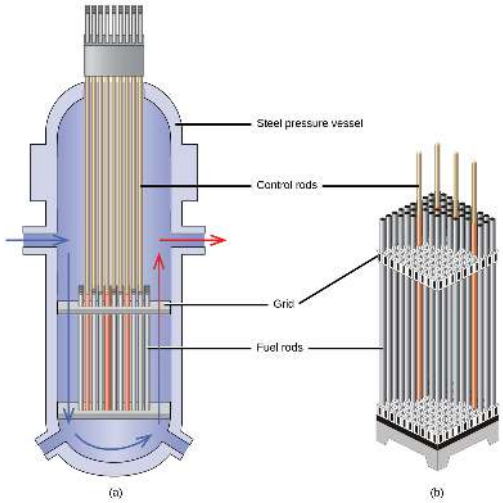


Figure 21.8.7: The nuclear reactor core shown in (a) contains the fuel and control rod assembly shown in (b). (credit: modification of work by E. Generalic)

Shield and Containment System

During its operation, a nuclear reactor produces neutrons and other radiation. Even when shut down, the decay products are radioactive. In addition, an operating reactor is thermally very hot, and high pressures result from the circulation of water or another coolant through it. Thus, a reactor must withstand high temperatures and pressures, and must protect operating personnel from the radiation. Reactors are equipped with a containment system (or shield) that consists of three parts:

1. The reactor vessel, a steel shell that is 3–20-centimeters thick and, with the moderator, absorbs much of the radiation produced by the reactor
2. A main shield of 1–3 meters of high-density concrete
3. A personnel shield of lighter materials that protects operators from γ rays and X-rays

In addition, reactors are often covered with a steel or concrete dome that is designed to contain any radioactive materials might be released by a reactor accident.



Video* 21.8.1*: *Click here to watch a 3-minute video from the Nuclear Energy Institute on how nuclear reactors work.*

Nuclear power plants are designed in such a way that they cannot form a supercritical mass of fissionable material and therefore cannot create a nuclear explosion. But as history has shown, failures of systems and safeguards can cause catastrophic accidents, including chemical explosions and nuclear meltdowns (damage to the reactor core from overheating). The following Chemistry in Everyday Life feature explores three infamous meltdown incidents.

Nuclear Accidents

The importance of cooling and containment are amply illustrated by three major accidents that occurred with the nuclear reactors at nuclear power generating stations in the United States (Three Mile Island), the former Soviet Union (Chernobyl), and Japan (Fukushima).

In March 1979, the cooling system of the Unit 2 reactor at Three Mile Island Nuclear Generating Station in Pennsylvania failed, and the cooling water spilled from the reactor onto the floor of the containment building. After the pumps stopped, the reactors overheated due to the high radioactive decay heat produced in the first few days after the nuclear reactor shut down. The temperature of the core climbed to at least 2200 °C, and the upper portion of the core began to melt. In addition, the zirconium alloy cladding of the fuel rods began to react with steam and produced hydrogen:

$$\mathrm{Zr}(s) + 2\,\mathrm{H_2O}(g) \longrightarrow \mathrm{ZrO_2}(s) + 2\,\mathrm{H_2}(g) \tag{21.8.2}$$

The hydrogen accumulated in the confinement building, and it was feared that there was danger of an explosion of the mixture of hydrogen and air in the building. Consequently, hydrogen gas and radioactive gases (primarily krypton and xenon) were vented from the building. Within a week, cooling water circulation was restored and the core began to cool. The plant was closed for nearly 10 years during the cleanup process.

Although zero discharge of radioactive material is desirable, the discharge of radioactive krypton and xenon, such as occurred at the Three Mile Island plant, is among the most tolerable. These gases readily disperse in the atmosphere and thus do not produce highly radioactive areas. Moreover, they are noble gases and are not incorporated into plant and animal matter in the food chain. Effectively none of the heavy elements of the core of the reactor were released into the environment, and no cleanup of the area outside of the containment building was necessary (Figure 21.8.8).

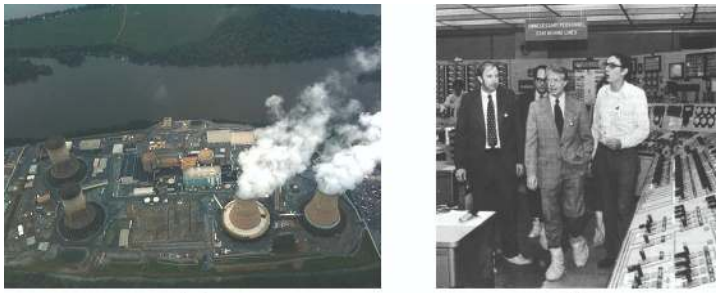


Figure 21.8.8: (a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control room a few days after the accident in 1979.

Another major nuclear accident involving a reactor occurred in April 1986, at the Chernobyl Nuclear Power Plant in Ukraine, which was still a part of the former Soviet Union. While operating at low power during an unauthorized experiment with some of its safety devices shut off, one of the reactors at the plant became unstable. Its chain reaction became uncontrollable and increased to a level far beyond what the reactor was designed for. The steam pressure in the reactor rose to between 100 and 500 times the full power pressure and ruptured the reactor. Because the reactor was not enclosed in a containment building, a large amount of radioactive material spewed out, and additional fission products were released, as the graphite (carbon) moderator of the core ignited and burned. The fire was controlled, but over 200 plant workers and firefighters developed acute radiation sickness and at least 32 soon died from the effects of the radiation. It is predicted that about 4000 more deaths will occur among emergency workers and former Chernobyl residents from radiation-induced cancer and leukemia. The reactor has since been encapsulated in steel and concrete, a now-decaying structure known as the sarcophagus. Almost 30 years later, significant radiation problems still persist in the area, and Chernobyl largely remains a wasteland.

In 2011, the Fukushima Daiichi Nuclear Power Plant in Japan was badly damaged by a 9.0-magnitude earthquake and resulting tsunami. Three reactors up and running at the time were shut down automatically, and emergency generators came online to power electronics and coolant systems. However, the tsunami quickly flooded the emergency generators and cut power to the pumps that circulated coolant water through the reactors. High-temperature steam in the reactors reacted with zirconium alloy to produce hydrogen gas. The gas escaped into the containment building, and the mixture of hydrogen and air exploded. Radioactive material was released from the containment vessels as the result of deliberate venting to reduce the hydrogen pressure, deliberate discharge of coolant water into the sea, and accidental or uncontrolled events.

An evacuation zone around the damaged plant extended over 12.4 miles away, and an estimated 200,000 people were evacuated from the area. All 48 of Japan's nuclear power plants were subsequently shut down, remaining shuttered as of December 2014. Since the disaster, public opinion has shifted from largely favoring to largely opposing increasing the use of nuclear power plants, and a restart of Japan's atomic energy program is still stalled (Figure 21.8.10).



(a) (b)

Figure 21.8.9: (a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by "Live Action Hero"/Flickr)

The energy produced by a reactor fueled with enriched uranium results from the fission of uranium as well as from the fission of plutonium produced as the reactor operates. As discussed previously, the plutonium forms from the combination of neutrons and the uranium in the fuel. In any nuclear reactor, only about 0.1% of the mass of the fuel is converted into energy. The other 99.9% remains in the fuel rods as fission products and unused fuel. All of the fission products absorb neutrons, and after a period of several months to a few years, depending on the reactor, the fission products must be removed by changing the fuel rods. Otherwise, the concentration of these fission products would increase and absorb more neutrons until the reactor could no longer operate.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

Contributors and Attributions

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

21.8: Nuclear Fission is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

21.9: Nuclear Fusion

Skills to Develop

- Describe the nuclear reactions in a nuclear fusion reaction
- Quantify the energy released or absorbed in a fusion reaction

The process of converting very light nuclei into heavier nuclei is also accompanied by the conversion of mass into large amounts of energy, a process called fusion. The principal source of energy in the sun is a net fusion reaction in which four hydrogen nuclei fuse and produce one helium nucleus and two positrons. This is a net reaction of a more complicated series of events:

$$\underbrace{4\,{}^{1}_{1}\mathrm{H}}_{4\times 1.00794\ u} \longrightarrow \underbrace{{}^{4}_{2}\mathrm{He}}_{4.0012\ u} + \underbrace{2\,{}^{0}_{1}\beta^{+}}_{2\times 0.0005487\ u} \tag{21.9.1}$$

A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into thermal energy during the fusion via Einstein's $E = mc^2$ equation. This reaction produces about 3.6 × 10^{11} kJ of energy per mole of ${}^{4}_{2}\mathrm{He}$ produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of ${}^{235}\mathrm{U}$ (1.8 × 10^{10} kJ), and over **3 million times larger** than the energy produced by the (chemical) combustion of one mole of octane ($\Delta H = -5471\ kJ$):

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O \tag{21.9.2}$$

It has been determined that the nuclei of the heavy isotopes of hydrogen, a deuteron, ${}^{2}_{1}\mathrm{H}$ and a triton, ${}^{3}_{1}\mathrm{H}$, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

$${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{1}_{0}\mathrm{n} \tag{21.9.3}$$

This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of 1.69 × 10^{9} kilojoules per mole of ${}^{4}_{2}\mathrm{He}$ formed. The very high temperature is necessary to give the nuclei enough kinetic energy to overcome the very strong repulsive forces resulting from the positive charges on their nuclei so they can collide.

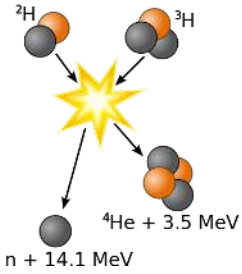


Figure 21.9.1: Fusion of deuterium with tritium creating helium-4, freeing a neutron, and releasing 17.59 MeV of energy, as an appropriate amount of mass changing forms to appear as the kinetic energy of the products, in agreement with kinetic $E = \Delta mc^2$, where Δm is the change in rest mass of particles.[Image use with permission via Wikipedia (Wykis)

The most important fusion process in nature is the one that powers stars. In the 20th century, it was realized that the energy released from nuclear fusion reactions accounted for the longevity of the Sun and other stars as a source of heat and light. The fusion of nuclei in a star, starting from its initial hydrogen and helium abundance, provides that energy and synthesizes new nuclei as a byproduct of that fusion process. The prime energy producer in the Sun is the fusion of hydrogen to form helium, which occurs at a solar-core temperature of 14 million kelvin. The net result is the fusion of four protons into one alpha particle, with the release of two positrons, two neutrinos (which changes two of the protons into neutrons), and energy (Figure 21.9.2).

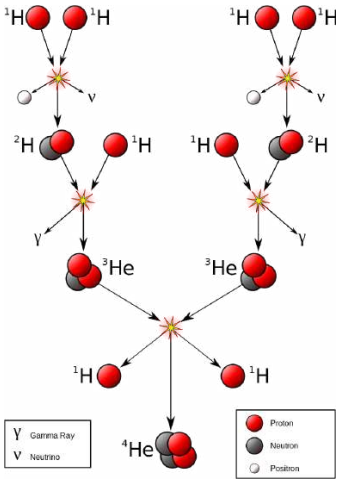


Figure 21.9.2: (left) The Sun is a main-sequence star, and thus generates its energy by nuclear fusion of hydrogen nuclei into helium. In its core, the Sun fuses 620 million metric tons of hydrogen each second. (right) The proton-proton chain dominates in stars the size of the Sun or smaller.

Example 21.9.1

Calculate the energy released in each of the following hypothetical processes.

a. $3\,{}^{4}_{2}\mathrm{He} \rightarrow {}^{12}_{6}\mathrm{C}$
b. $6\,{}^{1}_{1}\mathrm{H} + 6\,{}^{1}_{0}\mathrm{n} \rightarrow {}^{12}_{6}\mathrm{C}$
c. $6\,{}^{2}_{1}\mathrm{D} \rightarrow {}^{12}_{6}\mathrm{C}$

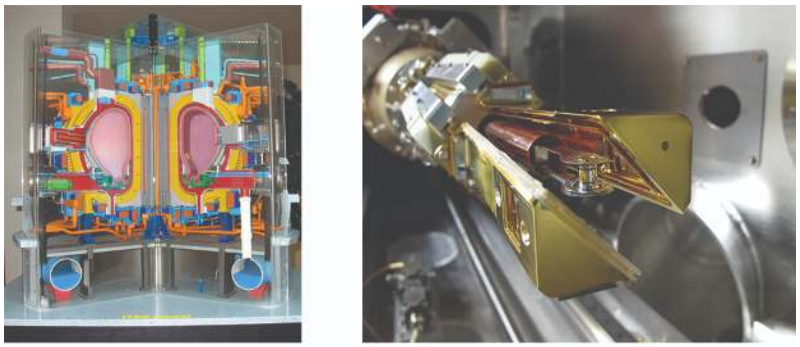
Discuss your results.

a. *Q*a = 3 * 4.0026 - 12.000) amu * (1.4924E-10 J/amu)
= 1.17E-12 J
b. *Q*b = (6*(1.007825 + 1.008665) - 12.00000) amu * (1.4924E-10 J/amu)
= 1.476E-11 J
c. *Q*c = 6*2.014102 - 12.00000 amu * (1.4924E-10 J/amu)
= 1.263E-11 J

Fusion of He to give C releases the least amount of energy, because the fusion to produce He has released a large amount. The difference between the second and the third is the binding energy of deuterium. The conservation of mass-and-energy is well illustrated in these calculations. On the other hand, the calculation is based on the conservation of mass-and-energy.

Nuclear Reactors

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.



(a) (b)

Figure 21.9.3: (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving large-scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

Another much more beneficial way to create fusion reactions is in a fusion reactor, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (Figure 21.9.3). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. At the time of this writing, there are no self-sustaining fusion reactors operating in the world, although small-scale controlled fusion reactions have been run for very brief periods.

Contributors

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

21.9: Nuclear Fusion is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

21.E: Nuclear Chemistry (Exercises)

21.1: Radioactivity

Q21.1.1

Why are many radioactive substances warm to the touch? Why do many radioactive substances glow?

Q21.1.2

Describe the differences between nonionizing and ionizing radiation in terms of the intensity of energy emitted and the effect each has on an atom or molecule after collision. Which nuclear decay reactions are more likely to produce ionizing radiation? nonionizing radiation?

Q21.1.3

Would you expect nonionizing or ionizing radiation to be more effective at treating cancer? Why?

S21.1.3

Ionizing radiation is higher in energy and causes greater tissue damage, so it is more likely to destroy cancerous cells.

Q21.1.4

Historically, concrete shelters have been used to protect people from nuclear blasts. Comment on the effectiveness of such shelters.

Q21.1.5

Gamma rays are a very high-energy radiation, yet α particles inflict more damage on biological tissue. Why?

Q21.1.6

List the three primary sources of naturally occurring radiation. Explain the factors that influence the dose that one receives throughout the year. Which is the largest contributor to overall exposure? Which is the most hazardous?

S21.1.6

Three primary naturally occurring radiations are radium, uranium and thorium, each all having long half lives. Inhalation of air, ingestion of food and water,terrestrial radation from the ground and cosmic radiation from space are all factors tat influence the does that a person receives throughout the year. Inhalation of the air is the largest contributor to exposure. Radiation can damage DNA or kill cells. When radiation is exposed to your body, it will collide with atoms and this will change and damage your DNA.

Q21.1.7

Because radon is a noble gas, it is inert and generally unreactive. Despite this, exposure to even low concentrations of radon in air is quite dangerous. Describe the physical consequences of exposure to radon gas. Why are people who smoke more susceptible to these effects?

Q21.1.8

Most medical imaging uses isotopes that have extremely short half-lives. These isotopes usually undergo only one kind of nuclear decay reaction. Which kind of decay reaction is usually used? Why? Why would a short half-life be preferred in these cases?

Beta decay. Alfa decay can be easily stopped by paper, which means it can not be used to see inside people's body. Also, Gamma rays are really dangerous for human, that even a short period of time exploding to it will have negative effect on human body. Thus, Beta decay is the perfect choice. It can be used to see through human's body and stopped by aluminum or some other metals.

Since all these radioactive decays are harmful for human body, if the half time of these reactions are short, the time exploding to these reactions will be short too.

Q21.1.9

Which would you prefer: one exposure of 100 rem, or 10 exposures of 10 rem each? Explain your rationale.

S21.1.9

Ten exposures of 10 rem are less likely to cause major damage.

Q21.1.10

A 2.14 kg sample of rock contains 0.0985 g of uranium. How much energy is emitted over 25 yr if 99.27% of the uranium is ^{238}U, which has a half-life of 4.46×10^9 yr, if each decay event is accompanied by the release of 4.039 MeV? If a 180 lb individual absorbs all of the emitted radiation, how much radiation has been absorbed in rads?

Q21.1.11

There is a story about a “radioactive boy scout” who attempted to convert thorium-232, which he isolated from about 1000 gas lantern mantles, to uranium-233 by bombarding the thorium with neutrons. The neutrons were generated via bombarding an aluminum target with α particles from the decay of americium-241, which was isolated from 100 smoke detectors. Write balanced nuclear reactions for these processes. The “radioactive boy scout” spent approximately 2 h/day with his experiment for 2 yr. Assuming that the alpha emission of americium has an energy of 5.24 MeV/particle and that the americium-241 was undergoing 3.5×10^6 decays/s, what was the exposure of the 60.0 kg scout in rads? The intrepid scientist apparently showed no ill effects from this exposure. Why?

241/95 Am---> 4/2 He + 237/93Np---> 4/2He + 233/91Pa----> 1/0n+ 232/91Th---> 1/1 H + 233/92 U

By adding alpha particles to the products side of the reaction, he was able to reduce the mass number by 4 and the atomic number by 2 to get the products he wanted. Bombardment with neutrons and 1 H was required to lower to the mass number to get Th and then raise both the mass number and the atomic number to yield Uranium.

2 hours*365*2= 1460 hours of exposure.*60min/1hr*60s/1min= 5.26*10^6s of exposure

1MeV= (1.6022*10^-13 Joules) * (5.24 MeV/particle)*2 particles= 1.679*10^-12 Joules.

(1.679*10^-12 Joules) * (1 amu/ 1.4924*10^-10 Joules)= 2.51*10^-13 amu

E=mc^2

E=(2.51*10^-13 amu)(1.66*10^-22kg/amu)(2.9998*10^8m/s)^2= (3.75*10^-18 kgm^2/s)*(3.5*10^6 decays/s)= 1.31*10^-11 joules of exposure per second.

The scientist showed no ill effects from this exposure because if we multiple the energy in joules of exposure per second, 1.31*10^-11, by the total amount of seconds of exposure, 5.26*10^6s, we find that he was only exposed to 6.9*10^-5 joules of radiation throughout the span of two years. This is a very small amount of radiation for such a long span of time.

In order to plug in the values for this equation, we must convert the given MeV to Joules with the known conversion rate. Similarly, we must convert Joules to amu with another known conversion rate. Then we can plug in the values and multiply by c^2 but we must not forget to multiple the amu by the conversion rate to kg in order to yield Joules. After all of this is done, we multiple the amount of Joules of exposure per second by the total amount of exposure in seconds in order to find out the total amount of exposure over the two year span.

21.2: Patterns of Nuclear Stability

Q21.2.1

How do chemical reactions compare with nuclear reactions with respect to mass changes? Does either type of reaction violate the law of conservation of mass? Explain your answers.

Q21.2.2

Why is the amount of energy released by a nuclear reaction so much greater than the amount of energy released by a chemical reaction?

Q21.2.3

Explain why the mass of an atom is less than the sum of the masses of its component particles.

Q21.2.4

The stability of a nucleus can be described using two values. What are they, and how do they differ from each other?

Q21.2.5

In the days before true chemistry, ancient scholars (alchemists) attempted to find the philosopher's stone, a material that would enable them to turn lead into gold. Is the conversion of Pb → Au energetically favorable? Explain why or why not.

Q21.2.6

Describe the energy barrier to nuclear fusion reactions and explain how it can be overcome.

Q21.2.7

Imagine that the universe is dying, the stars have burned out, and all the elements have undergone fusion or radioactive decay. What would be the most abundant element in this future universe? Why?

Q21.2.8

Numerous elements can undergo fission, but only a few can be used as fuels in a reactor. What aspect of nuclear fission allows a nuclear chain reaction to occur?

Q21.2.9

How are transmutation reactions and fusion reactions related? Describe the main impediment to fusion reactions and suggest one or two ways to surmount this difficulty.

Q21.2.10

Using the information provided in Chapter 33, complete each reaction and calculate the amount of energy released from each in kilojoules.

a. $^{238}\text{Pa} \rightarrow ? + \beta^-$
b. $^{216}\text{Fr} \rightarrow ? + \alpha$
c. $^{199}\text{Bi} \rightarrow ? + \beta^+$

Q21.2.22

Using the information provided in Chapter 33, complete each reaction and calculate the amount of energy released from each in kilojoules.

a. $^{194}\text{Tl} \rightarrow ? + \beta^+$
b. $^{171}\text{Pt} \rightarrow ? + \alpha$
c. $^{214}\text{Pb} \rightarrow ? + \beta^-$

Q21.2.23

Using the information provided in Chapter 33, complete each reaction and calculate the amount of energy released from each in kilojoules per mole.

a. $^{234}_{91}\text{Pa} \rightarrow ? + {}^{0}_{-1}\beta$
b. $^{226}_{88}\text{Ra} \rightarrow ? + {}^{4}_{2}\alpha$

Q21.2.24

Using the information provided in Chapter 33, complete each reaction and then calculate the amount of energy released from each in kilojoules per mole.

a. $^{60}_{27}\text{Co} \rightarrow ? + {}^{0}_{-1}\beta$ (The mass of cobalt-60 is 59.933817 amu.)
b. technicium-94 (mass = 93.909657 amu) undergoing fission to produce chromium-52 and potassium-40

Q21.2.25

Using the information provided in Chapter 33, predict whether each reaction is favorable and the amount of energy released or required in megaelectronvolts and kilojoules per mole.

a. the beta decay of bismuth-208 (mass = 207.979742 amu)
b. the formation of lead-206 by alpha decay

Q21.2.26

Using the information provided, predict whether each reaction is favorable and the amount of energy released or required in megaelectronvolts and kilojoules per mole.

a. alpha decay of oxygen-16
b. alpha decay to produce chromium-52

Q21.2.27

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{87}Sr if the measured mass of ^{87}Sr is 86.908877 amu.

a. the calculated mass
b. the mass defect
c. the nuclear binding energy
d. the nuclear binding energy per nucleon

Q21.2.30

The experimentally determined mass of ^{29}S is 28.996610 amu. Find each of the following.

a. the calculated mass
b. the mass defect
c. the nuclear binding energy
d. the nuclear binding energy per nucleon

Q21.2.31

Calculate the amount of energy that is released by the neutron-induced fission of ^{235}U to give ^{141}Ba, ^{92}Kr (mass = 91.926156 amu), and three neutrons. Report your answer in electronvolts per atom and kilojoules per mole.

Q21.2.31

Calculate the amount of energy that is released by the neutron-induced fission of ^{235}U to give ^{90}Sr, ^{143}Xe, and three neutrons. Report your answer in electronvolts per atom and kilojoules per mole.

Q21.2.33

Calculate the amount of energy released or required by the fusion of helium-4 to produce the unstable beryllium-8 (mass = 8.00530510 amu). Report your answer in kilojoules per mole. Do you expect this to be a spontaneous reaction?

Q21.2.34

Calculate the amount of energy released by the fusion of ^{6}Li and deuterium to give two helium-4 nuclei. Express your answer in electronvolts per atom and kilojoules per mole.

Q21.2.35

How much energy is released by the fusion of two deuterium nuclei to give one tritium nucleus and one proton? How does this amount compare with the energy released by the fusion of a deuterium nucleus and a tritium nucleus, which is accompanied by ejection of a neutron? Express your answer in megaelectronvolts and kilojoules per mole. Pound for pound, which is a better choice for a fusion reactor fuel mixture?

Numerical Answers

1

a. $^{238}_{91}\mathrm{Pa} \rightarrow {}^{238}_{92}\mathrm{U} + {}^{0}_{-1}\beta$; -5.540×10^{-16} kJ
b. $^{216}_{87}\mathrm{Fr} \rightarrow {}^{212}_{85}\mathrm{At} + {}^{4}_{2}\alpha$; -1.470×10^{-15} kJ
c. $^{199}_{83}\mathrm{Bi} \rightarrow {}^{199}_{82}\mathrm{Pb} + {}^{0}_{+1}\beta$; -5.458×10^{-16} kJ

3.

a. $^{234}_{91}\mathrm{Pa} \rightarrow {}^{234}_{92}\mathrm{U} + {}^{0}_{-1}\beta$; 2.118×10^{8} kJ/mol
b. $^{226}_{88}\mathrm{Ra} \rightarrow {}^{222}_{86}\mathrm{Rn} + {}^{4}_{2}\alpha$; 4.700×10^{8} kJ/mol

5.

a. The beta decay of bismuth-208 to polonium is endothermic (ΔE = 1.400 MeV/atom, 1.352×10^{8} kJ/mol).
b. The formation of lead-206 by alpha decay of polonium-210 is exothermic (ΔE = −5.405 MeV/atom, -5.218×10^{8} kJ/mol).

7. 757 MeV/atom, 8.70 MeV/nucleon

9.

a. 53.438245 amu
b. 0.496955 amu
c. 463 MeV/atom
d. 8.74 MeV/nucleon

11. −173 MeV/atom; 1.67×10^{10} kJ/mol

13. ΔE = $+ 9.0 \times 10^{6}$ kJ/mol beryllium-8; no

15. D–D fusion: ΔE = −4.03 MeV/tritium nucleus formed = -3.89×10^{8} kJ/mol tritium; D–T fusion: ΔE = −17.6 MeV/tritium nucleus = -1.70×10^{9} kJ/mol; D–T fusion

21.3: Nuclear Transmutations

Q21.3.1

Why do scientists believe that hydrogen is the building block of all other elements? Why do scientists believe that helium-4 is the building block of the heavier elements?

Q21.3.2

How does a star produce such enormous amounts of heat and light? How are elements heavier than Ni formed?

Q21.3.3

Propose an explanation for the observation that elements with even atomic numbers are more abundant than elements with odd atomic numbers.

S21.3.3

The raw material for all elements with Z > 2 is helium (Z = 2), and fusion of helium nuclei will always produce nuclei with an even number of protons.

Q21.3.4

During the lifetime of a star, different reactions that form different elements are used to power the fusion furnace that keeps a star “lit.” Explain the different reactions that dominate in the different stages of a star’s life cycle and their effect on the temperature of

the star.

Q21.3.5

A line in a popular song from the 1960s by Joni Mitchell stated, “We are stardust….” Does this statement have any merit or is it just poetic? Justify your answer.

Q21.3.6

If the laws of physics were different and the primary element in the universe were boron-11 (Z = 5), what would be the next four most abundant elements? Propose nuclear reactions for their formation.

Q21.3.7

Write a balanced nuclear reaction for the formation of each isotope.

a. ^{27}Al from two ^{12}C nuclei
b. ^{9}Be from two ^{4}He nuclei

Q21.3.8

At the end of a star’s life cycle, it can collapse, resulting in a supernova explosion that leads to the formation of heavy elements by multiple neutron-capture events. Write a balanced nuclear reaction for the formation of each isotope during such an explosion.

a. ^{106}Pd from nickel-58
b. selenium-79 from iron-56

Q21.3.9

When a star reaches middle age, helium-4 is converted to short-lived beryllium-8 (mass = 8.00530510 amu), which reacts with another helium-4 to produce carbon-12. How much energy is released in each reaction (in megaelectronvolts)? How many atoms of helium must be “burned” in this process to produce the same amount of energy obtained from the fusion of 1 mol of hydrogen atoms to give deuterium?

21.4: Rates of Radioactive Decay

Q21.4.1

What do chemists mean by the half-life of a reaction?

Q21.4.2

If a sample of one isotope undergoes more disintegrations per second than the same number of atoms of another isotope, how do their half-lives compare?

Q21.4.3

Half-lives for the reaction A + B → C were calculated at three values of $[A]_0$, and [B] was the same in all cases. The data are listed in the following table:

$[A]_0$ (M)	$t_{½}$ (s)
0.50	420
0.75	280
1.0	210

Does this reaction follow first-order kinetics? On what do you base your answer?

S21.4.3

1. No; the reaction is second order in A because the half-life decreases with increasing reactant concentration according to $t_{1/2} = 1/k[A_0]$.

Q21.4.4

Ethyl-2-nitrobenzoate ($NO_2C_6H_4CO_2C_2H_5$) hydrolyzes under basic conditions. A plot of [$NO_2C_6H_4CO_2C_2H_5$] versus *t* was used to calculate *t*½, with the following results:

[$NO_2C_6H_4CO_2C_2H_5$] (M/cm^3)	*t*½ (s)
0.050	240
0.040	300
0.030	400

Is this a first-order reaction? Explain your reasoning.

Q21.4.5

Azomethane ($CH_3N_2CH_3$) decomposes at 600 K to C_2H_6 and N_2. The decomposition is first order in azomethane. Calculate *t*½ from the data in the following table:

Time (s)	$P_{CH_3N_2CH_3}$ (atm)
0	8.2×10^{-2}
2000	3.99×10^{-2}
4000	1.94×10^{-2}

How long will it take for the decomposition to be 99.9% complete?

S21.4.5

$t_{1/2} = 1.92 \times 10^3$ s or 1920 s; 19100 s or 5.32 hrs.

Q21.4.6

The first-order decomposition of hydrogen peroxide has a half-life of 10.7 h at 20°C. What is the rate constant (expressed in s^{-1}) for this reaction? If you started with a solution that was 7.5×10^{-3} M H_2O_2, what would be the initial rate of decomposition (M/s)? What would be the concentration of H_2O_2 after 3.3 h?

21.E: Nuclear Chemistry (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

Appendix 1: Google Sheets

Topic hierarchy

1: Google Sheets Basics

Appendix 1: Google Sheets is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

1: Google Sheets Basics

Navigating Google Sheets

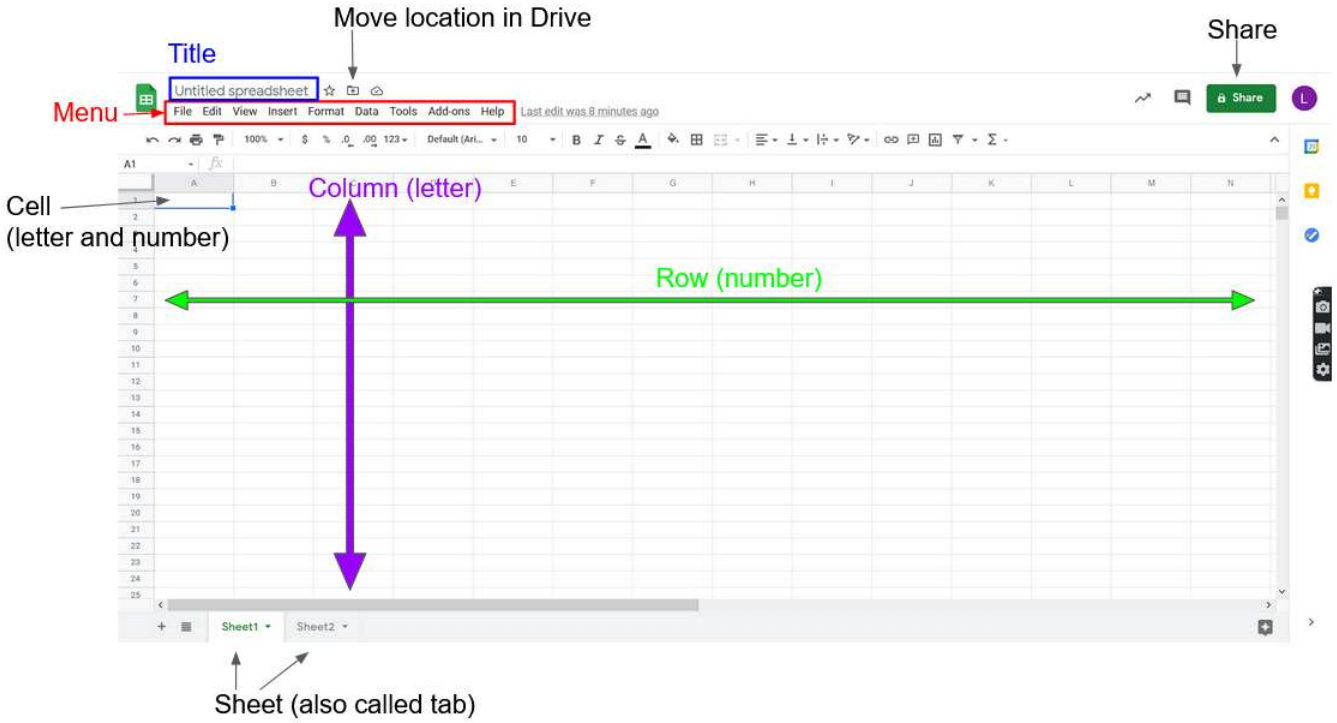


Figure 1.1: Parts of a Google Sheet labeled (Poirot)

Make a Google Sheet

First thing we will be doing is making a google sheet. There's multiple ways to access sheets but we will start with the way that is easiest to keep organized.



Video 1.1: 0:11 video on making a Google Sheet in Drive. (https://youtu.be/TAYVbgreE8s)

Step 1. Open your google drive

Step 2. Click +New in the top left corner which will open a drop down menu

Step 3. Select Google Sheets which will open your sheet in a new tab

Copy a Google Sheet

Making a copy of a sheet is a very useful tool. You can use previous sheets as a template for new data or to have an original copy to save when sharing a sheet.



Video 1.2: 0:38 video on copying and naming a Google Sheet (https://youtu.be/MIPYCvl9-Fw)

1. Open the sheet you want to make a copy of
2. In the menu, click File and then Make a copy.
3. This will open the box where you can name your new sheet. (For students I recommend including your name in the title to help whoever is grading your sheet stay organized)
4. Use folder to select where to save your new copy
5. Click on OK to make your copy which will open in a new tab

Google Sheets: Tabs

Tabs (Sheets) are a great way to organize data within one spreadsheet.

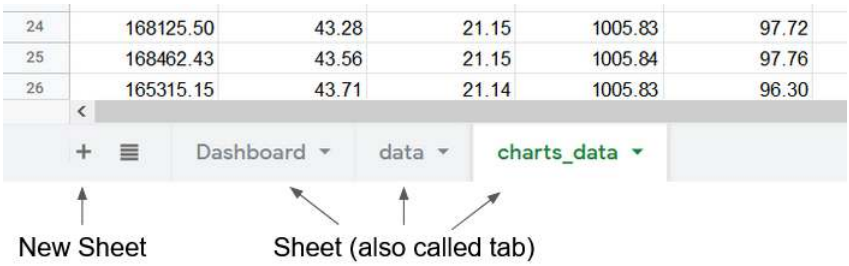


Figure 1.2: Sheets and New Sheet



Video 1.3: 2:48 Video tutorial on tabs. (https://youtu.be/WTUd8rZ2WHE)

Make new Tab (Sheet) in Spreadsheet

TimeStamp: Video 3 0:08

1. Click the plus button on the bottom left corner of the screen
2. Right click and select Rename

It is best practice to name sheets as all one word. This will make things a lot easier later on when referencing sheets later on. You can use and underscore (_) to replace a space.

Duplicate a Tab

TimeStamp: Video 3 0:37

1. Right click on the tab you wish to make a copy of
2. Select Duplicate to make a copy
3. Right Click the new tab and select Rename

Organizing Tabs

To move a tab click on the tab and drag it to rearrange. **TimeStamp:** Video 3: 1:03

To hide a sheet Right click on the tab then select Hide Sheet. This will hide the sheet from view. **TimeStamp:** Video 3: 1:15

To unhide a sheet go to the menu and select View. Go down to Hidden Sheets to select the sheet you want to unhide. **TimeStamp:** Video 3: 1:23

To protect a sheet (meaning choosing who can edit a tab) Right click on the tab then select Protect sheet. This will open a menu to the right, click Set Permissions to choose who can edit this sheet then press done. **TimeStamp:** Video 3: 1:33

You can combine Protect sheet and Hide sheet to prevent anyone from being able to open a sheet **TimeStamp:** Video 3: 2:15

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Liliane Poirot

1: Google Sheets Basics is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

Index

B

Balancing Redox Equations
19.2: Oxidation-Reduction Reactions
battery
19.4: Electrochemical Cell Fundamentals
body centered cubic
12.1: Crystal Lattices and Unit Cells
boiling point elevation
13.5: Colligative Properties
buffer
17.1: Common Ion Effect
17.2: Controlling pH- Buffer Solutions
buffer capacity
17.2: Controlling pH- Buffer Solutions

C

Chelation
20.7: Chelation
colligative property
13.5: Colligative Properties
common ion effect
17.1: Common Ion Effect
17.4: Solubility of Salts
concentration
13.2: Units of Concentration
Counting Electrons
19.10: Counting Electrons
Crystal Defects
12.1: Crystal Lattices and Unit Cells

D

defects
12.1: Crystal Lattices and Unit Cells

E

electrochemical cells
19.3: Electrochemical Cells
electrolysis
19.9: Electrolysis
Electron Transfer Reactions
19: Electron Transfer Reactions
entropy
18.2: Dispersal of Energy- Entropy
equilibrium constant
15.2: Equilibrium Constant and Reaction Quotient

F

Face Centered Cubic
12.1: Crystal Lattices and Unit Cells
formation constants
20.7: Chelation
freezing point depression
13.5: Colligative Properties

G

Gibbs free energy
18.5: Second Law and Gibbs Free Energy
18.6: Gibbs Free Energy

H

Half Equivalence
17.3: Acid-Base Titrations
Hydrated Salts
11.2: Ion-Dipole Forces
hydrogen bonds
11.5: Hydrogen Bonds

I

integrated rate law
14.5: Integrated Rate Law
Interstitial Defects
12.1: Crystal Lattices and Unit Cells

M

metallic bonding
12.3: Bonding in Metals and Semiconductors

N

Nernst equation
19.7: Electrochemical Cells under Nonstandard Conditions

O

osmotic pressure
13.5: Colligative Properties
oxidizing agent
19.2: Oxidation-Reduction Reactions

R

rate constant
14.4: Effect of Concentration on Reaction Rate
rate equation
14.2: Rates of Chemical Reactions
rate law
14.4: Effect of Concentration on Reaction Rate
reaction quotient
15.2: Equilibrium Constant and Reaction Quotient
redox
19.2: Oxidation-Reduction Reactions
reducing agent
19.2: Oxidation-Reduction Reactions

S

second law of thermodynamics
18.5: Second Law and Gibbs Free Energy
semiconductor
12.3: Bonding in Metals and Semiconductors
solubility
17.4: Solubility of Salts
solubility product
17.4: Solubility of Salts
solutions
13: Solutions
solvation
13.3: Solvation Processes
spontaneous process
18.1: Spontaneity and Energy Transfer
standard hydrogen electrode
19.5: Standard Electrochemical Potentials
standard reduction potential
19.5: Standard Electrochemical Potentials
Substitutional Defects
12.1: Crystal Lattices and Unit Cells

T

titration
17.3: Acid-Base Titrations

U

unit cell
12.1: Crystal Lattices and Unit Cells

V

vapor pressure
13.5: Colligative Properties
voltaic cell
19.3: Electrochemical Cells

Glossary

anion | Negatively charged ion

aqueous | solution with water as solvent

boiling point | Temperature at which vapor pressure of a liquid equals the ambient temperature. (11.6.4)

bond dipole moment | A vector representing the separation of charge in a bond that depends on the difference in electronegativity and the distance between the two nuclei being bonded

bond dissociation energy | the energy released when one mole of a bond is broken. You must draw Lewis dot structures to identify the bonds (sec 8.9.4). You can use bond dissociation enthalpies to determine enthalpies of reaction.

cation | Positively charged ion

Clausius-Clapeyron Equation | exponential equation relating vapor pressure of a liquid to the temperature and its enthalpy of vaporization (11.6.3.4)

colligative | colligative properties are properties like vapor pressure, boiling and melting points, osmosis, which are affected by adding solutes to a substance (sec 13.5)

Compressible | A compressible substance does not resist compression. If you "squeeze" a compressible substance its volume changes. Gases are compressible

condense | Exothermic phase change where a gas converts to a liquid

Coulomb's law | Inverse square law relating the force of interaction between two static charges to the product of the charges and the square of the reciprocal of the distance between them. $F=k\frac{Q_1Q_2}{r^2}$

covalent bond | Bond between two nonmetals with equal sharing of electron density. Results when two nonmetals of similar electronegativity ($\Delta\chi$ <0.5 share electrons in a common orbital

critical point | A point on a the liquid-gas equilibrium transition line of a PT phase diagram above which the boundary between the two phases disappear.

density | Density in chemistry means the ratio of the mass to the volume of a substance. If a substance is incompressible (solids and liquids), its density can be used to help identify it. Gases on the other hand fill a container, and so their density is not a constant.

deposition | Exothermic phase change of a gas directly converting to a solid.

dipole | a vector property of a molecule representing the net dipole resulting from the sum of all the bond dipoles in a molecule. Uses the unit of Debye

dipole-dipole force | intermolecular attraction between two permanent dipoles (section 11.3)

dipole-induced dipole | force or attraction between a polar molecule and an adjacent (nonpolar) molecule that it induces a dipole on. (section 11.4.3)

distillate | the more volatile coponent that is condensed during distillation (sec 13.1.3)

electron affinity | electron affinity is a change in energy when a gaseous atom or ion gains an electron. Electron affinities may be exothermic or endothermic. (sec 7.3.4)

electronegativity | Concept introduced by Linus Pauling describing the relative power an atom has to attract electrons to itself when bonded to other atoms. For the common elements in the periodic table Fluorine has the highest electronegativity (4) and Cesium and Francium (0.7) have the lowest. High electronegative atoms attract electrons for atoms with lower electronegatively. This is a relative scale and there are no units. The symbol for electronegativity is χ

endothermic | process where system gains energy from surroundings

enthalpy | The sum of a system's internal energy U and the product of its pressure P and volume V. (sec 5.4.3) $H=U+PV$.

enthalpy of formation | $(\Delta H_f)^o$, The standard state enthalpy of formation is the enthalpy change when 1 mole of a substance is formed from it's constituent elements in their standard state. The standard state is 1 bar and 298K. (sec. 7.7.3) these values can be obtained in a Standard Table of Thermodynamic Properties

exothermic | process where system releases heat to the surroundings

formal charge | The charge that would result on an atom due to the number of valence electrons it adds a molecule minus the number actually around it (add electrons donated minus the number of bonds and lone pair electrons). (section 8.4)

freeze | exothermic phase change from liquid to solid.

fusion | the same as melting (when referring to physical changes)

hydrogen bond | intermolecular force that exists when hydrogen is bonded to a strongly electronegative atom like F, O or N. The electronegative atom must have a lone pair of electrons, which are attracted to the hydrogen of a different bonding pair($(\delta+)$. (11.5)

hydrophilic | water loving- polar or charged part of a molecule that is soluble in water

hydrophobic | water fearing - nonpolar part of a molecule that does

incompressible | Something that resists compression. If you "squeeze" and incompressible substance its intermolecular forces prevent its volume from contracting, and so it has a relatively constant density. Solids and liquids are typically considered to be incompressible.

induced dipole | dipole induced on a non polar molecule by an external field, which could be from an adjacent dipole.

instantaneous dipole-induced dipole | short range force of attraction between two non polar molecules where an instantaneous dipole in one molecule induces a dipole in another. These are often called dispersive or London dispersion forces. (section 11.4.4)

ion-dipole | Intermolecular force of attraction between an ion and a polar molecule (section 11.2)

ionic bond | Bond resulting from net attractive force of positive cations to negative anions.

ionization energy | Ionization energy is the energy required to move an electron from a lone atom or ion in the gas phase. Ionization energies aer always endothermic (sec 7.3.3)

isobar | system at constant pressure,

isotherm | system at constant temperature

kinetic molecular theory | The kinetic molecular theory describes an ideal gas (10.5)

melting | endothermic phase change from a solid to a liquid

nonvolatile | substance that does not have a vapor pressure above its surface.

normal boiling point | boiling point when vapor pressure above a liquid equals 1 atm

oscillation | Movement back and forth at constant speed.

polar bond | bond between two atoms of different electronegativity.

polar molecule | A molecule with a net overall dipole

Polarizability | measure of the ability of an external electric field (charge) to distort a molecules charge distribution (electron cloud) (section 11.4.2)

solute | In a liquid phase solution the solute is the substance that is dissolved into the solvent by intermolecular forces. There can be more than one solute in a solution

solution | homogenous mixture

solvent | In a liquid phase solution the solute is the substance present in greatest proportions. Aqueous solutions have water as the solute, even if it is not in the greatest proportions.

sublimation | Endothermic phase change of a solid to a gas. Dry ice (solid CO_2) sublimes

supercritical fluid | At high temperature and high pressure the boundary between a liquid and gas disappears and you have a supercritical fluid (sec sec 11.6.5 and sec 11.5.2)

temperature | Temperature is an intensive property of matter related to its "hotness" or "coldness"

triple point | A point on the PT phase diagram where 3 phases can coexist in equilibrium.

Van der Waals force | Weak, short range attractive forces between molecules, including dipole-dipole, dipole induced dipole and London dispersion forces (section 11.4.5)

vapor pressure | Two meanings. We will normally say the vapor pressure is the equilibrium vapor pressure when the rate a volatile substance evaporates off a surface equals the rate the gas phase particles condense onto the surface. It also just means the pressure due to the particles in the gas phase. (11.6.3)

viscosity | measure of liquids resistance to flow

volatile | substance with a vapor pressure above its surface (substance that evaporates or sublimes)

Detailed Licensing

Overview

Title: Text

Webpages: 114

Applicable Restrictions: Noncommercial

All licenses found:

- CC BY-NC-SA 4.0: 63.2% (72 pages)
- Undeclared: 35.1% (40 pages)
- CC BY-NC-SA 3.0: 0.9% (1 page)
- CC BY 4.0: 0.9% (1 page)

By Page

- Text - *CC BY-NC-SA 4.0*
  - Front Matter - *CC BY-NC-SA 4.0*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: General Information - *Undeclared*
    - 1: Hypothes.is - *Undeclared*
  - 10: Review - *CC BY-NC-SA 4.0*
    - 10.1: Lewis Dot Structures - *CC BY-NC-SA 4.0*
    - 10.2: VSEPR - *CC BY-NC-SA 4.0*
    - 10.3: Molecular Polarity - *CC BY-NC-SA 4.0*
  - 11: Intermolecular Forces and Liquids - *CC BY-NC-SA 4.0*
    - 11.0: Prelude - *Undeclared*
    - 11.1: States of Matter and Intermolecular Forces - *CC BY-NC-SA 4.0*
    - 11.2: Ion-Dipole Forces - *CC BY-NC-SA 4.0*
    - 11.3: Dipole-Dipole Forces - *CC BY-NC-SA 4.0*
    - 11.4: NonPolar Molecules and IMF - *CC BY-NC-SA 4.0*
    - 11.5: Hydrogen Bonds - *CC BY-NC-SA 4.0*
    - 11.6: Properties of Liquids - *CC BY-NC-SA 4.0*
  - 12: Solids - *CC BY-NC-SA 4.0*
    - 12.0: Prelude - *Undeclared*
    - 12.1: Crystal Lattices and Unit Cells - *CC BY-NC-SA 4.0*
    - 12.2: Ionic Solids - *CC BY-NC-SA 4.0*
    - 12.3: Bonding in Metals and Semiconductors - *CC BY-NC-SA 4.0*
    - 12.4: Network and Amorphous Solids - *CC BY-NC-SA 4.0*
    - 12.5: Phase Diagrams - *CC BY-NC-SA 4.0*
  - 13: Solutions - *CC BY-NC-SA 4.0*
    - 13.1: Prelude - *Undeclared*
    - 13.2: Units of Concentration - *CC BY-NC-SA 4.0*
    - 13.3: Solvation Processes - *CC BY-NC-SA 4.0*
    - 13.4: Pressure and Temperature Effects on Solubility - *CC BY-NC-SA 4.0*
    - 13.5: Colligative Properties - *CC BY-NC-SA 4.0*
    - 13.6: Colloidal Mixtures - *Undeclared*
  - 14: Rates of Chemical Reactions - *CC BY-NC-SA 4.0*
    - 14.1: Prelude - *CC BY-NC-SA 4.0*
    - 14.2: Rates of Chemical Reactions - *CC BY-NC-SA 4.0*
    - 14.3: Reaction Conditions and Rate - *CC BY-NC-SA 4.0*
    - 14.4: Effect of Concentration on Reaction Rate - *CC BY-NC-SA 4.0*
    - 14.5: Integrated Rate Law - *CC BY-NC-SA 4.0*
    - 14.6: Energetics and Reaction Rates - *CC BY-NC-SA 4.0*
    - 14.7: Reaction Mechanisms - *CC BY-NC-SA 4.0*
  - 15: Equilibria - *CC BY-NC-SA 4.0*
    - 15.1: Chemical Equilibrium - *CC BY-NC-SA 4.0*
    - 15.2: Equilibrium Constant and Reaction Quotient - *CC BY-NC-SA 4.0*
      - Clicker1 - *Undeclared*
    - 15.3: Determining an Equilibrium Constant - *CC BY-NC-SA 4.0*
    - 15.4: Using Equilibrium Constants in Calculations - *CC BY-NC-SA 4.0*
    - 15.5: Equilibrium Constants and Coupled Reactions - *CC BY-NC-SA 4.0*
    - 15.6: Disturbing a Chemical Equilibrium - *CC BY-NC-SA 4.0*
  - 16: Acids and Bases - *CC BY-NC-SA 4.0*
    - 16.1: Brønsted-Lowry Concept of Acids and Bases - *CC BY-NC-SA 4.0*

- 16.2: Water and the pH Scale - *CC BY-NC-SA 4.0*
- 16.3: Equilibrium Constants for Acids and Bases - *CC BY-NC-SA 4.0*
- 16.4: Acid-Base Properties of Salts - *CC BY-NC-SA 4.0*
- 16.5: Acid-Base Equilibrium Calculations - *CC BY-NC-SA 4.0*
- 16.6: Molecular Structure, Bonding, and Acid-Base Behavior - *CC BY-NC-SA 3.0*
- 16.7: Lewis Concept of Acids and Bases - *CC BY-NC-SA 4.0*

17: Aqueous Equilibria - *CC BY-NC-SA 4.0*
- 17.1: Common Ion Effect - *CC BY-NC-SA 4.0*
- 17.2: Controlling pH- Buffer Solutions - *CC BY-NC-SA 4.0*
- 17.3: Acid-Base Titrations - *CC BY-NC-SA 4.0*
- 17.4: Solubility of Salts - *CC BY-NC-SA 4.0*
- 17.5: Precipitation Reactions - *CC BY-NC-SA 4.0*
- 17.6: Equilibria Involving Complex Ions - *CC BY-NC-SA 4.0*
- 17.7: Solubility and Complex Ions - *CC BY-NC-SA 4.0*

18: Entropy and Free Energy - *CC BY-NC-SA 4.0*
- 18.1: Spontaneity and Energy Transfer - *CC BY-NC-SA 4.0*
- 18.2: Dispersal of Energy- Entropy - *CC BY-NC-SA 4.0*
- 18.3: Entropy - A Microscopic Understanding - *CC BY 4.0*
- 18.4: Entropy Measurements and Values - *CC BY-NC-SA 4.0*
- 18.5: Second Law and Gibbs Free Energy - *CC BY-NC-SA 4.0*
- 18.6: Gibbs Free Energy - *CC BY-NC-SA 4.0*

19: Electron Transfer Reactions - *CC BY-NC-SA 4.0*
- 19.1: Electrical Fundamentals - *CC BY-NC-SA 4.0*
- 19.2: Oxidation-Reduction Reactions - *CC BY-NC-SA 4.0*
- 19.3: Electrochemical Cells - *CC BY-NC-SA 4.0*
- 19.4: Electrochemical Cell Fundamentals - *CC BY-NC-SA 4.0*
- 19.5: Standard Electrochemical Potentials - *CC BY-NC-SA 4.0*
- 19.6: Electrochemistry and Thermodynamics - *CC BY-NC-SA 4.0*
- 19.7: Electrochemical Cells under Nonstandard Conditions - *CC BY-NC-SA 4.0*
- 19.8: Corrosion - *CC BY-NC-SA 4.0*
- 19.9: Electrolysis - *CC BY-NC-SA 4.0*
- 19.10: Counting Electrons - *CC BY-NC-SA 4.0*

20: Coordination Chemistry - *Undeclared*
- 20.1: Werner's Theory of Coordination Compounds - *Undeclared*
- 20.2: Ligands - *Undeclared*
- 20.3: Nomenclature - *Undeclared*
- 20.4: Isomerism - *Undeclared*
- 20.5: Optical Isomerism in Metal Complexes - *Undeclared*
- 20.6: Stability Aspects of Complex-Ion Equilibria - *Undeclared*
- 20.7: Chelation - *Undeclared*
- 20.8: Bonding in Octahedral Complex Ions- Crystal Field Theory - *Undeclared*
- 20.9: Bonding in Non-Octahedral Complex Ions- Crystal Field Theory - *Undeclared*
- 20.10: Magnetic Behavior of Atoms, Molecules, and Materials - *Undeclared*
- 20.11: Magnetic Behavior of Complex Ions - *Undeclared*
- 20.12: Optical Properties of Coordination Compounds (Color) - *Undeclared*

21: Nuclear Chemistry - *Undeclared*
- 21.1: Components of the Nucleus - *Undeclared*
- 21.2: Nuclear Reactions - *Undeclared*
- 21.3: Nuclear Radiation - *Undeclared*
- 21.4: Rates of Radioactive Decay - *Undeclared*
- 21.5: Stability of the Atomic Nucleus - *Undeclared*
- 21.6: The Origin of the Elements - *Undeclared*
- 21.7: Transmutation of the Elements - *Undeclared*
- 21.8: Nuclear Fission - *Undeclared*
- 21.9: Nuclear Fusion - *Undeclared*
- 21.E: Nuclear Chemistry (Exercises) - *Undeclared*

Appendix 1: Google Sheets - *Undeclared*
- 1: Google Sheets Basics - *Undeclared*

Back Matter - *CC BY-NC-SA 4.0*
- Index - *Undeclared*
- Glossary - *Undeclared*
- Detailed Licensing - *Undeclared*