CHM 363: PHYSICAL CHEMISTRY 1



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Chm363: Physical Chemistry 1 GC

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TABLE OF CONTENTS

Licensing

1: Energy Levels and Spectroscopy

- 1.1: Electromagnetic Radiation
- 1.2: The Wave Theory of Light
- 1.3: Bohr's Theory of the Hydrogen Emission Spectrum
- 1.4: Hydrogen's Atomic Emission Spectrum
- 1.5: The Schrödinger Wave Equation
- 1.6: Particle in a One-Dimensional Box
- 1.7: Electronic Spectroscopy
- 1.8: The Harmonic Oscillator Approximates Molecular Vibrations
- 1.9: The Harmonic Oscillator and Infrared Spectra
- 1.10: Microwave Spectroscopy

2: Atomic Structure

- 2.1: The Schrödinger Wave Equation for the Hydrogen Atom
- 2.2: Many-Electron Atoms and the Periodic Table
- 2.3: Quantum-Mechanical Tunneling

3: Chemical Bond

- 3.1: Lewis Structures
- 3.2: Valence Bond Theory
- 3.3: Hybridization of Atomic Orbitals
- 3.4: Molecular Orbital Theory
- 3.5: Diatomic Molecules
- 3.6: Electronegativity and Dipole Moment
- 3.7: Photoelectron Spectroscopy

4: Gases

- 4.1: The Perfect Gas
- 4.2: Real Gases (Deviations From Ideal Behavior)
- 4.3: van der Waals and Redlich-Kwong Equations of State
- 4.4: The Law of Corresponding States
- 4.5: The Repulsive Term in the Lennard-Jones Potential

5: Boltzmann

- 5.1: The Boltzmann Factor is used to Approximate the Fraction of Particles in a Large System
- 5.2: The Boltzmann Distribution represents a Thermally Equilibrated Distribution
- 5.3: The Average Ensemble Energy is Equal to the Observed Energy of a System
- 5.4: Heat Capacity at Constant Volume is the Change in Internal Energy with Temperature
- 5.5: Partition Functions can be Decomposed into Partition Functions of Each Degree of Freedom
- 5.6: Translational Partition Functions of Monotonic Gases
- 5.7: Most Atoms are in the Ground Electronic State
- 5.8: The Energy of a Diatomic/Polyatomic Molecule Can Be Approximated as a Sum of Separate Terms

- 5.9: Most Molecules are in the Ground Vibrational State
- 5.10: Most Molecules are Rotationally Excited at Ordinary Temperatures
- 5.11: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number

6: The First Law

- 6.1: Internal Energy
- 6.2: Enthalpy
- 6.3: Thermochemistry
- 6.4: State Functions and Exact Differentials
- 6.5: Adiabatic Changes

7: Entropy and The Second Law of Thermodynamics

- 7.1: Energy Does not Determine Spontaneity
- 7.2: The Second Law of Thermodynamics
- 7.3: We Must Always Devise a Reversible Process to Calculate Entropy Changes
- 7.4: The Famous Equation of Statistical Thermodynamics is S=k ln W
- 7.5: Entropy Can Be Expressed in Terms of a Partition Function
- 7.6: The Statistical Definition of Entropy is Analogous to the Thermodynamic Definition
- 7.7: Thermodynamics Provides Insight into the Conversion of Heat into Work

8: The Third Law, Absolute Entropy, and the Gibbs Free Energy of Formation

- 8.1: Heat Capacity as a Function of Temperature
- 8.2: The Third Law
- 8.3: Absolute Entropy
- 8.4: Evaluating Entropy Changes Using Thermochemical Cycles

9: Helmholtz and Gibbs Energies

- 9.1: Helmholtz Energy
- 9.2: Gibbs Energy Determines the Direction of Spontaneity at Constant Pressure and Temperature
- 9.3: The Maxwell Relations
- 9.4: Thermodynamic Functions have Natural Variables
- 9.5: The Enthalpy of an Ideal Gas is Independent of Pressure
- 9.6: The Gibbs-Helmholtz Equation

10: Phase Equilibria

- 10.1: A Phase Diagram Summarizes the Solid-Liquid-Gas Behavior of a Substance
- 10.2: Gibbs Energies and Phase Diagrams
- 10.3: The Chemical Potentials of a Pure Substance in Two Phases in Equilibrium
- 10.4: The Clausius-Clapeyron Equation

11: Solutions Liquid Liquid

- 11.1: A Mixture is a Combination of Two or More Substances
- 11.2: The Gibbs-Duhem Equation Relates Chemical Potential and Composition at Equilibrium
- 11.3: Chemical Potential of Each Component Has the Same Value in Each Phase in Which the Component Appears
- 11.4: Ideal Solutions obey Raoult's Law
- 11.5: Most Solutions are Not Ideal

- 11.6: Vapor Pressures of Volatile Binary Solutions
- 11.7: Activities of Nonideal Solutions

12: Chemical Equilibrium

- 12.1: Reaction Quotient and Equilibrium Constant
- 12.2: Equilibrium Results when Gibbs Energy is Minimized
- 12.3: The Equilibrium Constant
- 12.4: An Equilibrium Constant is a Function of Temperature Only
- 12.5: Reaction Quotient and Equilibrium Constant Ratio Determines Reaction Direction
- 12.6: The Sign of ΔG and not ΔG° Determines the Direction of Reaction Spontaneity
- 12.7: The van 't Hoff Equation
- 12.8: Equilibrium Constants in Terms of Partition Functions

13: The Kinetic Theory of Gases

- 13.1: The Average Translational Kinetic Energy of a Gas
- 13.2: The Distribution of Molecular Speeds is Given by the Maxwell-Boltzmann Distribution
- 13.3: Mean Free Path
- 13.4: Rates of Gas-Phase Chemical Reactions

14: Chemical Kinetics I - Rate Laws

- 14.1: The Time Dependence of a Chemical Reaction is Described by a Rate Law
- 14.2: First-Order Reactions Show an Exponential Decay of Reactant Concentration with Time
- 14.3: Different Rate Laws Predict Different Kinetics
- 14.4: Arrhenius Equation
- 14.5: Eyring equation

15: Chemical Kinetics II- Reaction Mechanisms

- 15.1: A Mechanism is a Sequence of Elementary Reactions
- 15.2: The Steady-State Approximation
- 15.3: Rate Laws Do Not Imply Unique Mechanism
- 15.4: The Lindemann Mechanism
- 15.5: Some Reaction Mechanisms Involve Chain Reactions
- 15.6: A Catalyst Affects the Mechanism and Activation Energy
- 15.7: The Michaelis-Menten Mechanism for Enzyme Catalysis

16: Math Chapters

- 16.1: Probability and Statistics
- 16.2: Spherical Coordinates
- 16.3: Partial Differentiation

Index

Glossary

Detailed Licensing

Detailed Licensing

Licensing

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

CHAPTER OVERVIEW

1: Energy Levels and Spectroscopy

1.1: Electromagnetic Radiation
1.2: The Wave Theory of Light
1.3: Bohr's Theory of the Hydrogen Emission Spectrum
1.4: Hydrogen's Atomic Emission Spectrum
1.5: The Schrödinger Wave Equation
1.6: Particle in a One-Dimensional Box
1.7: Electronic Spectroscopy
1.8: The Harmonic Oscillator Approximates Molecular Vibrations
1.9: The Harmonic Oscillator and Infrared Spectra
1.10: Microwave Spectroscopy

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1.1: Electromagnetic Radiation

As you read the print off this computer screen now, you are reading pages of fluctuating energy and magnetic fields. Light, electricity, and magnetism are all different forms of electromagnetic radiation.

Introduction

Electromagnetic radiation is a form of energy that is produced by oscillating electric and magnetic disturbance, or by the movement of electrically charged particles traveling through a vacuum or matter. The electric and magnetic fields come at right angles to each other and combined wave moves perpendicular to both magnetic and electric oscillating fields thus the disturbance. Electron radiation is released as photons, which are bundles of light energy that travel at the speed of light as quantized harmonic waves. This energy is then grouped into categories based on its wavelength into the electromagnetic spectrum. These electric and magnetic waves travel perpendicular to each other and have certain characteristics, including amplitude, wavelength, and frequency.

General Properties of all electromagnetic radiation:

1. Electromagnetic radiation can travel through empty space. Most other types of waves must travel through some sort of substance. For example, sound waves need either a gas, solid, or liquid to pass through in order to be heard.
2. The speed of light is always a constant. (Speed of light : 2.99792458 x 10^8 m s^{-1})
3. Wavelengths are measured between the distances of either crests or troughs. It is usually characterized by the Greek symbol λ.

Waves and their Characteristics

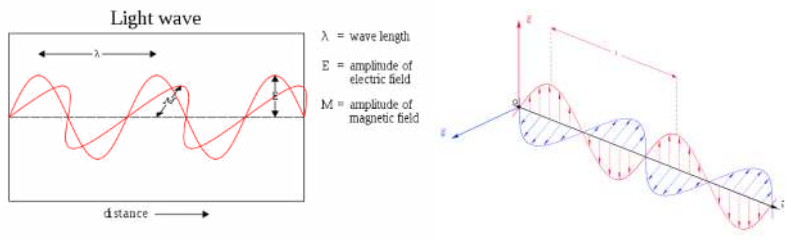


Fig. 1 & 2: Electromagnetic Waves

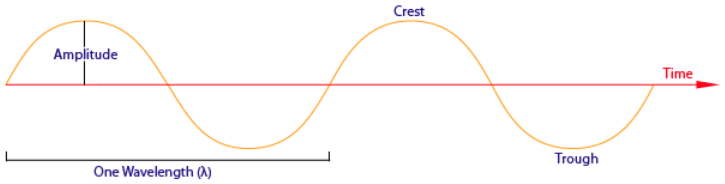


Fig. 3: An EM Wave

Amplitude

Amplitude is the distance from the maximum vertical displacement of the wave to the middle of the wave. This measures the magnitude of oscillation of a particular wave. In short, the amplitude is basically the height of the wave. Larger amplitude means higher energy and lower amplitude means lower energy. Amplitude is important because it tells you the intensity or brightness of a wave in comparison with other waves.

Wavelength

Wavelength (λ) is the distance of one full cycle of the oscillation. Longer wavelength waves such as radio waves carry low energy; this is why we can listen to the radio without any harmful consequences. Shorter wavelength waves such as x-rays carry higher energy that can be hazardous to our health. Consequently lead aprons are worn to protect our bodies from harmful radiation when we undergo x-rays. This wavelength frequently relationship is characterized by:

$$c = \lambda\nu \tag{1.1.1}$$

where

- c is the speed of light,
- λ is wavelength, and
- ν is frequency.

Shorter wavelength means greater frequency, and greater frequency means higher energy. Wavelengths are important in that they tell one what type of wave one is dealing with.

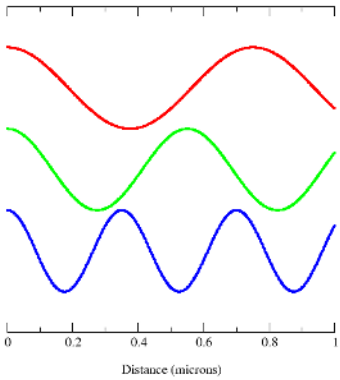


Fig. 4: Different Wavelengths and Frequencies

Remember, **Wavelength tells you the type of light** and **Amplitude tells you about the intensity of the light**

Frequency

Frequency is defined as the number of cycles per second, and is expressed as sec^{-1} or Hertz (Hz). Frequency is directly proportional to energy and can be express as:

$$E = h\nu \tag{1.1.2}$$

where

- E is energy,
- h is Planck's constant, (h= 6.62607 x 10^{-34} J), and
- ν is frequency.

Period

Period (T) is the amount of time a wave takes to travel one wavelength; it is measured in seconds (s).

Velocity

The velocity of wave in general is expressed as:

$$velocity = \lambda\nu \tag{1.1.3}$$

For Electromagnetic wave, the velocity in vacuum is $2.99 \times 10^8\ m/s$ or $186,282$ miles/second.

Electromagnetic spectrum

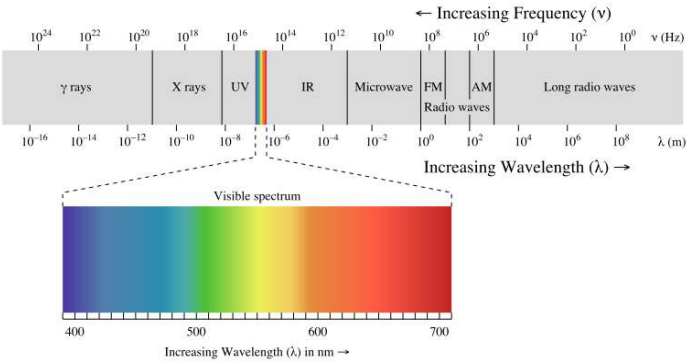


***Figure 24.5.1**: Electromagnetic spectrum with light highlighted. from Wikipedia.*

As a wave's wavelength increases, the frequency decreases, and as wave's wavelength decreases, the frequency increases. When electromagnetic energy is released as the energy level increases, the wavelength decreases and frequency decreases. Thus, electromagnetic radiation is then grouped into categories based on its wavelength or frequency into the electromagnetic spectrum. The different types of electromagnetic radiation shown in the electromagnetic spectrum consists of radio waves, microwaves, infrared waves, visible light, ultraviolet radiation, X-rays, and gamma rays. The part of the electromagnetic spectrum that we are able to see is the visible light spectrum.

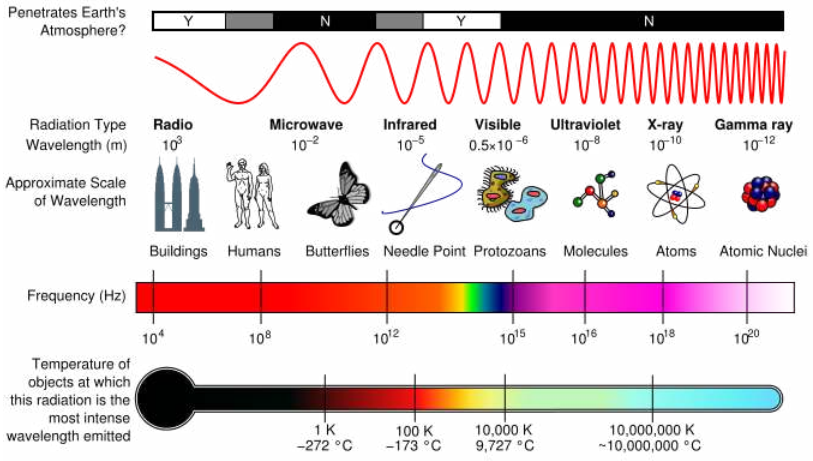


Fig. 6: Electromagnetic Spectrum with Radiation Types

Radiation Types

Radio Waves are approximately 10^3 m in wavelength. As the name implies, radio waves are transmitted by radio broadcasts, TV broadcasts, and even cell phones. Radio waves have the lowest energy levels. Radio waves are used in remote sensing, where hydrogen gas in space releases radio energy with a low frequency and is collected as radio waves. They are also used in radar systems, where they release radio energy and collect the bounced energy back. Especially useful in weather, radar systems are used to can illustrate maps of the surface of the Earth and predict weather patterns since radio energy easily breaks through the atmosphere. ;

Microwaves can be used to broadcast information through space, as well as warm food. They are also used in remote sensing in which microwaves are released and bounced back to collect information on their reflections.

Microwaves can be measured in centimeters. They are good for transmitting information because the energy can go through substances such as clouds and light rain. Short microwaves are sometimes used in Doppler radars to predict weather forecasts.

Infrared radiation can be released as heat or thermal energy. It can also be bounced back, which is called near infrared because of its similarities with visible light energy. Infrared Radiation is most commonly used in remote sensing as infrared sensors collect thermal energy, providing us with weather conditions.

This picture represents a snap shot in mid-infrared light.

Visible Light is the only part of the electromagnetic spectrum that humans can see with an unaided eye. This part of the spectrum includes a range of different colors that all represent a particular wavelength. Rainbows are formed in this way; light passes through matter in which it is absorbed or reflected based on its wavelength. Thus, some colors are reflected more than other, leading to the creation of a rainbow.

Color Region	Wavelength (nm)
Violet	380-435
Blue	435-500
Cyan	500-520
Green	520-565
Yellow	565-590
Orange	590-625
Red	625-740

Fig. 7: The color regions of the Visible Spectrum

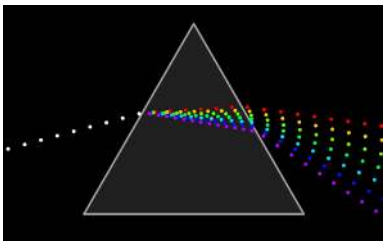


Fig. 8: Dispersion of Light Through A Prism

Ultraviolet, Radiation, X-Rays, and Gamma Rays are all related to events occurring in space. UV radiation is most commonly known because of its severe effects on the skin from the sun, leading to cancer. X-rays are used to produce medical images of the body. Gamma Rays can used in chemotherapy in order to rid of tumors in a body since it has such a high energy level. The shortest waves, Gamma rays, are approximately 10^{-12} m in wavelength. Out this huge spectrum, the human eyes can only detect waves from 390 nm to 780 nm.

Equations of Waves

The mathematical description of a wave is:

$$y = A\sin(kx - \omega t) \tag{1.1.4}$$

where A is the amplitude, k is the wave number, x is the displacement on the x-axis.

$$k = \frac{2\pi}{\lambda} \tag{1.1.5}$$

where λ is the wavelength. Angular frequency described as:

$$\omega = 2\pi\nu = \frac{2\pi}{T} \tag{1.1.6}$$

where ν is frequency and period (T) is the amount of time for the wave to travel one wavelength.

Interference

An important property of waves is the ability to combine with other waves. There are two type of interference: constructive and destructive. Constructive interference occurs when two or more waves are in phase and and their displacements add to produce a higher amplitude. On the contrary, destructive interference occurs when two or more waves are out of phase and their displacements negate each other to produce lower amplitude.

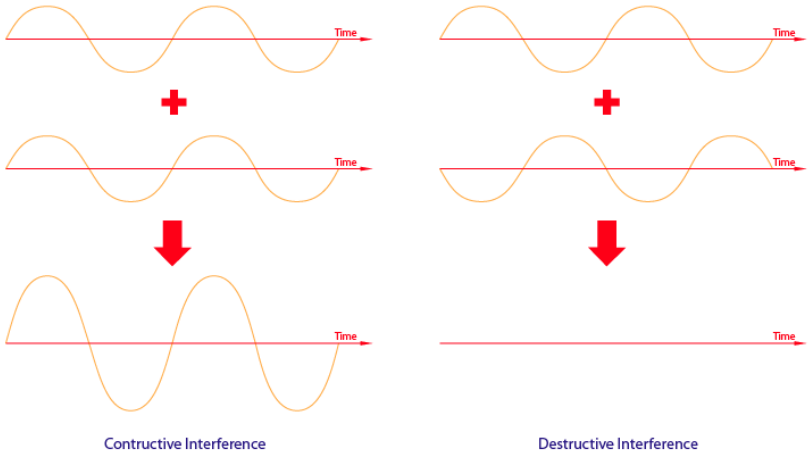
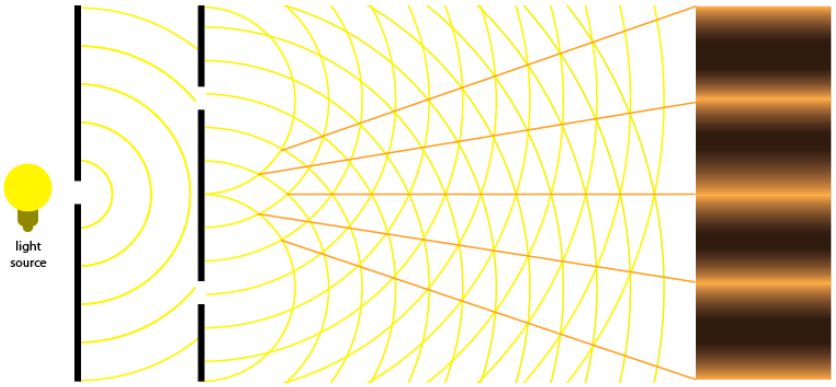


Figure 9 & 10: Constructive and Destructive Interference

Interference can be demonstrated effectively through the double slit experiment. This experiment consists of a light source pointing toward a plate with one slit and a second plate with two slits. As the light travels through the slits, we notice bands of alternating intensity on the wall behind the second plate. The banding in the middle is the most intense because the two waves are perfectly in phase at that point and thus constructively interfere. The dark bands are caused by out of phase waves which result in destructive interference. This is why you observe nodes on figure 4. In a similar way, if electrons are used instead of light, electrons will be represented both as waves and particles.



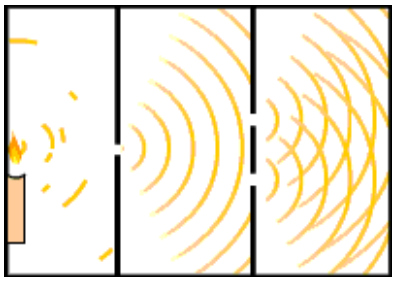


Fig. 11 & 12: Double-Slit Interference Experiment

Wave-Particle Duality

Electromagnetic radiation can either acts as a wave or a particle, a photon. As a wave, it is represented by velocity, wavelength, and frequency. Light is an EM wave since the speed of EM waves is the same as the speed of light. As a particle, EM is represented as a photon, which transports energy. When a photon is absorbed, the electron can be moved up or down an energy level. When it moves up, it absorbs energy, when it moves down, energy is released. Thus, since each atom has its own distinct set of energy levels, each element emits and absorbs different frequencies. Photons with higher energies produce shorter wavelengths and photons with lower energies produce longer wavelengths.

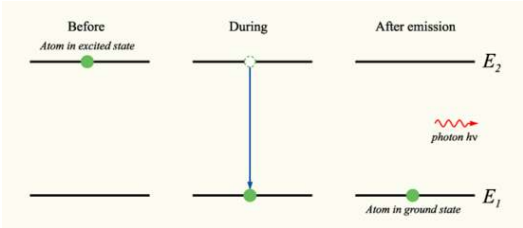


Fig. 13: Photon Before and After Emission

Ionizing and Non-Ionizing Radiation

Electromagnetic Radiation is also categorized into two groups based, ionizing and non-ionizing, on the severity of the radiation. Ionizing radiation holds a great amount of energy to remove electrons and cause the matter to become ionized. Thus, higher frequency waves such as the X-rays and gamma-rays have ionizing radiation. However, lower frequency waves such as radio waves, do not have ionizing radiation and are grouped as non-ionizing.

Electromagnetic Radiation and Temperature

Electromagnetic radiation released is related to the temperature of the body. Stephan-Boltzmann Law says that if this body is a black body, one which perfectly absorbs and emits radiation, the radiation released is equal to the temperature raised to the fourth power. Therefore, as temperature increases, the amount of radiation released increases greatly. Objects that release radiation very well also absorb radiation at certain wavelengths very well. This is explained by the Kirchhoff's Law. Wavelengths are also related to temperature. As the temperature increases, the wavelength of maximum emission decreases.

Problems

1. What is the wavelength of a wave with a frequency of 4.28 Hz?
2. What is the frequency of a wave with a wavelength of 200 cm?
3. What is the frequency of a wave with a wavelength of 500 pm?
4. What is the wavelength of a wave with a frequency of 2.998×10^5 Hz?
5. A radio transmits a frequency of 100 Hz. What is the wavelength of this wave?

Answers:

1. 700m
2. 1.5×10^8 Hz

3. 4.0×10^{17} Hz
4. 100m
5. 2.998×10^{6} m

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1.2: The Wave Theory of Light

Learning Objectives

- to learn about the characteristics of electromagnetic waves. Light, X-Rays, infrared and microwaves among the types of electromagnetic waves.

Scientists discovered much of what we know about the structure of the atom by observing the interaction of atoms with various forms of radiant, or transmitted, energy, such as the energy associated with the visible light we detect with our eyes, the infrared radiation we feel as heat, the ultraviolet light that causes sunburn, and the x-rays that produce images of our teeth or bones. All these forms of radiant energy should be familiar to you. We begin our discussion of the development of our current atomic model by describing the properties of waves and the various forms of electromagnetic radiation.



Figure 1.1.1 A Wave in Water When a drop of water falls onto a smooth water surface, it generates a set of waves that travel outward in a circular direction.

Properties of Waves

A wave is a periodic oscillation that transmits energy through space. Anyone who has visited a beach or dropped a stone into a puddle has observed waves traveling through water (Figure 1.1.1). These waves are produced when wind, a stone, or some other disturbance, such as a passing boat, transfers energy to the water, causing the surface to oscillate up and down as the energy travels outward from its point of origin. As a wave passes a particular point on the surface of the water, anything floating there moves up and down.

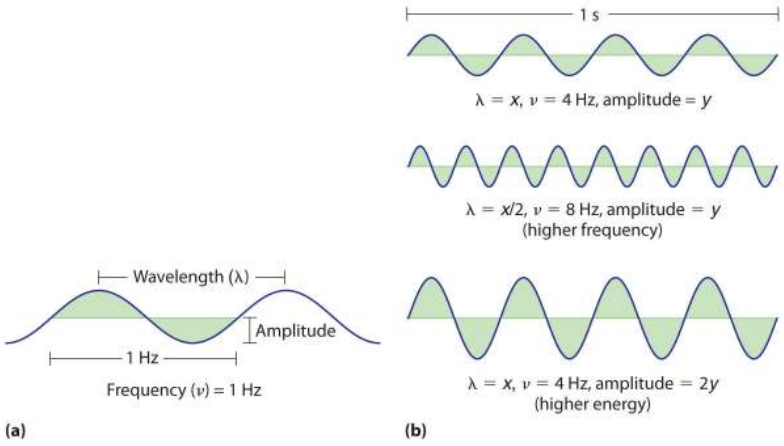


Figure 1.1.2: Important Properties of Waves (a) Wavelength (λ in meters), frequency (ν, in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.

Waves have characteristic properties (Figure 1.1.2). As you may have noticed in Figure 1.1.1, waves are periodic, that is, they repeat regularly in both space and time. The distance between two corresponding points in a wave—between the midpoints of two peaks, for example, or two troughs—is the wavelength (λ), distance between two corresponding points in a wave—between the midpoints of two peaks or two troughs. $\boldsymbol{\lambda}$ is the lowercase Greek lambda, and $\boldsymbol{\nu}$ is the lowercase Greek nu. Wavelengths are described by a unit of distance, typically meters. The frequency (ν), the number of oscillations (i.e., of a wave) that pass a particular

point in a given period of time. of a wave is the number of oscillations that pass a particular point in a given period of time. The usual units are oscillations persecond (1/s = s^{-1}), which in the SI system is called the hertz (Hz). It is named after German physicist Heinrich Hertz (1857–1894),a pioneer in the field of electromagnetic radiation. The amplitude (the vertical height of a wave, which is defined as half the peak-to-trough height), or vertical height, of a wave is defined as half the peak-to-trough height; as the amplitude of a wave with a given frequency increases, so does its energy. As you can see in Figure 1.1.2 , two waves can have the same amplitude but different wavelengths and vice versa. The distance traveled by a wave per unit time is its speed (v), the distance traveled by a wave per unit time, which is typically measured in meters per second (m/s). The speed of a wave is equal to the product of its wavelength and frequency:

(wavelength)(frequency) = speed

$$\lambda\nu = v \tag{1.1.1a}$$

$$\left(\frac{meters}{\cancel{wave}}\right)\left(\frac{\cancel{wave}}{second}\right) = \frac{meters}{second} \tag{1.1.1b}$$

Be careful not to confuse the symbols for the speed, v, with the frequency, ν. Water waves are slow compared to sound waves, which can travel through solids, liquids, and gases. Whereas water waves may travel a few meters per second, the speed of sound in dry air at 20°C is 343.5 m/s. Ultrasonic waves, which travel at an even higher speed (>1500 m/s) and have a greater frequency, are used in such diverse applications as locating underwater objects and the medical imaging of internal organs.

Electromagnetic Radiation

Water waves transmit energy through space by the periodic oscillation of matter (the water). In contrast, energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields is known as electromagnetic radiation, which is energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields. (Figure 1.1.3). Some forms of electromagnetic radiation are shown in Figure 1.1.4. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which is the speed with which all forms of electromagnetic radiation travel in a vacuum, a fundamental physical constant with a value of 2.99792458 × 10^8 m/s (which is about 3.00 ×10^8 m/s or 1.86 × 10^5 mi/s). This is about a million times faster than the speed of sound.

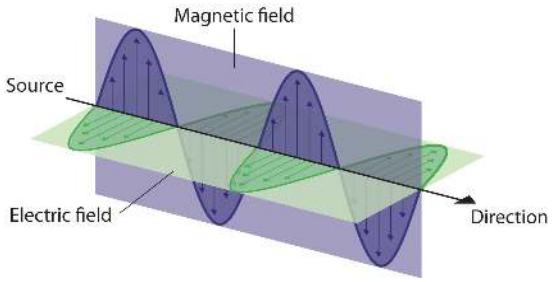


Figure 1.1.3: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Because the various kinds of electromagnetic radiation all have the same speed (c), they differ in only wavelength and frequency. As shown in Figure 1.1.4 and Table 1.1.1 , the wavelengths of familiar electromagnetic radiation range from 10^1 m for radio waves to 10^{-12} m for gamma rays, which are emitted by nuclear reactions. By replacing v with c in Equation 6.1.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$c = \lambda\nu$$
$$\nu = \frac{c}{\lambda} \tag{1.1.2}$$

For example, the frequency of radio waves is about 10^8 Hz, whereas the frequency of gamma rays is about 10^{20} Hz. Visible light, which is electromagnetic radiation that can be detected by the human eye, has wavelengths between about 7 × 10^{-7} m (700 nm, or 4.3 × 10^{14} Hz) and 4 × 10^{-7} m (400 nm, or 7.5 × 10^{14} Hz). Note that when frequency increases, wavelength decreases; c being a constant stays the same. Similarly when frequency decreases, the wavelength increases.

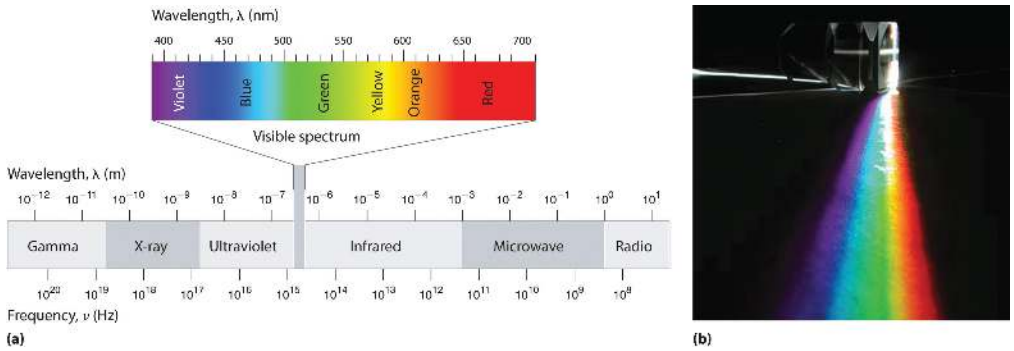


Figure 1.1.4: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.

Within this visible range our eyes perceive radiation of different wavelengths (or frequencies) as light of different colors, ranging from red to violet in order of decreasing wavelength. The components of white light—a mixture of all the frequencies of visible light—can be separated by a prism, as shown in part (b) in Figure 1.1.4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 1.1.1: Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Wavelength (m)	Type of Radiation
picometer	pm	10^{-12}	gamma ray
angstrom	Å	10^{-10}	x-ray
nanometer	nm	10^{-9}	x-ray
micrometer	μm	10^{-6}	infrared
millimeter	mm	10^{-3}	infrared
centimeter	cm	10^{-2}	microwave
meter	m	10^{0}	radio

As you will soon see, the energy of electromagnetic radiation is directly proportional to its frequency and inversely proportional to its wavelength:

$$E \propto \nu \tag{1.1.3}$$

$$E \propto \frac{1}{\lambda} \tag{1.1.4}$$

Whereas visible light is essentially harmless to our skin, ultraviolet light, with wavelengths of ≤ 400 nm, has enough energy to cause severe damage to our skin in the form of sunburn. Because the ozone layer absorbs sunlight with wavelengths less than 350 nm, it protects us from the damaging effects of highly energetic ultraviolet radiation.

> The energy of electromagnetic radiation **increases** with **increasing** frequency and **decreasing** wavelength.

Example 1.1.1

Your favorite FM radio station, WXYZ, broadcasts at a frequency of 101.1 MHz. What is the wavelength of this radiation?

Given: frequency

Asked for: wavelength

Strategy:

Substitute the value for the speed of light in meters per second into Equation 1.1.2 to calculate the wavelength in meters.

Solution:

From Equation 1.1.2 , we know that the product of the wavelength and the frequency is the speed of the wave, which for electromagnetic radiation is 2.998×10^8 m/s:

$$\lambda\nu = c = 2.998 \times 10^8 m/s$$

Thus the wavelength λ is given by

$$\lambda = \frac{c}{\nu} = \left(\frac{2.988 \times 10^8\ m/\cancel{s}}{101.1\ \cancel{MHz}}\right)\left(\frac{1\ \cancel{MHz}}{10^6\ \cancel{s^{-1}}}\right) = 2.965\ m$$

Exercise 1.1.1

As the police officer was writing up your speeding ticket, she mentioned that she was using a state-of-the-art radar gun operating at 35.5 GHz. What is the wavelength of the radiation emitted by the radar gun?

Click to Check Answer

8.45 mm

External Videos & Examples

- **Light Speed, Wavelength and Frequency by Doc Schuster - Explains wavelength and frequency**
- **Waves in General by JaHu Productions - a bit faster. Also discusses sound waves**
- **Calculating Frequency Given Wavelength - Johnny Cantrell**
- **Wavelength Frequency Problems - Cayer Chem**
- **Quantum Chemistry - Ohio State**
- **Quantum Chemistry Quizzes - mhe education**
- **AP Chemistry Chapter 7 Review - Science Geek**
- **Quantum Theory of the Atom Practice Quiz - Northrup**

Answers for these quizzes are included. There are also questions covering more topics in Chapter 6.

Summary

- Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation.

A basic knowledge of the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A wave is a periodic oscillation by which energy is transmitted through space. All waves are periodic, repeating regularly in both space and time. Waves are characterized by several interrelated properties: wavelength (λ), the distance between successive waves; frequency (ν), the number of waves that pass a fixed point per unit time; speed (v), the rate at which the wave propagates through space; and amplitude, the magnitude of the oscillation about the mean position. The speed of a wave is equal to the product of its wavelength and frequency. Electromagnetic radiation consists of two perpendicular waves, one electric and one magnetic, propagating at the speed of light (c). Electromagnetic radiation is radiant energy that includes radio waves, microwaves, visible light, x-rays, and gamma rays, which differ in their frequencies and wavelengths.

Contributors

- Modified by Joshua Halpern (Howard University)

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1.3: Bohr's Theory of the Hydrogen Emission Spectrum

Overview

- To introduce the concept of absorption and emission line spectra and describe the Balmer equation to describe the visible lines of atomic hydrogen.
- Describe Rydberg's theory for the hydrogen spectra.
- Interpret the hydrogen spectrum in terms of the energy states of electrons.

The first person to realize that white light was made up of the colors of the rainbow was Isaac Newton, who in 1666 passed sunlight through a narrow slit, then a prism, to project the colored spectrum on to a wall. This effect had been noticed previously, of course, not least in the sky, but previous attempts to explain it, by Descartes and others, had suggested that the white light became colored when it was refracted, the color depending on the angle of refraction. Newton clarified the situation by using a second prism to reconstitute the white light, making much more plausible the idea that the white light was composed of the separate colors. He then took a monochromatic component from the spectrum generated by one prism and passed it through a second prism, establishing that no further colors were generated. That is, light of a single color did not change color on refraction. He concluded that white light was made up of all the colors of the rainbow, and that on passing through a prism, these different colors were refracted through slightly different angles, thus separating them into the observed spectrum.

Atomic Line Spectrum

The spectrum of *hydrogen*, which turned out to be crucial in providing the first insight into atomic structure over half a century later, was first observed by Anders Angstrom in Uppsala, Sweden, in 1853. His communication was translated into English in 1855. Angstrom, the son of a country minister, was a reserved person, not interested in the social life that centered around the court. Consequently, it was many years before his achievements were recognized, at home or abroad (most of his results were published in Swedish).

Most of what is known about atomic (and molecular) structure and mechanics has been deduced from spectroscopy. Figure 1.4.1 shows two different types of spectra. A continuous spectrum can be produced by an incandescent solid or gas at high pressure (blackbody radiation, for example, is a continuum). An emission spectrum can be produced by a gas at low pressure excited by heat or by collisions with electrons. An absorption spectrum results when light from a continuous source passes through a cooler gas, consisting of a series of dark lines characteristic of the composition of the gas.

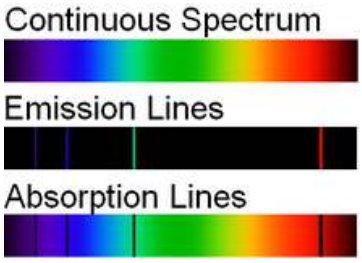


Figure **1.3.1** : Continuous spectrum and two types of line spectra. from Wikipedia.

In 1802, William Wollaston in England had discovered (perhaps by using a thinner slit or a better prism) that in fact the solar spectrum itself had tiny gaps - there were many thin dark lines in the rainbow of colors. These were investigated much more systematically by Joseph von Fraunhofer, beginning in 1814. He increased the dispersion by using more than one prism. He found an "almost countless number" of lines. He labeled the strongest dark lines A, B, C, D, etc. Frauenhofer between 1814 and 1823 discovered nearly 600 dark lines in the solar spectrum viewed at high resolution and designated the principal features with the letters A through K, and weaker lines with other letters (Table **1.3.1**). Modern observations of sunlight can detect many thousands of lines. It is now understood that these lines are caused by absorption by the outer layers of the Sun.

Table **1.3.1** : Major Fraunhofer lines, and the elements they are associated with

Designation	Element	Wavelength (nm)
y	O_2	898.765
Z	O_2	822.696
A	O_2	759.370
B	O_2	686.719
C	H	656.281
a	O_2	627.661
D_1	Na	589.592
D_2	Na	588.995
D_3 or d	He	587.5618

Fraunhofer Absorption Lines

The Fraunhofer lines are typical spectral absorption lines. These dark lines are produced whenever a cold gas is between a broad spectrum photon source and the detector. In this case, a decrease in the intensity of light in the frequency of the incident photon is seen as the photons are absorbed, then re-emitted in random directions, which are mostly in directions different from the original one. This results in an *absorption line*, since the narrow frequency band of light initially traveling toward the detector, has been turned into heat or re-emitted in other directions.

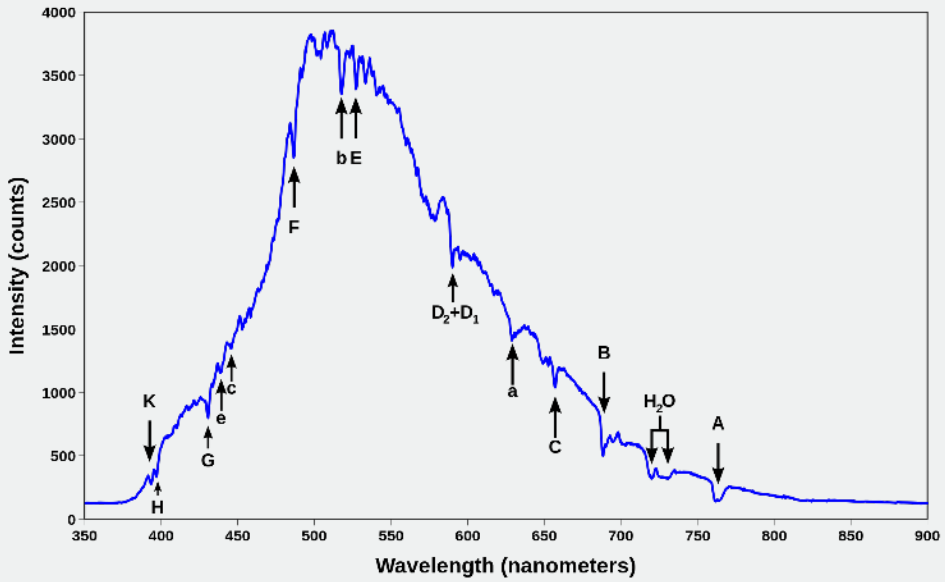


Figure **1.3.2**: Spectrum of blue sky. Dips are present at the Fraunhofer line wavelengths. from Wikipedia.

By contrast, if the detector sees photons emitted directly from a glowing gas, then the detector often sees photons emitted in a narrow frequency range by quantum emission processes in atoms in the hot gas, resulting in an *emission line*. In the Sun, Fraunhofer lines are seen from gas in the outer regions of the Sun, which are too cold to directly produce emission lines of the elements they represent.

Gases heated to incandescence were found by Bunsen, Kirkhoff and others to emit light with a series of sharp wavelengths. The emitted light analyzed by a spectrometer (or even a simple prism) appears as a multitude of narrow bands of color. These so called *line spectra* are characteristic of the atomic composition of the gas. The line spectra of several elements are shown in Figure **1.3.3**.

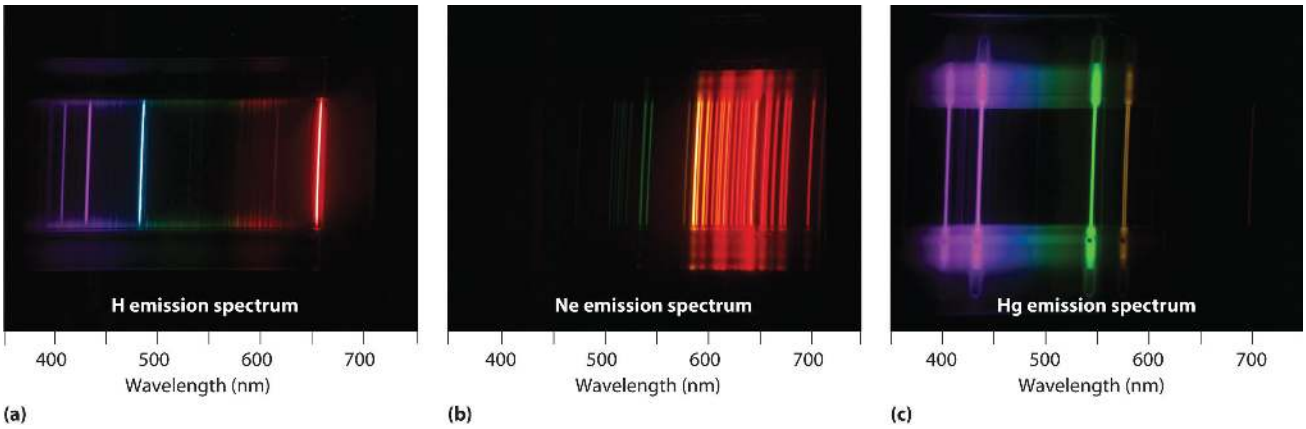


Figure **1.3.3**: The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) helium; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest lines in the mercury spectrum are at 181 and 254 nm, also in the UV. These are not shown.

The Balmer Series of Hydrogen

Obviously, if any pattern could be discerned in the spectral lines for a specifc atom (in contract to the mixture that Fraunhofer lines represent), that might be a clue as to the internal structure of the atom. One might be able to build a model. A great deal of effort went into analyzing the spectral data from the 1860's on. The big breakthrough was made by Johann Balmer, a math and Latin teacher at a girls' school in Basel, Switzerland. Balmer had done no physics before, and made his great discovery when he was almost sixty.



Figure **1.3.4**: The visible hydrogen emission spectrum lines in the Balmer series. The red line at the right is the H_α *line and the two leftmost lines are considered to be ultraviolet as they have wavelengths less than 400 nm. from Wikipedia.*

Balmer decided that the most likely atom to show simple spectral patterns was the lightest atom, hydrogen. Angstrom had measured the four visible spectral lines to have wavelengths 656.21, 486.07, 434.01 and 410.12 nm (Figure **1.3.4**). Balmer concentrated on just these four numbers, and found they were represented by the formula:

$$\lambda = b\left(\frac{n_2^2}{n_2^2-4}\right) \tag{1.3.1}$$

where

- b = 364.56 nm and
- $n_2 = 3, 4, 5, 6$.

The first four wavelengths of Equation **1.3.1** (with n_2=3,4,5,6) were in excellent agreement with the experimental lines from Angstrom (Table **1.3.2**). Balmer predicted that other lines exist in the infrared that correspond to *n* = 7, 8, etc., and in fact some of them had already been observed, unbeknown to Balmer.

Table **1.3.2** : The Balmer Series of Hydrogen Emission Lines

n_2	3	4	5	6	7	8	9	10
λ	*656*	*486*	*434*	*410*	397	389	383	380
color	*red*	*teal*	*blue*	*indigo*	violet	not visible	not visible	not visible

The n_2 integer in the Balmer series extends theoretically to infinity and the series resents a monotonically increasing energy (and frequency) of the absorption lines with increasing n_2 values. Moreover, the energy difference between successive lines decreased as n_2 increases (Figure 1.4.4). This behavior converges to a highest possible energy as Example **1.3.1** demonstrates. If the lines are

plot according to their λ on a linear scale, you will get the appearance of the spectrum in Figure **1.3.4**; these lines are called the **Balmer series**.

Balmer's general formula (Equation 1.3.1) can be rewritten in terms of the inverse wavelength typically called the *wavenumber* ($\tilde{\nu}$).

$$\tilde{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{4} - \frac{1}{n_2^2} \right) \tag{1.3.2}$$

where

- $n_2 = 3, 4, 5, 6$ and
- R_H is the Rydberg constant (discussed below) and is equal to 109,737 cm^{-1}.

He further conjectured that the 4 could be replaced by 9, 16, 25, … and this also turned out to be true - but these lines, further into the infrared, were not detected until the early twentieth century, along with the ultraviolet lines.

Wavenumbers

The relation between wavelength and frequency for electromagnetic radiation is

$$\lambda \nu = c \tag{1.3.3}$$

In the SI system of units the wavelength, \lambda\) is measured in meters (m) and since wavelengths are usually very small one often uses the nanometer (nm) which is $10^{-9}\ m$. The frequency (ν) in the SI system is measured in reciprocal seconds 1/s − which is called a Hertz (after the discover of the photoelectron effect) and is represented by Hz.

It is common to use the reciprocal of the wavelength in centimeters as a measure of the frequency of radiation. This unit is called a wavenumber and is represented by ($\tilde{\nu}$) and is defined by

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \tag{1.3.4}$$

Wavenumbers is a convenient unit in spectroscopy because it is directly proportional to energy.

$$E = \frac{hc}{\lambda} \tag{1.3.5}$$

$$E = hc \times \frac{1}{\lambda} \tag{1.3.6}$$

$$E = hc\tilde{\nu} \tag{1.3.7}$$

$$E \propto \tilde{\nu} \tag{1.3.8}$$

Balmer Series

Calculate the longest and shortest wavelengths (in nm) emitted in the Balmer series of the hydrogen atom emission spectrum.

Solution

From the behavior of the Balmer equation (Equation 1.3.1 and Table **1.3.2**), the value of n_2 that gives the longest (i.e., greatest) wavelength (λ) is the smallest value possible of n_2, which is $n_2 = 3$ for this series. This results in

$$\lambda_{longest} = (364.56\ nm) \left(\frac{9}{9-4} \right) \tag{1.3.9}$$

$$\lambda_{longest} = (364.56\ nm)\,(1.8) = 656.2\ nm \tag{1.3.10}$$

This is also known as the H_α line of atomic hydrogen and is bight red (Figure 1.4.4).

For the shortest wavelength, it should be recognized that the shortest wavelength (greatest energy) is obtained at the limit of greatest (n_2\):

$$\lambda_{shortest} = \lim_{n_2 \to \infty} (364.56\ nm) \left(\frac{n_2^2}{n_2^2 - 4} \right) \tag{1.3.11}$$

This can be solved via L'Hôpital's Rule, or alternatively the limit can be expressed via the equally useful energy expression (Equation 1.4.2) and simply solved:

$$\tilde{\nu}_{greatest} = \lim_{n_2 \to \infty} R_H \left(\frac{1}{4} - \frac{1}{n_2^2} \right) \tag{1.3.12}$$

$$\tilde{\nu}_{greatest} = \lim_{n_2 \to \infty} R_H \left(\frac{1}{4} \right) = 27,434\ cm^{-1} \tag{1.3.13}$$

Since $\frac{1}{\tilde{\nu}} = \lambda$ in units of cm, this converts to 364 nm as the shortest wavelength possible for the Balmer series.

The Balmer series is particularly useful in astronomy because the Balmer lines appear in numerous stellar objects due to the abundance of hydrogen in the universe, and therefore are commonly seen and relatively strong compared to lines from other elements.

The Generalized Rydberg Equation

In an amazing demonstration of mathematical insight, in 1885 Balmer came up with a simple formula for predicting the wavelength of any of the lines in atomic Hydrogen in what we now know as the Balmer series (Equation 1.3.2). Three years later, Rydberg generalized this so that it was possible to determine the wavelengths of any of the lines in the hydrogen emission spectrum. Rydberg suggested that all atomic spectra formed families with this pattern (he was unaware of Balmer's work). It turns out that there are families of spectra following Rydberg's pattern, notably in the alkali metals, sodium, potassium, etc., but not with the precision the hydrogen atom lines fit the Balmer formula, and low values of n_2 predicted wavelengths that deviate considerably.

Rydberg's general equation is as follows:

$$\tilde{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{1.3.14}$$

where

- R_H is the *Rydberg* constant and is equal to 109,737 cm^{-1}.
- n_1 and n_2 are integers (whole numbers) with $n_2 > n_1$.

For the Balmer lines, $n_1 = 2$ and n_2 can be any whole number between 3 and infinity. The various combinations of numbers that can be substituted into this formula allow the calculation the wavelength of any of the lines in the hydrogen emission spectrum; there is close agreement between the wavelengths generated by this formula and those observed in a real spectrum.

Other Series

The results given by Balmer and Rydberg for the spectrum in the visible region of the electromagnetic radiation start with $n_2 = 3$, and $n_1^2 = 2$. Is there a different series with the following formula (e.g., $n_1 = 1$?

$$\frac{1}{\lambda} = R_H \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \tag{1.3.15}$$

The values for n_2 and wavenumber $\tilde{\nu}$ for this series would be:

Table 1.3.3: The Lyman Series of Hydrogen Emission Lines ($n_1 = 1$)

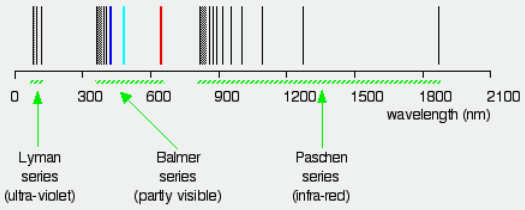
n_2	2	3	4	5	...
λ (nm)	121	102	97	94	...
$\tilde{\nu}$ (cm-1)	82,2291	97,530	102,864	105,332	...

These lines are in the UV region, and they are not visible, but they are detected by instruments; these lines form a **Lyman series**. The existences of the Lyman series and Balmer's series suggest the existence of more series. For example, the series with $n_2^2 = 3$ and n_1^2 = 4, 5, 6, 7, ... is called **Pashen series**.

Note

The spectral lines are grouped into series according to n_1 values. Lines are named sequentially starting from the longest wavelength/lowest frequency of the series, using Greek letters within each series. For example, the ($n_1 = 1/n_2 = 2$) line is called "Lyman-alpha" (Ly-α), while the ($n_1 = 3/n_2 = 7$) line is called "Paschen-delta" (Pa-δ). The first six series have specific names:

- Lyman series with $n_1 = 1$
- Balmer series with $n_1 = 2$
- Paschen series (or Bohr series) with $n_1 = 3$
- Brackett series with $n_1 = 4$
- Pfund series with $n_1 = 5$
- Humphreys series with $n_1 = 6$



The spectral series of hydrogen based of the Rydberg Equation (on a logarithmic scale).

Example 1.3.2: The Lyman Series

The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the *n* = 1 orbit. Calculate the wavelength of the lowest-energy line in the Lyman series to three significant figures. In what region of the electromagnetic spectrum does it occur?

Given: lowest-energy orbit in the Lyman series

Asked for: wavelength of the lowest-energy Lyman line and corresponding region of the spectrum

Strategy:

A. Substitute the appropriate values into Equation 1.5.1 (the Rydberg equation) and solve for λ.
B. Locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

$$\frac{1}{\lambda} = \Re\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{1.3.16}$$

A For the Lyman series, $n_1 = 1$.

$$\frac{1}{\lambda} = \Re\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 1.097 \times m^{-1}\left(\frac{1}{1} - \frac{1}{4}\right) = 8.228 \times 10^6\ m^{-1} \tag{1.3.17}$$

Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit is particularly convenient. The infrared range is roughly 200 - 5,000 cm^{-1}, the visible from 11,000 to 25.000 cm^{-1} and the UV between 25,000 and 100,000 cm^{-1}. The units of cm^{-1} are called wavenumbers, although people often verbalize it as inverse centimeters. We can convert the answer in part A to cm^{-1}.

$$\tilde{\nu} = \frac{1}{\lambda} = 8.228 \times 10^6 \cancel{m^{-1}} \left(\frac{\cancel{m}}{100\ cm} \right) = 82,280\ cm^{-1} \tag{1.3.18}$$

and

$$\lambda = 1.215 \times 10^{-7}\ m = 122\ nm \tag{1.3.19}$$

This emission line is called Lyman alpha. It is the strongest atomic emission line from the sun and drives the chemistry of the upper atmosphere of all the planets producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating O_2 molecules to O atoms which react with other O_2 molecules to form stratospheric ozone

B This wavelength is in the ultraviolet region of the spectrum.

? Exercise 1.3.2: The Pfund Series

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the \(*n_1* = 5\) orbit. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer: 4.65 × 10^3 nm; infrared

The above discussion presents only a phenomenological description of hydrogen emission lines and fails to provide a probe of the nature of the atom itself. Clearly a continuum model based on classical mechanics is not applicable.

Contributors and Attributions

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1.4: Hydrogen's Atomic Emission Spectrum

A hydrogen discharge tube is a slim tube containing hydrogen gas at low pressure with an electrode at each end. If a high voltage (5000 volts) is applied, the tube lights up with a bright pink glow. If the light is passed through a prism or diffraction grating, it is split into its various colors. This is a small part of the hydrogen emission spectrum. Most of the spectrum is invisible to the eye because it is either in the infrared or the ultraviolet region of the electromagnetic spectrum.

The photograph shows part of a hydrogen discharge tube on the left, and the three most apparent lines in the visible part of the spectrum on the right. (Ignore the "smearing," particularly to the left of the red line. This is caused by flaws in the way the photograph was taken. See note below.)

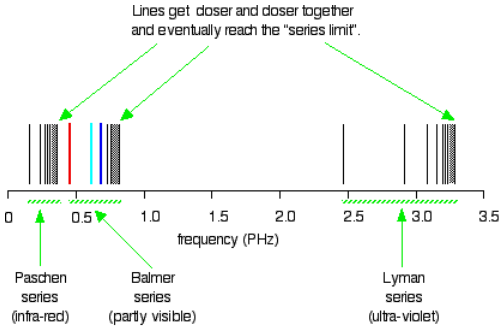


This photograph is by courtesy of Dr Rod Nave of the Department of Physics and Astronomy at Georgia State University, Atlanta.

Extending hydrogen's emission spectrum into the UV and IR

The hydrogen spectrum is complex, comprising more than the three lines visible to the naked eye. It is possible to detect patterns of lines in both the ultraviolet and infrared regions of the spectrum as well. These fall into a number of "series" of lines named after the person who discovered them. The diagram below shows three of these series, but there are others in the infrared to the left of the Paschen series shown in the diagram.

The diagram is quite complicated. Consider first at the Lyman series on the right of the diagram; this is the broadest series, and the easiest to decipher.



The frequency scale is marked in PHz—petaHertz. Peta means "10^{15} times". The value 3 PHz is equal to 3×10^{15} Hz. The quantity "hertz" indicates "cycles per second".

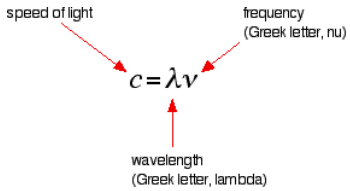
The Lyman series is a series of lines in the ultraviolet region. The lines grow closer and closer together as the frequency increases. Eventually, they are so close together that it becomes impossible to see them as anything other than a continuous spectrum. This is suggested by the shaded part on the right end of the series. At one particular point, known as the series limit, the series ends.

In Balmer series or the Paschen series, the pattern is the same, but the series are more compact. In the Balmer series, notice the position of the three visible lines from the photograph further up the page.

Frequency and Wavelength

The hydrogen spectrum is often drawn using wavelengths of light rather than frequencies. Unfortunately, because of the mathematical relationship between the frequency of light and its wavelength, two completely different views of the spectrum are

obtained when it is plotted against frequency or against wavelength. The mathematical relationship between frequency and wavelength is the following:



Rearranging this gives equations for either wavelength or frequency:

$$\lambda = \frac{c}{\nu} \tag{1.4.1}$$

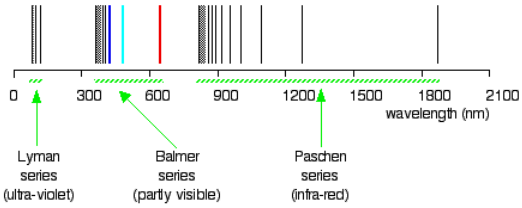
or

$$\nu = \frac{c}{\lambda} \tag{1.4.2}$$

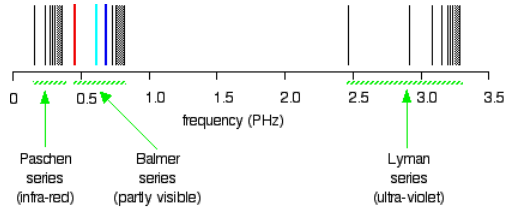
There is an inverse relationship between the two variables—a high frequency means a low wavelength and vice versa.

Drawing the hydrogen spectrum in terms of wavelength

This is what the spectrum looks like plotted in terms of wavelength instead of frequency:



Compare this to the same spectrum in terms of frequency:



When juxtaposed, the two plots form a confusing picture. The remainder of the article employs the spectrum plotted against frequency, because in this spectrum it is much easier visualize what is occurring in the atom.

The Balmer and Rydberg Equations

In an amazing demonstration of mathematical insight, in 1885 Balmer came up with a simple formula for predicting the wavelength of any of the lines in what we now know as the Balmer series. Three years later, Rydberg generalized this so that it was possible to determine the wavelengths of any of the lines in the hydrogen emission spectrum. Rydberg's equation is as follows:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{1.4.3}$$

where

- R_H is the *Rydberg* constant.
- n_1 and n_2 are integers (whole numbers). n_2 is always greater than n_1. In other words, if n_1 is, say, 2 then n_2 can be any whole number between 3 and infinity.

The various combinations of numbers that can be substituted into this formula allow the calculation the wavelength of any of the lines in the hydrogen emission spectrum; there is close agreement between the wavelengths generated by this formula and those observed in a real spectrum.

A modified version of the Rydberg equation can be used to calculate the frequency of each of the lines:

$$\nu = \frac{c}{\lambda}$$

$$= c \times \frac{1}{\lambda}$$

$$\text{If } \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

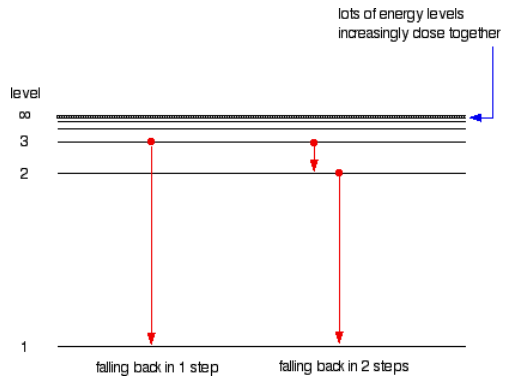
$$\nu = c.R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

The origin of the hydrogen emission spectrum

The lines in the hydrogen emission spectrum form regular patterns and can be represented by a (relatively) simple equation. Each line can be calculated from a combination of simple whole numbers. Why does hydrogen emit light when excited by a high voltage and what is the significance of those whole numbers?

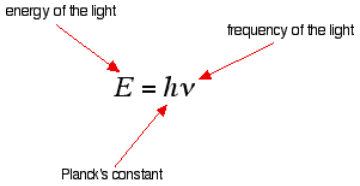
When unexcited, hydrogen's electron is in the first energy level—the level closest to the nucleus. But if energy is supplied to the atom, the electron is excited into a higher energy level, or even removed from the atom altogether. The high voltage in a discharge tube provides that energy. Hydrogen molecules are first broken up into hydrogen atoms (hence the atomic hydrogen emission spectrum) and electrons are then promoted into higher energy levels.

Suppose a particular electron is excited into the third energy level. It would tend to lose energy again by falling back down to a lower level. It can do this in two different ways. It could fall all the way back down to the first level again, or it could fall back to the second level and then, in a second jump, down to the first level.



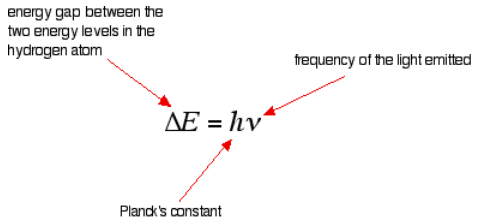
Assigning particular electron jumps to individual lines in the spectrum

If an electron falls from the 3-level to the 2-level, it must lose an amount of energy exactly equal to the energy difference between those two levels. That energy which the electron loses is emitted as light (which "light" includes UV and IR as well as visible radiation). Each frequency of light is associated with a particular energy by the equation:



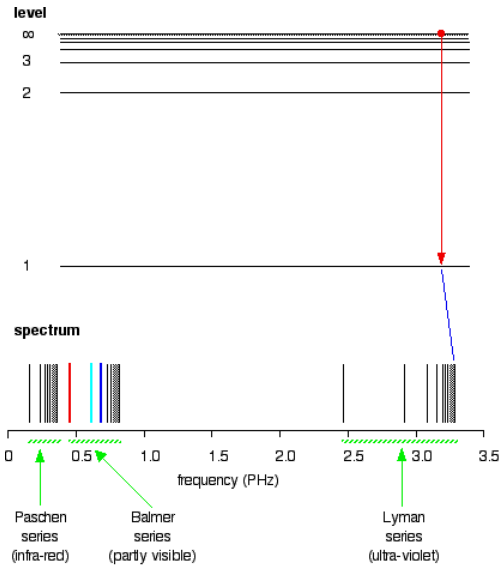
The higher the frequency, the higher the energy of the light. If an electron falls from the 3-level to the 2-level, red light is seen. This is the origin of the red line in the hydrogen spectrum. From the frequency of the red light, its energy can be calculated. That energy must be exactly the same as the energy gap between the 3-level and the 2-level in the hydrogen atom.

The last equation can therefore be rewritten as a measure of the energy gap between two electron levels:

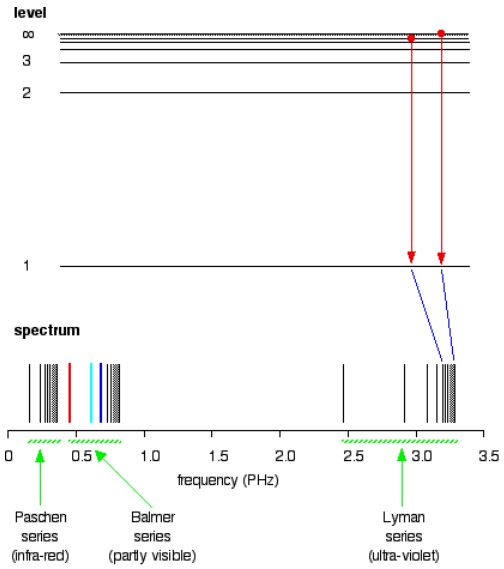


The greatest possible fall in energy will therefore produce the highest frequency line in the spectrum. The greatest fall will be from the infinity level to the 1-level. (The significance of the infinity level will be made clear later.)

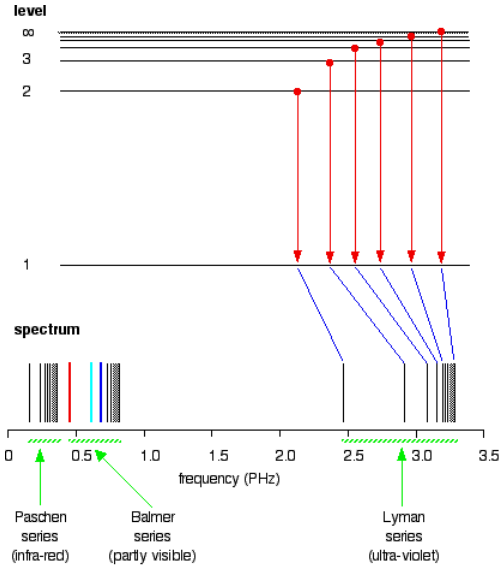
The next few diagrams are in two parts, with the energy levels at the top and the spectrum at the bottom.



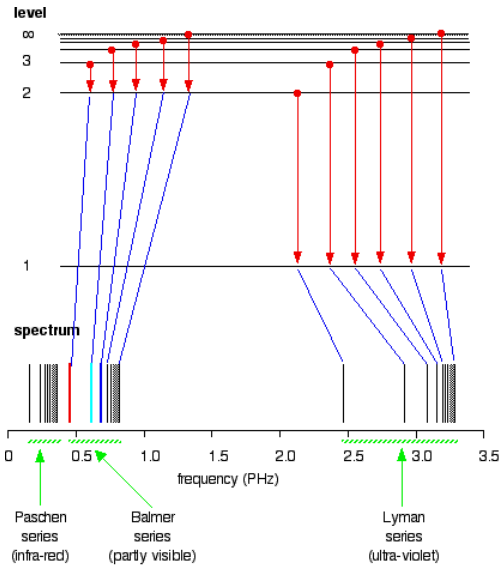
If an electron falls from the 6-level, the difference is slightly less than before, and so the frequency is slightly lower (because of the scale of the diagram, it is impossible to depict the levels beyond 7).



All other possible jumps to the first level make up the whole Lyman series. The spacings between the lines in the spectrum reflect the changes in spacings between the energy levels.



If the same is done for the 2-level, the Balmer series is shown. These energy gaps are all much smaller than in the Lyman series, and so the frequencies produced are also much lower.



The Paschen series is made up of the transitions to the 3-level, but they are omitted to avoid cluttering the diagram.

The significance of the numbers in the Rydberg equation

In the Rydberg equation, n_1 and n_2 represent the energy levels at either end of the jump that produces a particular line in the spectrum.

- In the Lyman series, $\boldsymbol{n_1 = 1}$, because electrons transition to the 1-level to produce lines in the Lyman series.
- In the Balmer series, $\boldsymbol{n_1 = 2}$, because electrons fall to the 2-level.

n_2 is the level being jumped from. In the case before, in which a red line is produced by electrons falling from the 3-level to the 2-level, n_2 is equal to 3.

The significance of the infinity level

The infinity level represents the highest possible energy an electron can have as a part of a hydrogen atom. If the electron exceeds that energy, it is no longer a part of the atom. The infinity level represents the point at which ionization of the atom occurs to form a positively charged ion.

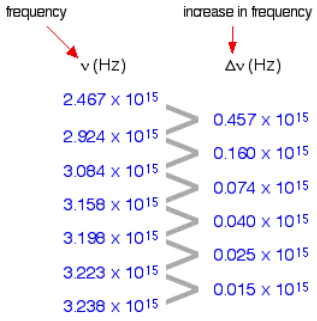
Using the spectrum to find the ionization energy of hydrogen

When there is no additional energy supplied to it, hydrogen atom's electron is found at the 1-level. This is known as its ground state. If enough energy is supplied to move the electron up to the infinity level, the atom is ionized. The ionization energy per electron is therefore a measure of the difference in energy between the 1-level and the infinity level. In above diagrams, that particular energy jump produces the series limit of the Lyman series.

The frequency of the Lyman series limit can be used to calculate the energy required to promote the electron in one atom from the 1-level to the point of ionization. This energy can then be used to calculate the ionization energy per mole of atoms. A problem with this approach is that the frequency of a series limit is quite difficult to find accurately from a spectrum because the lines are so close together in that region that the spectrum looks continuous.

Finding the frequency of the series limit graphically

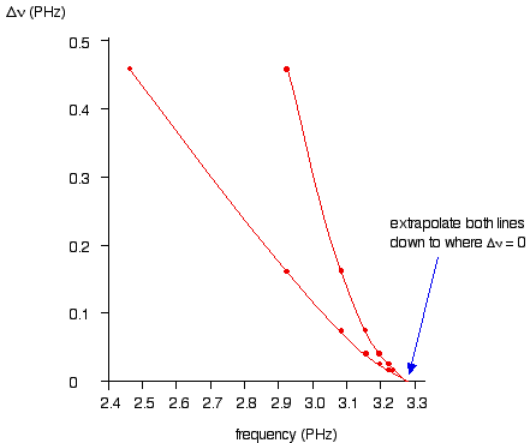
The following is a list of the frequencies of the seven most widely spaced lines in the Lyman series, together with the increase in frequency between successive lines.



As the lines become closer together, the increase in frequency is lessened. At the series limit, the gap between the lines is zero. Consequently, if the increase in frequency is plotted against the actual frequency, the curve can be extrapolated to the point at which the increase becomes zero, the frequency of the series limit.

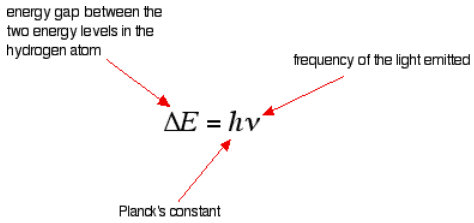
In fact, two graphs can be plotted from the data in the table above. The frequency difference is related to two frequencies. For example, the figure of 0.457 is found by subtracting 2.467 from 2.924. Which of the two values should be plotted against 0.457 does not matter, as long as consistency is maintained—the difference must always be plotted against either the higher or the lower figure. At the limit, the two frequency numbers are the same.

As illustrated in the graph below, plotting both of the possible curves on the same graph makes it easier to decide exactly how to extrapolate the curves. Because these are curves, they are much more difficult to extrapolate than straight lines.



Both lines indicate a series limit at about 3.28 x 10^{15} Hz.

With this information, it is possible calculate the energy needed to remove a single electron from a hydrogen atom. Recall the equation above:



The energy gap between the ground state and the point at which the electron leaves the atom can be determined by substituting the frequency and looking up the value of Planck's constant from a data book.

$$\Delta E = h\nu \tag{1.4.4}$$
$$= (6.626 \times 10^{-34})(3.28 \times 10^{15}) \tag{1.4.5}$$
$$= 2.173 \times 10^{-18}\ J \tag{1.4.6}$$

This is the ionization energy for a single atom. To find the normally quoted ionization energy, this value is multiplied by the number of atoms in a mole of hydrogen atoms (the Avogadro constant) and then dividing by 1000 to convert joules to kilojoules.

$$Ionization\ energy = (2.173 \times 10^{-18})(6.022 \times 10^{23})(\frac{1}{1000}) \tag{1.4.7}$$
$$= 1310\ kJ\ mol^{-1} \tag{1.4.8}$$

This compares well with the normally quoted value for hydrogen's ionization energy of 1312 kJ mol^{-1}.

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1.5: The Schrödinger Wave Equation

Beginning in the early 20th century, physicists began to acknowledge that matter--much like electromagnetic radiation--possessed wave-like behaviors. While electromagnetic radiation were well understood to obey Maxwell's Equations, matter obeyed no known equations.

Introduction

In 1926, the Austrian physicist Erwin Schrödinger formulated what came to be known as the (time-dependent) Schrödinger Equation:

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \frac{-\hbar}{2m}\nabla^2\Psi(x,t) + V(x)\Psi(x,t) \tag{1.5.1}$$

Equation 1.5.1 effectively describes matter as a wave that fluctuates with both displacement and time. Since the imaginary portion of the equation dictates its time dependence, it is sufficed to say that for most purposes it can be treated as time-independent. The result is seen in Equation 1.5.2:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{1.5.2}$$

Although this time-independent Schrödinger Equation can be useful to describe a matter wave in free space, we are most interested in waves when confined to a small region, such as an electron confined in a small region around the nucleus of an atom. Several different models have been developed that provide a means by which to study a matter-wave when confined to a small region: the particle in a box (infinite well), finite well, and the Hydrogen atom. We will discuss each of these in order to develop a greater understanding for how a wave behaves when it is in a bound state.

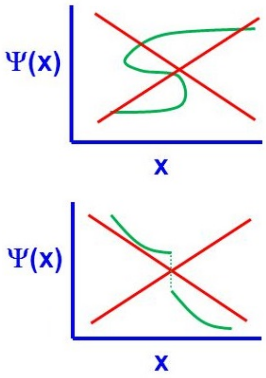


Figure 1.5.1 : Two unacceptable wavefunctions. (left) This is not a single-valued function and (right) this is a non-continuous function

There are four general aspects that are applicable to an acceptable wavefunction

1. An acceptable wavefunction will be the solution of the Schrödinger equation (either Equations 1.5.1 or 1.5.2).
2. An acceptable wavefunction must be normalizable so will approaches zero as position approaches infinity.
3. An acceptable wavefunction must be a continuous function of position.
4. An acceptable wavefunction will have a continuous slope (Figure 1.5.1).

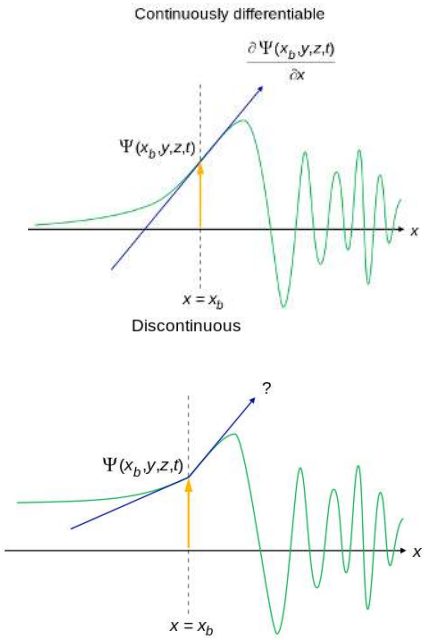


Figure 1.5.2 : Wavefunction continuity in space

Interpretation of the Wavefunction

Since wavefunctions can in general be complex functions, the physical significance cannot be found from the function itself because the $\sqrt{-1}$ is not a property of the physical world. Rather, the physical significance is found in the product of the wavefunction and its complex conjugate, i.e. the absolute square of the wavefunction, which also is called the square of the modulus.

$$\psi^*(r,t)\psi(r,t) = |\psi(r,t)|^2 \tag{1.5.3}$$

where r is a vector (x, y, z) specifying a point in three-dimensional space. The square is used, rather than the modulus itself, just like the intensity of a light wave depends on the square of the electric field. At one time it was thought that for an electron described by the wavefunction $\psi(r)$, the quantity $e\psi^*(r_i)\psi(r_i)d\tau$ was the amount of charge to be found in the volume $d\tau$ located at r_i. However, Max Born found this interpretation to be inconsistent with the results of experiments.

The Born interpretation, which generally is accepted today, is that $\psi^*(r_i)\psi(r_i)\ d\tau$ is the probability that the electron is in the volume dτ located at r_i. The Born interpretation therefore calls the wavefunction the probability amplitude, the absolute square of the wavefunction is called the probability density, and the probability density times a volume element in three-dimensional space ($d\tau$) is the probability. The idea that we can understand the world of atoms and molecules only in terms of probabilities is disturbing to some, who are seeking more satisfying descriptions through ongoing research.

Normalization of the Wavefunction

A probability is a real number between 0 and 1. An outcome of a measurement which has a probability 0 is an impossible outcome, whereas an outcome which has a probability 1 is a certain outcome. The probability of a measurement of x yielding a result between $-\infty$ and $+\infty$ is

$$P_{x\in-\infty:\infty}(t) = \int_{-\infty}^{\infty} |\psi(x,t)|^2 dx. \tag{1.5.4}$$

However, a measurement of x *must* yield a value between $-\infty$ and $+\infty$, since the particle has to be located somewhere. It follows that $P_{x\in-\infty:\infty}(t) = 1$, or

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = 1, \tag{1.5.5}$$

which is generally known as the *normalization condition* for the wavefunction.

Example 1.5.1: Normalizing a Gaussian wavefunction

Normalize the wavefunction of a Gaussian wave packet, centered on $x = x_o$, and of characteristic width σ: i.e.,

$$\psi(x) = \psi_0 \mathrm{e}^{-(x-x_0)^2/(4\sigma^2)}. \tag{1.5.6}$$

Solution

To determine the normalization constant ψ_0, we simply substitute Equation 1.5.6 into Equation 1.5.5, to obtain

$$|\psi_0|^2 \int_{-\infty}^{\infty} \mathrm{e}^{-(x-x_0)^2/(2\sigma^2)} dx = 1. \tag{1.5.7}$$

Changing the variable of integration to $y = (x - x_0)/(\sqrt{2}\sigma)$, we get

$$|\psi_0|^2 \sqrt{2}\sigma \int_{-\infty}^{\infty} \mathrm{e}^{-y^2} dy = 1. \tag{1.5.8}$$

However,

$$\int_{-\infty}^{\infty} \mathrm{e}^{-y^2} dy = \sqrt{\pi}, \tag{1.5.9}$$

which implies that

$$|\psi_0|^2 = \frac{1}{(2\pi\sigma^2)^{1/2}}. \tag{1.5.10}$$

Hence, a general **normalized** Gaussian wavefunction takes the form

$$\psi(x) = \frac{e^{\mathrm{i}\phi}}{(2\pi\sigma^2)^{1/4}} e^{-(x-x_0)^2/(4\sigma^2)} \tag{1.5.11}$$

where ϕ is an arbitrary real phase-angle.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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1.6: Particle in a One-Dimensional Box

A particle in a 1-dimensional box is a fundamental quantum mechanical approximation describing the translational motion of a single particle confined inside an infinitely deep well from which it *cannot* escape.

Introduction

The particle in a box problem is a common application of a quantum mechanical model to a simplified system consisting of a particle moving horizontally within an infinitely deep well from which it cannot escape. The solutions to the problem give possible values of E and ψ that the particle can possess. E represents allowed energy values and $\psi(x)$ is a wavefunction, which when squared gives us the probability of locating the particle at a certain position within the box at a given energy level.

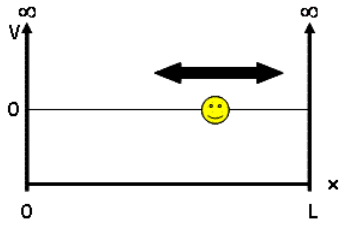
Recipe for Quantum Mechanics

To solve the problem for a particle in a 1-dimensional box, we must follow our *Big, Big recipe for Quantum Mechanics*:

1. Define the Potential Energy, V
2. Solve the Schrödinger Equation
3. Solve for the wavefunctions
4. Solve for the allowed energies

Step 1: Define the Potential Energy V

The potential energy is *0 inside the box* (V=0 for 0<x<L) and *goes to infinity at the walls of the box* (V=∞ for x<0 or x>L). We assume the walls have infinite potential energy to ensure that the particle has zero probability of being at the walls or outside the box. Doing so significantly simplifies our later mathematical calculations as we employ these **boundary conditions** when solving the Schrödinger Equation.



Step 2: Solve the Schrödinger Equation

The time-independent Schrödinger equation for a particle of mass m moving in one direction with energy E is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x)$$

with

- $\hbar$ is the reduced Planck constant where $\hbar=\frac{h}{2\pi}$
- m is the mass of the particle
- $\psi(x)$ is the stationary time-independent wavefunction
- $V(x)$ is the potential energy as a function of position
- E is the energy, a real number

This equation can be modified for a particle of mass m free to move parallel to the x-axis with zero potential energy (V = 0 everywhere) resulting in the quantum mechanical description of free motion in one dimension:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}=E\psi(x) \tag{1.6.1}$$

This equation has been well studied and gives a general solution of:

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

where A, B, and k are constants.

Step 3: Define the Wavefunction

The solution to the Schrödinger equation we found above is the general solution for a 1-dimensional system. We now need to apply our **boundary conditions** to find the solution to our particular system. According to our boundary conditions, the probability of finding the particle at $x = 0$ or $x = L$ is zero. When $x = 0$, then $\sin(0) = 0$ and $\cos(0) = 1$; therefore, B *must equal 0* to fulfill this boundary condition giving:

$$\psi(x) = A\sin(kx) \tag{1.6.2}$$

We can now solve for our constants (A and k) systematically to define the wavefunction.

Solving for k

Differentiate the wavefunction with respect to x:

$$\frac{d\psi}{dx} = kA\cos(kx)$$

Differentiate the wavefunction again with respect to x:

$$\frac{d^2\psi}{dx^2} = -k^2A\sin(kx)$$

Since $\psi(x) = A\sin(kx)$, then

$$\frac{d^2\psi}{dx^2} = -k^2\psi$$

If we then solve for k by comparing with the Schrödinger equation above, we find:

$$k = \left(\frac{8\pi^2mE}{h^2}\right)^{1/2}$$

Now we plug k into our wavefunction (Equation 1.6.2):

$$\psi = A\sin\left(\frac{8\pi^2mE}{h^2}\right)^{1/2}x$$

Solving for A

To determine A, we have to apply the boundary conditions again. Recall that the *probability of finding a particle at* $x = 0$ *or* $x = L$ *is zero.*

When $x = L$:

$$0 = A\sin\left(\frac{8\pi^2mE}{h^2}\right)^{1/2}L$$

This is only true when

$$\left(\frac{8\pi^2mE}{h^2}\right)^{1/2}L = n\pi$$

where $n = 1, 2, 3, ...$

Plugging this back in gives us:

$$\psi = A\sin\frac{n\pi}{L}x$$

To determine A, recall that the total probability of finding the particle inside the box is 1, meaning there is no probability of it being outside the box. When we find the probability and set it equal to 1, we are *normalizing* the wavefunction.

$$\int_0^L \psi^2 dx = 1$$

For our system, the normalization looks like:

$$A^2 \int_0^L \sin^2\left(\frac{n\pi}{L}\right) x\, dx = 1$$

Using the solution for this integral from an integral table, we find our normalization constant, A:

$$A = \sqrt{\frac{2}{L}}$$

Which results in the normalized wavefunctions for a particle in a 1-dimensional box:

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \tag{1.6.3}$$

where $n = 1, 2, 3, ...$

Step 4: Determine the Allowed Energies

Solving for the energy of each ψ requires substituting Equation 1.6.3 into Equation 1.6.1 to get the allowed energies for a particle in a box:

$$E_n = \frac{n^2 h^2}{8mL^2} \tag{1.6.4}$$

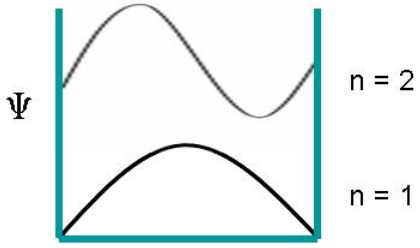
Equation 1.6.4 is a very important result and tells us that:

1. The energy of a particle is quantized.
2. The lowest possible energy of a particle is **NOT** zero. This is called the **zero-point energy** and means the particle can never be at rest because it always has some kinetic energy.

This is also consistent with the Heisenberg Uncertainty Principle: if the particle had zero energy, we would know where it was in both space and time.

What does all this mean?

The wavefunction for a particle in a box at the $n = 1$ and $n = 2$ energy levels look like this:



The probability of finding a particle a certain spot in the box is determined by squaring ψ. The probability distribution for a particle in a box at the $n = 1$ and $n = 2$ energy levels looks like this:



Notice that the number of **nodes** (places where the particle has zero probability of being located) increases with increasing energy n. Also note that as the energy of the particle becomes greater, the quantum mechanical model breaks down as the energy levels get closer together and overlap, forming a continuum. This continuum means the particle is free and can have any energy value. At such high energies, the classical mechanical model is applied as the particle behaves more like a continuous wave. Therefore, the particle in a box problem is an example of Wave-Particle Duality.

Example 1.6.1

What is the ΔE between the $n = 4$ and $n = 5$ states for an F_2 molecule trapped within in a one-dimension well of length 3.0 cm? At what value of n does the energy of the molecule reach $1/4k_BT$ at 450 K, and what is the separation between this energy level and the one immediately above it?

Solution

Since this is a one-dimensional particle in a box problem, the particle has only kinetic energy (V = 0), so the permitted energies are:

$$E_n = \frac{n^2h^2}{8mL^2}$$

with $n = 1, 2, ...$

The energy difference between $n = 4$ and $n = 5$ is then

$$\begin{aligned}\Delta E &= E_5 - E_4 \\ &= \frac{5^2h^2}{8mL^2} - \frac{4^2h^2}{8mL^2}\end{aligned}$$

Using Equation 1.6.4 with the mass of F_2 (37.93 amu = $6.3 \times 10^{-26}\ kg$) and the length of the box ($L = 3 \times 3.0 \times 10^{-2}\ \mathrm{m}^2$):

$$\begin{aligned}\Delta E &= \frac{9h^2}{8mL^2} \\ &= \frac{9(6.626 \times 10^{-34}\ \mathrm{kg \cdot m^2 \cdot s^{-1}})^2}{8(6.30938414 \times 10^{-26}\ \mathrm{kg})(3.0 \times 10^{-2}\ \mathrm{m^2})^2} \\ &= 8.70 \times 10^{-39}\ J\end{aligned}$$

The n value for which the energy reaches $\frac{1}{4}k_BT$:

$$\begin{aligned}\frac{n^2h^2}{8mL^2} &= \frac{1}{4}k_BT \\ n &= 1.79 \times 10^9\end{aligned}$$

The separation between $n + 1$ and n:

$$\begin{aligned}\Delta E &= E_{n+1} - E_n \\ &= \frac{(n+1)^2h^2 - (n)^2h^2}{8mL^2} \\ &= \frac{(2n+1)h^2}{8mL^2} \\ &= 3.47 \times 10^{-30}\ J\end{aligned}$$

Important Facts to Learn from the Particle in the Box

- The energy of a particle is quantized. This means it can only take on discreet energy values.
- The lowest possible energy for a particle is **NOT** zero (even at 0 K). This means the particle *always* has some kinetic energy.
- The square of the wavefunction is related to the probability of finding the particle in a specific position for a given energy level.
- The probability changes with increasing energy of the particle and depends on the position in the box you are attempting to define the energy for
- In classical physics, the probability of finding the particle is independent of the energy and the same at all points in the box

References

1. Chang, Raymond. *Physical Chemistry for the Biosciences*. Sansalito, CA: University Science, 2005.

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1.7: Electronic Spectroscopy

This page explains what happens when organic compounds absorb UV or visible light, and why the wavelength of light absorbed varies from compound to compound.

Molecular Absorption of Light

When we were talking about the various sorts of molecular orbitals present in organic compounds earlier, you will have come across this diagram showing their relative energies:

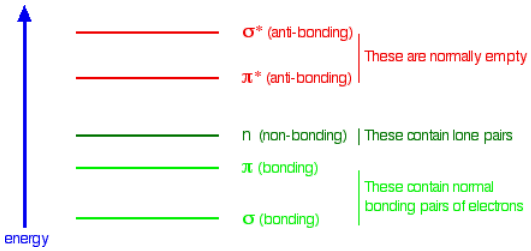


Figure **1.7.1**: The diagram is not intended to be to scale - it just shows the relative placing of the different orbitals.

When light passes through the compound, energy from the light is used to promote an electron from a bonding or non-bonding orbital into one of the empty anti-bonding orbitals. The possible electron jumps that light might cause are:

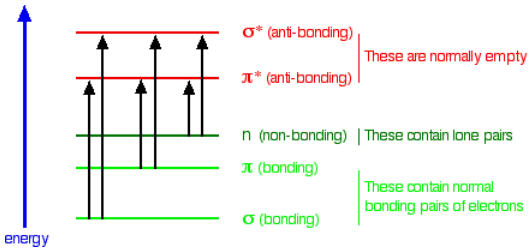


Figure **1.7.2**: Promotion of an electron via different electron transitions

In each possible case, an electron is excited from a full orbital into an empty anti-bonding orbital. Each jump takes energy from the light, and a big jump obviously needs more energy than a small one. Each wavelength of light has a particular energy associated with it. If that particular amount of energy is just right for making one of these energy jumps, then that wavelength will be absorbed - its energy will have been used in promoting an electron.

An absorption spectrometer works in a range from about 200 nm (in the near ultra-violet) to about 800 nm (in the very near infra-red). Only a limited number of the possible electron jumps absorb light in that region. Look again at the possible jumps. This time, the important jumps are shown in black, and a less important one in grey. The grey dotted arrows show jumps which absorb light outside the region of the spectrum we are working in.

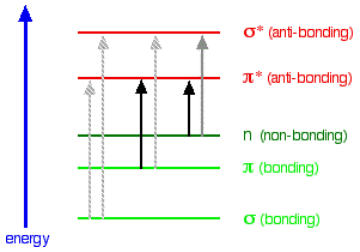


Figure **1.7.3**: Promotion of an electron via different electron transitions scaled by energies.

Remember that bigger jumps need more energy and so absorb light with a shorter wavelength. The jumps shown with grey dotted arrows absorb UV light of wavelength less that 200 nm. The important jumps are:

- from π bonding orbitals to π anti-bonding orbitals;
- from non-bonding orbitals to π anti-bonding orbitals;
- from non-bonding orbitals to sigma anti-bonding orbitals.

That means that in order to absorb light in the region from 200 - 800 nm (which is where the spectra are measured), the molecule must contain either π bonds or atoms with non-bonding orbitals. Remember that a non-bonding orbital is a lone pair on, say, oxygen, nitrogen or a halogen. Groups in a molecule which absorb light are known as chromophores.

What does an absorption spectrum look like

The diagram below shows a simple UV-visible absorption spectrum for buta-1,3-diene - a molecule we will talk more about later. Absorbance (on the vertical axis) is just a measure of the amount of light absorbed. The higher the value, the more of a particular wavelength is being absorbed.

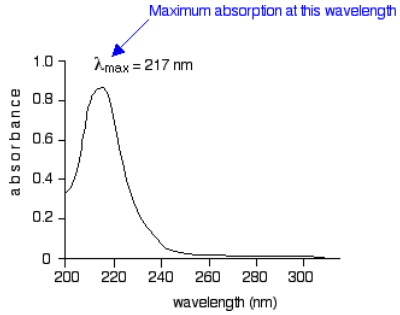


Figure **1.7.4**: UV-visible absorption spectrum for buta-1,3-diene

You will see that absorption peaks at a value of 217 nm. This is in the ultra-violet and so there would be no visible sign of any light being absorbed - buta-1,3-diene is colorless. In buta-1,3-diene, CH_2=CH-CH=CH_2, there are no non-bonding electrons. That means that the only electron jumps taking place (within the range that the spectrometer can measure) are from π bonding to π anti-bonding orbitals.

A chromophore such as the carbon-oxygen double bond in ethanal, for example, obviously has π electrons as a part of the double bond, but also has lone pairs on the oxygen atom. That means that both of the important absorptions from the last energy diagram are possible. You can get an electron excited from a π bonding to a π anti-bonding orbital, or you can get one excited from an oxygen lone pair (a non-bonding orbital) into a π anti-bonding orbital.

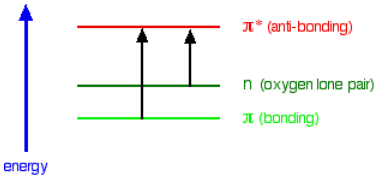


Figure **1.7.4**: A simplified diagram showing $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions

The non-bonding orbital has a higher energy than a π bonding orbital. That means that the jump from an oxygen lone pair into a π anti-bonding orbital needs less energy. That means it absorbs light of a lower frequency and therefore a higher wavelength. For example, ethanal can therefore absorb light of two different wavelengths:

- the π bonding to π anti-bonding absorption peaks at 180 nm. These $n \rightarrow \pi^*$ transitions involve moving an electron from a nonbonding electron pair to a antibonding *pi^*\) orbital. They tend to have molar absorbtivities less than 2000
- the non-bonding to π anti-bonding absorption peaks at 290 nm. These $\pi \rightarrow \pi^*$ transitions involve moving an electron from a bonding $\pi*$ orbital to an antibonding π^* orbital. They tend to have molar absorptivities on the order of 10,000.

Both of these absorptions are in the ultra-violet, but most spectrometers will not pick up the one at 180 nm because they work in the range from 200 - 800 nm.

Conjugation and Delocalization

Consider these three molecules:

CH_2=CH_2	CH_2=CH-CH=CH_2	CH_2=CH-CH=CH-CH=CH_2
ethene	buta-1,3-diene	hexa-1,3,5-triene

Ethene contains a simple isolated carbon-carbon double bond, but the other two have conjugated double bonds. In these cases, there is delocalization of the π bonding orbitals over the whole molecule. Now look at the wavelengths of the light which each of these molecules absorbs.

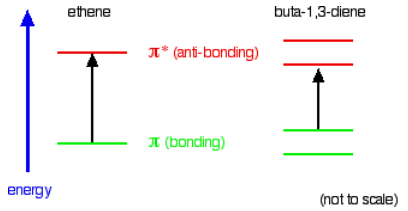
molecule	wavelength of maximum absorption (nm)
ethene	171
buta-1,3-diene	217
hexa-1,3,5-triene	258

All of the molecules give similar UV-visible absorption spectra - the only difference being that the absorptions move to longer and longer wavelengths as the amount of delocalization in the molecule increases. Why is this? You can actually work out what must be happening.

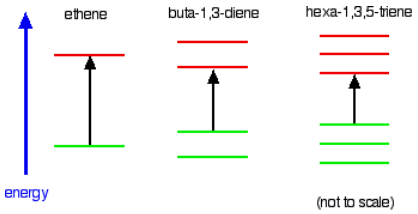
- The maximum absorption is moving to longer wavelengths as the amount of delocalization increases.
- Therefore maximum absorption is moving to shorter frequencies as the amount of delocalization increases.
- Therefore absorption needs less energy as the amount of delocalization increases.
- Therefore there must be less energy gap between the bonding and anti-bonding orbitals as the amount of delocalization increases.

. . . and that's what is happening.

Compare ethene with buta-1,3-diene. In ethene, there is one π bonding orbital and one π anti-bonding orbital. In buta-1,3-diene, there are two π bonding orbitals and two π anti-bonding orbitals. This is all discussed in detail on the introductory page that you should have read.



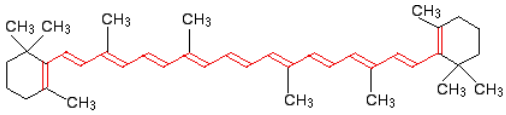
The highest occupied molecular orbital is often referred to as the HOMO - in these cases, it is a π bonding orbital. The lowest unoccupied molecular orbital (the LUMO) is a π anti-bonding orbital. Notice that the gap between these has fallen. It takes less energy to excite an electron in the buta-1,3-diene case than with ethene. In the hexa-1,3,5-triene case, it is less still.



If you extend this to compounds with really massive delocalization, the wavelength absorbed will eventually be high enough to be in the visible region of the spectrum, and the compound will then be seen as colored. A good example of this is the orange plant pigment, beta-carotene - present in carrots, for example.

Why is beta-carotene orange?

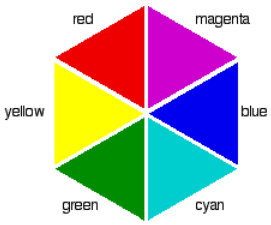
Beta-carotene has the sort of delocalization that we've just been looking at, but on a much greater scale with 11 carbon-carbon double bonds conjugated together. The diagram shows the structure of beta-carotene with the alternating double and single bonds shown in red.



The more delocalization there is, the smaller the gap between the highest energy π bonding orbital and the lowest energy π anti-bonding orbital. To promote an electron therefore takes less energy in beta-carotene than in the cases we've looked at so far - because the gap between the levels is less. Remember that less energy means a lower frequency of light gets absorbed - and that's equivalent to a longer wavelength. Beta-carotene absorbs throughout the ultra-violet region into the violet - but particularly strongly in the visible region between about 400 and 500 nm with a peak about 470 nm. The wavelengths associated with the various colors are approximately:

color region	wavelength (nm)
violet	380 - 435
blue	435 - 500
cyan	500 - 520
green	520 - 565
yellow	565 - 590
orange	590 - 625
red	625 - 740

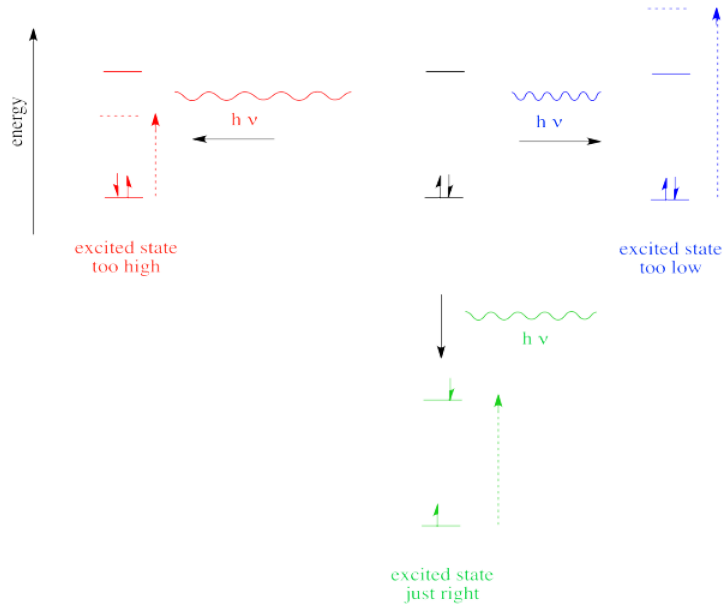
So if the absorption is strongest in the violet to cyan region, what color will you actually see? It is tempting to think that you can work it out from the colors that are left - and in this particular case, you wouldn't be far wrong. Unfortunately, it is not as simple as that! Sometimes what you actually see is quite unexpected. Mixing different wavelengths of light does not 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. If you arrange some colors in a circle, you get a "color wheel". The diagram shows one possible version of this. An internet search will throw up many different versions!



colors directly opposite each other on the color wheel are said to be complementary colors. Blue and yellow are complementary colors; red and cyan are complementary; and so are green and magenta. Mixing together two complementary colors of light will give you white light. What this all means is that if a particular color is absorbed from white light, what your eye detects by mixing up all the other wavelengths of light is its complementary color. In the beta-carotene case, the situation is more confused because you are absorbing such a range of wavelengths. However, if you think of the peak absorption running from the blue into the cyan, it would be reasonable to think of the color you would see as being opposite that where yellow runs into red - in other words, orange.

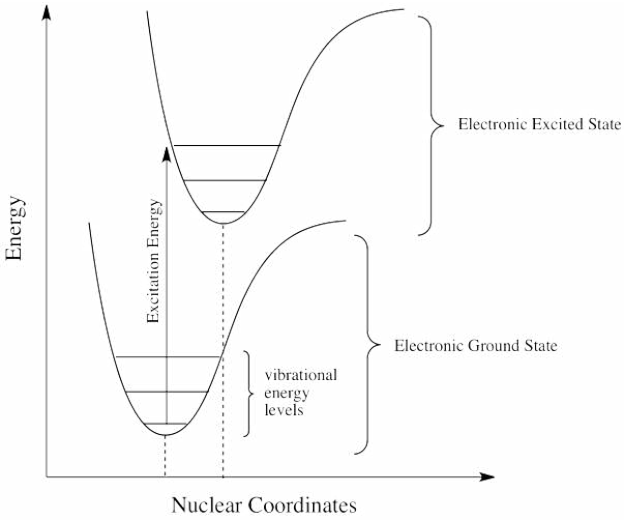
Franck-Condon: Electronic and Vibrational Coupling

So far, we have come across one big rule of photon absorbance. To be absorbed, a photon's energy has to match an energy difference within the compound that is absorbing it.



In the case of visible or ultraviolet light, the energy of a photon is roughly in the region that would be appropriate to promote an electron to a higher energy level. Different wavelengths would be able to promote different electrons, depending on the energy difference between an occupied electronic energy level and an unoccupied one. Other types of electromagnetic radiation would not be able to promote an electron, but they would be coupled to other events. For example, absorption of infrared light is tied to vibrational energy levels. Microwave radiation is tied to rotational energy levels in molecules. Thus, one reason a photon may or may not be absorbed has to do with whether its energy corresponds to the available energy differences within the molecule or ion that it encounters.

Photons face other limitations. One of these is a moderate variation on our main rule. It is called the Frank Condon Principle. According to this idea, when an electron is excited from its normal position, the ground state, to a higher energy level, the optimal positions of atoms in the molecule may need to shift. Because electronic motion is much faster than nuclear motion, however, any shifting of atoms needed to optimize positions as they should be in the excited state will have to wait until after the electron gets excited. In that case, when the electron lands and the atoms aren't yet in their lowest energy positions for the excited state, the molecule will find itself in an excited vibrational state as well as an excited electronic state.



That means the required energy for excitation does not just correspond to the difference in electronic energy levels; it is fine-tuned to reach a vibrational energy level, which is quantized as well.

- The Franck Condon Principle states that electronic transitions are vertical.

- A vertical transition is one in which non of the nuclei move while the electron journeys from one state to another.
- A vertical transition may begin in a vibrational ground state of an electronic ground state and end in a vibrational excited state of an electronic excited state.

Contributors and Attributions

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- Jim Clark (Chemguide.co.uk)

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1.8: The Harmonic Oscillator Approximates Molecular Vibrations

Learning Objectives

- Understand the utility and limits of using the quantum harmonic oscillator as a model for molecular vibrations

The quantum harmonic oscillator is one of the most important model systems in quantum mechanics. This is due in partially to the fact that an arbitrary potential curve $V(x)$ can usually be *approximated* as a harmonic potential at the vicinity of a stable equilibrium point. Furthermore, it is one of the few quantum-mechanical systems for which an exact, analytical solution exists. Solving other potentials typically require either approximations or numerical approaches to identify the corresponding eigenstates and eigenvalues (i.e., wavefunctions and energies).

A general potential energy ($V(x)$) curve for a molecular vibration can be expanded as a Taylor series

$$V(x) = V(x_0) + \left.\frac{dV(x)}{dx}\right|_{x_0}^{x} (x - x_0) + \frac{1}{2!}\left.\frac{d^2V(x)}{dx^2}\right|_{x_0}^{x} (x - x_0)^2 + \ldots + \frac{1}{n!}\left.\frac{d^nV(x)}{dx^n}\right|_{x_0}^{x} (x - x_0)^n \tag{1.8.1}$$

It is important to note that this approximation is only good for x near x_0, and that x_0 stands for the equilibrium bond distance. $V(x)$ is often (but not always) shortened to the cubic term and can be rewritten as

$$V(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 \tag{1.8.2}$$

where $V(x_0) = 0$, k is the harmonic force constant (harmonic term), and γ is the first anharmonic term (i.e., cubic). As Figure 5.3.2 demonstrates, the harmonic oscillator (red curve) is a good approximation for the exact potential energy of a vibration (blue curve).

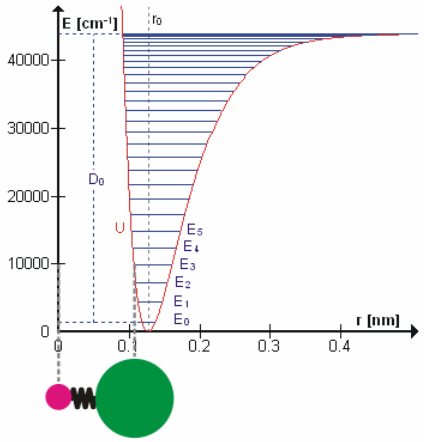


Figure 5.3.1 : The vibration of the **HCl** molecule is really an anharmonic oscillator, but can be approximated as a harmonic oscillator at low energies. In this animation, **HCl** is vibrating at the E_3 energy level. D_0 is dissociation energy here, r_0 bond length, V potential energy. Energy is expressed in wavenumbers. The hydrogen chloride molecule is attached to the coordinate system to show bond length changes on the curve. (CC BY-SA 3.0; Darekk2 via Wikipedia).

Adding anharmonic perturbations to the harmonic oscillator (Equation 1.8.2) better describes molecular vibrations. Anharmonic oscillation is defined as the deviation of a system from harmonic oscillation, or an oscillator not oscillating in simple harmonic motion. Anharmonic oscillation is described as the restoring force is no longer proportional to the displacement. Adding the cubic term (Figure 5.3.2 ; green curve) improves the harmonic oscillation approximation especially under greater displacement from equilibrium.

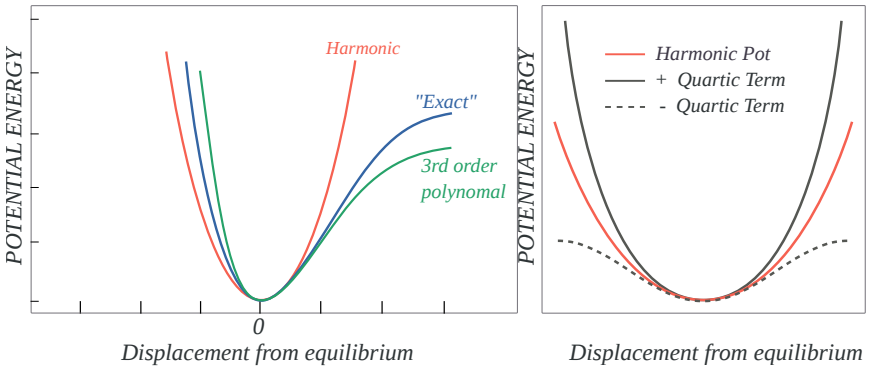


Figure 5.3.2 : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

Naturally, adding higher order anharmonic terms, like quartic terms (Figure **1.8.2;**) improve the approximation. Almost all diatomics have experimentally determined potentials for their lowest energy states. $\mathbf{H_2}$, $\mathbf{Li_2}$, $\mathbf{O_2}$, $\mathbf{N_2}$, and $\mathbf{F_2}$ with terms up to $n < 10$ determined of Equation 1.8.1.

Figure 5.3.1 shows the the general potential with (numerically) calculated energy levels (E_0, E_1 etc.). D_o is the dissociation energy, which is different from the well depth D_e. These vibrational energy levels of this plot can be calculated using the harmonic oscillator model (i.e., Equation 5.3.1 with the Schrödinger equation) and have the general form

$$E_v = \left(v + \frac{1}{2}\right) v_e - \left(v + \frac{1}{2}\right)^2 v_e x_e + \left(v + \frac{1}{2}\right)^3 v_e y_e + \text{higher terms}$$

where v is the vibrational quantum number and x_e and y_e are the first and second anharmonicity constants, respectively.

The $v = 0$ level is the vibrational ground state. Because this potential is less confining than a parabola used in the harmonic oscillator, the energy levels become **less widely** spaced at high excitation (Figure 5.3.1 ; top of potential).

Limitations of the Harmonic Oscillator Model for Molecular Vibrations

The harmonic oscillation is a great approximation of a molecular vibration, but has key limitations:

- Due to equal spacing of energy, all transitions occur at the **same** frequency (i.e. single line spectrum). However experimentally many lines are often observed (called overtones).
- The harmonic oscillator does not predict bond dissociation; you cannot break it no matter how much energy is introduced.

Morse Potentials are better Approximations of Vibrational Motion

A more powerful approach than just "patching up" the harmonic oscillator solution with anharmonic corrections is to adopt a different potential ($V(x)$). One such approach is the Morse potential, named after physicist Philip M. Morse, and a better approximation for the vibrational structure of the molecule than the harmonic oscillator because it explicitly includes the effects of *bond breaking* and accounts for the anharmonicity of real bonds (Figure 5.3.4).

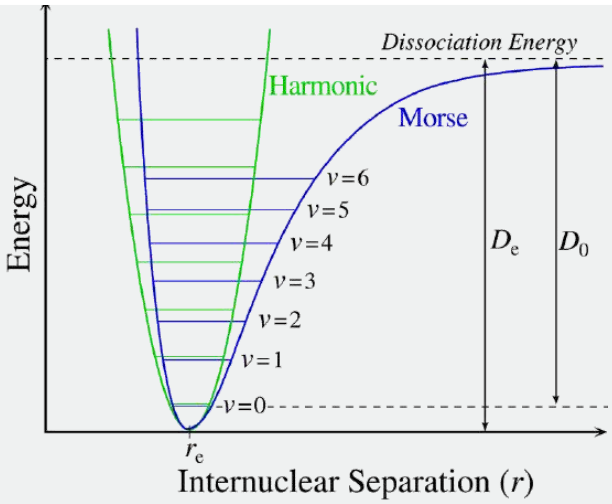


Figure 5.3.4 : The Morse potential (blue) and harmonic oscillator potential (green). Unlike the energy levels of the harmonic oscillator potential, which are evenly spaced by ħω, the Morse potential level spacing decreases as the energy approaches the dissociation energy. The dissociation energy D_e is larger than the true energy required for dissociation D_0 due to the zero point energy of the lowest ($v = 0$) vibrational level. from Wikipedia.

The Morse Potential is a good approximation to $V(x)$ and is best when looking for a general formula for all x from 0 to ∞, not just applicable for the local region around the x_o:

$$V(x) = D(1 - e^{-\beta(x-x_0)})^2 \tag{1.8.3}$$

with $V(x = x_0) = 0$ and $V(x = \infty) = D$.

The Morse Potential (Figure 5.3.4) approaches zero at infinite r_e and equals $-D_e$ at its minimum (i.e. $r = r_e$). It clearly shows that the Morse potential is the combination of a short-range repulsion term (small r values) and a long-range attractive term (large r values).

Solving the Schrödinger Equation with the Morse Potential (Equation **1.8.3**) is not trivial, but can be done analytically.

$$\hat{H}\,|\psi\rangle = E_n|\,\psi\rangle$$

with

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V} \\ &= \frac{-\hbar^2 d^2}{2m\,dx^2} + D(1 - e^{-\beta(x-x_0)})^2\end{aligned}$$

The solutions and energies for the Morse potential will not be used in this course and will not be discussed in more detail.

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1.9: The Harmonic Oscillator and Infrared Spectra

Learning Objectives

- Understand how the quantum harmonic oscillator model can be used to interpret the infrared spectra of diatomic molecules
- Understand the origin of the transition moment integral and selection rules and how they are related

Infrared (IR) spectroscopy is one of the most common and widely used spectroscopic techniques employed mainly by inorganic and organic chemists due to its usefulness in determining structures of compounds and identifying them. Chemical compounds have different chemical properties due to the presence of different functional groups. IR spectroscopy is one of the most common and widely used spectroscopic techniques. Absorbing groups in the infrared region absorb within a certain wavelength region. The absorption peaks within this region are usually sharper when compared with absorption peaks from the ultraviolet and visible regions. In this way, IR spectroscopy can be very sensitive to determination of functional groups within a sample since different functional group absorbs different particular frequency of IR radiation. Also, each molecule has a characteristic spectrum often referred to as the fingerprint. A molecule can be identified by comparing its absorption peak to a data bank of spectra. IR spectroscopy is very useful in the identification and structure analysis of a variety of substances, including both organic and inorganic compounds. It can also be used for both qualitative and quantitative analysis of complex mixtures of similar compounds.

1.9.1: IR Spectroscopy

Transitions between vibrational energy levels can be induced about by absorption or emission of radiation. To understand this, knowledge of both the initial and final eigenstates is needed. The energy of the v^{th} eigenstate of a harmonic oscillator can be written as

$$E_v = \left(v + \frac{1}{2}\right) \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \tag{1.9.1}$$

where h is Planck's constant and v is the vibrational quantum number and ranges from 0, 1, 2, 3,..., ∞. Equation 1.9.1 is often rewritten as

$$E_v = \left(v + \frac{1}{2}\right) h\nu_m \tag{1.9.2}$$

where ν_m is the vibrational frequency of the vibration. Equation 1.9.2 is often written as

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega$$

where ω is the angular frequency (i.e., $2\pi\nu$).

Transitions in vibrational energy levels can be brought about by absorption of radiation, provided the energy of the radiation ($h\nu_{photon}$) **exactly** matches the difference in energy ($\Delta E_{vv'}$) between the vibrational quantum state v to quantum state v'. This can be expressed as

$$\begin{aligned} h\nu_{photon} &= \Delta E_{vv'} \\ &= E_{v'} - E_v \\ &= \left(v' + \frac{1}{2}\right) h\nu_m - \left(v + \frac{1}{2}\right) h\nu_m \\ &= (v' - v)\, h\nu_m \end{aligned} \tag{1.9.3}$$

Let's consider only transitions between adjacent eigenstates (discussed in more details below) so

$$v' - v = \pm 1$$

which is positive if an IR photon is absorbed and negative if it is emitted. For the absorption of a IR photon, Equation 1.9.3 simplifies to

$$h\nu_{photon} = h\nu_m$$

$$= \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \tag{1.9.4}$$

The frequency of radiation ν_{photon} that will bring about this change is **identical** to the classical vibrational frequency of the bond ν.

The Wavenumber as a Unit of Energy

The cm^{-1} is the wavenumber scale and it can also be defined as 1/wavelength in cm. A wavenumber is often used due to its direct relationship with both frequency and energy. The frequency of the absorbed radiation causes the molecular vibrational frequency for the absorption process:

$$\bar{\nu}(cm^{-1}) = \frac{1}{\lambda(\mu m)} \times 10^4 \left(\frac{\mu m}{cm}\right) \tag{1.9.5}$$

$$= \frac{\nu\,(Hz)}{c\,(cm/s)} \tag{1.9.6}$$

Equation 1.9.3 can be modified so that the radiation can be expressed in wavenumbers

$$\tilde{\nu}_m = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \tag{1.9.7}$$

where c is the velocity of light (cm/s) and $\tilde{\nu}$ is the wavenumber of an absorption maximum (cm^{-1}).

Example 5.5.1: Hydrogen Halides

The force constants for typical diatomic molecules are in the range between 400 to 2000 $N \cdot m^{-1}$.

Molecule	HF	HCl	HBr	HI	CO	NO
Force constant, k ($N.m^{-1}$)	970	480	410	320	1860	1530

For the diatomic molecules listed above, calculate the following:

a. angular frequency ($rad \cdot s^{-1}$)
b. natural frequency (Hz)
c. period (s)
d. separation between energy levels
e. wavelength λ of the electromagnetic radiation absorbed in the transition $v = 0 \rightarrow v = 1$.

Solution

For **HCl**:

a. angular frequency

$$\omega = 5.45 \times 10^{14} rad \cdot s^{-1}$$

b. natural frequency:

$$\nu = \frac{\omega}{2\pi} = 8.68 \times 10^{13}$$

c. period (s):

$$T = \frac{1}{\nu} = 1.15 \times 10^{-14}$$

d. separation between energy levels:

$$\Delta E = E_{v=1} - E_{v=0} = \hbar\omega = 5.75 \times 10^{-20}\ J$$

e. wavelength λ of the electromagnetic radiation absorbed in the transition $v = 0 \rightarrow v = 1$:

$$3.46 \times 10^{-6}\, m$$

The electromagnetic radiation released (and absorbed) for vibrations is primarily in the infrared (IR) part of the spectrum. Calculating the above properties for the other molecules remains as an exercise.

Note: We did not designate the specific isotopes in the hydrogen halides above because that information was not required to solve these questions.

IR deals with the interaction between a molecule and radiation from the electromagnetic region ranging (4000- 40 cm^{-1}). The IR region of the electromagnetic spectrum ranges in wavelength from 2 -15 µm. Conventionally the IR region is subdivided into three regions (Table 5.5.1): near IR, mid IR and far IR. Most of the IR used originates from the mid IR region.

Table 5.5.1: Regions of the IR Spectrum

Region	Wavelength	Wavenumbers ($\tilde{\nu}$), cm^{-1}	Frequencies (v), HZ
Near	0.78 -2.5	12800 - 4000	3.8 x 10^{14} - 1.2 x 10^{14}
Middle	2.5 - 50	4000 - 200	3.8 x 10^{14} - 1.2 x 10^{14}
Far	50 -100	200 -10	3.8 x 10^{14} - 1.2 x 10^{14}
Most Used	2.5 -15	4000 -670	3.8 x 10^{14} - 1.2 x 10^{14}

? Example 5.5.2: Hydrogen Chloride

The $H^{35}Cl$ equilibrium bond length is 0.127 nm and the $v = 0$ to $v = 1$ transition is observed in the infrared at 2,886 cm^{-1}. Compute the vibrational energy of $H^{35}Cl$ in its lowest state.

a. Compute the classical limit for the stretching of the HCl bond from its equilibrium length in this state.
b. What percent of the equilibrium bond length is this extension?

Solution

The $H{-}Cl$ bond length is $0.127\, nm = 1.27 \times 10^{-10} m$ and the IR transition is observed at $2886\, cm^{-1}$. We first convert this to Hertz

$$2886\, cm^{-1}(3 \times 10^{10} cm/s) = 8.646 \times 10^{13} s^{-1} = 8.646 \times 10^{13}\, Hz$$

The equations for the energy of the vth eigenstate of a harmonic oscillator is

$$E_v = (v + 1/2)\hbar\omega$$

So the ground state ($v = 0$) energy is

$$E_0 = \frac{1}{2}\hbar\omega$$

with

$$\begin{aligned} \omega &= 2\pi\nu \\ &= 5.54 \times 10^{14}\, rad/s \end{aligned}$$

We can then extra the ground state vibrational energy (aka zero-point energy) from

$$\begin{aligned} E_o &= \frac{1}{2}\hbar\omega \\ &= \frac{1}{2}\hbar(5.54 \times 10^{14} rad/s) \\ &= 2.916 \times 10^{-20}\ J \end{aligned}$$

The classical limit of the stretch is denoted as Q_0, this can be equated as potential energy in relation to the total E_0 found above as, at E_0, all of the energy would be potential energy in the form of the stretch. In comparison to the classic spring potential

$$V = \frac{1}{2}kQ_0^2$$

As described above, we can relate the two as

$$\frac{1}{2}\hbar\omega = \frac{1}{2}kQ_0^2$$

or,

$$2.916 \times 10^{-20} J = \frac{1}{2}481Q_0^2$$

where $Q_0 = 1.10 \times 10^{-11} m = 0.0110\, nm$.

Lastly, this classical limit to length can be compared to the equilibrium bond length by a simple relation of

$$\begin{aligned} \text{Percent bond length} &= \frac{Q_0}{x_{eq}} \times 100\% \\ &= \frac{0.0110\, nm}{0.127\, nm} \times 100\% \\ &= 8.66\% \end{aligned}$$

1.9.2: Selection Rules for IR Transitions

Photons can be absorbed or emitted, and the harmonic oscillator can transition from one vibrational energy state to another. Which transitions between vibrational states are allowed? When discussing the Bohr hydrogen atom in Chapter 1, we identified multiple transitions between different states as being responsible for the line spectra emission of the hydrogen atom. No limitations were identified so that any transition between any starting state and ending state was possible and this resulted in a complex pattern in the spectra. As we will identify later on, when considering mulit-electron atoms, there are **selection rules** that limits which transitions will be observed (i.e., are allowed).

A similar situation exist for the harmonic oscillator and IR transitions and a set of selection rules must be satisfied to ensure a particular transition is allowed. Selection rules result from evaluating a **transition moment integral** that expresses the probability of a transition from the v to the v' eigenstates:

$$\mu_T = \langle \psi_{v'} \left| \hat{\mu}(x) \right| \psi_v \rangle \tag{1.9.8}$$

$$= \int_{-\infty}^{\infty} \psi_{v'}^*(x) \hat{\mu}(x) \psi_v(x) dx \tag{1.9.9}$$

When the transition moment integral is zero for two specific eigenstates (i.e., $\psi_v(x)$ and $\psi_v'(x)$), then the probability of observing that transition is zero. In this case, this transition is called a **forbidden transition** (i.e., it will not be obversed). Transitions with low probabilities are call "weakly allowed transitions" since they will have small amplitudes in spectra and transitions with high probabilities are "strongly allowed transitions" and will exhibit high amplitudes in spectra.

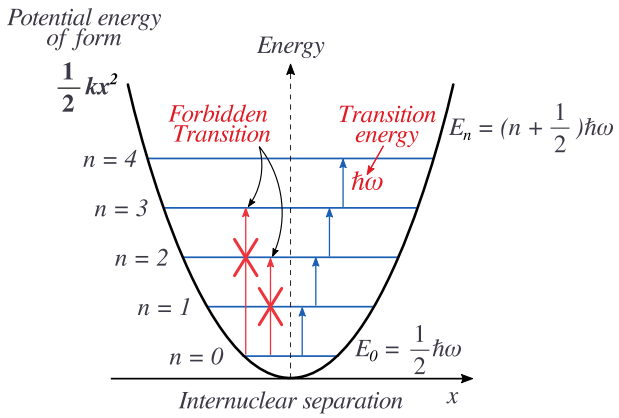


Figure 5.5.1: Possible transitions for a harmonic oscillator. Allowed transitions are labeled with blue arrows and forbidden transitions are labeled with red arrows. (CC BY-NC; Ümit Kaya via LibreTexts)

To evaluate Equation 1.9.9, we need to express the dipole moment operator, $\hat{\mu}$, in terms of the magnitude of the vibration x. The dipole moment operator is defined as

$$\hat{\mu} = \sum_{electrons} e\vec{r} + \sum_{nuclei} q\vec{R} \tag{1.9.10}$$

where the two sums are over all the electrons and nuclei and involve the particle charge ($-e$ or q) multiplying the position vector ($\vec{r}$ or $\vec{R}$, respectively). We can obtain this dipole moment operator in terms of the magnitude of the displacement coordinate, x, in a simple way by using a **Taylor series expansion** for the dipole moment around the equlibrium position ($x = 0$).

$$\hat{\mu}(x) = \mu_{x=0} + \left.\frac{d\mu(x)}{dx}\right|_{x=0} x + \left.\frac{d^2\mu(x)}{dx^2}\right|_{x=0} x^2 + \cdots \tag{1.9.11}$$

Retaining only the first two terms and substituting into Equation 1.9.9 produces

$$\mu_T = \mu_{x=0} \int_{-\infty}^{\infty} \psi_{v'}(x)\psi_v(x)dx + \left.\frac{d\mu(x)}{dx}\right|_{x=0} \int_{-\infty}^{\infty} x\psi^*_{v'}(x)\psi_v(x)dx \tag{1.9.12}$$

where $\mu_{x=0}$ is the **dipole moment** of the molecule when the nuclei are at their equilibrium positions, and

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0}$$

is the *linear* change in the dipole moment due to the displacement of the nuclei in the normal mode. The derivative is the linear change because it multiplies x and not a higher power of x in Equation 1.9.11. Both μ and

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0}$$

are moved outside of the integral because they are constants that no longer depend on x because they are evaluated at $x = 0$.

The integral in the first term in Equation 1.9.12 is 0 because any two harmonic oscillator wavefunctions are *orthogonal*. The integral in the second term of Equation 1.9.12 is zero except when $v' = v \pm 1$ as demonstrated in Exercise 5.5.1 . Also note that the second term is zero if

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0} = 0 \tag{1.9.13}$$

Hence we can identify two "rules" that need to be satisfied for an IR photon to be absorb (or emitted) by a vibrating molecule.

Rules for IR Absorption

For IR absorption to occur two conditions must be met:

1. There must be a **change** in the dipole moment of the molecule as a result of a molecular vibration (or rotation). The change (or oscillation) in the dipole moment allows interaction with the alternating electrical component of the IR radiation. Symmetric molecules (or bonds) do not absorb IR radiation since there is no dipole moment.
2. If the frequency of the radiation ν_{photon} matches the natural frequency of the vibration (ν_m), the IR photon can be absorbed and the amplitude of the vibration increases.

? Exercise 5.5.1

Use one of the Hermite polynomial recursion relations to verify that the second integral in Equation 1.9.12 is 0 unless $v' = v \pm 1$.

If we are to observe absorption of infrared radiation due to a vibrational transition in a molecule, the transition moment cannot be zero. This condition requires that the dipole moment derivative Equation 1.9.13 **cannot** be zero and that the vibrational quantum number change by one unit. The normal coordinate motion must cause the dipole moment of the molecule to change in order for a molecule to absorb infrared radiation. If the normal coordinate oscillation does not cause the dipole moment to change then $\mu_T = 0$ and no infrared absorption is observed. So we can

$$\underbrace{\Delta v = \pm 1}_{\text{For allowed transitions}} \tag{1.9.14}$$

Consider oxygen and nitrogen molecules. Because they are symmetrical, their dipole moments are zero, $\mu = 0$. Since the vibrational motion (only bond stretching for a diatomic molecule) preserves this symmetry, the change in the dipole moment due to the vibrational motion also is zero, $\frac{d\mu(x)}{dx} = 0$. Consequently, oxygen and nitrogen do not absorb infrared radiation as a result of vibrational motion.

? Exercise 5.5.2

Explain why the molar absorptivity or molar extinction coefficients (ϵ) in Beer's Law for the IR absorption of some vibrations are greater than others.

Answer

Qualitatively, if the probability of transition is large, then the molar absorptivity is large. And similar if the transition were not allowed, then there will be no intensity and no observed peak in the spectrum. Transitions can be "partially allowed" as well, and these bands appear with a lower intensity than the full allowed transitions.

When looking at the Beer's Law

$$A = \epsilon\, c\, l$$

where A is absorbance. ϵ is the molar absorptivity, c is the molar concentration and l is the optical path length

We are only looking at the change in the molar absorptivity as the IR absorptions of vibrations vary. To do this we have to look at the transition moment integral

$$\mu_T = \langle \psi_{v'} \,|\, \hat{\mu}(x) \,|\, \psi_v \rangle$$

When the transition moment integral is zero, there is no transition as it is not allowed under the selection rules. This means that the IR is not absorbing any vibrations and therefore the molar absorptivity is zero, which means that absorbance according to Beer's Law is zero. As the transition moment integral increases, the molar absorptivity also increases and the overall absorbance increases.

The case $v' = v + 1$ corresponds to going from one vibrational state to a higher energy one by absorbing a photon with energy $h\nu$. The case $v' = v - 1$ corresponds to a transition that emits a photon with energy $h\nu$. In the harmonic oscillator model infrared spectra are very simple; only the fundamental transitions, $\Delta = \pm 1$, are allowed. The associated transition energy is $\hbar\omega$, according to

Equation 1.9.4. The transition energy is the change in energy of the oscillator as it moves from one vibrational state to another, and it equals the photon energy.

$$\begin{aligned}\Delta E &= E_{final} - E_{initial} \\ &= h\nu_{photon} \\ &= \hbar\omega_{oscillator}\end{aligned}$$

For perfect harmonic oscillators, the only possible allowed transitions are $\Delta = \pm 1$ with all other transitions forbidden (Figure 5.5.1). This conclusion predicts that the vibrational absorption spectrum of a diatomic molecule consists of a single line since the energy levels are equally spaced in the harmonic oscillator model (Figure 5.5.1). If the vibration were anharmonic, then the levels would not be equally spaced and then transitions from $v = 0$ to $v = 1$ and from $v = 1$ to $v = 2$, etc. would occur at different frequencies.

> *Only the fundamental transitions, $\Delta = \pm 1$, are observed in infrared spectra within harmonic oscillator model.*

The actual IR spectrum is more complex, especially at high resolution. There is a fine structure due to the rotational states of the molecule. These states will be discussed in the next chapter. The spectrum is enriched further by the appearance of lines due to transitions corresponding to $\Delta = \pm n$ where $n > 1$. These transitions are called **overtone** transitions and their appearance in spectra despite being forbidden in the harmonic oscillator model is due to the anharmonicity of molecular vibrations. Anharmonicity means the potential energy function is not strictly the harmonic potential. The first overtone, $\Delta v = 2$, generally appears at a frequency slightly less than twice that of the fundamental, i.e. the frequency due to the $\Delta v = 1$ transition.

? Exercise 5.5.3: Hydrogen Chloride

Compute the approximate transition frequencies in wavenumber units for the first and second overtone transitions in HCl given that the fundamental is at 2,886 cm^{-1}.

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1.10: Microwave Spectroscopy

Microwave rotational spectroscopy uses microwave radiation to measure the energies of rotational transitions for molecules in the gas phase. It accomplishes this through the interaction of the electric dipole moment of the molecules with the electromagnetic field of the exciting microwave photon.

Introduction

To probe the pure rotational transitions for molecules, scientists use microwave rotational spectroscopy. This spectroscopy utilizes photons in the microwave range to cause transitions between the quantum rotational energy levels of a gas molecule. The reason why the sample must be in the gas phase is due to intermolecular interactions hindering rotations in the liquid and solid phases of the molecule. For microwave spectroscopy, molecules can be broken down into 5 categories based on their shape and the inertia around their 3 orthogonal rotational axes. These 5 categories include diatomic molecules, linear molecules, spherical tops, symmetric tops and asymmetric tops.

Classical Mechanics

The **Hamiltonian solution** to the rigid rotor is

$$H = T \tag{1.10.1}$$

since,

$$H = T + V \tag{1.10.2}$$

Where T is kinetic energy and V is potential energy. Potential energy, V, is 0 because there is no resistance to the rotation (similar to a particle in a box model).

Since $H = T$, we can also say that:

$$T = \frac{1}{2}\sum m_i v_i^2 \tag{1.10.3}$$

However, we have to determine v_i in terms of rotation since we are dealing with rotation. Since,

$$\omega = \frac{v}{r} \tag{1.10.4}$$

where ω = angular velocity, we can say that:

$$v_i = \omega X r_i \tag{1.10.5}$$

Thus we can rewrite the T equation as:

$$T = \frac{1}{2}\sum m_i v_i \left(\omega X r_i\right) \tag{1.10.6}$$

Since ω is a scalar constant, we can rewrite the T equation as:

$$T = \frac{\omega}{2}\sum m_i \left(v_i X r_i\right) = \frac{\omega}{2}\sum l_i = \omega\frac{L}{2} \tag{1.10.7}$$

where l_i is the **angular momentum** of the *ith* particle, and **L** is the angular momentum of the *entire system*. Also, we know from physics that,

$$L = I\omega \tag{1.10.8}$$

where **I** is the moment of inertia of the rigid body relative to the axis of rotation. We can rewrite the T equation as,

$$T = \omega\frac{I\omega}{2} = \frac{1}{2}I\omega^2 \tag{1.10.9}$$

The internal Hamiltonian, H, is:

$$H = \frac{i^2\hbar^2}{2I} \tag{1.10.10}$$

and the Schrödinger Equation for rigid rotor is:

$$\frac{i^2\hbar^2}{2I}\psi = E\psi \tag{1.10.11}$$

Thus, we get:

$$E_n = \frac{J(J+1)h^2}{8\pi^2 I} \tag{1.10.12}$$

where J is a rotational quantum number and $\hbar$ is the reduced Planck's constant. However, if we let:

$$B = \frac{h}{8\pi^2 I} \tag{1.10.13}$$

where B is a rotational constant, then we can substitute it into the E_n equation and get:

$$E_n = J(J+1)Bh \tag{1.10.14}$$

Considering the transition energy between two energy levels, the difference is a multiple of 2. That is, from $J = 0$ to $J = 1$, the $\Delta E_{0\to1}$ is 2Bh and from J = 1 to J = 2, the $\Delta E_{1\to2}$ is 4Bh.

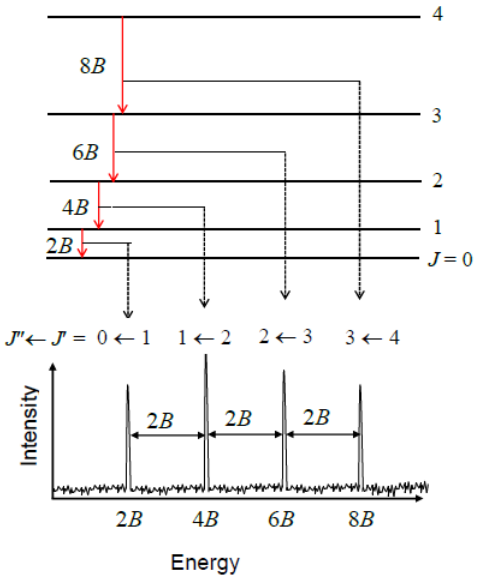


Figure **1.10.1**: Energy levels and line positions calculated in the rigid rotor approximation. This diagram illustrates how transitions between the rotational energy levels of molecules map onto the energies at which these transitions are observed during laboratory experiments. (CC CS-BY 3.0; Nnrw).

Theory

When a gas molecule is irradiated with microwave radiation, a photon can be absorbed through the interaction of the photon's electronic field with the electrons in the molecules. For the microwave region this energy absorption is in the range needed to cause transitions between rotational states of the molecule. However, only molecules with a permanent dipole that changes upon rotation can be investigated using microwave spectroscopy. This is due to the fact that their must be a charge difference across the molecule for the oscillating electric field of the photon to impart a torque upon the molecule around an axis that is perpendicular to this dipole and that passes through the molecules center of mass.

This interaction can be expressed by the transition dipole moment for the transition between two rotational states

$$\text{Probability of Transition} = \int \psi_{rot}(F)\hat{\mu}\psi_{rot}(I)d\tau \tag{1.10.15}$$

Where $\Psi_{rot(F)}$ is the complex conjugate of the wave function for the final rotational state, $\Psi_{rot(I)}$ is the wave function of the initial rotational state , and μ is the dipole moment operator with Cartesian coordinates of μ_x, μ_y, μ_z. For this integral to be nonzero the integrand must be an even function. This is due to the fact that any odd function integrated from negative infinity to positive infinity, or any other symmetric limits, is always zero.

In addition to the constraints imposed by the transition moment integral, transitions between rotational states are also limited by the nature of the photon itself. A photon contains one unit of angular momentum, so when it interacts with a molecule it can only impart one unit of angular momentum to the molecule. This leads to the selection rule that a transition can only occur between rotational energy levels that are only one quantum rotation level (J) away from another[1].

$$\Delta J = \pm 1 \tag{1.10.16}$$

The transition moment integral and the selection rule for rotational transitions tell if a transition from one rotational state to another is allowed. However, what these do not take into account is whether or not the state being transitioned from is actually populated, meaning that the molecule is in that energy state. This leads to the concept of the Boltzmann distribution of states. The Boltzmann distribution is a statistical distribution of energy states for an ensemble of molecules based on the temperature of the sample[2].

$$\frac{n_J}{n_0} = \frac{e^{(-E_{rot}(J)/RT)}}{\sum_{J=1}^{J=n} e^{(-E_{rot}(J)/RT)}} \tag{1.10.17}$$

where $E_{rot(J)}$ is the molar energy of the J rotational energy state of the molecule,

- R is the gas constant,
- T is the temperature of the sample.
- n(J) is the number of molecules in the J rotational level, and
- n_0 is the total number of molecules in the sample.

This distribution of energy states is the main contributing factor for the observed absorption intensity distributions seen in the microwave spectrum. This distribution makes it so that the absorption peaks that correspond to the transition from the energy state with the largest population based on the Boltzmann equation will have the largest absorption peak, with the peaks on either side steadily decreasing.

Degrees of Freedom

A molecule can have three types of degrees of freedom and a total of 3N degrees of freedom, where N equals the number of atoms in the molecule. These degrees of freedom can be broken down into 3 categories[3].

- **Translational**: These are the simplest of the degrees of freedom. These entail the movement of the entire molecule's center of mass. This movement can be completely described by three orthogonal vectors and thus contains 3 degrees of freedom.
- **Rotational**: These are rotations around the center of mass of the molecule and like the translational movement they can be completely described by three orthogonal vectors. This again means that this category contains only 3 degrees of freedom. However, in the case of a linear molecule only two degrees of freedom are present due to the rotation along the bonds in the molecule having a negligible inertia.
- **Vibrational**: These are any other types of movement not assigned to rotational or translational movement and thus there are 3N – 6 degrees of vibrational freedom for a nonlinear molecule and 3N – 5 for a linear molecule. These vibrations include bending, stretching, wagging and many other aptly named internal movements of a molecule. These various vibrations arise due to the numerous combinations of different stretches, contractions, and bends that can occur between the bonds of atoms in the molecule.

Each of these degrees of freedom is able to store energy. However, In the case of rotational and vibrational degrees of freedom, energy can only be stored in discrete amounts. This is due to the quantized break down of energy levels in a molecule described by quantum mechanics. In the case of rotations the energy stored is dependent on the rotational inertia of the gas along with the corresponding quantum number describing the energy level.

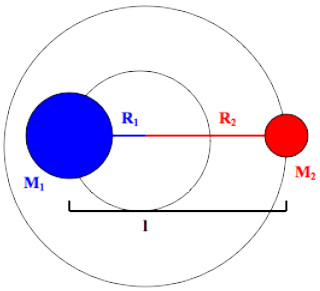
Rotational Symmetries

To analyze molecules for rotational spectroscopy, we can break molecules down into 5 categories based on their shapes and their moments of inertia around their 3 orthogonal rotational axes:[4]

1. Diatomic Molecules
2. Linear Molecules
3. Spherical Tops
4. Symmetrical Tops
5. Asymmetrical Tops

Diatomic Molecules

The rotations of a diatomic molecule can be modeled as a rigid rotor. This rigid rotor model has two masses attached to each other with a fixed distance between the two masses.



It has an inertia (I) that is equal to the square of the fixed distance between the two masses multiplied by the reduced mass of the rigid rotor.

$$I_e = \mu r_e^2 \tag{1.10.18}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{1.10.19}$$

Using quantum mechanical calculations it can be shown that the energy levels of the rigid rotator depend on the inertia of the rigid rotator and the quantum rotational number J[2].

$$E(J) = B_e J(J+1) \tag{1.10.20}$$

$$B_e = \frac{h}{8\pi^2 c I_e} \tag{1.10.21}$$

However, this rigid rotor model fails to take into account that bonds do not act like a rod with a fixed distance, but like a spring. This means that as the angular velocity of the molecule increases so does the distance between the atoms. This leads us to the **nonrigid rotor model** in which a centrifugal distortion term (D_e) is added to the energy equation to account for this stretching during rotation.

$$E(J)(cm^{-1}) = B_e J(J+1) – D_e J^2 (J+1)^2 \tag{1.10.22}$$

This means that for a diatomic molecule the transitional energy between two rotational states equals

$$E = B_e[J'(J'+1) - J''(J''+1)] - D_e[J'^2(J'+1)^2 - J''^2(J'+1)^2] \tag{1.10.23}$$

Where J' is the quantum number of the final rotational energy state and J'' is the quantum number of the initial rotational energy state. Using the selection rule of $\Delta J = \pm 1$ the spacing between peaks in the microwave absorption spectrum of a diatomic molecule will equal

$$E_R = (2B_e - 4D_e) + (2B_e - 12D_e)J'' - 4D_e J''^3 \tag{1.10.24}$$

Linear Molecules

Linear molecules behave in the same way as diatomic molecules when it comes to rotations. For this reason they can be modeled as a non-rigid rotor just like diatomic molecules. This means that linear molecule have the same equation for their rotational energy levels. The only difference is there are now more masses along the rotor. This means that the inertia is now the sum of the distance between each mass and the center of mass of the rotor multiplied by the square of the distance between them[2].

$$I_e = \sum_{j=1}^{n} m_j r_{ej}^2 \tag{1.10.25}$$

Where m_j is the mass of the jth mass on the rotor and r_{ej} is the equilibrium distance between the j^{th} mass and the center of mass of the rotor.

Spherical Tops

Spherical tops are molecules in which all three orthogonal rotations have equal inertia and they are highly symmetrical. This means that the molecule has no dipole and for this reason spherical tops do not give a microwave rotational spectrum.

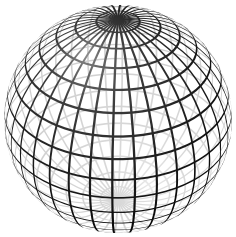
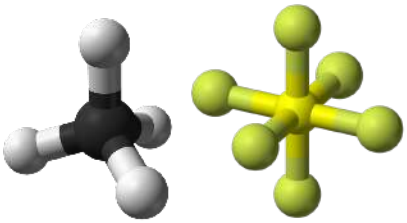


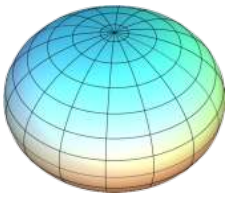
Figure 1.10.2: Geometrical example of a spherical top

Examples:



Symmetrical Tops

Symmetrical tops are molecules with two rotational axes that have the same inertia and one unique rotational axis with a different inertia. Symmetrical tops can be divided into two categories based on the relationship between the inertia of the unique axis and the inertia of the two axes with equivalent inertia. If the unique rotational axis has a greater inertia than the degenerate axes the molecule is called an oblate symmetrical top. If the unique rotational axis has a lower inertia than the degenerate axes the molecule is called a prolate symmetrical top. For simplification think of these two categories as either frisbees for oblate tops or footballs for prolate tops.



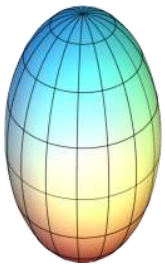


Figure* 1.10.3*: *Symmetric Tops: (Left) Geometrical example of an oblate top and (right) a prolate top. Images used with permission from Wikipedia.com.*

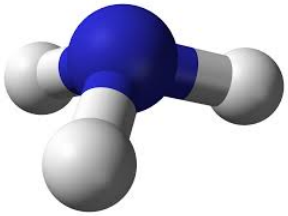


Figure 1.10.4: Examples of symmetric tops. Benzene (oblate) XeF_4 (oblate) $ClCH_3$ (prolate) NH_3 (prolate)

In the case of linear molecules there is one degenerate rotational axis which in turn has a single rotational constant. With symmetrical tops now there is one unique axis and two degenerate axes. This means an additional rotational constant is needed to describe the energy levels of a symmetrical top. In addition to the rotational constant an additional quantum number must be introduced to describe the rotational energy levels of the symmetric top. These two additions give us the following rotational energy levels of a prolate and oblate symmetric top

$$E_{(J,K)}(cm^{-1}) = B_e * J(J+1) + (A_e - B_e)K^2 \tag{1.10.26}$$

Where B_e is the rotational constant of the unique axis, A_e is the rotational constant of the degenerate axes, J is the total rotational angular momentum quantum number and K is the quantum number that represents the portion of the total angular momentum that lies along the unique rotational axis. This leads to the property that K is always equal to or less than J. Thus we get the two selection rules for symmetric tops

$$\Delta J = 0, \pm 1 \tag{1.10.27}$$

$$\Delta K = 0 \tag{1.10.28}$$

when $K \neq 0$

$$\Delta J = \pm 1 \tag{1.10.29}$$

$$\Delta K = 0 \tag{1.10.30}$$

when $K = 0$

However, like the rigid rotor approximation for linear molecules, we must also take into account the elasticity of the bonds in symmetric tops. Therefore, in a similar manner to the rigid rotor we add a centrifugal coupling term, but this time we have one for each quantum number and one for the coupling between the two.

$$E_{(J,K)}(cm^{-1}) = B_e J(J+1) - D_{eJ}J^2(J+1)^2 + (A_e - B_e) * K^2 \tag{1.10.31}$$

$$-D_{ek}K^4 - D_{ejk}J(J+1)K^2 \tag{1.10.32}$$

Asymmetrical Tops

Asymmetrical tops have three orthogonal rotational axes that all have different moments of inertia and most molecules fall into this category. Unlike linear molecules and symmetric tops these types of molecules do not have a simplified energy equation to determine the energy levels of the rotations. These types of molecules do not follow a specific pattern and usually have very complex microwave spectra.

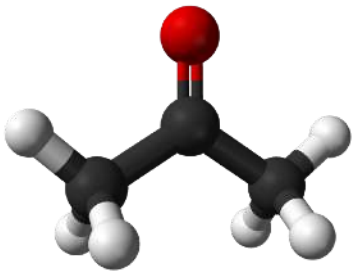


Figure 1.10.5: Molecular examples of asymmetrical tops. (left) water and (right) acetone

Additional Rotationally Sensitive Spectroscopies

In addition to microwave spectroscopy, IR spectroscopy can also be used to probe rotational transitions in a molecule. However, in the case of IR spectroscopy the rotational transitions are coupled to the vibrational transitions of the molecule. One other spectroscopy that can probe the rotational transitions in a molecule is Raman spectroscopy, which uses UV-visible light scattering to determine energy levels in a molecule. However, a very high sensitivity detector must be used to analyze rotational energy levels of a molecule.

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CHAPTER OVERVIEW

2: Atomic Structure

2.1: The Schrödinger Wave Equation for the Hydrogen Atom

2.2: Many-Electron Atoms and the Periodic Table

2.3: Quantum-Mechanical Tunneling

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2.1: The Schrödinger Wave Equation for the Hydrogen Atom

Introduction (Schrödinger equation for 1 e- system)

The hydrogen atom, consisting of an electron and a proton, is a two-particle system, and the internal motion of two particles around their center of mass is equivalent to the motion of a single particle with a reduced mass ($m = \frac{m_1 m_2}{m_1 + m_2}$). This reduced particle is located at $\vec{r}$, where $\vec{r}$ is the vector specifying the position of the electron relative to the position of the proton. The length r of $\vec{r}$ is the distance between the proton and the electron, and the direction of r is given by the orientation of the vector pointing from the proton to the electron. Since the proton is much more massive than the electron, we will assume that the reduced mass equals the electron mass and the proton is located at the center of mass.

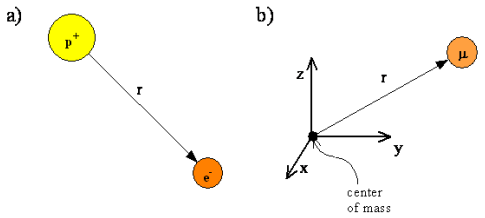


Figure 2.1.1: a) The proton (p^+) and electron (e^-) of the hydrogen atom. b) Equivalent reduced particle with reduced mass μ at distance r from center of mass.

Starting with the general Schrödinger equation:

$$\frac{-\hbar^2}{2m}\nabla^2\Psi(\vec{r}) + V(\vec{r})\Psi(\vec{r}) = E\Psi(\vec{r}) \tag{2.1.1}$$

we need an expression for the potential. This is just Coulomb attraction and depends only on the separation distance r:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \tag{2.1.2}$$

where r is the distance between the electron and the proton. The Coulomb potential energy depends inversely on the distance between the electron and the nucleus and does not depend on any angles. Such a potential is called a central potential. Substituting in to equation 2.1.1 this gives us:

$$\frac{-\hbar^2}{2m}\nabla^2\Psi(\vec{r}) + \frac{e^2}{4\pi\epsilon_0 r}\Psi(\vec{r}) = E\Psi(\vec{r}) \tag{2.1.3}$$

Because of the spherical symmetry of the equation it turns out to be better to switch from Cartesian coordinates x, y, z to spherical coordinates in terms of a radius r, as well as angles ϕ, which is measured from the positive x axis in the xy plane and may be between 0 and 2π, and θ, which is measured from the positive z axis towards the xy plane and may be between 0 and π.

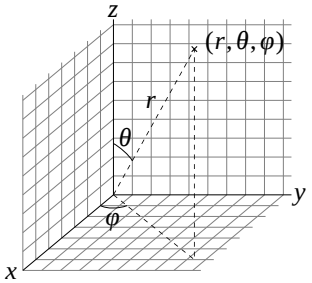


Figure 2.1.2: Spherical Coordinates

This generates a much more complicated, but easier to solve equation:

$$\left\{-\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r}\right\}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{2.1.4}$$

The second two terms in the square brackets of this equation only depend on the angles. This lead people to try separating the equation into two parts, one that depends on the angles (θ and φ) and one that depends on the distance (r). This does work, just as the

wavefunction for a particle in a multidimensional box can be represented as the product of wavefunctions that depend on each coordinate separately.

Solutions

The solutions to this equation take the form of products of two functions as shown in equation 2.1.5.

$$\psi_{nlm_l}(r,\theta,\varphi) = R_n(r)Y_{lm}(\theta,\varphi) \tag{2.1.5}$$

The $Y_{lm_l}(\theta,\varphi)$ are a the Spherical Harmonic functions (Table M4), which were well known before quantum mechanics was developed. The Spherical Harmonic functions provide information about the angular probability distribution of the electron around the proton, and the radial function $R_n(r)$ describes how far the electron is away from the proton.

The state of the electron is specified by the three quantum numbes n, l, and m_l. For this case of a single electron atom the energy E_n depends only on n, although the other quantum numbers are required for the full description of the wavefunction:

$$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2} \tag{2.1.6}$$

with $n = 1, 2, 3...\infty$.

It is found that the possible values of l are constrained by n and the possible values of m_l are constrained by l. We will see when we consider multi-electron atoms that these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

The Three Quantum Numbers

Schrödinger's approach requires three quantum numbers (n, l, and m_l) to specify a wavefunction for the electron. The quantum numbers provide information about the spatial distribution of an electron. Although n can be any positive integer (NOT zero), only certain values of l and m_l are allowed for a given value of n.

The principal quantum number (n): This quantum number indicates the energy of the electron (equation 2.1.6) and the average distance of an electron from the nucleus. n is restricted to the positive integers:

$$n = 1,\ 2,\ 3,\ 4,\ \ldots \tag{2.1.7}$$

As n increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of n are easier to remove from an atom. All wave functions that have the same value of n are said to constitute a principal ***shell***, because those electrons have similar average distances from the nucleus. The principal quantum number n corresponds to the n used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

The Azimuthal Quantum Number (l): This quantum number indicates the shape of the region of space occupied by an electron and the electrons total orbital angular momentum. The allowed values of l are integers that depend on the value of n and can range from 0 to n − 1:

$$l = 0,\ 1,.,2,\ 3,\ ..\ (n-1) \tag{2.1.8}$$

For example, if n = 1, l can be only 0; if n = 2, l can be 0 or 1; and so forth. For a given atom, all wave functions that have the same values of both n and l form a ***subshell***. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

The total angular momentum of the electron has the value:

$$J = \sqrt{l(l+1)}\hbar \tag{2.1.9}$$

Thus the angular momentum of the electron is quantized.

The Magnetic Quantum Number (m_l): This quantum number indicates the orientation of the region of space occupied by an electron with respect to an applied magnetic field. The allowed integer values of m_l depend on the value of l and can range from $-l$ to l:

$$m = -l,\ -l+1,\ldots.0,\ \ldots.l-1,l \tag{2.1.10}$$

For example, if $l = 0$, m_l can be only 0; if l = 1, m_l can be −1, 0, or +1; and if l = 2, m_l can be −2, −1, 0, +1, or +2.

Each wave function with an allowed combination of n, l, and m_l values describes an ***atomic orbital***, a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

Because the electron is charged and has an angular momentum it can interact with a magnetic field. If the direction of the magnetic field is taken to be along the z-axis then the component (projection) of the angular momentum along the z-axis is:

$$J_z = m_l \hbar \tag{2.1.11}$$

This is the same quantization of J_z as seen for the particle on a ring.

Example 2.1.1: Number of subshells

How many subshells and orbitals are contained within the principal shell with n = 4?

Given: value of n

Asked for: number of subshells and orbitals in the principal shell

Strategy:

A. Given n = 4, calculate the allowed values of l. From these allowed values, count the number of subshells.

B. For each allowed value of l, calculate the allowed values of ml. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Solution

A We know that l can have all integral values from 0 to n − 1. If n = 4, then l can equal 0, 1, 2, or 3. Because the shell has four values of l, it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of ml.

B For l = 0, ml can be only 0, and thus the l = 0 subshell has only one orbital. For l = 1, ml can be 0 or ±1; thus the l = 1 subshell has three orbitals. For l = 2, ml can be 0, ±1, or ±2, so there are five orbitals in the l = 2 subshell. The last allowed value of l is l = 3, for which ml can be 0, ±1, ±2, or ±3, resulting in seven orbitals in the l = 3 subshell. The total number of orbitals in the n = 4 principal shell is the sum of the number of orbitals in each subshell and is equal to n2:

$$\underset{(l=0)}{1} + \underset{(l=1)}{3} + \underset{(l=2)}{5} + \underset{(l=3)}{7} = 16 \text{ orbitals} = (4 \text{ principal shells})^2$$

Exercise 2.1.1

How many subshells and orbitals are in the principal shell with n = 3?

Answer: three subshells; nine orbitals

Rather than specifying all the values of n and l every time we refer to a subshell or an orbital, chemists use an abbreviated system with lowercase letters to denote the value of l for a particular subshell or orbital:

l	0	1	2	3
Designation	s	p	d	f

The principal quantum number is named first, followed by the letter s, p, d, or f as appropriate. These orbital designations are derived from corresponding spectroscopic characteristics of lines involving them: *s*harp, *p*rincipal, *d*iffuse, and *f*undamental. A 1s orbital has n = 1 and l = 0; a 2p subshell has n = 2 and l = 1 (and has three 2p orbitals, corresponding to m_l = −1, 0, and +1); a 3d subshell has n = 3 and l = 2 (and has five 3d orbitals, corresponding to m_l = −2, −1, 0, +1, and +2); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table **2.1.1**):

- Each principal shell has n subshells. For n = 1, only a single subshell is possible (1s); for n = 2, there are two subshells (2s and 2p); for n = 3, there are three subshells (3s, 3p, and 3d); and so forth. Every shell has an ns subshell, any shell with $n \geq 2$ also has an np

subshell, and any shell with $n \geq 3$ also has an *nd* subshell. Because a 2*d* subshell would require both $n = 2$ and $l = 2$, which is not an allowed value of l for $n = 2$, a 2*d* subshell does not exist.

- Each subshell has $2l + 1$ orbitals. This means that all *ns* subshells contain a single *s* orbital, all *np* subshells contain three *p* orbitals, all *nd* subshells contain five *d* orbitals, and all *nf* subshells contain seven *f* orbitals.

> **Note**
>
> Each principal shell has n subshells, and each subshell has $2l + 1$ orbitals.

Table **2.1.1**: Allowed values of n, l, and m_l through n = 4

n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	4
	1	2*p*	−1, 0, 1	3	
3	0	3*s*	0	1	9
	1	3*p*	−1, 0, 1	3	
	2	3*d*	−2, −1, 0, 1, 2	5	

4	0	4*s*	0	1
	1	4*p*	−1, 0, 1	3
	2	4*d*	−2, −1, 0, 1, 2	5
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7

16

The Radial Component

The first six radial functions are provided in Table **2.1.2**. Note that the functions in the table exhibit a dependence on Z, the atomic number of the nucleus. Other one electron systems have electronic states analogous to those for the hydrogen atom, and inclusion of the charge on the nucleus allows the same wavefunctions to be used for all one-electron systems. For hydrogen, $Z = 1$ and for helium, $Z = 2$.

Table **2.1.2**: Hydrogen-like atomic wavefunctions for n values $1, 2, 3$: Z is the atomic number of the nucleus, and $\rho = \frac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

n	l	m_l	Radial Component
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\rho}$
2	0	0	$\psi_{200} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} (2-\rho)e^{\frac{-\rho}{2}}$
2	1	0	$\psi_{210} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \rho e^{-\rho/2}\cos(\theta)$
2	1	±1	$\psi_{21\pm 1} = \frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \rho e^{-\rho/2}\sin(\theta)e^{\pm i\phi}$
3	0	0	$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} (27-18\rho+2\rho^2)e^{-\rho/3}$
3	1	0	$\psi_{310} = \frac{1}{81}\sqrt{\frac{2}{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} (6r-\rho^2)e^{-\rho/3}\cos(\theta)$
3	1	±1	$\psi_{31\pm 1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} (6\rho-\rho^2)e^{-r/3}\sin(\theta)e^{\pm i\phi}$
3	2	0	$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \rho^2 e^{-\rho/3}(3cos^2(\theta)-1)$
3	2	±1	$\psi_{32\pm 1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \rho^2 e^{-\rho/3}\sin(\theta)\cos(\theta)e^{-}$
3	2	±2	$\psi_{32\pm 2} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \rho^2 e^{-\rho/3}\sin^2(\theta)e^{\pm 2i\phi}$

Visualizing the variation of an electronic wavefunction with r, θ, and ϕ is important because the absolute square of the wavefunction depicts the charge distribution (electron probability density) in an atom or molecule. The charge distribution is central to chemistry because it is related to chemical reactivity. For example, an electron deficient part of one molecule is attracted to an electron rich region of another molecule, and such interactions play a major role in chemical interactions ranging from substitution and addition reactions to protein folding and the interaction of substrates with enzymes.

Plots of the radial functions, R(r), for the 1s, 2s, and 2p orbitals plotted in figure **2.1.2** (left). The quantity $R(r)^*R(r)$ gives the radial probability density; i.e., the probability density for the electron to be at a point located the distance r from the proton. Radial probability densities for three types of atomic orbitals are plotted in figure **2.1.2** (middle). The probability of finding an electron at a

particular distance from the nucleus is the integral of $R(r)^*R(r)$ over the surface of the sphere of radius r, $P(r) = 4\pi r^2 R(r)^*R(r)$, which is plotted in figure **2.1.2** (right).

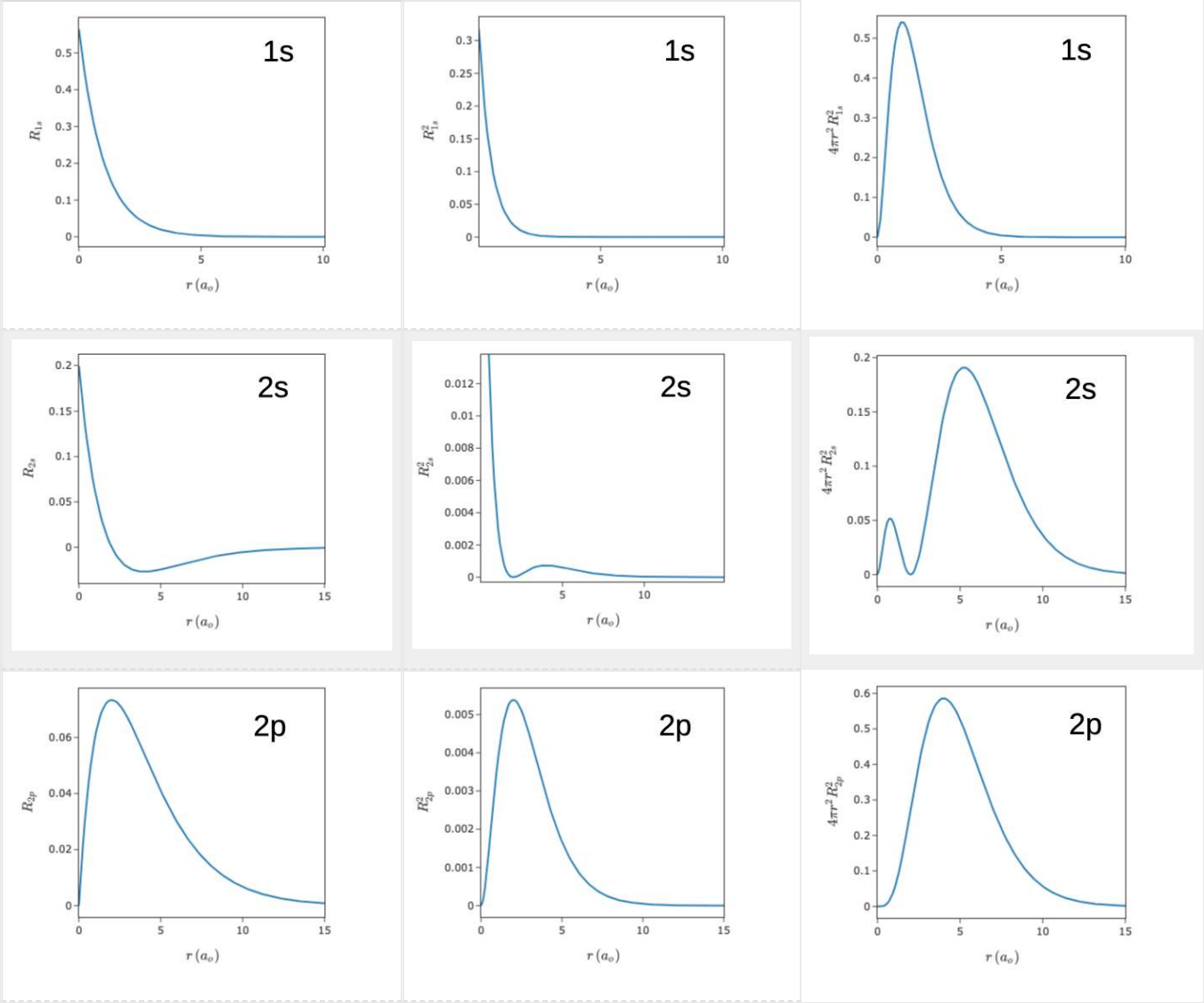


Figure **2.1.2**: (left) **Radial function**, R(r), for the 1s, 2s, and 2p orbitals. (middle) **Radial probability densities** for the 1s, 2s, and 2p orbitals.(right) **Radial distribution functions** for the 1s, 2s, and 2p orbitals. Units on the x-axis are Bohrs = 0.529 Å = a_o.

For the hydrogen atom, the peak in the radial probability plot (right colum in figure **2.1.2**) occurs at r = 0.529 Å (52.9 pm), which is exactly the radius calculated by Bohr for the n = 1 orbit. Thus the *most probable radius* obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg uncertainty principle.

> Notice that because the surface area of a sphere with radius of zero is zero, **there is no probability of finding the electron at the nucleus** (r = 0). See the right hand column in figure **2.1.2**. This quantum prediction can be thought of as an explanation for why atoms do not collapse into a single uncharged particle.

Figure **2.1.3** compares the electron probability densities for the hydrogen 1*s*, 2*s*, and 3*s* orbitals in 3-D. Note that all three are spherically symmetrical. For the 2*s* and 3*s* orbitals, however (and for all other *s* orbitals as well), the electron probability density does not fall off smoothly with increasing *r*. Instead, a series of minima and maxima are observed in the radial probability plots (part (c) in

Figure 2.1.3). The minima correspond to spherical nodes (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability.

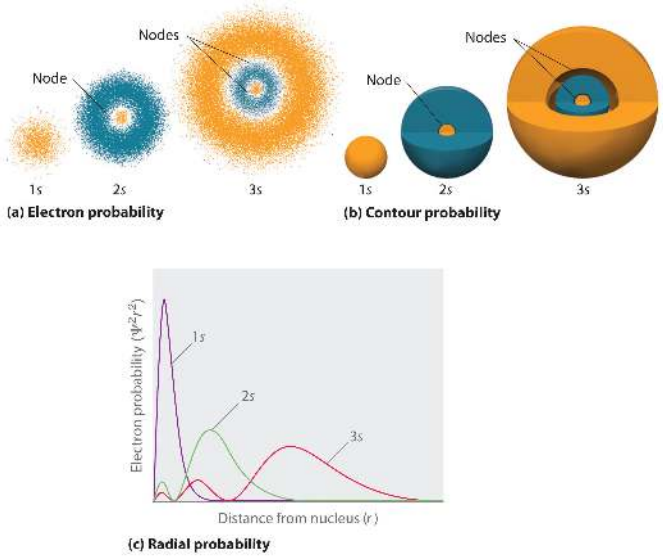


Figure 2.1.3: Probability Densities for the 1 s, 2 s, and 3*s* Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1*s*, 2*s*, and 3*s* orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (*r*) in all directions (radial probability), the most probable radius increases as*n* increases, but the 2*s* and 3*s* orbitals have regions of significant electron probability at small values of *r*.

The Angular Component

The angular component of the wavefunction $Y_{lm_l}(\theta,\phi)$ in Equation 2.1.5 does much to give an orbital its distinctive shape. Y is typically normalized so the the integral of Y^2 over the unit sphere is equal to one. In this case, Y^2 serves as a probability function. The probability function can be interpreted as the probability that the electron will be found on the ray emitting from the origin that is at angles (θ,ϕ) from the axes. The probability function can also be interpreted as the probability distribution of the electron being at position (θ,ϕ) on a sphere of radius *r*, given that it is *r* distance from the nucleus. $Y_{l,m_l}(\theta,\phi)$ are also the wavefunction solutions to Schrödinger's equation for a rigid rotor consisting of rotating bodies, for example a diatomic molecule. These are called Spherical Harmonic functions (Table M4).

s Orbitals (l=0)

Three things happen to *s* orbitals as *n* increases (figure 2.1.3):

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the *s* orbitals also become higher in energy as *n* increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density. Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2*s* and 3*s* orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding.

p Orbitals (l=1)

Only *s* orbitals are spherically symmetrical. As the value of *l* increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the 2*p* subshell has $l = 1$, with three values of m_l (−1, 0, and +1), there are three 2*p* orbitals).

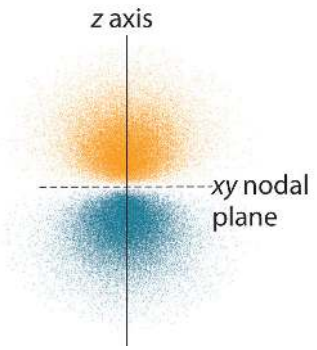


Figure 2.1.4: Illustration of a slice through a p_z orbital, where the dot density indicates the relative probability of finding the electron. The colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen 2*p* orbitals is shown in Figure 2.1.4. Because this orbital has two lobes of electron density arranged along the *z* axis, with an electron density of zero in the *xy* plane (i.e., the *xy* plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 2.1.5, the other two 2*p* orbitals have identical shapes, but they lie along the *x* axis ($2p_x$) and *y* axis ($2p_y$), respectively. Note that each *p* orbital has just one nodal plane. In each case, the phase of the wave function for each of the 2*p* orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the *phase* of the wave that describes the electron motion, *not* to positive or negative charges.

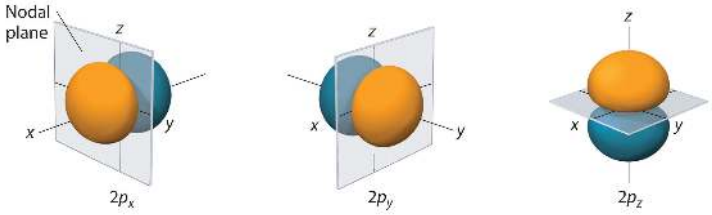


Figure 2.1.5: The Three Equivalent 2 p Orbitals of the Hydrogen Atom. The surfaces shown enclose 90% of the total electron probability for the $2p_x$, $2p_y$, and $2p_z$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each 2*p* orbital. The phase of the wave function is positive (orange) in the region of space where *x*, *y*, or *z* is positive and negative (blue) where *x*, *y*, or *z* is negative.

Just as with the *s* orbitals, the size and complexity of the *p* orbitals for any atom increase as the principal quantum number *n* increases. The shapes of the 90% probability surfaces of the 3*p*, 4*p*, and higher-energy *p* orbitals are, however, essentially the same as those shown in figure 2.1.5, but with additional radial nodes.

Note: Orbitals specified by m_l are not the same as those usually labeled p_x, p_y or p_z

The p_x, p_y and p_z orbitals are **not the solutions to the Schrödinger equation associated with m_l = -1, 0 and 1**. They are valid wavefunctions built from linear combinations of the m_l = -1, 0, 1 wavefunctions in order to get real valued functions. See the table of Spherical Harmonics and Real Valued Spherical Harmonics.

d Orbitals (l=2)

Subshells with $l = 2$ have five *d* orbitals; the first principal shell to have a *d* subshell corresponds to $n = 3$. The five *d* orbitals have m_l values of −2, −1, 0, +1, and +2. The surfaces enclosing the 90% probability of finding the electron for the five real-valued linear combinations of the complex orbitals specified by m_l are shown in figure 2.1.6.

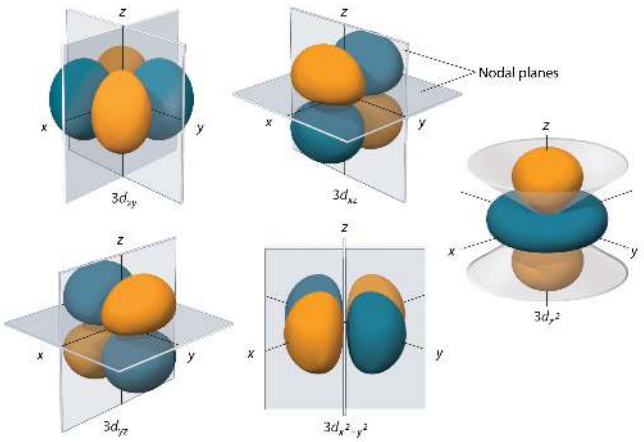


Figure **2.1.6**: The five equivalent 3d orbitals of the hydrogen atom. The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth 3d orbital, $3d_{z^2}$, has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.

The hydrogen 3d orbitals have more complex shapes than the 2p orbitals. All five 3d orbitals contain two nodal surfaces, as compared to one for each p orbital and zero for each s orbital. In three of the d orbitals, the lobes of electron density are oriented between the x and y, x and z, and y and z planes; these orbitals are referred to as the $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals, respectively. A fourth d orbital has lobes lying along the x and y axes; this is the $3d_{x^2-y^2}$ orbital. The fifth 3d orbital, called the $3d_{z^2}$ orbital, has a unique shape: it looks like a $2p_z$ orbital combined with an additional doughnut of electron probability lying in the xy plane. Despite its peculiar shape, the $3d_{z^2}$ orbital is mathematically equivalent to the other four and has the same energy. In contrast to p orbitals, the phase of the wave function for d orbitals is the same for opposite pairs of lobes. As shown in Figure **2.1.6**, the phase of the wave function is positive for the two lobes of the dz^2 orbital that lie along the z axis, whereas the phase of the wave function is negative for the doughnut of electron density in the xy plane. Like the s and p orbitals, as n increases, the size of the d orbitals increases, but the overall shapes remain similar to those depicted in figure **2.1.6**.

f Orbitals (l=3)

Principal shells with n = 4 can have subshells with l = 3 and m_l values of −3, −2, −1, 0, +1, +2, and +3. These subshells consist of seven *f* orbitals. Each *f* orbital has three nodal surfaces, so their shapes are complex (not shown).

Energies

As noted previously, the energy for a single electron atom depend only on n, the principal quantum number. The solutions reproduce the same quantized expression for hydrogen atom energy levels that was obtained from the Bohr model of the hydrogen atom.

$$E = -\frac{Z^2}{n^2} Rhc \tag{2.1.12}$$

or

$$E_n = -\frac{Z^2 \mu e^4}{8\epsilon_0^2 h^2 n^2} \tag{2.1.13}$$

The relative energies of the atomic orbitals with $n \leq 4$ for a hydrogen atom are plotted in Figure **2.1.7** ; note that the orbital energies depend on *only* the principal quantum number n and are all less than zero, indicating attraction to the nucleus. Consequently, the energies of the 2*s* and 2*p* orbitals of hydrogen are the same; the energies of the 3*s*, 3*p*, and 3*d* orbitals are the same; and so forth. The orbital energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are *4* orbitals with different electron density distributions in the n = 2 principal shell (one 2*s* and three 2*p* orbitals), *9* in the n = 3 principal shell, and *16* in the n = 4 principal shell.

For a single electron atom, the energy of that electron is a function of only the principal quantum number (Equation 2.1.12).

The different values of l and m_l for the individual orbitals within a given principal shell are not important for understanding the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic field. As we have just seen, however, quantum mechanics also predicts that in the hydrogen atom, all orbitals with the same value of n (e.g., the three 2p orbitals) are degenerate, meaning that they have the same energy. Figure **2.1.7** shows that the energy levels become closer and closer together as the value of n increases, as expected because of the $1/n^2$ dependence of orbital energies.

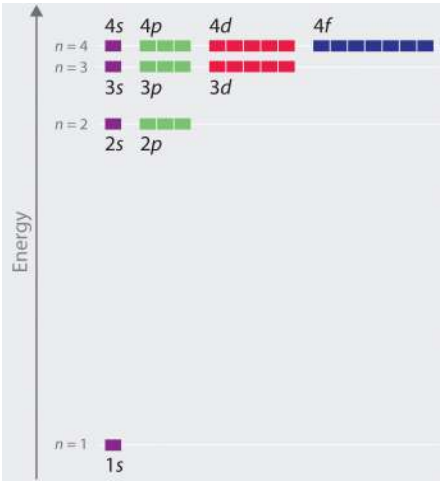


Figure **2.1.7**: Orbital energy level diagram for the hydrogen atom. Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of n.

In general, both energy and radius decrease as the nuclear charge increases. Thus the most stable orbitals (those with the lowest energy) are those closest to the nucleus. For example, in the ground state of the hydrogen atom, the single electron is in the 1s orbital, whereas in the first excited state, the atom has absorbed energy and the electron has been promoted to one of the n = 2 orbitals. In ions with only a single electron, the energy of a given orbital depends on only n, and all subshells within a principal shell, such as the p_x, p_y, and p_z orbitals, are degenerate.

Note: Bohr vs. Schrödinger

It is interesting to compare the results obtained by solving the Schrödinger equation with Bohr's model of the hydrogen atom. There are several ways in which the Schrödinger model and Bohr model differ.

1. First, and perhaps most strikingly, the Schrödinger model does not produce well-defined orbits for the electron. The wavefunctions only give us the probability for the electron to be at various directions and distances from the proton.
2. Second, the quantization of angular momentum is different from that proposed by Bohr. Bohr proposed that the angular momentum is quantized in integer units of $\hbar$, while the Schrödinger model leads to an angular momentum of $(l(l+1)\hbar^2)^{\frac{1}{2}}$.
3. Third, the quantum numbers appear naturally during solution of the Schrödinger equation while Bohr had to postulate the existence of quantized energy states. Although more complex, the Schrödinger model leads to a better correspondence between theory and experiment over a range of applications that was not possible for the Bohr model.

Electron Spin: The Fourth Quantum Number

The quantum numbers n, l, m_l are not sufficient to fully characterize the physical state of the electrons in an atom. In 1926, Otto Stern and Walther Gerlach carried out an experiment that could not be explained in terms of the three quantum numbers n, l, m_l and showed that there is, in fact, another quantum-mechanical degree of freedom that needs to be included in the theory. The experiment is illustrated in the Figure **2.1.8**. A beam of atoms (e.g. hydrogen or silver atoms) is sent through a spatially inhomogeneous magnetic field with a definite field gradient toward one of the poles. It is observed that the beam splits into two beams as it passes through the field region.

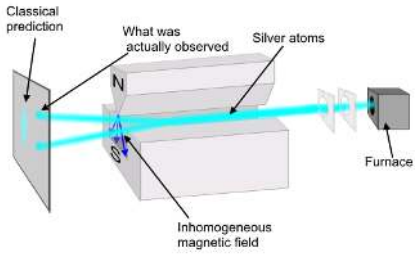


Figure **2.1.8**: The Stern-Gerlach apparatus. from Wikipedia

The fact that the beam splits into 2 beams suggests that the electrons in the atoms have a degree of freedom capable of coupling to the magnetic field. That is, an electron has an *intrinsic magnetic moment* $\boldsymbol{M}$ arising from a degree of freedom that has no classical analog. The magnetic moment must take on only 2 values according to the Stern-Gerlach experiment. The intrinsic property that gives rise to the magnetic moment is called *spin*, $\boldsymbol{S}$; unlike position and momentum, which have clear classical analogs, spin does not. The implication of the Stern-Gerlach experiment is that we need to include a fourth quantum number, $\boldsymbol{m_s}$ in our description of the physical state of the electron. That is, in addition to give its principal, angular, and magnetic quantum numbers, we also need to say if it is a spin-up electron or a spin-down electron.

Note: Spin is a Quantum Phenomenon

Unlike position and momentum, which have clear classical analogs, spin does not. Spin may be thought of as a relativistic phenomenon. Solutions to the relativistic form of the wave equation for an electron (Dirac equation) do require the inclusion of a spin quantum number.[1] This is related to the relativistic effect that leads to the generation of a magnetic field by moving charged particles.[2] For most situations it is not necessary to use the relativistic formulation and spin is just added as an extra quantum number with two values.

George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978), proposed that the splittings were caused by an electron spinning about its axis, much as Earth spins about its axis. When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet. Electrons are not spinning as they are a wave, but they do have a magnetic moment. The name electron spin stuck, despite not being particularly accurate.

The magnetic moment has two possible orientations, described by the fourth quantum number, $m_s = +½$ (up) and $m_s = −½$ (down). The subscript *s* is for spin. An electron behaves like a magnet that has one of two possible orientations, aligned either with the magnetic field or against it. The implications of electron spin for chemistry were recognized almost immediately by an Austrian physicist, Wolfgang Pauli (1900–1958; Nobel Prize in Physics, 1945), who determined that each orbital can contain no more than two electrons. This is usually referred to as **the Pauli exclusion principle**.

Pauli Exclusion Principle

No two electrons in an atom can have the same values of all four quantum numbers ($\boldsymbol{n}$, $\boldsymbol{l}$, $\boldsymbol{m_l}$, $\boldsymbol{m_s}$).

By giving the values of *n*, *l*, and m_l, we specify a particular orbital (e.g., 1*s* with $n = 1$, $l = 0$, $m_l = 0$). Because m_s has only two possible values (+½ or −½), two electrons, *and only two electrons*, can occupy any given orbital, one with spin up and one with spin down. With this information, we can proceed to construct the entire periodic table, which was originally based on the physical and chemical properties of the known elements.

Example 2.1.2

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in a 2*p* orbital and predict the maximum number of electrons the 2*p* subshell can accommodate.

Given: orbital

Asked for: allowed quantum numbers and maximum number of electrons in orbital

Strategy:

A. List the quantum numbers (n, l, m_l) that correspond to an $n = 2p$ orbital. List all allowed combinations of (n, l, m_l).
B. Build on these combinations to list all the allowed combinations of (n, l, m_l, m_s).
C. Add together the number of combinations to predict the maximum number of electrons the 2p subshell can accommodate.

Solution:

A For a 2p orbital, we know that $n = 2$, $l = n - 1 = 1$, and $m_l = -l$, $(-l + 1)$,…, $(l - 1)$, l. There are only three possible combinations of (n, l, m_l): (2, 1, 1), (2, 1, 0), and (2, 1, −1).

B Because m_s is independent of the other quantum numbers and can have values of only +½ and −½, there are six possible combinations of (n, l, m_l, m_s): (2, 1, 1, +½), (2, 1, 1, −½), (2, 1, 0, +½), (2, 1, 0, −½), (2, 1, −1, +½), and (2, 1, −1, −½).

C Hence the 2p subshell, which consists of three 2p orbitals (2p_x, 2p_y, and 2p_z), can contain a total of six electrons, two in each orbital.

? Exercise 2.1.2

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for a 6s orbital, and predict the total number of electrons it can contain.

Answer: (6, 0, 0, +½), (6, 0, 0, −½); two electrons

References

1. Leonard I. Schiff, *Quantum Mechanics*, 3rd Ed. (McGraw-Hill, New York, 1968) Pp. 480 - 481.

2. Paul Lorain and Dale Corson, *Electromagnetic Fields and Waves*, 2nd Ed. (W. H. Freeman and Co. New York, 1970) Chpt 6.

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2.2: Many-Electron Atoms and the Periodic Table

Quantum mechanics can account for the periodic structure of the elements, by any measure a major conceptual accomplishment for any theory. Although accurate computations become increasingly more challenging as the number of electrons increases, the general patterns of atomic behavior can be predicted with remarkable accuracy.

Figure **2.2.1** shows a schematic representation of a helium atom with two electrons whose coordinates are given by the vectors r_1 and r_2. The electrons are separated by a distance $r_{12} = |r_1 - r_2|$. The origin of the coordinate system is fixed at the nucleus. As with the hydrogen atom, the nuclei for multi-electron atoms are so much heavier than an electron that the nucleus is assumed to be the center of mass. Fixing the origin of the coordinate system at the nucleus allows us to exclude translational motion of the center of mass from our quantum mechanical treatment.

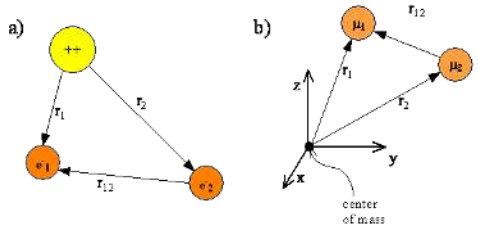


Figure **2.2.1 :** a) The nucleus (++) and electrons (e-) of the helium atom. b) Equivalent reduced particles with the center of mass (approximately located at the nucleus) at the origin of the coordinate system. Note that μ_1 and $\mu_2 \approx m_e$.

The Schrödinger equation operator for the hydrogen atom serves as a reference point for writing the Schrödinger equation for atoms with more than one electron. Start with the same general form we used for the hydrogen atom Hamiltonian

$$(\hat{T} + \hat{V})\psi = E\psi \tag{2.2.1}$$

Include a kinetic energy term for each electron and a potential energy term for the attraction of each negatively charged electron for the positively charged nucleus and a potential energy term for the mutual repulsion of each pair of negatively charged electrons. The He atom Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + V(r_1) + V(r_2) + V(r_{12})\right)\psi = E\psi \tag{2.2.2}$$

where

$$V(r_1) = -\frac{2e^2}{4\pi\epsilon_0 r_1} \tag{2.2.3}$$

$$V(r_2) = -\frac{2e^2}{4\pi\epsilon_0 r_2} \tag{2.2.4}$$

$$V(r_{12}) = +\frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{2.2.5}$$

Equation 2.2.2 can be extended to any atom or ion by including terms for the additional electrons and replacing the He nuclear charge +2 with a general charge Z; e.g.

$$V(r_1) = -\frac{Ze^2}{4\pi\epsilon_0 r_1} \tag{2.2.6}$$

Equation 2.2.2 then becomes

$$\left(-\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_i V(r_i) + \sum_{i \neq j} V(r_{ij})\right)\psi = E\psi \tag{2.2.7}$$

Given what we have learned from the previous quantum mechanical systems we've studied, we predict that exact solutions to the multi-electron Schrödinger equation would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue. These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the

hydrogen wavefunctions and their associated energies describe the ground and excited states of the hydrogen atom. We would predict quantum numbers to be involved, as well.

The fact that electrons interact through their electron-electron repulsion means that an exact wavefunction for a multi-electron system would be a single function that depends **simultaneously** upon the coordinates of all the electrons; i.e., a multi-electron wavefunction:

$$\Psi(r_1, r_2, \cdots r_i) \tag{2.2.8}$$

Unfortunately, the electron-electron repulsion terms make it impossible to find an exact solution to the Schrödinger equation for many-electron atoms. The most basic ansatz to the exact solutions involve writing a multi-electron wavefunction as a **simple product of single**-electron wavefunctions

$$\psi(r_1, r_2, \cdots, r_i) = \varphi_1(r_1)\varphi_2(r_2)\cdots\varphi_i(r_i) \tag{2.2.9}$$

Obtaining the energy of the atom in the state described by that wavefunction as the **sum** of the energies of the one-electron components.

By writing the multi-electron wavefunction as a product of single-electron functions in Equation 2.2.9, we conceptually transform a multi-electron atom into a collection of individual electrons located in individual orbitals whose spatial characteristics and energies can be separately identified. For atoms these single-electron wavefunctions are called atomic orbitals. For molecules, as we will see in the next chapter, they are called molecular orbitals. While a great deal can be learned from such an analysis, it is important to keep in mind that such a discrete, compartmentalized picture of the electrons is an approximation, albeit a powerful one.

Electron Configurations

The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom and is formulated via the *Aufbau* principle, which means "building-up" in German. Aufbau principles determine the order in which atomic orbitals are filled as the atomic number is increased. For the hydrogen atom, the order of increasing orbital energy is given by $1s < 2s = 2p < 3s = 3p = 3d$, etc. The dependence of energy on n alone leads to extensive degeneracy, which is however removed for orbitals in many-electron atoms. Thus $2s$ lies below $2p$, as already observed in helium. Similarly, $3s$, $3p$ and $3d$ increase energy in that order, and so on. The $4s$ is lowered sufficiently that it becomes comparable to $3d$. The general ordering of atomic orbitals is summarized in the following scheme:

$$\begin{aligned} &1s < 2s < 2p < 3s < 3p < 4s \sim 3d < 4p < 5s \sim 4d \\ &< 5p < 6s \sim 5d \sim 4f < 6p < 7s \sim 6d \sim 5f \end{aligned} \tag{2.2.10}$$

and illustrated in Figure 2.2.2. This provides enough orbitals to fill the ground states of all the atoms in the periodic table. For orbitals designated as comparable in energy, e.g., $4s \sim 3d$, the actual order depends which other orbitals are occupied. The energy of atomic orbitals increases as the principal quantum number, n, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of l differ so that the energy of the orbitals increases within a shell in the order $s < p < d < f$. Figure 2.2.2 depicts how these two trends in increasing energy relate. The $1s$ orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the $2s$ and then $2p$, $3s$, and $3p$ orbitals, showing that the increasing n value has more influence on energy than the increasing l value for small atoms. However, this pattern does not hold for larger atoms. The $3d$ orbital is higher in energy than the $4s$ orbital. Such overlaps continue to occur frequently as we move up the chart.

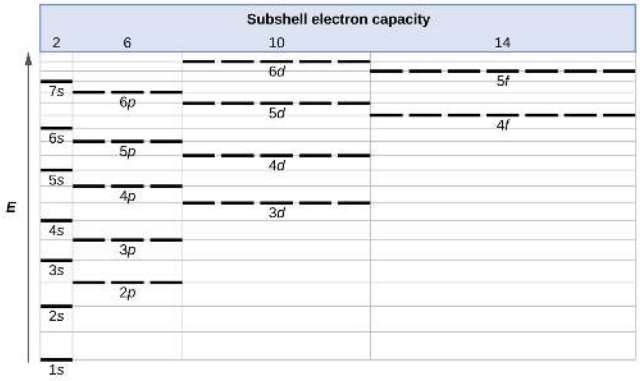


Figure **2.2.2**: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. The arrangement of electrons in the orbitals of an atom is called the electron configuration of the atom. We describe an electron configuration with a symbol that contains three pieces of information (Figure **2.2.3**):

1. The number of the principal quantum shell, *n*,
2. The letter that designates the orbital type (the subshell, *l*), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a *p* subshell ($l = 1$) with a principal quantum number (n) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the *d* subshell (i.e., $l = 2$) of the principal shell for which $n = 3$.

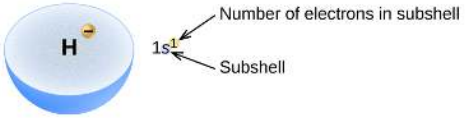


Figure **2.2.3**: The diagram of an electron configuration specifies the subshell (n and l value, with letter symbol) and superscript number of electrons.

To determine the electron configuration for any particular atom, we can “build” the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the Aufbau principle, from the German word *Aufbau* (“to build up”). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure **2.2.4**), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure **2.2.3** illustrates the traditional way to remember the filling order for atomic orbitals.

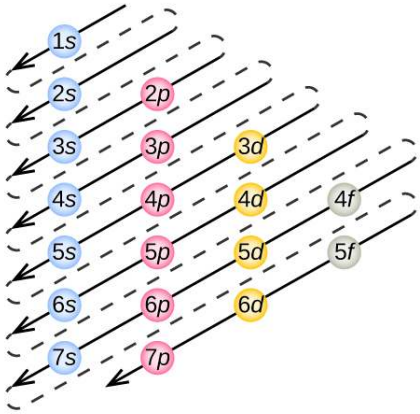
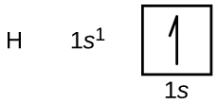


Figure **2.2.4**: The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed by the quantum numbers (no 1p or 2d, and so forth). Finally, draw diagonal lines from top to bottom as shown.

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. Orbital diagrams are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to either Figure **2.2.4**, we would expect to find the electron in the 1*s* orbital. By convention, the $m_s = +\frac{1}{2}$ value is usually filled first. The electron configuration and the orbital diagram are:

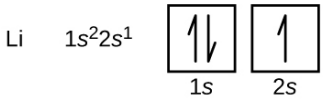


Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron (n = 1, l = 0, m_l = 0, $m_s = +\frac{1}{2}$). The second electron also goes into the 1*s* orbital and fills that orbital. The second electron has the same n, l, and m_l quantum numbers, but must have the opposite spin quantum number, $m_s = -\frac{1}{2}$. This is in accord with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:

In this figure, the element symbol H e is followed by the electron configuration, “1 s superscript 2.” An orbital diagram is provided that consists of a single square. The square is labeled below as “1 s.” It contains a pair of half arrows: one pointing up and the other down.

The n = 1 shell is completely filled in a helium atom.

The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1*s* orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2*s* orbital (Figure **2.2.4**). Thus, the electron configuration and orbital diagram of lithium are:

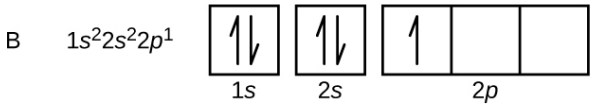


An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2*s* orbital.

In this figure, the element symbol B e is followed by the electron configuration, “1 s superscript 2 2 s superscript 2.” An orbital diagram is provided that consists of two individual squares. The first square is labeled below as, “1 s.” The second square is similarly labeled, “2 s.” Both squares contain a pair of half arrows: one pointing up and the other down.

An atom of boron (atomic number 5) contains five electrons. The n = 1 shell is filled with two electrons and three electrons will occupy the n = 2 shell. Because any *s* subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There are three degenerate 2*p* orbitals (m_l = −1, 0, +1) and the electron can occupy any one of these *p*

orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.



Carbon (atomic number 6) has six electrons. Four of them fill the 1*s* and 2*s* orbitals. The remaining two electrons occupy the 2*p* subshell. We now have a choice of filling one of the 2*p* orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, *p* orbitals. The orbitals are filled as described by Hund's rule: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2*p* orbitals have identical n, l, and m_s quantum numbers and differ in their m_l quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:

In this figure, the element symbol C is followed by the electron configuration, "1 s superscript 2 2 s superscript 2 2 p superscript 2." The orbital diagram consists of two individual squares followed by 3 connected squares in a single row. The first blue square is labeled below as, "1 s." The second is similarly labeled, "2 s." The connected squares are labeled below as, "2 p." All squares not connected to each other contain a pair of half arrows: one pointing up and the other down. The first two squares in the group of 3 each contain a single upward pointing arrow.

Nitrogen (atomic number 7) fills the 1*s* and 2*s* subshells and has one electron in each of the three 2*p* orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2*p* orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2*p* orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the $n = 1$ and the $n = 2$ shells are filled. The electron configurations and orbital diagrams of these four elements are:

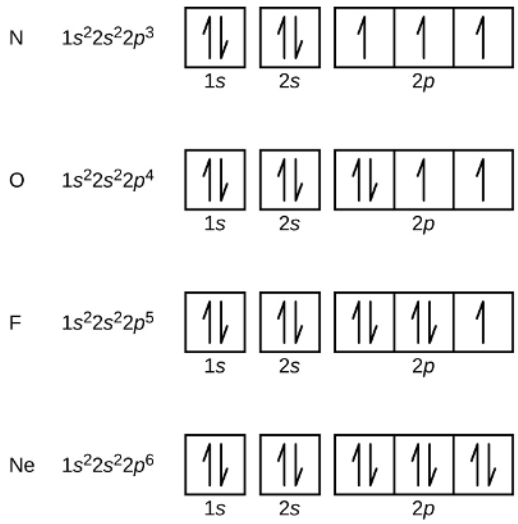


Figure **2.2.5**). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1\ s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is $[Ne]3s^1$.

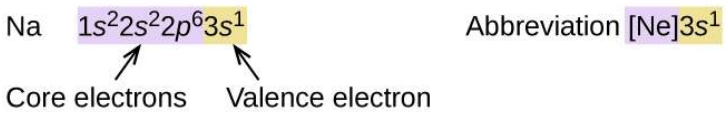


Figure **2.2.5**: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as $[He]2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence *s* subshell outside a filled set of inner shells.

$$\begin{aligned} \mathbf{Li} &: \mathbf{[He]}\, 2s^1 \\ \mathbf{Na} &: \mathbf{[Ne]}\, 3s^1 \end{aligned} \qquad (2.2.11)$$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a [Ne]$3s^2$ configuration, is analogous to its family member beryllium, [He]$2s^2$. Both atoms have a filled *s* subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration [Ne]$3s^23p^1$, is analogous to its family member boron, [He]$2s^22p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to $n = 3$. Figure

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the 3*d* subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [*d* orbitals], there are $2l + 1 = 5$ values of m_l, meaning that there are five *d* orbitals that have a combined capacity of 10 electrons). The 4*p* subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10 *d* electrons are successively added to the $(n – 1)$ shell next to the *n* shell to bring that $(n – 1)$ shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14 *f* electrons ($l = 3$, $2l + 1 = 7$ m_l values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the $(n – 2)$ shell to bring that shell from 18 electrons to a total of 32 electrons.

Example 2.2.1

Quantum Numbers and Electron Configurations What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, . . . The 15 electrons of the phosphorus atom will fill up to the 3*p* orbital, which will contain three electrons:



The last electron added is a 3*p* electron. Therefore, $n = 3$ and, for a *p*-type orbital, $l = 1$. The m_l value could be –1, 0, or +1. The three *p* orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of $+\frac{1}{2}$ for the spin quantum number; thus, $m_s = +\frac{1}{2}$.

Exercise 2.2.1

Identify the atoms from the electron configurations given:

a. [Ar]$4s^23d^5$
b. [Kr]$5s^24d^{10}5p^6$

Answer

(a) Mn (b) Xe

Effective Charge, Shielding and Penetration

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies.

If an electron is far from the nucleus (i.e., if the distance r between the nucleus and the electron is large), then at any given moment, most of the other electrons will be *between* that electron and the nucleus. Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Z_{eff}) that is *less* than the actual nuclear charge Z (Figure **2.2.6**). This effect is called electron shielding.

As the distance between an electron and the nucleus approaches infinity, Z_{eff} approaches a value of 1 because all the other $(Z - 1)$ electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{eff} \approx Z$. At intermediate values of r, the effective nuclear charge is somewhere between 1 and Z: $1 \le Z_{eff} \le Z$. Thus the actual Z_{eff} experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present. This leads to large differences in Z_{eff} for different elements, as shown in Figure 2.5.1 for the elements of the first three rows of the periodic table. Notice that only for hydrogen does $Z_{eff} = Z$, and only for helium are Z_{eff} and Z comparable in magnitude.

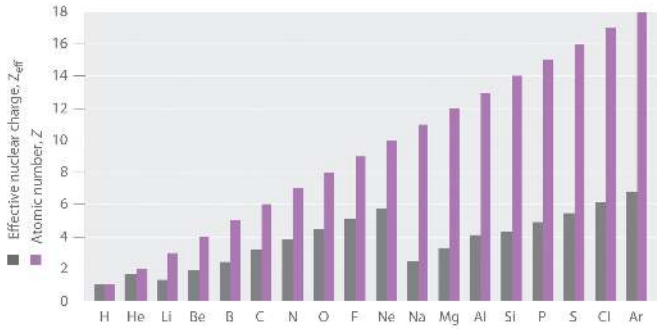


Figure **2.2.6**: Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the Periodic Table. Except for hydrogen, Z_{eff} is *always* less than Z, and Z_{eff} increases from left to right as you go across a row.

Because of the effects of shielding and the different radial distributions of orbitals with the same value of n but different values of l, the different subshells are not degenerate in a multielectron atom. For a given value of n, the ns orbital is always lower in energy than the np orbitals, which are lower in energy than the nd orbitals, and so forth. As a result, some subshells with higher principal quantum numbers are actually lower in energy than subshells with a lower value of n; for example, the 4s orbital is lower in energy than the 3d orbitals for most atoms.

Note

Except for the single electron containing hydrogen atom, in every other element Z_{eff} is always less than Z.

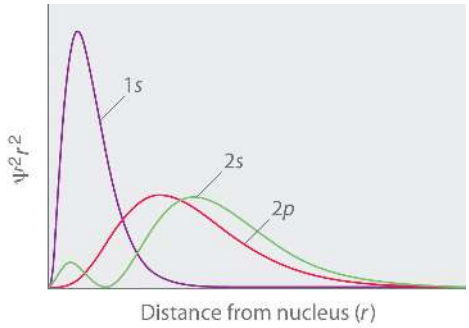


Figure **2.2.7**: Orbital Penetration. A comparison of the radial probability distribution of the 2 s and 2p orbitals for various states of the hydrogen atom shows that the 2s orbital penetrates inside the 1s orbital more than the 2p orbital does. Consequently, when an electron is in the small inner lobe of the 2s orbital, it experiences a relatively large value of Z_{eff}, which causes the energy of the 2s orbital to be lower than the energy of the 2p orbital.

Ionization Energy

Ionization energy is the energy required to remove an electron from a neutral atom in its gaseous phase. Conceptually, ionization energy is the opposite of electronegativity. The lower this energy is, the more readily the atom becomes a cation. Therefore, the higher this energy is, the more unlikely it is the atom becomes a cation. Generally, elements on the right side of the periodic table have a higher ionization energy because their valence shell is nearly filled. Elements on the left side of the periodic table have low ionization energies because of their willingness to lose electrons and become cations. Thus, ionization energy increases from left to right on the periodic table.

Another factor that affects ionization energy is *electron shielding*. Electron shielding describes the ability of an atom's inner electrons to shield its positively-charged nucleus from its valence electrons. When moving to the right of a period, the number of electrons increases and the strength of shielding increases. As a result, it is easier for valence shell electrons to ionize, and thus the ionization energy decreases down a group. Electron shielding is also known as *screening*.

Note

- The ionization energy of the elements within a period generally increases from left to right. This is due to valence shell stability.
- The ionization energy of the elements within a group generally decreases from top to bottom. This is due to electron shielding.
- The noble gases possess very high ionization energies because of their full valence shells as indicated in the graph. Note that helium has the highest ionization energy of all the elements.

Some elements have several ionization energies; these varying energies are referred to as the first ionization energy, the second ionization energy, third ionization energy, etc. The first ionization energy is the energy requiredto remove the outermost, or highest, energy electron, the second ionization energy is the energy required to remove any subsequent high-energy electron from a gaseous cation, etc. Below are the chemical equations describing the first and second ionization energies:

First Ionization Energy:

$$X_{(g)} \rightarrow X^{+}_{(g)} + e^{-} \tag{2.2.12}$$

Second Ionization Energy:

$$X^{+}_{(g)} \rightarrow X^{2+}_{(g)} + e^{-} \tag{2.2.13}$$

Generally, any subsequent ionization energies (2nd, 3rd, etc.) follow the same periodic trend as the first ionization energy.

Ionization energies decrease as atomic radii increase. This observation is affected by n (the principal quantum number) and Z_{eff} (based on the atomic number and shows how many protons are seen in the atom) on the ionization energy (I). The relationship is given by the following equation:

$$I = \frac{R_H Z^2_{eff}}{n^2} \tag{2.2.14}$$

- Across a period, Z_{eff} *increases* and n (principal quantum number) *remains the same*, so the ionization energy *increases*.
- Down a group, n *increases* and Z_{eff} *increases slightly;* the ionization energy *decreases*.

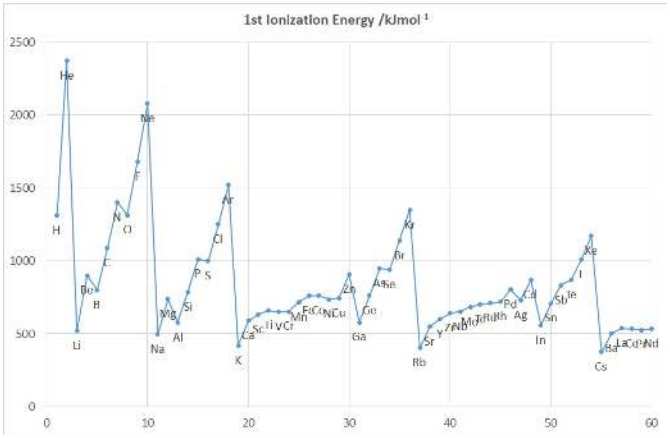


Figure **2.2.8**: Periodic trends in ionization energy.

The periodic structure of the elements is evident for many physical and chemical properties, including chemical valence, atomic radius, electronegativity, melting point, density, and hardness. The classic prototype for periodic behavior is the variation of the first ionization energy with atomic number, which is plotted in Figure **2.2.8**.

Electron Affinity

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

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \tag{2.2.15}$$

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

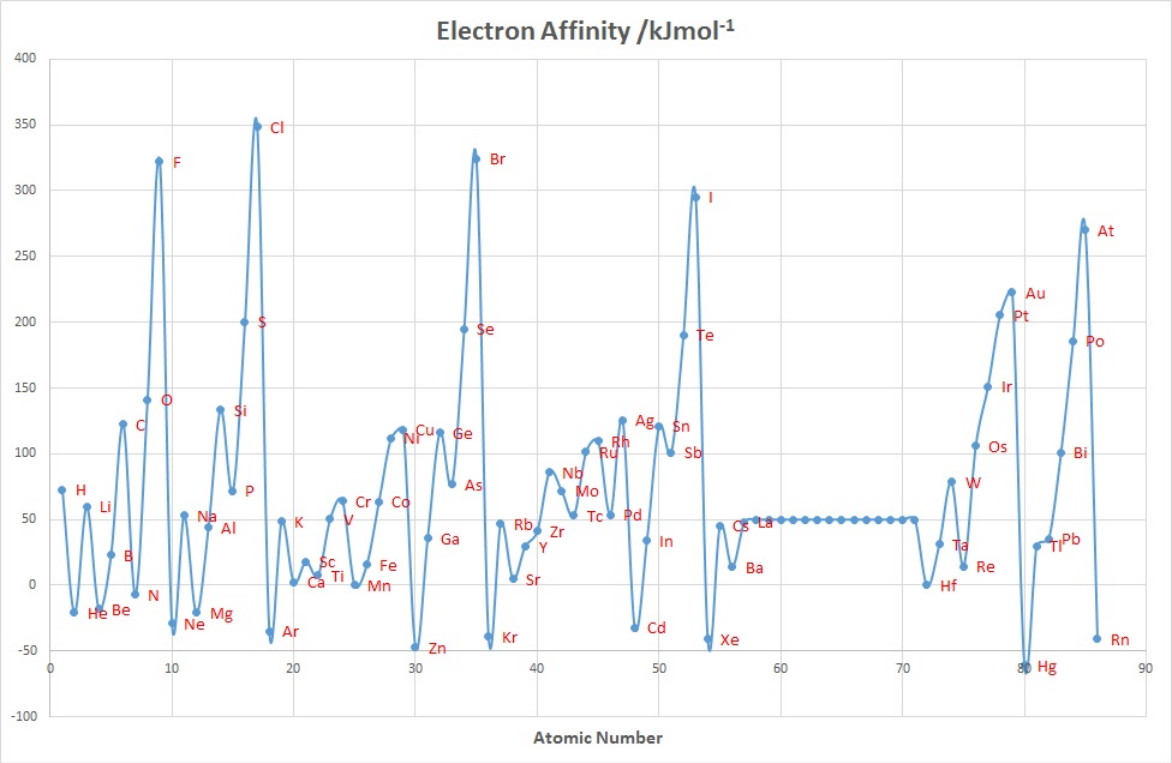


Figure* 2.2.9*: *Periodic trends in electron affinities.*

The periodic trends of electron affinity (Figure **2.2.9**) shows that chlorine has the most positive electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element, EA= 348.6 kJmol^{-1} and the Group 17 elements have the largest values overall. The addition of a second electron to an element is expected to be much less favored since there will be repulsion between the negatively charged electron and the overall negatively charged anion. For example, for O the values are:

$$O_{(g)} + e^{\rightarrow} O^{-}_{(g)} \quad EA = +141\ kJmol^{-1} \tag{2.2.16}$$

$$O^{-}_{(g)} + e^{-} \rightarrow O^{2-})(g) \quad EA = -798\ kJmol^{-1} \tag{2.2.17}$$

David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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2.3: Quantum-Mechanical Tunneling

Tunneling is a quantum mechanical phenomenon when a particle is able to penetrate through a potential energy barrier that is higher in energy than the particle's kinetic energy. This amazing property of microscopic particles play important roles in explaining several physical phenomena including radioactive decay. Additionally, the principle of tunneling leads to the development of Scanning Tunneling Microscope (STM) which had a profound impact on chemical, biological and material science research.

Violating Classical Mechanics

Consider a ball rolling from one valley to another over a hill (Figure **2.3.1**). If the ball has enough energy (E) to overcome the potential energy (V) at the top of the barrier between each valley, then it can roll from one valley to the other. This is the classical picture and is controlled by the simple Law of Conservation of Energy approach taught in beginning physics courses. However, If the ball does not have enough kinetic energy ($E < V$), to overcome the barrier it will never roll from one valley to the other. In contrast, when quantum effects are taken into effect, the ball can "tunnel" through the barrier to the other valley, even if its kinetic energy is less than the potential energy of the barrier to the top of one of the hills.

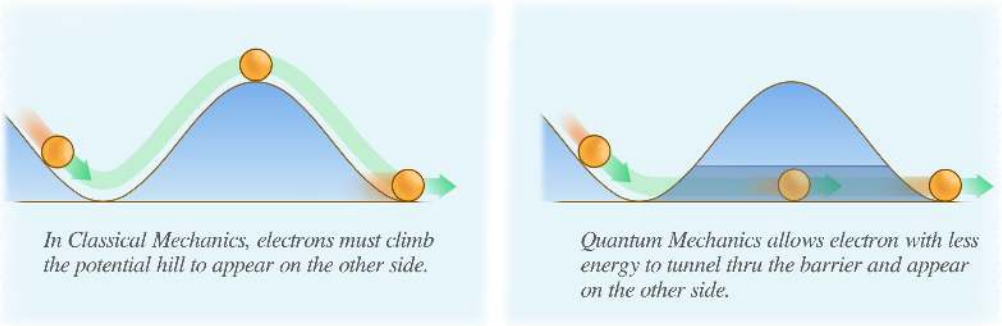


Figure **2.3.1**: Contrasting classical (over the barrier) motion vs. quantum (through the barrier) motion. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

The Heisenberg Uncertainty Principle in Action

The reason for the difference between classical and quantum motion comes from wave-particle nature of matter. One interpretation of this duality involves the Heisenberg uncertainty principle, which defines a limit on how precisely the position and the momentum of a particle can be known at the same time. This implies that there are no solutions with a probability of exactly zero (or one), though a solution may approach infinity if, for example, the calculation for its position was taken as a probability of 1, the other, i.e. its speed, would have to be infinity. Hence, the probability of a given particle's existence on the opposite side of an intervening barrier is non-zero, and such particles will appear on the 'other' (a semantically difficult word in this instance) side with a relative frequency proportional to this probability.

Microscopic particles such as protons, or electrons would behave differently as a consequence of wave-particle duality. Consider a particle with energy E that is confined in a box which has a barrier of height V. Classically, the box will prevent these particles from escaping due to the insufficiency in kinetic energy of these particles to get over the barrier. However, if the thickness of the barrier is thin, the particles have some probability of penetrating through the barrier **without** sufficient energy and appear on the other side of the box (Figure **2.3.2**).

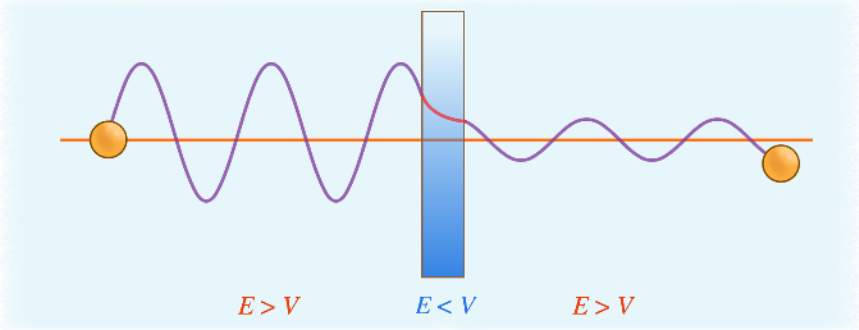


Figure **2.3.2**: Quantum tunneling through a barrier. The energy of the tunneled particle is the same but the amplitude is decreased. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

When it reaches a barrier it cannot overcome, a particle's wave function changes from sinusoidal to exponentially diminishing in form. The solution for the Schrödinger equation in such a medium (Figure **2.3.2**; blue region) is:

$$\psi = Ne^{-\beta x} \tag{2.3.1}$$

where

- N is a normalization constant and
- $\beta = \sqrt{\frac{2m(V-E)}{\hbar^2}}$

For a quantum particle to *appreciably* tunnel through a barrier three conditions must be met (Figure **2.3.2**):

1. The height of the barrier must be **finite** and the thickness of the barrier should be **thin**.
2. The potential energy of the barrier exceeds the kinetic energy of the particle ($E < V$).
3. The particle has wave properties because the wavefunction is able to penetrate through the barrier. This suggests that quantum tunneling only apply to microscopic objects such protons or electrons and does not apply to macroscopic objects.

If these conditions are met, there would be some probability of finding the particles on the other side of the barrier. Beginning as a sinusoidal wave, a particle begins tunneling through the barrier and goes into exponential decay until it exits the barrier and gets transmitted out the other side as a final sinusoidal wave with a smaller amplitude. The act of tunneling decreases the wave amplitude due the reflection of the incident wave when it comes into the contact with the barrier but does not affect the wave equation.

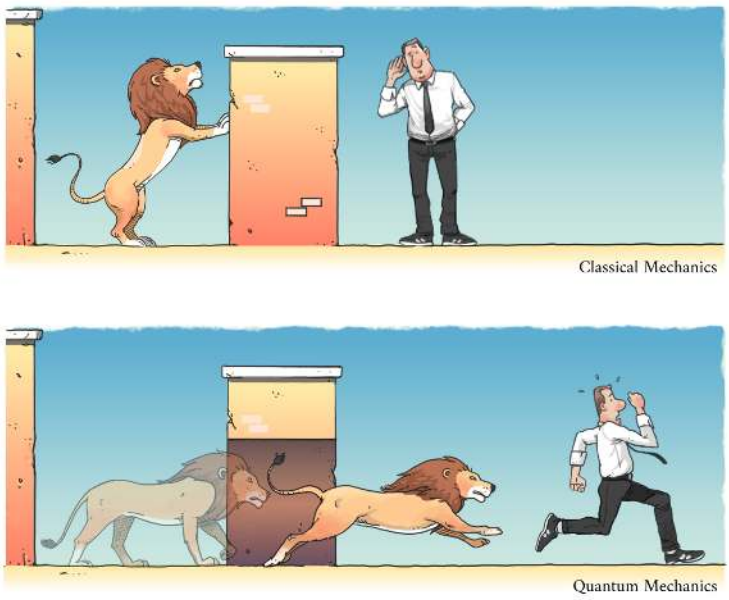


Figure 2.3.3: Quantum tunnelling of alion through a barrier is a quantum effect with no classical analog. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

The probability, P, of a particle tunneling through the potential energy barrier is derived from the Schrödinger Equation and is described as,

$$P = \exp\left(\frac{-4a\pi}{h}\sqrt{2m(V-E)}\right) \tag{2.3.2}$$

with $E < V$

where

- V is the potential barrier,
- E is the kinetic energy possessed by the particle, and
- a is the thickness of the barrier.
- m is mass of the particle
- h is Planks Constant ($6.6260 \times 10^{-34} m^2 kg/s$)

Therefore, the probability of an object tunneling through a barrier decreases with the object's increasing mass and with the increasing gap between the energy of the object and the energy of the barrier. And although the wave function never quite reaches 0 (as can be determined from the functionality), this explains how tunneling is frequent on nanoscale, but negligible at the macroscopic level. Equation 2.3.2 argues that the probability of tunneling decreases exponentially with the square root of the particles mass (particles with a small mass can effectively tunnel through barriers more easily than those with larger mass) and the thickness of the barrier (a)

Example 2.3.1

An electron having total kinetic energy E of 4.50 eV approaches a rectangular energy barrier with $V = 5.00\,eV$ and $L = 950\,pm$. Classically, the electron cannot pass through the barrier because $E < V$. Calculate probability of tunneling of this electron through the barrier.

Solution

This is a straightforward application of Equation 2.3.2.

$$P = \exp\left(\frac{-4a\pi}{h}\sqrt{2m(V-E)}\right)$$

The electronvolt (eV) is a unit of energy that is equal to approximately $1.6 \times 10^{-19}\ J$, which is the conversion used below.

The mass of an electron is $9.10 \times 10^{-31}\ kg$

$$P = \exp\left[\left(-\frac{(4)(950 \times 10^{-12}\ m)(\pi)}{6.6260 \times 10^{-34} m^2 kg/s}\right)\right.$$
$$\left.\sqrt{(2)(9.10 \times 10^{-31}\ kg)(5.00 - 4.50\ \cancel{eV})(1.60 \times 10^{-19} J/\cancel{eV})}\right]$$
$$= \exp^{-6.88} = 1.03 \times 10^{-3}$$

There is a ~0.1% probability of the electrons tunneling though the barrier.

Alpha Decay Radioactivity

Protons and neutrons in a nucleus have kinetic energy, but it is about 8 MeV less than that needed to get out from attractive nuclear potential (Figure 2.3.4). Hence, they are bound by an average of 8 MeV per nucleon. The slope of the hill outside the bowl is analogous to the repulsive Coulomb potential for a nucleus, such as for an α particle outside a positive nucleus. In α decay, two protons and two neutrons spontaneously break away as a ^{4}He unit. Yet the protons and neutrons do not have enough kinetic energy to classically get over the rim.

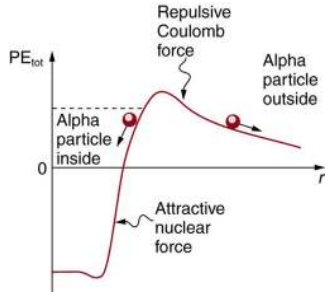


Figure 2.3.4: Nucleons within an atomic nucleus are bound or trapped by the attractive nuclear force, as shown in this simplified potential energy curve. An particle outside the range of the nuclear force feels the repulsive Coulomb force. The α particle inside the nucleus does not have enough kinetic energy to get over the rim, yet it does manage to get out by quantum mechanical tunneling. (CC BY; OpenStax)

The α article tunnels through a region of space it is forbidden to be in, and it comes out of the side of the nucleus. Like an electron making a transition between orbits around an atom, it travels from one point to another without ever having been in between (Figure 2.3.5). The wave function of a quantum mechanical particle varies smoothly, going from within an atomic nucleus (on one side of a potential energy barrier) to outside the nucleus (on the other side of the potential energy barrier). Inside the barrier, the wave function does not become zero but decreases exponentially, and we do not observe the particle inside the barrier. The probability of finding a particle is related to the square of its wave function, and so there is a small probability of finding the particle outside the barrier, which implies that the particle can tunnel through the barrier.

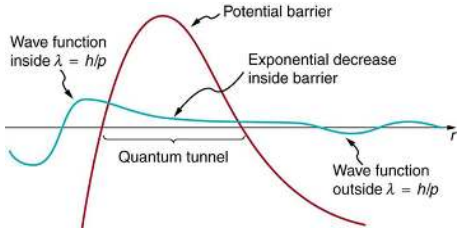


Figure 2.3.5: The wave function representing a quantum mechanical particle must vary smoothly, going from within the nucleus (to the left of the barrier) to outside the nucleus (to the right of the barrier). Inside the barrier, the wave function does not abruptly become zero; rather, it decreases exponentially. Outside the barrier, the wave function is small but finite, and there it smoothly becomes sinusoidal. Owing to the fact that there is a small probability of finding the particle outside the barrier, the particle can tunnel through the barrier. (CC BY; OpenStax)

Scanning Tunneling Microscopy (STM)

A metal tip usually made out of tungsten is placed between a very small distance above a conducting or semiconducting surface. This distance acts as a potential barrier for tunneling. The space between the tip and the surface normally is vacuum. When electrons tunnel from the metal tip to the surface, a current is created and monitored by a computer (Figure **2.3.6**). The current depends on the distance between the tip and the surface, which is controlled by a piezoelectric cylinder. If there is a strong current, the tip will move away from the surface. The increase of the potential barrier will decrease the probability of tunneling and decrease the current. If the current becomes too weak, the tip moves closer to the surface. The potential barrier will be reduced and the current will increase. The variations in the current as the tip moves over the sample are reconstructed by the computer to produce topological image of the scanned surface.

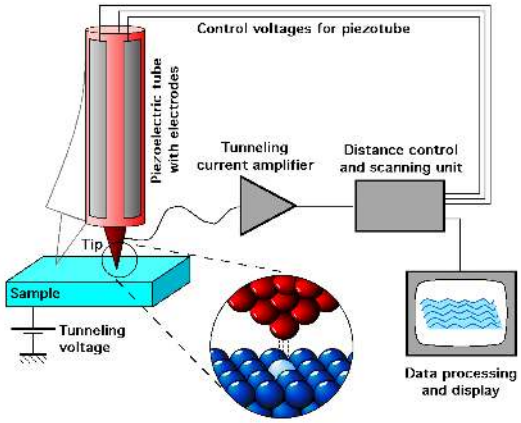


Figure **2.3.6**: Schematic diagram of a scanning tunneling microscope. (CC BY-SA 2.0 Austria; Michael Schmid via Wikipedia).

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CHAPTER OVERVIEW

3: Chemical Bond

3.1: Lewis Structures
3.2: Valence Bond Theory
3.3: Hybridization of Atomic Orbitals
3.4: Molecular Orbital Theory
3.5: Diatomic Molecules
3.6: Electronegativity and Dipole Moment
3.7: Photoelectron Spectroscopy

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3.1: Lewis Structures

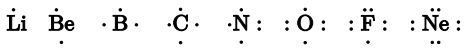
Chemical bond refers to the forces holding atoms together to form molecules and solids. This force is of an electric nature, and the attraction between electrons of one atom to the nucleus of another atom contributes to what is known as **chemical bonds**. Various theories regarding chemical bonds have been proposed over the past 300 years, during which our interpretation of the world has also changed. Some old concepts such as Lewis dot structure and valency are still rather useful in our understanding of the chemical properties of atoms and molecules, and new concepts involving quantum mechanics of chemical bonding interpret modern observations very well. You learn new concepts such as bond length, bond energy, bond order, covalent bond, ionic bond, polar and non-polar bond etc. These concepts help you understand the material world at the molecular level.

Of the three primary theories of bonding discussed in this class (Lewis Theory, Valance Bond Theory and Molecular orbital theory), Lewis theory does not take full advantage of the quantum mechanical concepts discussed previously. Key to this theory is the Lewis Structure, which is a very simplified representation of the electrons in a molecule and is use to show how the electrons are arranged around individual atoms in a molecule. Between 1916 and 1919, Gilbert Newton Lewis, Walther Kossel, and Irving Langmuir formulated a theory to explain chemical bonding. This theory is now called **Lewis Theory** and it is based on the following five principles:

1. **Valence electrons**, or the electrons in the outermost electron shell, have an essential role in chemical bonding.
2. **Ionic bonds** are formed between atoms when electrons are transferred from one atom to another. Ionic bond is a bond between nonmetals and metals .
3. **Covalent bonds** are formed between atoms when pairs of electrons are shared between atoms. A covalent bond is between two nonmetals.
4. Electrons are transferred/shared so that each atom may reach a more stable electron configuration, i.e., the noble gas configuration which contains 8 valence electrons; this is called **octet rule**.
5. Although many different Lewis structures can be constructed, those that are most stable have the lowest formal charge on the atoms.

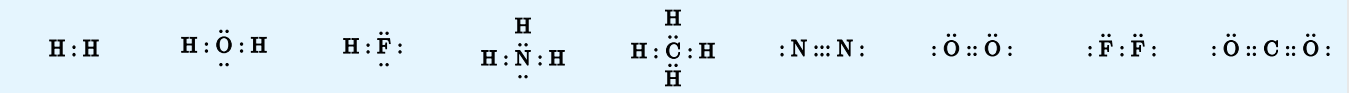
Writing out Lewis structures can be at times, tricky and somewhat difficult. Moreover, a compound can have multiple Lewis Structures that contribute to the shape of the overall compound, so one Lewis structure of a compound may not necessarily be exactly what the compound looks like. If you need a refresher on how to constructing Lewis Structures consult the following Modules: Writing Lewis Structures, Lewis Structures I and Lewis Structures II.

In Lewis Structures, valence electrons are represented as dots and only outer-shell electrons are considered (e.g., the valence electrons and not the core electrons). Single (covalent) bonds are made up of two shared electrons and are represented by two dots between the bonded atoms or a single line. Double bonds and triple bonds are represented as two and three lines/(pairs of electrons), respectively. Lone pairs on the outer rims of an atom are represented as two dots. This is because they are the ones involved in chemical reactions. For the 2nd and 3rd periods elements, the number of valence electrons range from 1 to 8. Lewis dot structure for them are as indicated:



(3.1.1)

Lewis made the valence electron visible with dots. Other examples include the following molecules:



Note

Lewis structure does NOT attempt to explain the geometry of molecules, how the bonds form, or how the electrons are shared between the atoms. It is the simplest and most limited theory on electronic structure.

Principle 1: Valence Electrons

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

The electron configuration of the oxygen atoms is

$$O: 1s^2 2s^2 2p^4 \tag{3.1.2}$$

As discussed before, this configuration may be shorted

$$O: [He] 2s^2 2p^4 \tag{3.1.3}$$

where the $[He]$ stands for the configuration of helium ($1s^2 2s^2$). The $1s$ electrons in oxygen (Equation 3.1.2) do not participate in bonding, i.e., chemistry, and are called **core electrons**. The other electrons (i.e., the $2s^2 2p^4$ part) are call **valence electrons** and are responsible for the making and breaking of chemical bonds.

The configuration of calcium with 20 electrons can be written

$$Ca: [Ar] 4s^2 \tag{3.1.4}$$

where the $[Ar]$ stands for the configuration of argon ($1s^2 2s^2 2p^6 3s^2 3p^6$). Electronic configurations that are the same as noble gases are very stable since they have a full octet (except helium with a full 1s orbital). The electrons in the argon-like closed shell of Equation 3.1.4 are the core electrons and the two electrons in the 4s orbital are valence electrons.

Example 3.1.1: Cobalt

What are the core and valence electrons in cobalt?

Solution

Start by writing the electron configuration of cobalt (i.e., 27 electrons):

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

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

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

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

Principle 2: Ionic Bonding

In ionic bonding, electrons are transferred from one atom to another resulting in the formation of positive and negative ions. The electrostatic attractions between the positive and negative ions hold the compound together. The predicted overall energy of the ionic bonding process, which includes the ionization energy of the metal and electron affinity of the nonmetal, is usually positive, indicating that the reaction is endothermic and unfavorable. However, this reaction is highly favorable because of their electrostatic attraction.

The energy of the electrostatic attraction (E), a measure of the force's strength, is inversely proportional to the internuclear distance between the charged particles (r):

$$E = k\frac{Q_1 Q_2}{r} \tag{3.1.5}$$

where each ion's charge is represented by the symbol Q. The proportionality constant k is equal to 2.31×10^{-28} J·m.

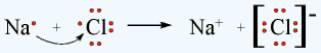
Example 3.1.2: Ionic Bonding in NaCl

For example, in the reaction of Na (sodium) and Cl (chlorine), each Cl atom takes one electron from a Na atom. Therefore each Na becomes a Na^+ cation and each Cl atom becomes a Cl^- anion. Due to their opposite charges, they attract each other to form an ionic lattice. The formula (ratio of positive to negative ions) in the lattice is **NaCl**.

$$2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$$

Sodium has one valence electron and chlorine has seven valence electrons; the two elements react such that the chlorine atom takes the valence electron from the sodium atom leaving the chlorine atom with one extra electron and thus negatively charged and the Sodium atom without an electron and thus positively charged. The two atoms then become ions and because of their opposite charges the ions are held together in an ionic bond (Equation 3.1.5).

The chlorine has a high affinity for electrons, and the sodium has a low ionization potential. Thus the chlorine gains an electron from the sodium atom. The Lewis Structure of this reaction is (here we will consider one chlorine atom, rather than Cl_2) is:

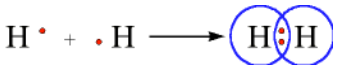


The arrow indicates the transfer of the electron from sodium to chlorine to form the Na^+ metal ion and the Cl^- chloride ion

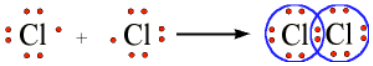
Principle 3: Covalent Bonding

Covalent bonding occurs when pairs of electrons are shared by atoms. Atoms will covalently bond with other atoms in order to gain more stability, which is gained by forming a full electron shell. By sharing their outer most (valence) electrons, atoms can fill up their outer electron shell and gain stability. Nonmetals will readily form covalent bonds with other nonmetals in order to obtain stability, and can form anywhere between one to three covalent bonds with other nonmetals depending on how many valence electrons they posses. Although it is said that atoms share electrons when they form covalent bonds, they do not usually share the electrons equally.

The diatomic hydrogen molecule (H_2) is the simplest model of a covalent bond, and is represented in Lewis structures as:



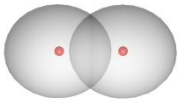
The ***shared pair*** of electrons provides ***each*** hydrogen atom with two electrons in its valence shell (the 1*s*) orbital. In a sense, it has the electron configuration of the noble gas helium. When two chlorine atoms covalently bond to form Cl_2Cl_2, the following sharing of electrons occurs:



Each chlorine atom shared the bonding pair of electrons and achieves the electron configuration of the noble gas argon. In Lewis structures the bonding pair of electrons is usually displayed as a line, and the unshared electrons as dots:



The shared electrons are not located in a fixed position between the nuclei. In the case of the H_2H_2 compound, the electron density is concentrated between the two nuclei:



The two atoms are bound into the H_2H_2 molecule mainly due to the attraction of the positively charged nuclei for the negatively charged electron cloud located between them.

Example 3.1.3: The Chlorate Ion

Draw the Lewis Structure for the chlorate ion (ClO_3^-).

Solution

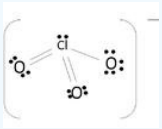
First, lets find the how many valence electrons chlorate has:

$$ClO_3^-: 7\ e^-\text{(from Cl)} + 3(6)\ e^-\text{(from 3 O atoms)} + 1\ \text{(from the total charge of -1)} = 26$$

There are 26 valence electrons. Next lets draw the basic framework of the molecule:



The molecule uses covalent bonds to hold together the atoms to the central Chlorine. The remaining electrons become non-bonding electrons. Since 6 electrons were used for the bonds, the 20 others become those un-bonding electrons to complete the octet:



The oxygen atom's shells fill up with 18 electrons, and the other 2 complete Chlorine's octet

Example 3.1.4: Formaldehyde

Constructing the Lewis Structure of the formaldehyde (H_2CO) molecule.

Solution

First find number of valence electrons:

$$H_2CO: 2(1)\ e^-\text{ (from the H atoms)} + 4\ e^-\text{ (from the C atom)} + 6\ e^-\text{ (from the O atom)}$$

There are 12 valence electrons. Next draw out the framework of the molecule:



To satisfy the octet of Carbon, one of the pairs of electrons on Oxygen must be moved to create a double bond with Carbon. Therefore our Lewis Structure would look as it does below:



The Hydrogen atoms are each filled up with their two electrons and both the Carbon and the Oxygen atoms' octets are filled.

Principle 4: The Octet Rule

The **octet rule** is a chemical **rule** of thumb that reflects observation that atoms of main-group elements tend to combine in such a way that each atom has eight electrons in its valence shell, giving it the same electronic configuration as a noble gas. The **Octet Rule** requires all atoms in a molecule to have 8 valence electrons--either by sharing, losing or gaining electrons--to become stable. For covalent bonds, atoms to share their electrons with each other to satisfy the octet rule. It requires eight electrons because that is the amount of electrons needed to fill a *s*- and *p*- orbital (electron configuration); also known as a noble gas configuration. Although it is important to remember the "magic number" is 8, but there are many octet rule exceptions.

Octet Rule

A stable arrangement is attended when the atom is surrounded by eight electrons. This octet can be made up by own electrons and some electrons which are donated (e.g, ionic bonding) or shared (covalent bonding). An atom continues to form bonds until an octet of electrons is reached.

For the first rows in the periodic table, the magic number 8 can easily be explained from quantum mechanics of the multiple electron atoms discussed previously. In particular, electrons possess four quantum numbers (usually n, l, m_l, and m_s), which are restricted as such:

$$n = 1, 2, 3, ... \tag{3.1.6}$$

$$l = 0, 1, 2, ..., n-1 \tag{3.1.7}$$

$$m_l = -l, -l+1, ..., 0, ..., l-1, l \tag{3.1.8}$$

$$m_s = -\frac{1}{2}, \frac{1}{2} \tag{3.1.9}$$

where

- n is the principal quantum number (dealing with energy states),
- l is the orbital quantum number (dealing with subshells),
- m_l is the orbital magnetic quantum number (direction of l) and
- m_s is the spin quantum number (direction of spin).

By the Pauli's Exclusion Principle all of these numbers cannot be the same for any two electrons in an atom. So in the $n = 2$ shell you can have two possible values for l, one possible value for m_l when $l = 0$, three possible values for m_l when $l = 1$, and two possible values for m_s. This sums to a total of eight possible value vectors:

$$(1 + 3) \cdot 2 = 8 \tag{3.1.10}$$

In the $n = 3$ shell, the Octet rule also holds for $l < 2$, which gives you sort of the same combinatorics all over again.

Since the quantum numbers cannot be the same for any electrons in an atom, adding an extra electron to an atom with eight electrons in its outermost shell forces the electron to occupy an orbital with a higher principal quantum number (n). Since the binding energy of the electron increases with n, this is energetically unfavorable to binding with an atom that has more space in its outermost shell. For example, for the nonmetals (and the 's' block metals) to achieve an octet, the number of valence electrons is equal to the group number (Table **3.1.1**).

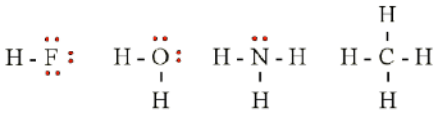
Table **3.1.1**: Select electronic properties of p-block elements of the 2nd row.

Element	Group	Valence electrons	Number of Covalent Bonds needed to form valence octet
F	17	7	1
O	16	6	2
N	15	5	3
C	14	4	4

Note: The 18 Electron Rule

The octet rule is not a law and it only works for a handful of elements, mainly the second-row p-block ones; there are many exceptions. Transition metals compounds often have 18 electrons on the metal atom because eighteen is the number of electrons in the nearest noble gas configuration in transition metals, which includes s + p + d electrons. The second and third row of transition metals have f electrons, too, but we usually simplify and don't worry about those electrons for electron counting purposes; we treat them like core electrons, not valence electrons.

Lewis theory successfully describe the covalent interactions between various nonmetal elements. Examples of hydride compounds of the elements in Table 12.2.1 (covalent compounds with hydrogen):



The sharing of a pair of electrons represents a single covalent bond, usually just referred to as a ***single bond***. However, in many molecules atoms attain complete octets by sharing more than one pair of electrons between them.

- Two electron pairs shared a ***double bond***
- Three electron pairs shared a ***triple bond***



Because each nitrogen contains five valence electrons, they need to share three pairs to each achieve a valence octet. The strong nitrogen triple bond makes the molecule fairly inert. Moreover, the N - N bond distance in N_2 is 1.10 Å, which is appreciably shorter than the average N-N single bonds (14.7Å).

Principle 5: Formal Charges

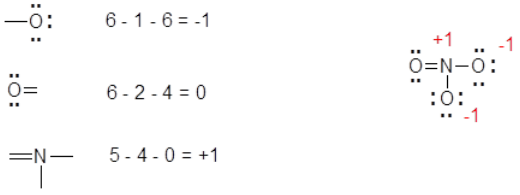
It is sometimes possible to write more than one Lewis structure for a substance that does not violate the octet rule, as we saw for CH_2O, but not every Lewis structure may be equally reasonable. In these situations, we can choose the most stable Lewis structure by considering the formal charge on the atoms, which is the difference between the number of valence electrons in the free atom and the number assigned to it in the Lewis electron structure. The formal charge is a way of computing the charge distribution within a Lewis structure; the sum of the formal charges on the atoms within a molecule or an ion must equal the overall charge on the molecule or ion. A formal charge does *not* represent a true charge on an atom in a covalent bond but is simply used to predict the most likely structure when a compound has more than one valid Lewis structure. To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- Nonbonding electrons are assigned to the atom on which they are located.
- Bonding electrons are divided equally between the bonded atoms.

For each atom, we then compute a formal charge:

$$\text{formal charge} = \underset{(\textit{free atom})}{\textit{valence } e^-} - \underset{(\textit{atom in Lewis structure})}{\left(\textit{nonbonding } e^- + \frac{\textit{bonding } e^-}{2}\right)} \tag{3.1.11}$$

The most favorable Lewis Structure has the smallest formal charge for the atoms, and negative formal charges tend to come from more electronegative atoms. An **example** of determining formal charge can be seen below with the nitrate ion, NO_3^-:



- The double bonded O atom has *6 electrons*: 4 non-bonding and 2 bonding (one electron for each bond). Since O should have 6 electrons, the *formal charge is 0*.
- The two singly bonded O atoms each have *7 electrons*: 6 non-bonding and 1 bonding electron. Since O should have 6 electrons, and there is one extra electron, those O atoms each have *formal charges of -1*.
- The N atom has 4 electrons: 4 bonding and 0 non-bonding electrons. Since N should have 5 electrons and there are only 4 electrons for this N, the N atom has a *formal charge of +1*.
- The charges add up to the overall charge of the ion. 0 + (-1) + (-1) + 1 = -1. Thus, these charges are correct, as the overall charge of nitrate is -1.

In general you want the fewest number of formal charges possible, i.e. formal charges of 0 for as many of the atoms in a structure as possible. Also the formal charges should match the electronegativity of the atom, that is negative charges should be on the more electronegative atoms and positive charges on the least electronegative atoms if possible. Charges of -1 and +1 on adjacent atoms can usually be removed by using a lone pair of electrons from the -1 atom to form a double (or triple) bond to the atom with the +1 charge.

Summary

Lewis Structures are visual representations of the bonds between atoms and illustrate the lone pairs of electrons in molecules. They can also be called Lewis dot diagrams and are used as a simple way to show the configuration of atoms within a molecule. Electrons are shown as "dots" or for bonding electrons as a line between the two atoms. The goal is to obtain the "best" electron configuration, *i.e.* the octet rule and formal charges need to be satisfied. Lewis structures can also be useful in predicting molecular geometry in conjunction with hybrid orbitals. A compound may have multiple resonance forms that are also all correct Lewis structures. This section will discuss the rules for writing out Lewis structures correctly.

Contributors and Attributions

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- Andreas Hagen (via StackExchange)

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3.2: Valence Bond Theory

Valence bond (VB) theory is one of two basic theories, along with molecular orbital (MO) theory, that were developed to use the methods of quantum mechanics to explain chemical bonding. It focuses on how the atomic orbitals of the dissociated atoms combine to give individual chemical bonds when a molecule is formed. In contrast, molecular orbital theory, which will be discussed elsewhere, predict wavefunctions that cover the entire molecule.

The simplest case to consider is the hydrogen molecule, H_2. When we say that the two hydrogen nuclei share their electrons to form a covalent bond, what we mean in VB theory terms is that the two spherical 1*s* orbitals (the grey spheres in Figure **3.2.1**) overlap and contain two electrons.

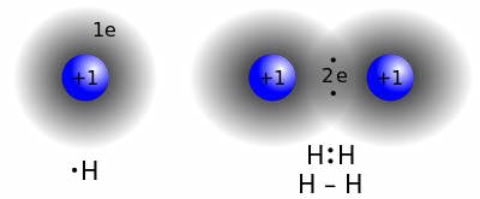


Figure **3.2.1**: These two electrons are now attracted to the positive charge of both of the hydrogen nuclei, with the result that they serve as a sort of 'chemical glue' holding the two nuclei together. from Wikipedia (credit: Jacek FH)

How far apart are the two nuclei? If they are too far apart, their respective 1*s* orbitals cannot overlap, and thus no covalent bond can form - they are still just two separate hydrogen atoms. As they move closer and closer together, orbital overlap begins to occur, and a bond begins to form. This lowers the **potential energy** of the system, as new, *attractive* positive-negative electrostatic interactions become possible between the nucleus of one atom and the electron of the second (Figure **3.2.2**). However, something else is happening at the same time: as the atoms get closer, the *repulsive* positive-positive interaction between the two nuclei also begins to increase.

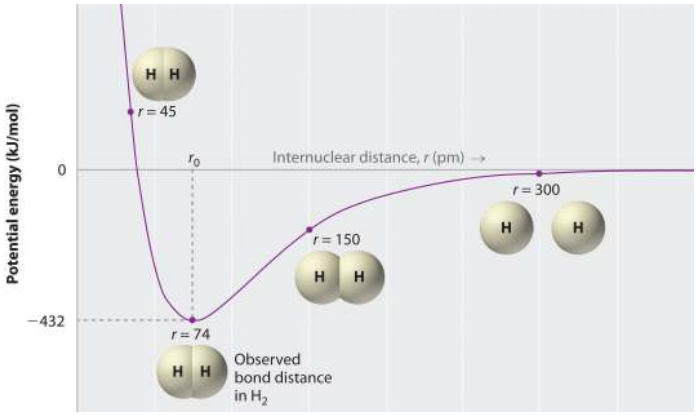


Figure **3.2.2**: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms. At long distances, both attractive and repulsive interactions are small. As the distance between the atoms decreases, the attractive electron–proton interactions dominate, and the energy of the system decreases. At the observed bond distance, the repulsive electron–electron and proton–proton interactions just balance the attractive interactions, preventing a further decrease in the internuclear distance. At very short internuclear distances, the repulsive interactions dominate, making the system less stable than the isolated atoms.

At first this repulsion is more than offset by the attraction between nuclei and electrons, but at a certain point, as the nuclei get even closer, the repulsive forces begin to overcome the attractive forces, and the potential energy of the system rises quickly. When the two nuclei are 'too close', we have an unstable, high-energy situation. There is a defined optimal distance between the nuclei in which the potential energy is at a minimum, meaning that the combined attractive and repulsive forces add up to the greatest overall attractive force. This optimal internuclear distance is the **bond length**; the distance is 74 pm for H_2. Likewise, the difference in potential energy between the lowest energy state (at the optimal internuclear distance) and the state where the two atoms are completely separated is called the **bond dissociation energy,** or, more simply**, bond strength**; the H_2 bond strength is 435 kJ/mol.

A comparison of some bond lengths and energies is shown in Table 3.2.1. We can find many of these bonds in a variety of molecules, and this table provides average values. For example, breaking the first C–H bond in CH4 requires 439.3 kJ/mol, while breaking the first C–H bond in $\mathbf{H{-}CH_2C_6H_5}$ (a common paint thinner) requires 375.5 kJ/mol.

Table 3.2.1: Representative Bond Energies and Lengths

Bond	Length (pm)	Energy (kJ/mol)		Bond	Length (pm)	Energy (kJ/mol)
H–H	74	436		C–O	140.1	358
H–C	106.8	413		$\mathbf{C=O}$	119.7	745
H–N	101.5	391		$\mathbf{C\equiv O}$	113.7	1072
H–O	97.5	467		H–Cl	127.5	431
C–C	150.6	347		H–Br	141.4	366
$\mathbf{C=C}$	133.5	614		H–I	160.9	298
$\mathbf{C\equiv C}$	120.8	839		O–O	148	146
C–N	142.1	305		$\mathbf{O=O}$	120.8	498
$\mathbf{C=N}$	130.0	615		F–F	141.2	159
$\mathbf{C\equiv N}$	116.1	891		Cl–Cl	198.8	243

Example 3.2.1: A Morse Potential Approximation

The Morse potential, named after physicist Philip M. Morse, is a convenient interatomic interaction approximation for the potential energy of a diatomic molecule.

$$V(r) = D_e \left[1 - e^{-\beta(r-r_e)}\right]^2$$

Here r is the distance between the atoms, r_e is the equilibrium bond distance, D_e is the well depth (defined relative to the dissociated atoms), and β controls the 'width' of the potential (the smaller β is, the larger the well). For H_2, the equilibrium bond length $r_e = 74.1\ pm$, the bond energy $D_e = 7.61 \times 10^{-19} J$, and the Morse potential parameter $\beta = 0.0193\ pm^{-1}$.

The force on the system is given by

$$F(r) = -\frac{dV(r)}{dr}$$

Calculate the force for H_2 and explain the status of the system (e.g., compressing, expanding, or stationary) at:

a. 45 pm,
b. 74 pm,
c. 150 pm, and
d. 500 pm.

Overlap

Valence bond theory describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms. We say that orbitals on two different atoms overlap when a portion of one orbital and a portion of a second orbital occupy the same region of space. According to valence bond theory, a covalent bond results when two conditions are met:

1. an orbital on one atom overlaps an orbital on a second atom and
2. the single electrons in each orbital combine to form an electron pair.

The mutual attraction between this negatively charged electron pair and the two atoms' positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.

In addition to the distance between two orbitals, the orientation of orbitals also affects their overlap (other than for two *s* orbitals, which are spherically symmetric). Greater overlap is possible when orbitals are oriented such that they overlap on a direct line between the two nuclei. Figure **3.2.3** illustrates this for two *p* orbitals from different atoms; the overlap is greater when the orbitals overlap end to end rather than at an angle.

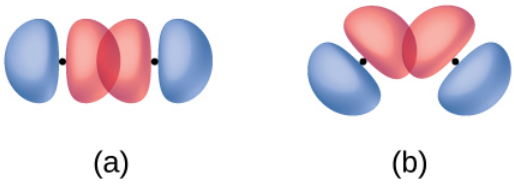


Figure **3.2.3**: (a) The overlap of two p orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.

The overlap of two *s* orbitals (as in H_2), the overlap of an *s* orbital and a *p* orbital (as in HCl), and the end-to-end overlap of two *p* orbitals (as in Cl_2) all produce sigma bonds (σ bonds), as illustrated in Figure **3.2.4**. A σ bond is a covalent bond in which the electron density is concentrated in the region along the internuclear axis; that is, a line between the nuclei would pass through the center of the overlap region. Single bonds in Lewis structures are described as σ bonds in valence bond theory.

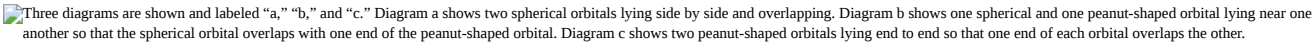
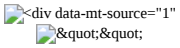

Three diagrams are shown and labeled "a," "b," and "c." Diagram a shows two spherical orbitals lying side by side and overlapping. Diagram b shows one spherical and one peanut-shaped orbital lying near one another so that the spherical orbital overlaps with one end of the peanut-shaped orbital. Diagram c shows two peanut-shaped orbitals lying end to end so that one end of each orbital overlaps the other.

Figure **3.2.4**: Sigma (σ) bonds form from the overlap of the following: (a) two s orbitals, (b) an s orbital and a p orbital, and (c) two p orbitals. The dots indicate the locations of the nuclei.

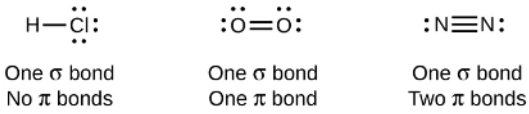
A pi bond (π bond) is a type of covalent bond that results from the side-by-side overlap of two *p* orbitals, as illustrated in Figure **3.2.5**. In a π bond, the regions of orbital overlap lie on opposite sides of the internuclear axis. Along the axis itself, there is a node, that is, a plane with no probability of finding an electron.



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Figure **3.2.5**: Pi (π) bonds form from the side-by-side overlap of two p orbitals. The dots indicate the location of the nuclei.

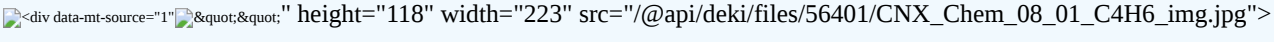
While all single bonds are σ bonds, multiple bonds consist of both σ and π bonds. As the Lewis structures in suggest, O_2 contains a double bond, and N_2 contains a triple bond. The double bond consists of one σ bond and one π bond, and the triple bond consists of one σ bond and two π bonds. Between any two atoms, the first bond formed will always be a σ bond, but there can only be one σ bond in any one location. In any multiple bond, there will be one σ bond, and the remaining one or two bonds will be π bonds. These bonds are described in more detail later in this chapter.



As seen in Table **3.2.2**, an average carbon-carbon single bond is 347 kJ/mol, while in a carbon-carbon double bond, the π bond increases the bond strength by 267 kJ/mol. Adding an additional π bond causes a further increase of 225 kJ/mol. We can see a similar pattern when we compare other σ and π bonds. Thus, each individual π bond is generally weaker than a corresponding σ bond between the same two atoms. In a σ bond, there is a greater degree of orbital overlap than in a π bond.

✔ Counting σ and π Bonds

Butadiene, C_6H_6, is used to make synthetic rubber. Identify the number of σ and π bonds contained in this molecule.



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Butadiene

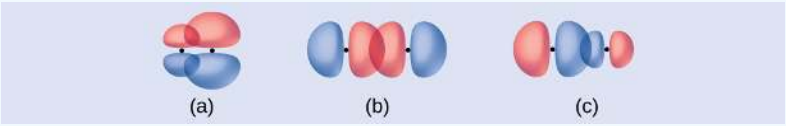
Solution

There are six σ C–H bonds and one σ C–C bond, for a total of seven from the single bonds. There are two double bonds that each have a π bond in addition to the σ bond. This gives a total nine σ and two π bonds overall.

? Exercise 3.2.2

Identify each illustration as depicting a σ or π bond:

a. side-by-side overlap of a 4*p* and a 2*p* orbital
b. end-to-end overlap of a 4*p* and 4*p* orbital
c. end-to-end overlap of a 4*p* and a 2*p* orbital



Answer

(a) is a π bond with a node along the axis connecting the nuclei while (b) and (c) are σ bonds that overlap along the axis.

The Valence Bond Wavefunction

In the hydrogen molecule, VB theory uses two electrons (electron 1 and electron 2) in two 1s atomic orbitals (ψ_a and ψ_b) on the hydrogen atoms(atom a and atom b). The simplest description of a H_2 molecule with two electrons and two nuclei is

$$\psi_{simple} = \psi_a(1)\psi_b(2) \tag{3.2.1}$$

Equation 3.2.1 means electron 1 is in ψ_a of atom a and electron 2 is in ψ_a on the atom b. Where ψ_a and ψ_b may be the $1s$ orbitals as the simplest wavefunction ($n = 1$, $l = 0$, m_l). The ψ_{simple} wavefunction predicts an energy that is about 6% of the experimental value at a bond length of 0.90 pm, which is considerably longer than the experimental value of 0.74 pm (Table 3.2.1). However, Equation 3.2.1 does not address the *indistinguishability* of the problem, i.e, we **cannot** distinguished each electron from the other.

Distinguishable vs. Indistinguishable Particles

Assume you have two particle A and B in states 1 and 2. If the two particle are *distinguishable*, then by exchanging the particles A and B, you will obtain a new state that will have the same properties as the old state. However, for *indistinguishable* particles, exchanging A and B is a transformation that does nothing and you have the same physical state. This means that for indistinguishable particles, particle labels are unphysical and they represent a redundancy in describing the physical state.

To account for the indistinguishable nature of the two electrons in the system, a covalent wavefunction that is better than Equation 3.2.1 can be constructed (ignoring spin effect):

$$\psi_{covalent} = \psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1) \tag{3.2.2}$$

Equation 3.2.2 means electron 1 is sometimes in ψ_a on atom a and electron 2 is on the atom b (left term of right hand side of Equation) and sometime electron 1 is sometimes in ψ_b on atom b and electron 2 is in ψ_a on the atom a (right term of right hand side of Equation). Notice that in contrast to Equation 3.2.1, if the two electron labels are switched, the wavefunction in Equation 3.2.2 does not change. The potential energy curve for the $\psi_{covalent}$ wavefunction predicts a bond energy that is about 72% at a bond length of 0.87 pm (Table 3.2.2), so the $\psi_{covalent}$ wavefunction is more accurate than ψ_{simple}.

To be more accurate within VB theory, the possibility that both electrons may be on atom a ($\psi_a(1)\psi_a(2)$) or on atom b ($\psi_b(1)\psi_b(2)$) should also be taken into account. This introduces an ionic contribution:

$$\psi_{ionic} = \psi_a(1)\psi_a(2) + \psi_b(2)\psi_b(1) \tag{3.2.3}$$

Notice that Equation 3.2.3 addresses indistinguishability since the wavefunction is unchanged if the two electron labels are switched. The more complete VB wavefunction is a linear combination of both $\psi_{covalent}$ and ψ_{ionic}:

$$\psi_{AB} = \Psi_{covalent} + \lambda\psi_{ionic} \tag{3.2.4}$$

where λ quantifies the amount of ionic character to the bond, e.g., if $\lambda = 0$, then the bond is purely covalent. The potential energy curve for the ψ_{AB} wavefunction predicts a bond energy that is ~80% of the experimental value and a reasonably accurate bond length of 0.77 pm (Table **3.2.1**). Additional tinkering with the wavefunction leads to even better results, but is beyond the scope of this discussion. It should be noted that the wavefunctions in Equations 3.2.2, 3.2.3, and 3.2.4 are unnormalized.

Table **3.2.2**: Valence Bond Theory Results for H_2

Wavefunction	Bond Energy (kJ mol-1)	Bond Length (pm)
Experiment	435	0.74
ψ_{simple}	25	0.90
$\psi_{covalent}$	301	0.87
ψ_{AB}	335	0.77

Two-Atom Bonds

The central gist of VB theory is that a covalent bond is formed between the **two** atoms by the overlap of half filled valence **atomic orbitals** of each atom containing one unpaired electron.

Example 3.2.3: Percent Ionic Character

Calculate the relative fraction of the contribution of the ionic character to the VB wavefunction. Assuming that the ionic character in HBr bond is 20%.

Solution

From Equation 3.2.4, the percent ionic character is given by:

$$\frac{\lambda^2}{1+\lambda^2} \times 100\%$$

Therefore,

$$20\% = 100\%\frac{\lambda^2}{1+\lambda^2}$$

$$20\% + 20\%\lambda^2 = 100\%\lambda^2$$

$$20\% = 100\%\lambda^2 – 20\lambda^2$$

$$20\% = 80\%\lambda^2$$

Therefore,

$$\lambda^2 = \frac{20}{80}$$

Hence, $\lambda = \sqrt{20/80} = 0.5$ and the fraction of contribution of ionic character to ψ_{AB} is 0.5 or 50%.

Linus Pauling used the pair bonding ideas of Lewis together with Heitler–London theory to develop two key concepts in VB theory: **resonance** and **orbital hybridization**. These will be addressed in later Modules.

Summary

Valence bond theory describes bonding as a consequence of the overlap of two separate atomic orbitals on different atoms that creates a region with one pair of electrons shared between the two atoms. When the orbitals overlap along an axis containing the nuclei, they form a σ bond. When they overlap in a fashion that creates a node along this axis, they form a π bond.

Contributors and Attributions

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- 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).
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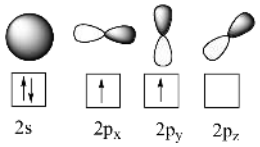
3.3: Hybridization of Atomic Orbitals

Hybridization was introduced to explain molecular structure when the valence bond theory failed to correctly predict them. It is experimentally observed that bond angles in organic compounds are close to 109°, 120°, or 180°. According to Valence Shell Electron Pair Repulsion (VSEPR) theory, electron pairs repel each other and the bonds and lone pairs around a central atom are generally separated by the largest possible angles.

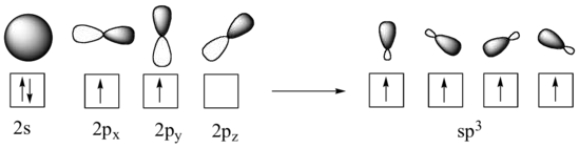
In this section, we will use a model called **valence bond theory** to describe bonding in molecules. In this model, bonds are considered to form from the overlapping of two atomic orbitals on different atoms, each orbital containing a single electron. In looking at simple inorganic molecules such as H_2 or HF, our present understanding of s and p atomic orbitals will suffice. In order to explain the bonding in organic molecules, however, we will need to introduce the concept of **hybrid orbitals**.

Hybrid orbitals: sp^3 hybridization and tetrahedral bonding

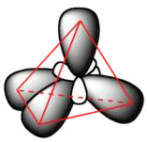
Now let's turn to methane, the simplest organic molecule. Recall the valence electron configuration of the central carbon:



This picture, however, is problematic. How does the carbon form four bonds if it has only two half-filled *p* orbitals available for bonding? A hint comes from the experimental observation that the four C-H bonds in methane are arranged with tetrahedral geometry about the central carbon, and that each bond has the same length and strength. In order to explain this observation, valence bond theory relies on a concept called **orbital hybridization**. In this picture, the four valence orbitals of the carbon (one 2*s* and three 2*p* orbitals) combine mathematically (remember: orbitals are described by equations) to form four equivalent **hybrid orbitals**, which are named **sp^3 orbitals** because they are formed from mixing one s and three p orbitals. In the new electron configuration, each of the four valence electrons on the carbon occupies a single sp^3 orbital.

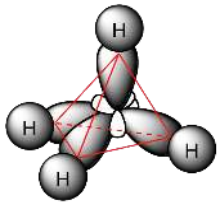


The sp^3 hybrid orbitals, like the *p* orbitals of which they are partially composed, are oblong in shape, and have two lobes of opposite sign. Unlike the *p* orbitals, however, the two lobes are of very different size. The larger lobes of the sp^3 hybrids are directed towards the four corners of a tetrahedron, meaning that the angle between any two orbitals is 109.5°.

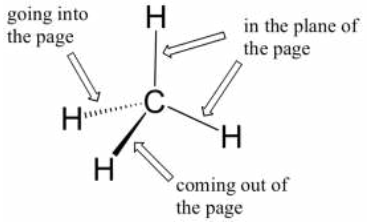


This geometric arrangement makes perfect sense if you consider that it is precisely this angle that allows the four orbitals (and the electrons in them) to be as far apart from each other as possible. This is simply a restatement of the Valence Shell Electron Pair Repulsion (VSEPR) theory that you learned in General Chemistry: electron pairs (in orbitals) will arrange themselves in such a way as to remain as far apart as possible, due to negative-negative electrostatic repulsion.

Each C-H bond in methane, then, can be described as an overlap between a half-filled 1*s* orbital in a hydrogen atom and the larger lobe of one of the four half-filled sp^3 hybrid orbitals in the central carbon. The length of the carbon-hydrogen bonds in methane is 1.09 Å (1.09×10^{-10} m).



While previously we drew a Lewis structure of methane in two dimensions using lines to denote each covalent bond, we can now draw a more accurate structure in three dimensions, showing the tetrahedral bonding geometry. To do this on a two-dimensional page, though, we need to introduce a new drawing convention: the solid / dashed wedge system. In this convention, a solid wedge simply represents a bond that is meant to be pictured emerging from the plane of the page. A dashed wedge represents a bond that is meant to be pictured pointing into, or behind, the plane of the page. Normal lines imply bonds that lie in the plane of the page.

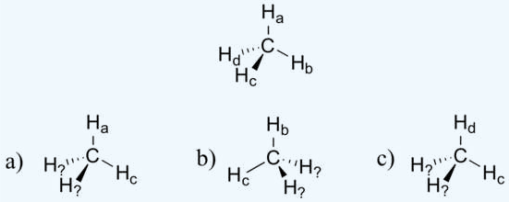


This system takes a little bit of getting used to, but with practice your eye will learn to immediately 'see' the third dimension being depicted.

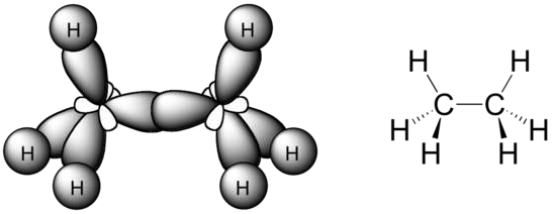
interactive 3D model of the bonding in methane

? Exercise

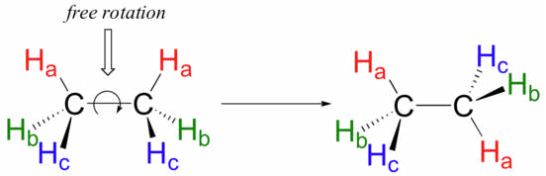
Imagine that you could distinguish between the four hydrogens in a methane molecule, and labeled them H_a through H_d. In the images below, the *exact same* methane molecule is rotated and flipped in various positions. Draw the missing hydrogen atom labels. (It will be much easier to do this if you make a model.)



In the ethane molecule, the bonding picture according to valence orbital theory is very similar to that of methane. Both carbons are sp^3-hybridized, meaning that both have four bonds arranged with tetrahedral geometry. The carbon-carbon bond, with a bond length of 1.54 Å, is formed by overlap of one sp^3 orbital from each of the carbons, while the six carbon-hydrogen bonds are formed from overlaps between the remaining sp^3 orbitals on the two carbons and the 1*s* orbitals of hydrogen atoms. All of these are sigma bonds.

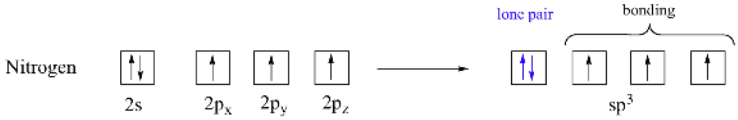


Because they are formed from the end-on-end overlap of two orbitals, *sigma bonds are free to rotate*. This means, in the case of ethane molecule, that the two methyl (CH_3) groups can be pictured as two wheels on a hub, each one able to rotate freely with respect to the other.

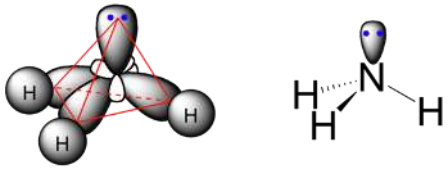


In another module we will learn more about the implications of rotational freedom in sigma bonds, when we discuss the 'conformation' of organic molecules.

The sp^3 bonding picture is also used to described the bonding in amines, including ammonia, the simplest amine. Just like the carbon atom in methane, the central nitrogen in ammonia is sp^3-hybridized. With nitrogen, however, there are five rather than four valence electrons to account for, meaning that three of the four hybrid orbitals are half-filled and available for bonding, while the fourth is fully occupied by a (non-bonding) pair of electrons.

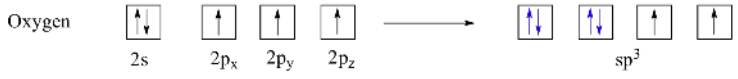


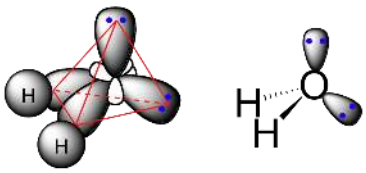
The bonding arrangement here is also tetrahedral: the three N-H bonds of ammonia can be pictured as forming the base of a trigonal pyramid, with the fourth orbital, containing the lone pair, forming the top of the pyramid.



Recall from your study of VSEPR theory in General Chemistry that the lone pair, with its slightly greater repulsive effect, 'pushes' the three N-H sigma bonds away from the top of the pyramid, meaning that the H-N-H bond angles are slightly less than tetrahedral, at 107.3˚ rather than 109.5˚.

VSEPR theory also predicts, accurately, that a water molecule is 'bent' at an angle of approximately 104.5˚. It would seem logical, then, to describe the bonding in water as occurring through the overlap of sp^3-hybrid orbitals on oxygen with 1sorbitals on the two hydrogen atoms. In this model, the two nonbonding lone pairs on oxygen would be located in sp^3 orbitals.





Some experimental evidence, however, suggests that the bonding orbitals on the oxygen are actually unhybridized 2*p* orbitals rather than sp^3 hybrids. Although this would seem to imply that the H-O-H bond angle should be 90˚ (remember that *p* orbitals are oriented perpendicular to one another), it appears that electrostatic repulsion has the effect of distorting this *p*-orbital angle to 104.5˚. Both the hybrid orbital and the nonhybrid orbital models present reasonable explanations for the observed bonding arrangement in water, so we will not concern ourselves any further with the distinction.

? Exercise

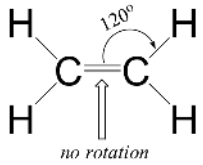
Draw, in the same style as the figures above, an orbital picture for the bonding in methylamine.

Solution

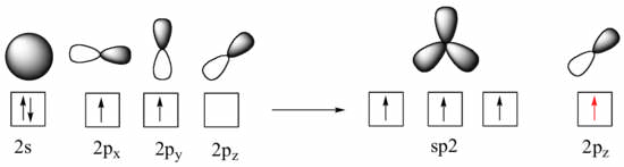
Formation of pi bonds - sp^2 and sp hybridization

The valence bond theory, along with the hybrid orbital concept, does a very good job of describing double-bonded compounds such as ethene. Three experimentally observable characteristics of the ethene molecule need to be accounted for by a bonding model:

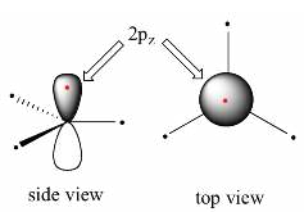
1. Ethene is a planar (flat) molecule.
2. Bond angles in ethene are approximately 120°, and the carbon-carbon bond length is 1.34 Å, significantly shorter than the 1.54 Å single carbon-carbon bond in ethane.
3. There is a significant barrier to rotation about the carbon-carbon double bond.



Clearly, these characteristics are not consistent with an sp^3 hybrid bonding picture for the two carbon atoms. Instead, the bonding in ethene is described by a model involving the participation of a different kind of hybrid orbital. Three atomic orbitals on each carbon – the 2*s*, $2p_x$ and $2p_y$ orbitals – combine to form three sp^2 hybrids, leaving the $2p_z$ orbital unhybridized.

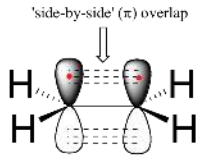


The three sp^2 hybrids are arranged with trigonal planar geometry, pointing to the three corners of an equilateral triangle, with angles of 120°between them. The unhybridized $2p_z$ orbital is *perpendicular* to this plane (in the next several figures, sp^2 orbitals and the sigma bonds to which they contribute are represented by lines and wedges; only the $2p_z$ orbitals are shown in the 'space-filling' mode).



another view

The carbon-carbon double bond in ethene consists of one sigma bond, formed by the overlap of two sp^2 orbitals, and a second bond, called a **π (pi) bond**, which is formed by the *side-by-side* overlap of the two unhybridized $2p_z$ orbitals from each carbon.

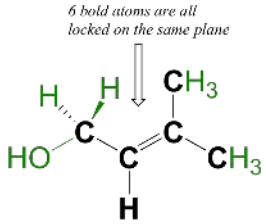


another view

interactive model

The pi bond does *not* have symmetrical symmetry. Because they are the result of side-by-side overlap (rather then end-to-end overlap like a sigma bond), *pi bonds are not free to rotate.* If rotation about this bond were to occur, it would involve disrupting the side-by-side overlap between the two $2p_z$ orbitals that make up the pi bond. The presence of the pi bond thus 'locks' the six atoms

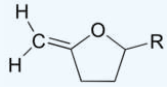
of ethene into the same plane. This argument extends to larger alkene groups: in each case, the six atoms of the group form a single plane.



Conversely, sigma bonds such as the carbon-carbon single bond in ethane (CH_3CH_3) exhibit free rotation, and can assume many different conformations, or shapes.

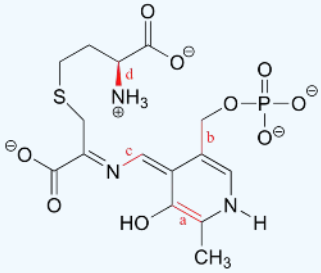
Example

Circle the six atoms in the molecule below that are 'locked' into the same plane.

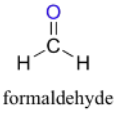


Exercise

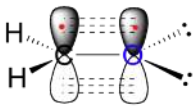
What kinds of orbitals are overlapping in bonds a-d indicated below?



A similar picture can be drawn for the bonding in carbonyl groups, such as formaldehyde. In this molecule, the carbon is sp^2-hybridized, and we will assume that the oxygen atom is also sp^2 hybridized. The carbon has three sigma bonds: two are formed by overlap between two of its sp^2 orbitals with the 1sorbital from each of the hydrogens, and the third sigma bond is formed by overlap between the remaining carbon sp^2 orbital and an sp^2 orbital on the oxygen. The two lone pairs on oxygen occupy its other two sp^2 orbitals.



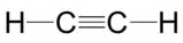
formaldehyde



interactive 3D model

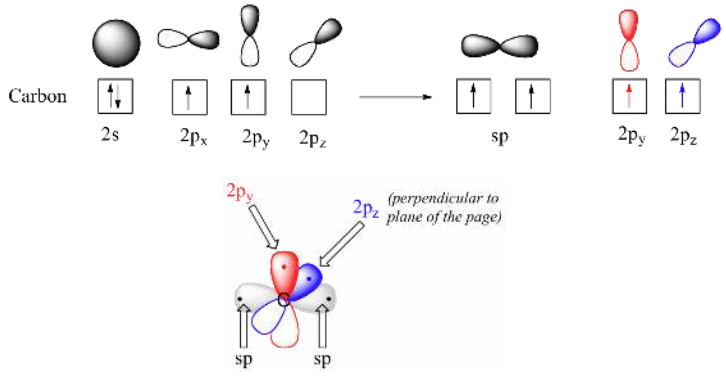
The pi bond is formed by side-by-side overlap of the unhybridized $2p_z$ orbitals on the carbon and the oxygen. Just like in alkenes, the $2p_z$ orbitals that form the pi bond are perpendicular to the plane formed by the sigma bonds.

Finally, the hybrid orbital concept applies well to triple-bonded groups, such as alkynes and nitriles. Consider, for example, the structure of ethyne (common name acetylene), the simplest alkyne.



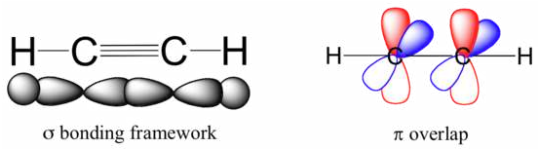
ethyne
(acetylene)

This molecule is linear: all four atoms lie in a straight line. The carbon-carbon triple bond is only 1.20Å long. In the hybrid orbital picture of acetylene, both carbons are **sp-hybridized**. In an sp-hybridized carbon, the 2*s* orbital combines with the $2p_x$ orbital to form two sp hybrid orbitals that are oriented at an angle of 180°with respect to each other (eg. along the x axis). The $2p_y$ and $2p_z$ orbitals remain unhybridized, and are oriented perpendicularly along the y and z axes, respectively.



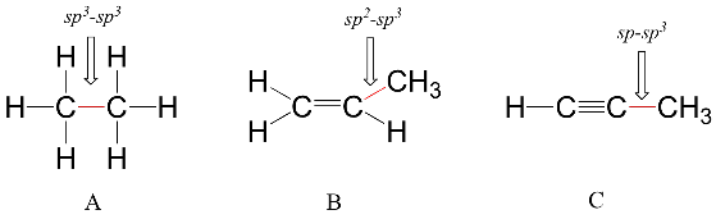
another view

The C-C sigma bond, then, is formed by the overlap of one sp orbital from each of the carbons, while the two C-H sigma bonds are formed by the overlap of the second sp orbital on each carbon with a 1*s* orbital on a hydrogen. Each carbon atom still has two half-filled $2p_y$ and $2p_z$ orbitals, which are perpendicular both to each other and to the line formed by the sigma bonds. These two perpendicular pairs of *p* orbitals form two pi bonds between the carbons, resulting in a triple bond overall (one sigma bond plus two pi bonds).



another view

The hybrid orbital concept nicely explains another experimental observation: single bonds adjacent to double and triple bonds are progressively shorter and stronger than 'normal' single bonds, such as the one in a simple alkane. The carbon-carbon bond in ethane (structure A below) results from the overlap of two sp^3 orbitals.



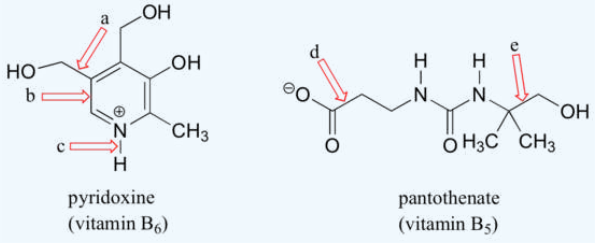
In alkene B, however, the carbon-carbon single bond is the result of overlap between an sp^2 orbital and an sp^3 orbital, while in alkyne C the carbon-carbon single bond is the result of overlap between an sp orbital and an sp^3 orbital. These are all single bonds, but the bond in molecule C is shorter and stronger than the one in B, which is in turn shorter and stronger than the one in A.

The explanation here is relatively straightforward. An sp orbital is composed of one *s* orbital and one *p* orbital, and thus it has 50% *s* character and 50% *p* character. sp^2 orbitals, by comparison, have 33% *s* character and 67% *p* character, while sp^3 orbitals have 25% *s* character and 75% *p* character. Because of their spherical shape, 2*s* orbitals are smaller, and hold electrons closer and 'tighter' to the nucleus, compared to 2*p* orbitals. Consequently, bonds involving sp + sp^3 overlap (as in alkyne C) are shorter and stronger than bonds involving sp^2 + sp^3 overlap (as in alkene B). Bonds involving sp^3-sp^3overlap (as in alkane A) are the longest and weakest of the group, because of the 75% '*p*' character of the hybrids.

Example

For each of the bonds indicated by arrows a-e in the figures below, describe the bonding picture by completing this sentence:

"The sigma bond indicated by this arrow is formed by the overlap of an _____ orbital of a _____atom and an _____orbital of a _____atom."



pyridoxine (vitamin B_6)

pantothenate (vitamin B_5)

Solution

Contributors and Attributions

- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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3.4: Molecular Orbital Theory

None of the approaches we have described so far can adequately explain why some compounds are colored and others are not, why some substances with unpaired electrons are stable, and why others are effective semiconductors. These approaches also cannot describe the nature of resonance. Such limitations led to the development of a new approach to bonding in which electrons are *not* viewed as being localized between the nuclei of bonded atoms but are instead delocalized throughout the entire molecule. Just as with the valence bond theory, the approach we are about to discuss is based on a quantum mechanical model.

Previously, we described the electrons in isolated atoms as having certain spatial distributions, called *orbitals*, each with a particular *orbital energy*. Just as the positions and energies of electrons in *atoms* can be described in terms of *atomic orbitals* (AOs), the positions and energies of electrons in *molecules* can be described in terms of molecular orbitals (MOs) A particular spatial distribution of electrons in a molecule that is associated with a particular orbital energy.—a spatial distribution of electrons *in a molecule* that is associated with a particular orbital energy. As the name suggests, molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called molecular orbital theory is a *delocalized* approach to bonding.

Although the molecular orbital theory is computationally demanding, the principles on which it is based are similar to those we used to determine electron configurations for atoms. The key difference is that in molecular orbitals, the electrons are allowed to interact with more than one atomic nucleus at a time. Just as with atomic orbitals, we create an energy-level diagram by listing the molecular orbitals in order of increasing energy. We then fill the orbitals with the required number of valence electrons according to the Pauli principle. This means that each molecular orbital can accommodate a maximum of two electrons with opposite spins.

The Hydrogen Molecule-Ion

Molecular orbital theory is a conceptual extension of the orbital model, which was so successfully applied to atomic structure. As was once playfully remarked, "a molecule is nothing more than an atom with more nuclei." This may be overly simplistic, but we do attempt, as far as possible, to exploit analogies with atomic structure. Our understanding of atomic orbitals began with the exact solutions of a prototype problem – the hydrogen atom. We will begin our study of homonuclear diatomic molecules beginning with another exactly solvable prototype, the hydrogen molecule-ion H_2^+. This species actually has a transient existence in electrical discharges through hydrogen gas and has been detected by mass spectrometry. It also has been detected in outer space. The Schrödinger equation for H_2^+ can be solved exactly within the Born-Oppenheimer approximation. For fixed internuclear distance R, this reduces to a problem of one electron in the field of two protons, designated A and B. We can write

$$\left\{-\frac{1}{2}\nabla^2\frac{1}{r_A}-\frac{1}{r_B}+\frac{1}{R}\right\}\psi(r)=E\psi(r) \tag{1}$$

where r_A and r_B are the distances from the electron to protons A and B, respectively. This equation was solved by Burrau (1927), after separating the variables in prolate spheroidal coordinates.

Molecular Orbitals Involving Only *ns* Atomic Orbitals

We begin our discussion of molecular orbitals with the simplest molecule, H_2, formed from two isolated hydrogen atoms, each with a $1s^1$ electron configuration. As discussed before, electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called *wave functions*. The 1*s* atomic orbitals on the two hydrogen atoms interact to form two new molecular orbitals, one produced by taking the *sum* of the two H 1*s* wave functions, and the other produced by taking their *difference*:

$$\begin{aligned} MO(1) &= AO(atom\ A) + AO(atom B) \\ MO(1) &= AO(atom\ A) - AO(atom B) \end{aligned} \tag{3.4.1}$$

The molecular orbitals created from the sum and the difference of two wavefunctions (atomic orbitals) from Equation 3.4.1 are called Linear Combinations of Atomic Orbitals (LCAOs). A molecule **must** have as many molecular orbitals as there are atomic orbitals.

Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1*s* orbitals is

called a σ_{1s} combination (pronounced “sigma one ess”) (part (a) and part (b) in Figure **3.4.1**). In a sigma (σ) orbital, A bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry, the electron density along the internuclear axis and between the nuclei has cylindrical symmetry; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1*s* denotes the atomic orbitals from which the molecular orbital was derived: The ≈ sign is used rather than an = sign because we are ignoring certain constants that are not important to our argument.

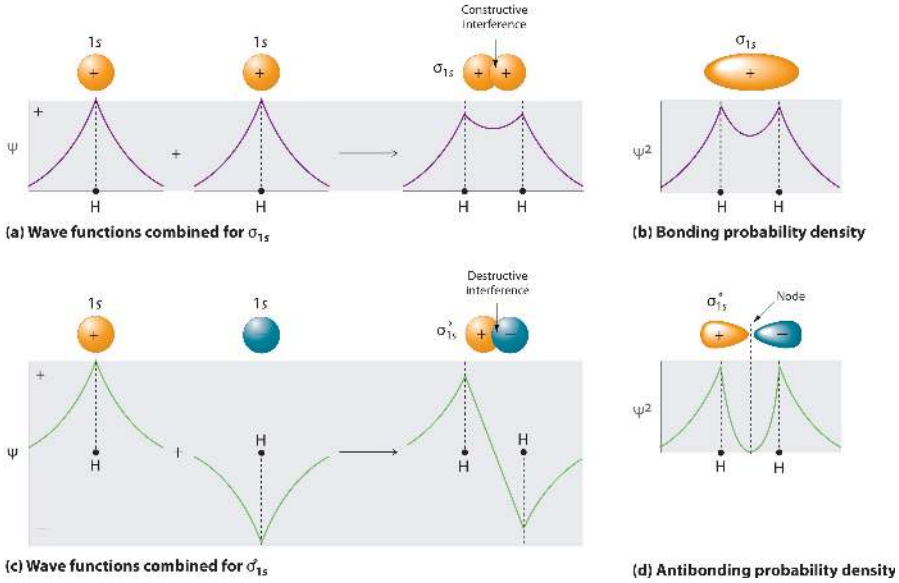


Figure **3.4.1**: Molecular Orbitals for the H_2 Molecule**.** (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1*s* atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the *square* of the wave function.) (c) This diagram shows the formation of an antibonding σ^*_{1s} *molecular orbital for* H_2 *as the difference of the wave functions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wave function* (Ψ^2) *for the* σ^*_{1s} *antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.*

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B) \tag{3.4.2}$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure **3.4.1**). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{1s} (“sigma one ess star”). In a sigma star (σ*) orbital An antibonding molecular orbital in which there is a region of zero electron probability (a nodal plane) perpendicular to the internuclear axis., there is a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$\sigma^*_{1s} \approx 1s\,(A) - 1s\,(B) \tag{3.4.3}$$

> A molecule must have as many molecular orbitals as there are atomic orbitals.

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wave functions. In contrast, electrons in the σ^*_{1s} orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the σ^*_{1s} orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wave functions).

> *Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.*

Energy-Level Diagrams

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1*s* atomic orbitals. Conversely, electrons in the σ^*_{1s} orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1*s* atomic orbitals. Consequently, the σ^*_{1s} molecular orbital has a *higher* energy than either of the hydrogen 1*s* atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1*s* atomic orbitals, and the σ^*_{1s} (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure **3.4.2**

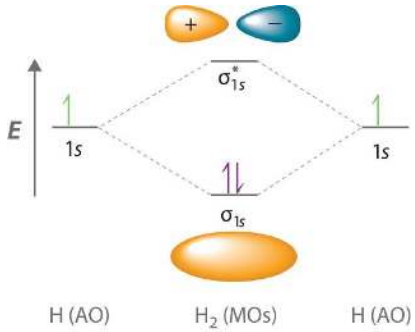


Figure **3.4.2**: Molecular Orbital Energy-Level Diagram for H_2. The two available electrons (one from each H atom) in this diagram fill the bonding $\sigma_{1\,s}$ molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1*s* atomic orbitals, the H_2 molecule is more stable (at a lower energy) than the two isolated H atoms.

> A bonding molecular orbital is *always* lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is *always* higher in energy (less stable).

To describe the bonding in a homonuclear diatomic molecule (a molecule that consists of two atoms of the same element) such as H_2, we use molecular orbitals; that is, for a molecule in which two identical atoms interact, we insert the total number of valence electrons into the energy-level diagram (Figure **3.4.2**). We fill the orbitals according to the Pauli principle and Hund's rule: each orbital can accommodate a maximum of two electrons with opposite spins, and the orbitals are filled in order of increasing energy. Because each H atom contributes one valence electron, the resulting two electrons are exactly enough to fill the σ_{1s} bonding molecular orbital. The two electrons enter an orbital whose energy is lower than that of the parent atomic orbitals, so the H_2 molecule is more stable than the two isolated hydrogen atoms. Thus molecular orbital theory correctly predicts that H_2 is a stable molecule. Because bonds form when electrons are concentrated in the space between nuclei, this approach is also consistent with our earlier discussion of electron-pair bonds.

Bond Order in Molecular Orbital Theory

In the Lewis electron structures, the number of electron pairs holding two atoms together was called the *bond order*. In the molecular orbital approach, bond order One-half the net number of bonding electrons in a molecule. is defined as one-half the *net* number of bonding electrons:

$$\textit{bond order} = \frac{\textit{number of bonding electrons} - \textit{number of antibonding electrons}}{2} \tag{3.4.4}$$

To calculate the bond order of H_2, we see from Figure **3.4.2** that the σ_{1s} (bonding) molecular orbital contains two electrons, while the σ^*_{1s} (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\frac{2-0}{2} = 1 \tag{3.4.5}$$

This result corresponds to the single covalent bond predicted by Lewis dot symbols. Thus molecular orbital theory and the Lewis electron-pair approach agree that a single bond containing two electrons has a bond order of 1. Double and triple bonds contain

four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams such as the one in Figure **3.4.2** to describe the bonding in other pairs of atoms and ions where n = 1, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's rule.

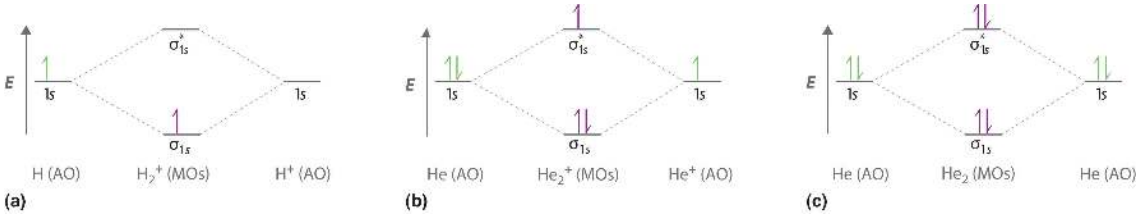


Figure **3.4.3**: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1 s Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

Part (a) in Figure **3.4.3** shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is (1-0)/2=1/2 Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table **3.4.1**, these predictions agree with the experimental data.

Part (b) in Figure **3.4.3** is the molecular orbital energy-level diagram for He_2^+. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the σ_{1s}^* antibonding orbital, giving a $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ electron configuration. This electron configuration gives a bond order of (2-1)/2=1/2. As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table **3.4.1**).

Table **3.4.1**: Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Molecule or Ion	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	not observed	not observed

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Part (c) in Figure **3.4.3** is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and σ_{1s}^* antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ electron configuration, with a predicted bond order of $(2-2) \div 2 = 0$, which indicates that the He_2 molecule has no net bond and is not a stable species. Experiments show that the He_2 molecule is actually *less* stable than two isolated He atoms due to unfavorable electron–electron and nucleus–nucleus interactions.

In molecular orbital theory, *electrons in antibonding orbitals effectively cancel the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature. In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory is able to accommodate systems with an odd number of electrons, such as the H_2^+ ion.

Note

In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.

Example 3.4.1

Use a molecular orbital energy-level diagram, such as those in Figure **3.4.3**, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

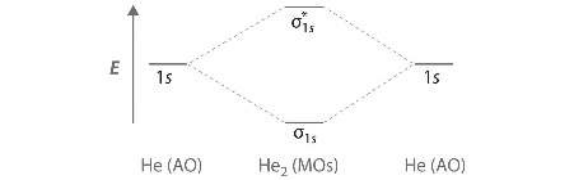
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

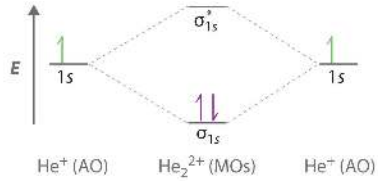
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1*s* atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a σ_{1s}^* antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:



B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^+ ions, each of which has a single valence electron in the 1*s* atomic orbital. We can now fill the molecular orbital diagram:



The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired. **C** So the bond order is

$$\frac{2-0}{2}=1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

Exercise 3.4.1

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer:

H_2^{2-} has a valence electron configuration of $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ with a bond order of 0. It is therefore predicted to be unstable.

So far, our discussion of molecular orbitals has been confined to the interaction of valence orbitals, which tend to lie farthest from the nucleus. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they do not need to be considered in a molecular orbital scheme. Also, when the inner orbitals are completely filled, they contain exactly enough electrons to completely fill both the bonding and antibonding molecular orbitals that

arise from their interaction. Thus the interaction of filled shells always gives a bond order of 0, so filled shells are not a factor when predicting the stability of a species. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

A molecular orbital diagram that can be applied to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure **3.4.4**, where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule in Figure **3.4.2**. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

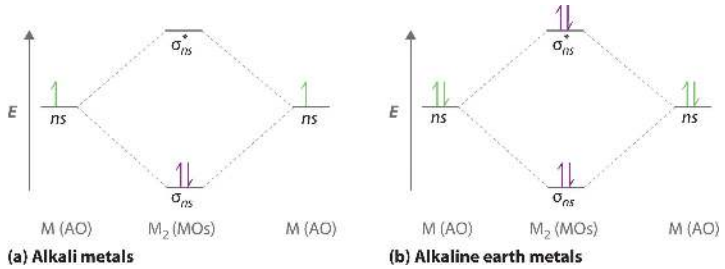


Figure **3.4.4**: Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ_{ns}* (nonbonding) levels, leading to a predicted bond order of 0.

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule in part (c) in Figure **3.4.3** As shown in part (b) in Figure **3.4.4**, this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{ns}* antibonding orbital and give a bond order of 0. Thus Be_2, Mg_2, Ca_2, Sr_2, and Ba_2 are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, Be_2 is stable.

✔ Example 3.4.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

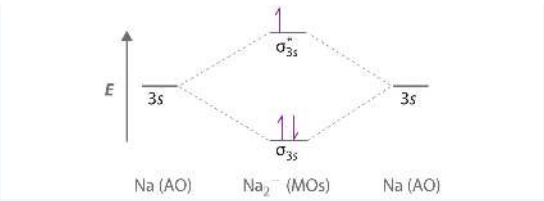
Strategy:

A. Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.
B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Because sodium has a [Ne]$3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1*s* atomic orbitals.

B The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s*} and a $(\sigma_{3s})^2 (\sigma^*_{3s})^1$ electron configuration.



C The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

? Exercise 3.4.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer: Ca_2^+ has a $(\sigma_{4s})^2 (\sigma^*_{4s})^1$ electron configurations and a bond order of 1/2 and should exist.

Contributors

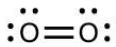
- Seymour Blinder (Professor Emeritus of Chemistry and Physics at the University of Michigan, Ann Arbor)

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3.5: Diatomic Molecules

For almost every covalent molecule that exists, we can now draw the Lewis structure, predict the electron-pair geometry, predict the molecular geometry, and come close to predicting bond angles. However, one of the most important molecules we know, the oxygen molecule O_2, presents a problem with respect to its Lewis structure. We would write the following Lewis structure for O_2:



This electronic structure adheres to all the rules governing Lewis theory. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself, O_2 is not magnetic, but it is attracted to magnetic fields. Thus, when we pour liquid oxygen past a strong magnet, it collects between the poles of the magnet and defies gravity. Such attraction to a magnetic field is called paramagnetism, and it arises in molecules that have unpaired electrons. And yet, the Lewis structure of O_2 indicates that all electrons are paired. How do we account for this discrepancy?

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 **3.5.1**), 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.

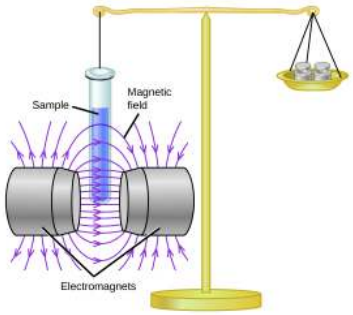


Figure **3.5.1**: A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

Experiments show that each O_2 molecule has two unpaired electrons. The Lewis-structure model does not predict the presence of these two unpaired electrons. Unlike oxygen, the apparent weight of most molecules decreases slightly in the presence of an inhomogeneous magnetic field. Materials in which all of the electrons are paired are diamagnetic and weakly repel a magnetic field. Paramagnetic and diamagnetic materials do not act as permanent magnets. Only in the presence of an applied magnetic field do they demonstrate attraction or repulsion.



***Video* 3.5.1:** *Water, like most molecules, contains all paired electrons. Living things contain a large percentage of water, so they demonstrate diamagnetic behavior. If you place a frog near a sufficiently large magnet, it will levitate. You can see videos of diamagnetic floating frogs, strawberries, and more (https://www.youtube.com/watch?v=A1vyB-O5i6E)*

Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the paramagnetism of the oxygen molecule. It also explains the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures. Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons. Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are delocalized over the entire molecule rather than being localized on its constituent atoms. MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators. Table **3.5.1** summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

Table **3.5.1** : Comparison of Bonding Theories

Valence Bond Theory	Molecular Orbital Theory
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from overlap of atomic orbitals (*s*, *p*, *d*…) and hybrid orbitals (*sp*, sp^2, sp^3…)	combines atomic orbitals to form molecular orbitals (σ, σ*, π, π*)
forms σ or π bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	

Molecular Orbitals Formed from *ns* and *np* Atomic Orbitals

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{3.5.1}$$

Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure **3.5.2**, it is the mathematical *difference* of their wave functions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{3.5.2}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z(A) + np_z(B) \tag{3.5.3}$$

In this combination, shown in part (b) in Figure **3.5.2**, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z(A) - np_z(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

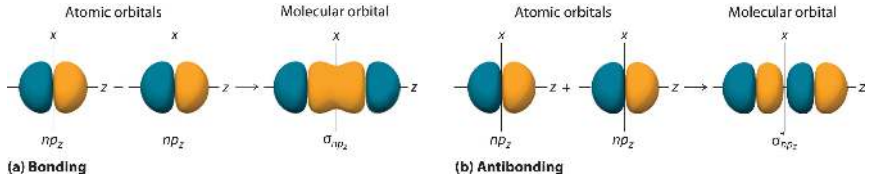


Figure **3.5.2**: Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate − + − +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis.

> Overlap of atomic orbital lobes with the *same sign* produces a bonding molecular orbital, regardless of whether it corresponds to the sum or the difference of the atomic orbitals.

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure **3.5.3**, we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_z} = np_x\,(A) + np_x\,(B) \tag{3.5.4}$$

$$\pi^*_{np_z} = np_x\,(A) - np_x\,(B) \tag{3.5.5}$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^*_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_z} and π_{np_y}molecular orbitals are a degenerate pair, as are the $\pi^*_{np_z}$ and $\pi^*_{np_y}$ molecular orbitals.

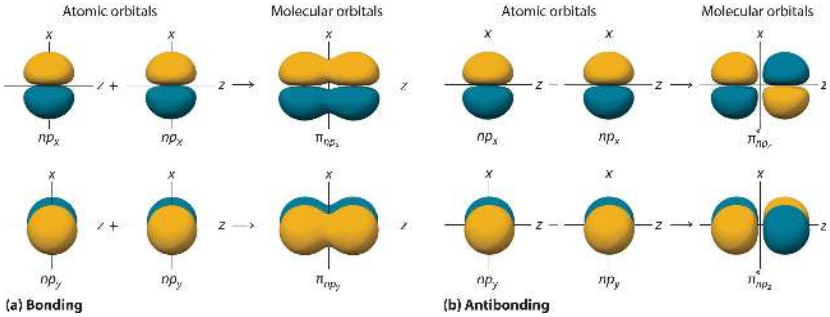


Figure **3.5.3**: Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Figure **3.5.4** is an energy-level diagram that can be applied to two identical interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

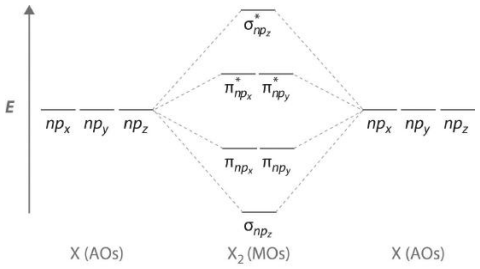


Figure **3.5.4**: The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals.

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure **3.5.5**, the sum of the two atomic wave functions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

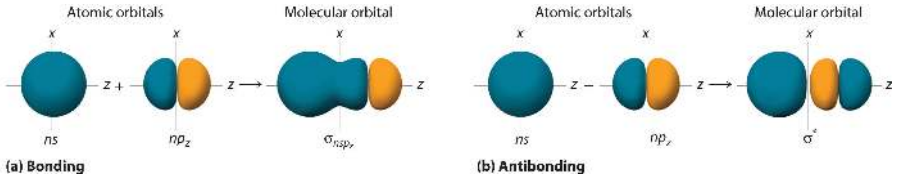


Figure **3.5.5**: Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Second Row Diatomic Molecules

If we combine the splitting schemes for the 2s and 2p orbitals, we can predict bond order in all of the diatomic molecules and ions composed of elements in the first complete row of the periodic table. Remember that only the valence orbitals of the atoms need be considered; as we saw in the cases of lithium hydride and dilithium, the inner orbitals remain tightly bound and retain their localized atomic character.

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (the law of conservation of orbitals).
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

> The number of molecular orbitals is **always** equal to the total number of atomic orbitals we started with.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in part (a) in Figure **3.5.6**; the $n = 1$ orbitals (σ_{1s} and σ_{1s}*) are located well below those of the $n = 2$ level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2*p* atomic orbitals because of the large difference in energy between the 2*s* and 2*p* atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2*p* orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^*_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rule. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π^* orbitals, for a total of 14 electrons. To determine what type of bonding the molecular orbital approach predicts F_2 to have, we must calculate the bond order. According to our diagram, there are 8 bonding electrons and 6 antibonding electrons, giving a bond order of $(8 - 6) \div 2 = 1$. Thus F_2 is predicted to have a stable F–F single bond, in agreement with experimental data.

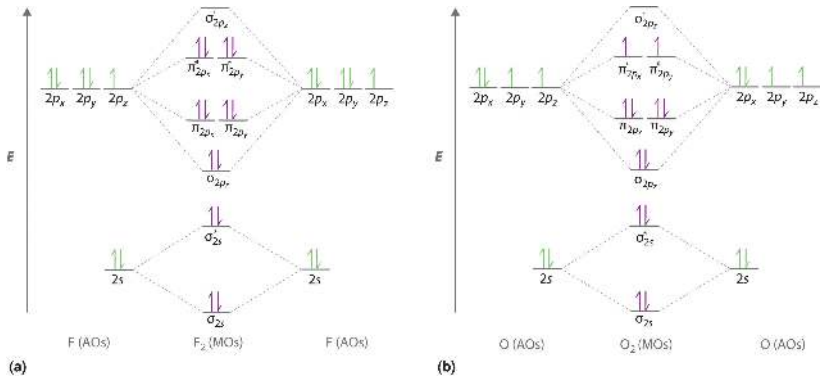
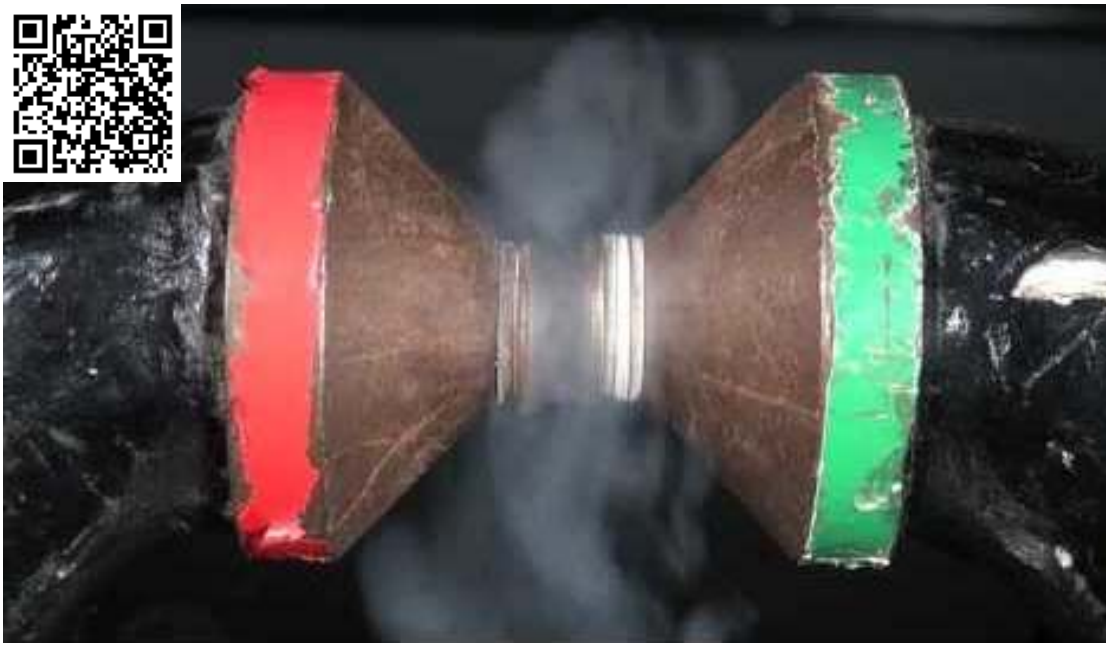


Figure **3.5.6**: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^*_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding orbitals, resulting in a bond order of 1. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^*_{np_x}, \pi^*_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2.

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. To obtain the molecular orbital energy-level diagram

for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in part (b) in Figure **3.5.6**. We again fill the orbitals according to Hund's rule and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}* orbitals, 2 more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals. According to Hund's rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of $(8 - 4) \div 2 = 2$, which corresponds to a double bond, in agreement with experimental data (Table 4.5): the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

None of the other bonding models can predict the presence of two unpaired electrons in O_2. Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Video **3.5.2**, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.



***Video* 3.5.2:** *Liquid O_2 Suspended between the Poles of a Magnet.Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates. Full video can be found at* https://www.youtube.com/watch?featur...&v=Lt4P6ctf06Q.

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*. Consequently, reactions of this type are usually exceedingly slow. If they were not so slow, all organic substances, including this book and you, would disappear in a puff of smoke!

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^*_{np_x}$ and $\pi^*_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p* atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the 2*pz* orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure **3.5.7** Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure **3.5.7**). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

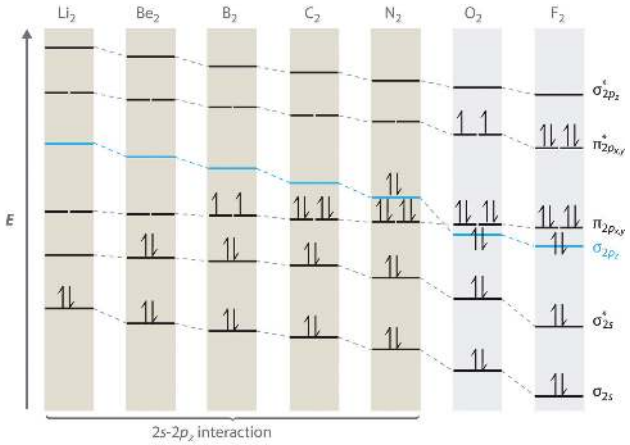


Figure **3.5.7**: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. For Li_2 through N_2, the σ_{2p_z} *orbital is higher in energy than the* $\pi_{2p_{x,y}}$ *orbitals. In contrast, the* σ_{2p_z} *orbital is lower in energy than the* $\pi_{2p_{x,y}}$ *orbitals for* O_2 *and* F_2 *due to the increase in the energy difference between the 2s and 2p atomic orbitals as the nuclear charge increases across the row.*

Completing the diagram for N_2 in the same manner as demonstrated previously, we find that the 10 valence electrons result in 8 bonding electrons and 2 antibonding electrons, for a predicted bond order of 3, a triple bond. Experimental data show that the N–N bond is significantly shorter than the F–F bond (109.8 pm in N_2 versus 141.2 pm in F_2), and the bond energy is much greater for N_2 than for F_2 (945.3 kJ/mol versus 158.8 kJ/mol, respectively). Thus the N_2 bond is much shorter and stronger than the F_2 bond, consistent with what we would expect when comparing a triple bond with a single bond.

Example 3.5.1

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

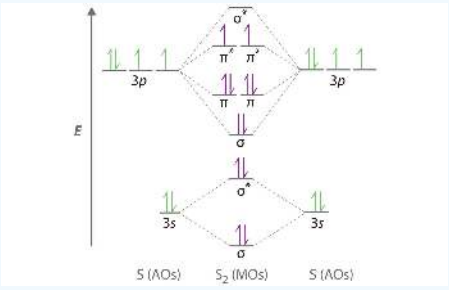
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a $[Ne]3s^23p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure **3.5.6** and Figure **3.5.7**, we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure **3.5.7**), the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_z} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^*_{3p_z}$ and $\pi^*_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2(\sigma^*_{3s})^2(\sigma_{3p_x})^2(\pi_{3p_{z,y}})^4(\pi^*_{3p^*_{z,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

? Exercise 3.5.1

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer

$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p_x})^2(\pi_{2p_{z,y}})^4(\pi^*_{2p^*_{z,y}})^4$ bond order of 1; no unpaired electrons

Molecular Orbitals for Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure **3.5.8**. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

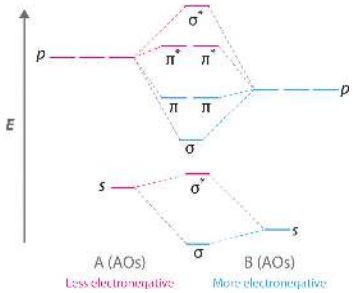


Figure **3.5.8**: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure **3.5.9**) shows that the general pattern is similar to that for the O_2 molecule (Figure **3.5.7**). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2*p* atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2 . Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N_2 and O_2 molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

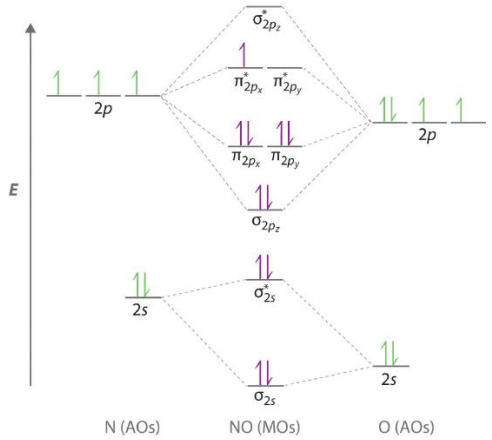


Figure **3.5.9**: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^*_{2p_x}, \pi^*_{2p_y}\right)$ pair of orbitals.

Molecular orbital theory can also tell us something about the *chemistry* of ***NO***. As indicated in the energy-level diagram in Figure **3.5.9**, NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, ***NO*** is easily oxidized to the NO^+ cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.

Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure **3.5.10** that the 1*s* orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3*s* atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1*s* and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can interact with the H 1*s* orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1*s* orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3*s*, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 − 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1*s* atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+} - Cl^{\delta-}$.

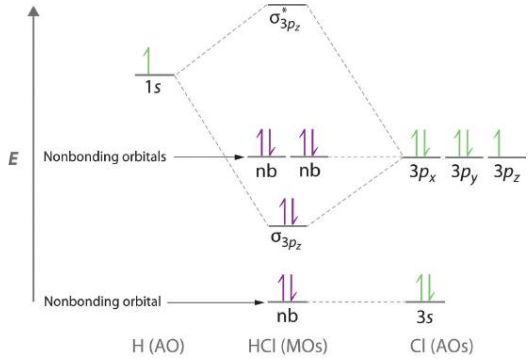


Figure **3.5.10**: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1 s atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

Electrons in nonbonding molecular orbitals have **no effect** on bond order.

✔ Example 3.5.2

Use a "skewed" molecular orbital energy-level diagram like the one in Figure **3.5.8** to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

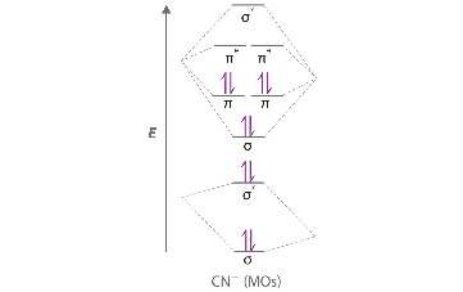
Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure **3.5.8** in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the −1 charge. Placing these electrons in an energy-level diagram like Figure **3.5.8** fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C. **B** The resulting valence electron configuration gives a predicted bond order of $(8 - 2) \div 2 = 3$, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

Exercise 3.5.2

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer

All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.

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3.6: Electronegativity and Dipole Moment

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

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

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

Bond dissociation energies. ΔE_d measured in kJ/mol, measure the energy required to break a mole of a particular kind of bond. A similar periodic trend exists for bond dissociation energies. Consider the hydrogen halides:

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

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

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

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

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

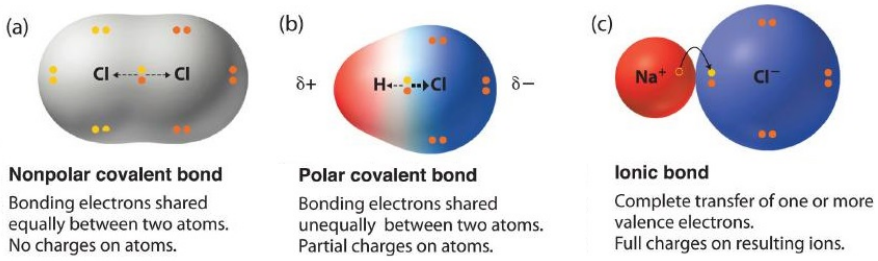


Figure **3.6.1 :** The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

The two idealized extremes of chemical bonding:

1. Ionic bonding—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and
2. Covalent bonding, in which electrons are shared equally between two atoms.

Most compounds, however, have polar covalent bonds, which means that electrons are shared unequally between the bonded atoms. Figure **3.6.1** compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+, or a partial negative charge, indicated by δ^-, and a bond between two atoms that possess partial charges is a polar bond.

Most real chemical bonds in nature are neither truly covalent nor truly ionic. Only homonuclear bonds are truly covalent, and nearly perfect ionic bonds can form between group I and group VII elements, for example, KF. Generally, however, bonds are partially covalent and partially ionic, meaning that there is partial transfer of electrons between atoms and partial sharing of electrons. To quantify how much ionic character (and how much covalent character) a bond possesses, electronegativity differences between the atoms in the bond can be used. In 1936, Linus Pauling came up a method for estimating atomic electronegativities forms the basis of our understanding of electronegativity today.

> Only **homonuclear** bonds are truly covalent, or as covalent as a bond can get. As discussed in Section 12.2, a quantum-mechanical treatment has shown that the two ionic structures (e.g., H^+H^- and H^-H^+ for H_2) also contribute via a resonance with the covalent structure $H-H$. However, this is often to a small extent, for example in H_2, each ionic structure contributes only ~2% to the bonding of the molecule.

Pauling Electronegativity

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

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

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

$$pure\ covalent\ contribution = \sqrt{\Delta E_{AA}\Delta E_{BB}} \tag{3.6.1}$$

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

$$\Delta E_{AB} - \sqrt{\Delta E_{AA}\Delta E_{BB}} \tag{3.6.2}$$

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

$$\Delta = \Delta E_{AB} - \sqrt{\Delta E_{AA}\Delta E_{BB}} \tag{3.6.3}$$

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

$$\chi_A - \chi_B = 0.102\sqrt{\Delta} \tag{3.6.4}$$

where Δ is measured in kJ/mol, and the constant 0.102 has units $mol^{1/2}/kJ^{1/2}$, so that the electronegativity difference is dimensionless. Thus, with some extra input information, he was able to generate a table of atomic electronegativities that are still used today and is Tablated in Table A2 (Figure **3.6.2**).

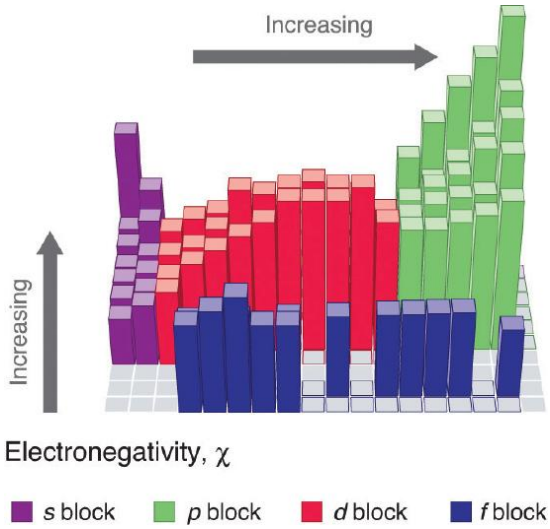


Figure **3.6.2**: Pauling Electronegativity Values of the s-, *p*-, *d*-, and *f*-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (1960).

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

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

As the electronegativity difference decreases, so does the ionic character of the bond. Hence its covalent character increases. It is possible to predict whether a given bond will be non-polar, polar covalent, or ionic based on the electronegativity difference, since the greater the difference, the more polar the bond (Figure **3.6.3**)

Electronegativity difference, ΔχP	Bond
Δχ < 0.4	covalent
0.4 < Δχ < 1.7	polar covalent
Δχ > 1.7	ionic

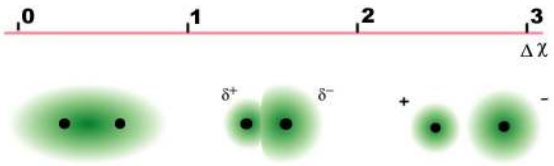


Figure **3.6.3**: Range of Bonds Polarity based on difference of Electronegativites

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

Dipole moment

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

$$K^+F^- \tag{3.6.5}$$

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

representation would be

$$H^{+\delta}F^{-\delta} \tag{3.6.6}$$

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

How much charge is actually transferred can be quantified by studying the *electric dipole moment* of the bond, which is a quantity that can be measured experimentally. The electric dipole moment for a diatomic with charges $Q_1 = Q = \delta e$ and $Q_2 = -Q = -\delta e$ on atoms 1 and 2, respectively, is

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

Hence, the magnitude of the dipole moment is

$$\mu = |\mu| = Q\,|r_1 - r_2| = QR \tag{3.6.7}$$

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

$$|\mu| = 0.41(1.602 \times 10^{-19} C)(0.926 \times 10^{-10} m) = 6.08 \times 10^{-30} C \cdot m \tag{3.6.8}$$

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

$$1\ D = 3.336 \times 10^{-30}\ \text{Coulomb} \cdot \text{meters} \tag{3.6.9}$$

> Historically, the Debye was defined in terms of the dipole moment resulting from two equal charges of opposite sign and separated by 1 Ångstrom ($10^{-10}\ m$) as 4.801 D from Equation 3.6.7. This value arises from
>
> $$\frac{(1.602 \times 10^{-19})(1 \times 10^{-10})}{3.336 \times 10^{-30}}$$
>
> where
>
> $$D = 3.336 \times 10^{-30}\ C\,m$$
>
> or
>
> $$1\ C\,m = 2.9979 \times 10^{29}\ D$$

Thus, for a diatomic with partial charges $+\delta$ and $-\delta$, the dipole moment in D is given by

$$\mu(D) = \frac{\delta * R(\mathring{A})}{0.2082\ \mathring{A}\ D^{-1}} \tag{3.6.10}$$

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

$$percent\ ionic\ character = 100\% * \delta \tag{3.6.11}$$

Typical dipole moments for simple diatomic molecules are in the range of 0 to 11 D (Table 3.6.1). Equation 3.6.11 can be expressed differently in terms of the expected dipole assuming a full charge separation (μ_{ionic}) compared to the experimental dipole moment (μ_{exp})

$$percent\ ionic\ character = 100\% * \frac{\mu_{exp}}{\mu_{ionic}} \tag{3.6.12}$$

Example 3.6.1: KBr

Calculate a theoretical dipole moment for the KBr molecule, assuming opposite charges of one fundamental unit located at each nucleus, and hence the percentage ionic character of KBr.

Solution

From Table **3.6.1**, the observed dipole moment of KBr is given as 10.41 D, (3.473 x 10^{-29} Coulomb-meters), which being close to the upper level of 11 indicates that it is a highly polar molecule. The interatomic distance between K^+ and Br^- is 282 pm. From this it is possible to calculate a theoretical dipole moment for the KBr molecule, assuming opposite charges of one fundamental unit located at each nucleus, and hence the percentage ionic character of KBr.

Dipole moment

$$\mu = q \times e \times d \text{ (in Coulomb-meters)} \tag{3.6.13}$$

- q = 1 for complete separation of unit charge
- e = 1.602 x 10^{-19} C
- d = 2.82 x 10^{-10} m for KBr (282 pm)

Hence calculated ionic dipole moment is

$$\mu_{KBr} = (1)(1.602 \times 10^{-19})(2.82 \times 10^{-10}) = 4.518 \times 10^{-29}\ Cm = 13.54\ D$$

The observed dipole moment is

$$\mu_{KBr} = 3.473 \times 10^{-29}\ Cm = 10.41\ D$$

the % ionic character from Equation 3.6.12 is

$$KBr = \frac{3.473 \times 10^{-29}}{4.518 \times 10^{-29}} \times 100\% = \frac{10.41\ D}{13.54\ D} \times 100\% = 76.87\%$$

and the % covalent character is therefore about 23% (100% - 77%).

Given the observed dipole moment is 10.41 D (3.473 x 10^{-29}) it is possible to estimate the charge distribution from the same equation by now solving for q.

Dipole moment μ = q * e * d Coulomb metre, but since q is no longer 1 we can substitute in values for μ and d to obtain an estimate for it.

$$q = \mu / (e * d) = 3.473 \text{ x } 10^{-29} / (1.602 \text{ x } 10^{-19} * 2.82 \text{ x } 10^{-10})$$

thus q = 3.473 x 10^{-29} / (4.518 x 10^{-29}) = 0.77 and the δ- and δ+ are -0.8 and +0.8 respectively.

Example 3.6.2: NaCl

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

A Compute the charge on each atom using the information given and Equation 8.4.2.

B Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$Q = \frac{\mu}{r} = 9.001 \cancel{D} \left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}} \right) \left(\frac{1}{236.1\ \cancel{pm}} \right) \left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) = 1.272 \times 10^{-19}\ C \tag{3.6.14}$$

Thus NaCl behaves as if it had charges of 1.272×10^{-19} C on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\%\ ionic\ character = \left(\frac{1.272 \times 10^{-19}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} \right) (100) = 79.39\% \simeq 79\% \tag{3.6.15}$$

Exercise 3.6.2: AgCl

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

Answer

55.5%

Table 3.6.1: Bond characteristics of select diatomics

diatomic	$\Delta\chi$	%ionic	bond dist (pm)	μ_{exp} (D)	μ_{ionic} (D)
Cl_2	0.0	0.0	200	0.00	9.60
IBr	0.3	5.9	247	0.70	11.86
HI	0.4	5.7	161	0.44	7.73
ICl	0.5	5.4	232	0.60	11.14
HBr	0.7	12.1	141	0.82	6.77
HCl	0.9	17.7	127	1.08	6.10
ClF	1.0	11.2	163	0.88	7.83
BrF	1.2	15.1	178	1.29	8.55
LiI	1.5	65.0	238	7.43	11.43
HF	1.9	41.2	92	1.82	4.42
LiBr	1.8	69.8	217	7.27	10.42
KI	1.7	73.7	305	10.80	14.65
LiCl	2.0	73.5	202	7.13	9.70
KBr	2.0	76.9	282	10.41	13.54
NaCl	2.1	79.4	236	9.00	11.33
KCl	2.2	80.1	267	10.27	12.82
CsCl	2.3	74.6	291	10.42	13.97
LiF	3.0	86.7	152	6.33	7.30
KF	3.2	82.5	217	8.60	10.42
CsF	3.3	64.4	255	7.88	12.25

Pauling proposed an empirical relationship (instead of the defintion in Equation 3.6.12) which relates the percent ionic character in a bond to the electronegativity difference.

$$percent\ ionic\ character = 100\% \left(1 - e^{(\Delta\chi/2)^2}\right) \tag{3.6.16}$$

This is shown as the curve in Figure 3.6.4 and is compared to the values for some diatomic molecules calculated from observed and calculated dipole moments.

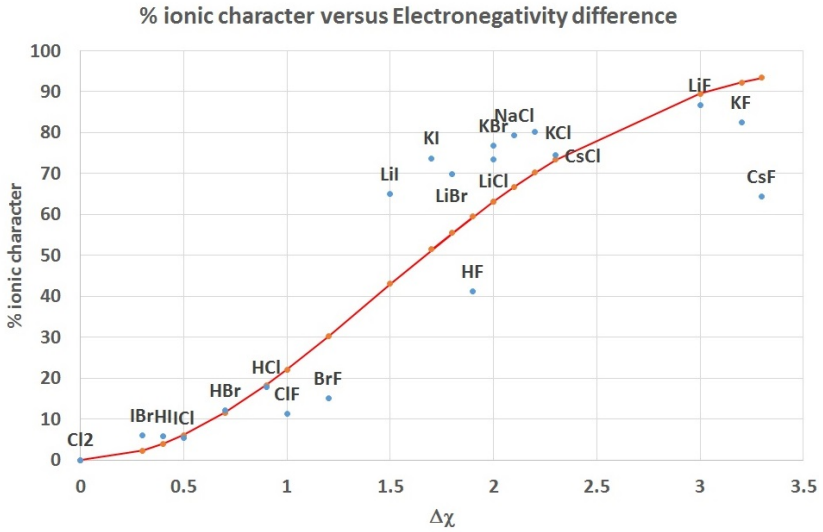


Figure 3.6.4: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms.In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

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

$$\mu(D) = \frac{0.41 * 0.926\ \mathring{A}}{0.2082\ \mathring{A}\ D^{-1}} = 1.82D \tag{3.6.17}$$

and its percent ionic character is 41%.

Example 3.6.3: Bond Polarity

Without consulting the table of electronegativities (use the periodic table), arrange the following bonds in order of decreasing polarity:

B—Cl, Ba—Cl, Be—Cl, Br—Cl, Cl—Cl.

Solution

We first need to arrange the elements in order of increasing electronegativity. Since the electronegativity increases in going up a column of the periodic table, we have the following relationships:

Ba < Be and Br < Cl

Also since the electronegativity increases across the periodic table, we have

Be < B

Since B is a group III element on the borderline between metals and non-metals, we easily guess that

B < Br

which gives us the complete order

Ba < Be < B < Br < Cl

Among the bonds listed, therefore, the Ba—Cl bond corresponds to the largest difference in electronegativity, i.e., to the most nearly ionic bond. The order of bond polarity is thus

Ba—Cl > Br—Cl > B—Cl > Br—Cl > Cl—Cl

where the final bond, Cl—Cl,is, of course, purely covalent.

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3.7: Photoelectron Spectroscopy

Learning Objectives

- Demonstrate how photoelectron spectroscopy can be used to resolve the absolute energies of molecular orbitals.

Photoelectron spectroscopy (PES) utilizes photo-ionization and analysis of the kinetic energy distribution of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample.

- **X-ray Photoelectron Spectroscopy** (XPS) uses soft x-rays (with a photon energy of 200-2000 eV) to examine electrons in *core*-levels.
- **Ultraviolet Photoelectron Spectroscopy** (UPS) using vacuum UV radiation (with a photon energy of 10-45 eV) to examine electrons in *valence* levels.

Both photoelectron spectroscopies are based upon a single photon in/electron out process. The energy of a photon of all types of electromagnetic radiation is given by the Planck–Einstein relation:

$$E = h\nu \tag{3.7.1}$$

where h is Planck constant and ν is the frequency (Hz) of the radiation. UPS is a powerful technique to exam molecular electron structure since we are interested in the molecular orbitals from polyatomic molecules (especially the valence orbitals) and is the topic of this page.

Photoelectron spectroscopy uses monochromatic sources of radiation (i.e. photons of fixed energy). In UPS the photon interacts with valence levels of the molecule or solid, leading to ionization by removal of one of these valence electrons. The kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted photoelectrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyzer and a photoelectron spectrum can thus be recorded.

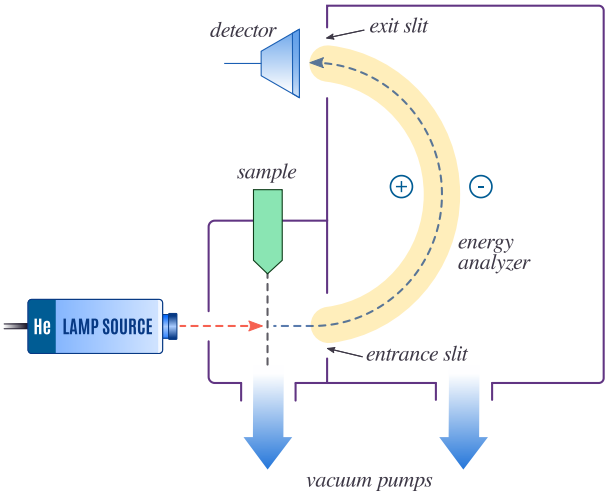


Figure 10.4.1: Diagram of a basic, typical PES instrument used in UPS, where the radiation source is an UV light source. When the sample is irradiated, the released photoelectrons pass through the lens system which slows them down before they enter the energy analyzer. The analyzer shown is a spherical deflection analyzer which the photoelectrons pass through before they are collected at the collector slit. (CC BY 4.0; Ümit Kaya via LibreTexts)

The process of photoionization can be considered in several ways. One way is to look at the overall process for a species A:

$$A + \text{photon} \rightarrow A^+ + e^- \tag{3.7.2}$$

Conservation of energy then requires that (after using Equation 3.7.1):

$$E(A) + h\nu = E(A^+) + E(e^-) \tag{3.7.3}$$

Since the free electron's energy is present solely as kinetic energy (KE) (i.e., there is no internal energy in a free electron)

$$E(e^-) = KE$$

Equation 3.7.3 can then be rearranged to give the following expression for the KE of the photoelectron:

$$KE = h\nu - [E(A^+) - E(A)] \tag{3.7.4}$$

The final term in brackets represents the difference in energy between the ionized and neutral species and is generally called the **vertical ionization energy** (IE) of the ejected electron; this then leads to the following commonly quoted equations:

$$KE = h\nu - IE \tag{3.7.5}$$

or

$$IE = h\nu - KE \tag{3.7.6}$$

The vertical ionization energy is a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level (i.e., a free electron). Photoelectron spectroscopy measures the relative energies of the ground and excited positive ion states that are obtained by removal of single electrons from the neutral molecule.

Note

Equation 3.7.5 may look familiar to you as it the same equation Einstein used to describe the photoelectric effect except the vertical ionization energy (IE) is substituted for workfunction Φ. Both vertical ionization energy and workfunctions are metrics for the binding energy of an electron in the sample.

At a fundamental level, ionization energies are well-defined thermodynamic quantities related to the heats of protonation, oxidation/reduction chemistry, and ionic and covalent bond energies. Ionization energies are closely related to the concepts of electronegativity, electron-richness, and the general reactivity of molecules. The energies and other characteristic features of the ionization bands observed in photoelectron spectroscopy provide some of the molecular orbitals detailed and specific quantitative information regarding the electronic structure and bonding in molecules.

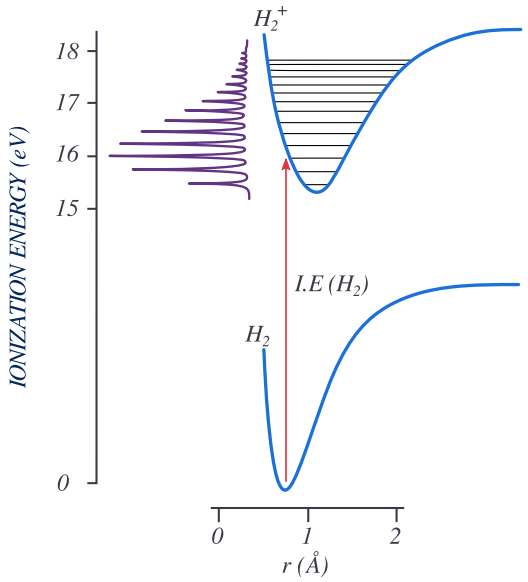


Figure 10.4.2: Vertical ionization process for molecular hydrogen. (CC BY 4.0; Ümit Kaya via LibreTexts)

Ionization is explicitly defined in terms of transitions between the ground state of a molecule and ion states as shown in Equation 3.7.6 and as illustrated in the Figure 10.4.2. Nonetheless, the information obtained from photoelectron spectroscopy is typically discussed in terms of the electronic structure and bonding in the ground states of neutral molecules, with ionization of electrons

occurring from bonding molecular orbitals, lone pairs, antibonding molecular orbitals, or atomic cores. These descriptions reflect the relationship of ionization energies to the molecular orbital model of electronic structure.

Ionization energies are directly related to the energies of molecular orbitals by Koopmans' theorem, which states that the negative of the eigenvalue of an occupied orbital from a Hartree-Fock calculation is equal to the *vertical ionization energy* to the ion state formed by removal of an electron from that orbital (Figure 10.4.3), provided the distributions of the remaining electrons do not change (i.e., frozen).

$$I_j = -\epsilon_j \tag{3.7.7}$$

There are many limitations to Koopmans' theorem, but in a first order approximation each ionization of a molecule can be considered as removal of an electron from an individual orbital. The ionization energies can then be considered as measures of orbital stabilities, and shifts can be interpreted in terms of orbital stabilizations or destabilizations due to electron distributions and bonding. Koopmans' theorem is implicated whenever an orbital picture is involved, but is not necessary when the focus is on the total electronic states of the positive ions.

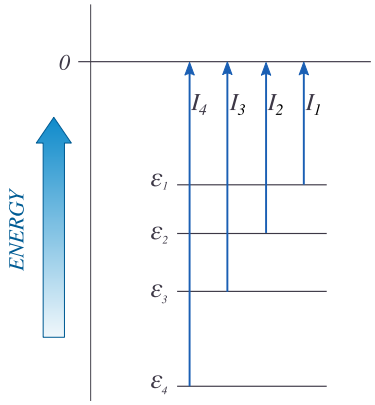


Figure 10.4.3: Within Koopmans' Theorem, the energies of the orbitals ϵ have an attractively simple physical interpretation: they give the amount of energy necessary to remove (ionize) the electron out of the molecular orbital, which corresponds to the negative of the experimentally observable ionization potential (I). (CC BY 4.0; Ümit Kaya via LibreTexts)

Koopmans' Theorem

Koopmans' theorem argues that the negative of the eigenvalue of an occupied orbital from a Hartree-Fock calculation is equal to the vertical ionization energy to the ion state formed by removal of an electron from that orbital.

Several different ionization energies can be defined, depending on the degree of vibrational excitation of the cations. In general, the following two types of ionization energies are considered (Figure 10.4.4):

- Adiabatic ionization energy corresponds to the ionization energy associated with this transition

  $$M(X, v''=0) + h\nu \rightarrow M^+(x, v'=0) + e^-$$

  Adiabatic ionization energy that is, the minimum energy required to eject an electron from a molecule in its ground vibrational state and transform it into a cation in the lowest vibrational level of an electronic state x of the cation.
- Vertical ionization energy corresponds to the ionization energy associated with this transition

  $$M(X, v''=0) + h\nu \rightarrow M^+(x, v'=n) + e^-$$

  where, the value n of the vibrational quantum number v' corresponds to the vibrational level whose wavefunction gives the largest overlap with the v" = 0 wavefunction. This is the most probable transition and usually corresponds to the vertical transition where the internuclear separations of the ionic state are similar to those of the ground state.

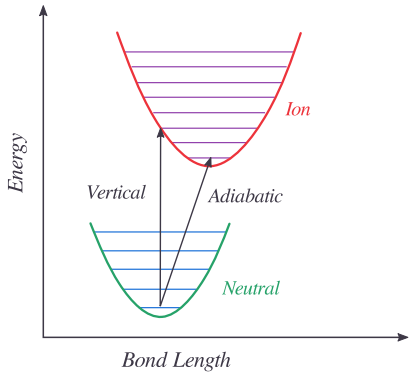


Figure 10.4.4: Difference between vertical and adiabatic ionization energies for a simple harmonic oscillator system. (CC BY 4.0; Ümit Kaya via LibreTexts)

The geometry of an ion may be different from the neutral molecule. The measured ionzation energy in a PES experiment can refer to the vertical ionization energy, in which case the ion is in the same geometry as the neutral, or to the adiabatic ionzaiton energy, in which case the ion is in its lowest energy, relaxed geometry (mostly the former though). This is illustrated in the Figure 10.4.4. For a diatomic the only geometry change possible is the bond length. The figure shows an ion with a slightly longer bond length than the neutral. The harmonic potential energy surfaces are shown in green (neutral) and red (ion) with vibrational energy levels. The vertical ionzation energy is **always greater** than the adiabatic ionzation energy.

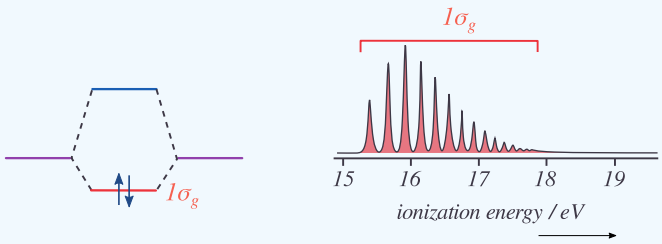
Differing Ionization Energies

You have been exposed to three metrics of ionization energies already, which are similar, but with distinct differences:

- The *ionization energy* (also called *adiabatic ionization energy*) is the lowest energy required to effect the removal of an electron from a molecule or atom, and corresponds to the transition from the lowest electronic, vibrational and rotational level of the isolated molecule to the lowest electronic, vibrational and rotational level of the isolated ion.
- The *binding energy* (also called *vertical ionization energy*) is the energy change corresponding to an ionization reaction leading to formation of the ion in a configuration which is the same as that of the equilibrium geometry of the ground state neutral molecule.
- The *workfunction* is the minimum energy needed to remove an electron from a (bulk) solid to a point in the vacuum.

Example 10.4.1: Molecular Hydrogen

As you remember, the molecular orbital description of molecular hydrogen involves two $|1s\rangle$ atomic orbitals generating a bonding $1\sigma_g$ and antibonding $2\sigma_u^*$ molecular orbitals. The two electrons that are responsible for the H_2 bond are occupied in the $1\sigma_g$.



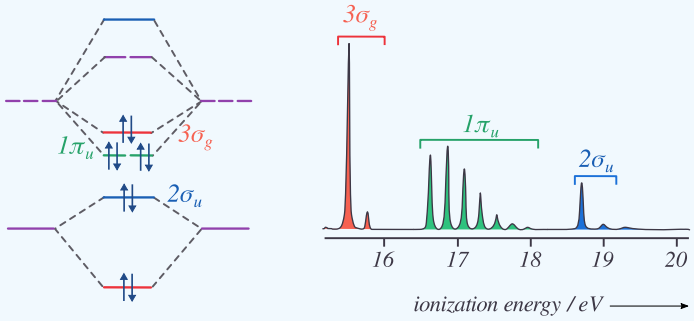
MO diagram and PES spectrum of H_2. (CC BY 4.0; Ümit Kaya via LibreTexts)

The PES spectrum has a single band that corresponds to the ionization of a $1\sigma_g$ electron. The multiple peaks are due to electrons ejecting from a range of stimulated vibrational energy levels. When extensive vibrational structure is resolved in a

PES molecular orbital, then the removal of an electron from that molecular orbital induces a significant change in the bonding (in this case an increase in the bond length since the bond order has been reduced).

Example 10.4.2: Molecular Nitrogen

Diatomic nitrogen is more complex than hydrogen since multiple molecular orbitals are occupied. Four molecular orbitals are occupied (the two $1\pi_u$ orbitals are both occupied). The UV photoelectron spectrum of N_2, has three bands corresponding to $3\sigma_g$, $1\pi_u$ and $2\sigma_u$ occupied molecular orbitals. Both $3\sigma_g$ and $2\sigma_u$ are weakly bonding and antibonding. The $1\sigma_g$ orbital is not resolved in this spectrum since the incident light $h\nu$ used did not have sufficient energy to ionize electrons in that deeply stabilized molecular orbital.



MO diagram and PES spectrum of N_2. (CC BY 4.0; Ümit Kaya via LibreTexts)

Note that extensive vibrational structure for the $1\pi_u$ band indicates that the removal of an electron from this molecular orbital causes a significant change in the bonding.

3.7.1: Hydrogen Chloride

The molecular energy level diagram for HCl is reproduced in Figure 10.4.5

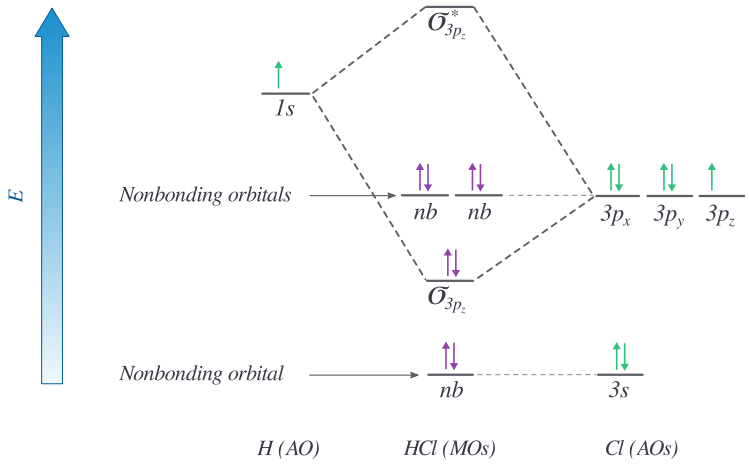


Figure 10.4.5: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts molecular orbitals strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1. (CC BY 4.0; Ümit Kaya via LibreTexts)

Important aspects of molecular orbital diagram in Figure 10.4.5:

- The H 1*s* energy lies well above the Cl 2*s* and 2*p* atomic orbitals;
- The valence electron configuration can be written $3\sigma^2 1\pi^4$;

- The H 1*s* orbital contributes only to the σ molecular orbitals, as does one of the Cl 2*p* orbitals (hence the lines in Figure 10.4.5 connecting these atomic orbitals and the 3σ and 4σ molecular orbitals);
- The remaining Cl 2*p* orbitals (ie those perpendicular to the bond axis) are unaffected by bonding, and these form the 1π molecular orbitals;
- The 1π orbitals are nonbonding - they are not affected energetically by the interaction between the atoms, and are hence neither bonding nor antibonding;
- The 3σ orbital is weakly bonding, and largely Cl 2*p*;
- The 3σ* orbital is antibonding, and primarily of H 1*s* character;

Figure 10.4.6 shows the analogous MO diagram and photoelectron spectrum for **HCl**. The spectrum has two bands corresponding to non-bonding 1*p* (or 1π) molecular orbitals (with negligible vibrational structure) and the 3*s* bonding molecular orbital (vibrational structure).

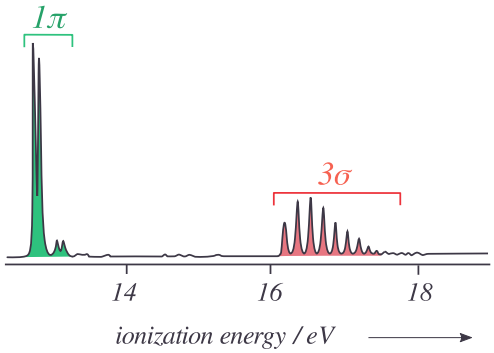


Figure 10.4.6: Photoelectron spectrum **HCl**. (CC BY 4.0; Ümit Kaya via LibreTexts)

The higher energy (more stabilized) core molecular orbitals are not observed since the incident photon energy $h\nu$ is below their ionization energies.

3.7.2: Water

In the simplified valence bond theory perspective of the water molecule, the oxygen atom form four sp^3 hybrid orbitals. Two of these are occupied by the two lone pairs on the oxygen atom, while the other two are used for bonding. Within the molecular orbital picture, the electronic configuration of the H_2O^+ molecule is $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$ where the symbols a_1, b_2 and b_1 are orbital labels based on molecular symmetry that will be discussed later (Figure 10.4.7). Within Koopmans' theorem:

- The energy of the $1b_1$ HOMO corresponds to the ionization energy to form the H_2O^+ ion in its ground state $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^1$.
- The energy of the second-highest molecular orbitals $3a_1$ refers to the ion in the excited state $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^2$.

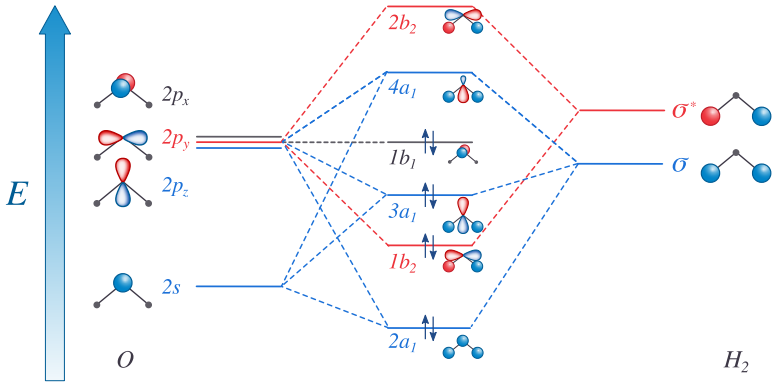


Figure 10.4.7: MO diagram for water. (CC BY 4.0; Ümit Kaya via LibreTexts)

The Hartree–Fock orbital energies (with sign changed) of these orbitals are tabulated below and compared to the experimental ionization energies.

Molecular orbital	Hartree–Fock orbital Energies (eV)	Experimental Ionization Energies (eV)
$2a_1$	36.7	32.2
$1b_2$	19.5	18.5
$3a_1$	15.9	14.7
$1b_1$	13.8	12.6

As explained above, the deviations between orbital energy and ionization energy is small and due to the effects of orbital relaxation as well as differences in electron correlation energy between the molecular and the various ionized states.

The molecular orbital perspective has the lone pair in different orbitals (one in a non-bonding orbital ($1b_1$ and one in the bonding orbitals). We tern to the photoelectron spectroscopy to help identify which theory is more accurate (i.e., describes reality better). The photoelectron spectrum of water in Figure 10.4.6 can be interpreted as having three major peaks with some fine structure arises from vibrational energy changes. The light source used in this experiment is not sufficiently energetic to ionize electrons from the lowest lying molecular orbitals.

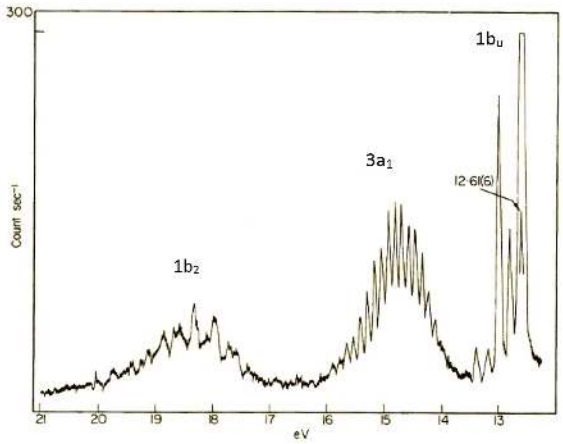


Figure 10.4.8: Photoelectron spectrum of water. Note the energy axes is flipped compared to other spectra on this page. This spectrum does not go to high enough energy to show the deep $2a_1$ molecular orbital.

If water was formed two identical O-H bonds and two lone pairs on the oxygen atom line valence bond theory predicts, then the PES in Figure 10.4.8 would have two (degenerate) peaks, one for the two bonds and one for the two lone pairs. The photoelectron spectrum clearly shows three peaks in the positions expected for the molecular orbitals in Figure 10.4.8.

If the molecular orbitals in Figure 10.4.7 represent the real electronic structure, how do we view the bonding? These molecular orbitals are delocalized and bare little relationship to the familiar 2-center bonds used in valence bond theory. For example, the $2a_1$ $1b_1$ and $3a_1$ molecular orbitals all have contributions from all three atoms, they are really 3-centered molecular orbitals. The bonds however can be thought of as representing a build up of the total electron density which loosely put is a total of all the orbital contributions. Despite this, we keep the ideas of hybridization and 2-center bonds because they are useful NOT because they represent reality

3.7.3: Summary

A photoelecton spectrum can show the relative energies of occupied molecular orbitals by ionization. (i.e. ejection of an electron). A photoelectron spectrum can also be used to determine energy spacing between vibrational levels of a given electronic state. Each orbital energy band has a structure showing ionization to different vibrational levels.

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CHAPTER OVERVIEW

4: Gases

4.1: The Perfect Gas

4.2: Real Gases (Deviations From Ideal Behavior)

4.3: van der Waals and Redlich-Kwong Equations of State

4.4: The Law of Corresponding States

4.5: The Repulsive Term in the Lennard-Jones Potential

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4.1: The Perfect Gas

At the macroscopic level, a complete physical description of a sample of a gas requires four quantities:

- ***temperature*** (T, expressed in kelvins),
- ***volume*** (V, expressed in liters),
- ***amount*** (n, expressed in moles), and
- ***pressure*** (P, in atmospheres).

These variables are *not* independent (i.e., they cannot be arbitrarily be varied). If we know the values of any *three* of these quantities, we can calculate the fourth and thereby obtain a full physical description of the gas. The volume of a container and the number of gas particles are relatively straightforward concepts, but pressure and temperature will each require some description.

Pressure

Any object, whether it is your computer, a person, or a sample of gas, exerts a force on any surface with which it comes in contact. If the surface exerts exactly that same force against the object, the object and the surface are in mechanical equilibrium. The air in a balloon, for example, exerts a force against the interior surface of the balloon that is equal to the force of the air pushing on the outside of the balloon plus the tensile stress from the balloon wall. If the air in a balloon is heated, the increased kinetic energy of the gas causes the balloon to expand because of the increased pressure (P) of the gas inside the balloon. This pressure is equal to the force (F) per unit area (A) of the balloon surface:

$$P = \frac{\text{Force}}{\text{Area}} = \frac{F}{A} \tag{4.1.1}$$

Pressure is dependent on *both* the force exerted *and* the size of the area to which the force is applied. We know from Equation 4.1.1 that applying the same force to a smaller area produces a higher pressure. When we use a hose to wash a car, for example, we can increase the pressure of the water by reducing the size of the opening of the hose with a thumb.

The units of pressure are derived from the units used to measure force and area. The SI unit for pressure, derived from the SI units for force (newtons) and area (square meters), is the newton per square meter (N/m^2), which is called the **Pascal (Pa)**, after the French mathematician Blaise Pascal (1623–1662):

$$1\ \text{Pa} = 1\ \text{N/m}^2 \tag{4.1.2}$$

Example 4.1.1

Assuming a paperback book has a mass of 2.00 kg, a length of 27.0 cm, a width of 21.0 cm, and a thickness of 4.5 cm, what pressure, in Pascals, does it exert on a surface if it is

a. lying flat?
b. standing on edge in a bookcase?

Strategy:

A. Calculate the force exerted by the book and then compute the area that is in contact with a surface.
B. Substitute these two values into Equation 4.1.1 to find the pressure exerted on the surface in each orientation.

Solution:

The force exerted by the book does *not* depend on its orientation. Recall that the force exerted by an object is $F = ma$, where m is its mass and a is its acceleration. In Earth's gravitational field, the acceleration is due to gravity (9.8067 m/s^2 at Earth's surface). In SI units, the force exerted by the book is therefore

$$F = ma = 2.00\ \text{kg} \times 9.8067 \frac{\text{m}}{\text{s}^2} = 19.6 \frac{\text{kg} \cdot \text{m}}{\text{s}^2} = 19.6\ \text{N} \tag{4.1.3}$$

A We calculated the force as 19.6 N. When the book is lying flat, the area is

$$A = 0.270\ \text{m} \times 0.210\ \text{m} = 0.0567\ \text{m}^2. \tag{4.1.4}$$

B The pressure exerted by the text lying flat is thus

$$P = \frac{F}{A} = \frac{19.6\ \text{N}}{0.0567\ \text{m}^2} = 3.46 \times 10^2 \text{Pa} \tag{4.1.5}$$

A If the book is standing on its end, the force remains the same, but the area decreases:

$$\text{A} = 21.0\ \text{cm} \times 4.5\ \text{cm} = 0.210\ \text{m} \times 0.045\ \text{m} = 9.5 \times 10^{-3}\ \text{m}^2 \tag{4.1.6}$$

B The pressure exerted by the text lying flat is thus

$$P = \frac{19.6\ \text{N}}{9.5 \times 10^{-3}\ \text{m}^2} = 2.06 \times 10^3\ \text{Pa} \tag{4.1.7}$$

Exercise 4.1.1

What pressure does a 60.0 kg student exert on the floor

a. when standing flat-footed in the laboratory in a pair of tennis shoes (the surface area of the soles is approximately 180 cm^2)?
b. as she steps heel-first onto a dance floor wearing high-heeled shoes (the area of the heel = 1.0 cm^2)?

Answers:

a. 3.27×10^4 Pa
b. 5.9×10^6 Pa

Barometric Pressure

Just as we exert pressure on a surface because of gravity, so does our atmosphere. We live at the bottom of an ocean of gases that becomes progressively less dense with increasing altitude. Approximately 99% of the mass of the atmosphere lies within 30 km of Earth's surface. Every point on Earth's surface experiences a net pressure called ***barometric pressure***. The pressure exerted by the atmosphere is considerable: a 1 m^2 column, measured from sea level to the top of the atmosphere, has a mass of about 10,000 kg, which gives a pressure of about 101 kPa.

Barometric pressure can be measured using a barometer, a device invented in 1643 by one of Galileo's students, Evangelista Torricelli (1608–1647). A barometer may be constructed from a long glass tube that is closed at one end. The glass tube is filled with mercury and placed upside down in a dish of mercury without allowing any air to enter the tube. Some of the mercury will run out of the tube, but a relatively tall column remains inside. Why doesn't all the mercury run out? Gravity is certainly exerting a downward force on the mercury in the tube, but the pull of gravity is opposed by the pressure of the atmosphere pushing down on the surface of the mercury in the dish, which has the net effect of pushing the mercury up into the tube. Because there is no air above the mercury inside the tube in a properly filled barometer (it contains a vacuum), there is no pressure pushing down on the column. Thus the mercury runs out of the tube until the pressure exerted by the mercury column itself exactly balances the pressure of the atmosphere. It can be said that at this point the column of mercury is in mechanical equilibrium with the atmosphere. The pressure exerted by the mercury column can be expressed as:

$$P = \frac{F}{A} = \frac{mg}{A} = \frac{\rho V \cdot g}{A} = \frac{\rho \cdot Ah \cdot g}{A} = \rho g h\ kPa \tag{4.1.8}$$

with

- g is the gravitational acceleration,
- m is the mass,
- ρ is the density,
- V is the volume,
- A is the bottom area, and
- h is height of the mercury column.

Mercury barometers have been used to measure barometric pressure for so long that they have their own unit for pressure: the millimeter of mercury (mmHg), often called the torr, after Torricelli. Standard barometric pressure is the barometric pressure

required to support a column of mercury exactly 760 mm tall; this pressure is also referred to as 1 atmosphere (atm). These units are also related to the pascal:

$$1\ \text{atm} = 760\ \text{mmHg} = 760\ \text{torr} = 1.01325 \times 10^5\ \text{Pa} = 101.325\ \text{kPa} \tag{4.1.9}$$

Exercise 4.1.2

Suppose you want to design a barometer to measure barometric pressure in an environment that is always hotter than 30°C. To avoid using mercury, you decide to use gallium, which melts at 29.76°C. At 35°C the density of mercury is 13.5 g/cm^3 and the density of liquid gallium is 6.11 g/cm^3. How tall a column of gallium do you need if P = 1.00 atm?

Answer: 1.69 m

Gas Sample Pressure

Barometers measure barometric pressure, but manometers measure the pressures of samples of gases contained in an apparatus. The key feature of a manometer is a U-shaped tube containing mercury (or occasionally another nonvolatile liquid). A closed-end manometer is shown schematically in part (a) in Figure **4.1.1**.

When the bulb contains no gas (i.e., when its interior is a near vacuum), the heights of the two columns of mercury are the same because the space above the mercury on the left is a near vacuum (it contains only traces of mercury vapor). If a gas is released into the bulb on the right, it will exert a pressure on the mercury in the right column, and the two columns of mercury will no longer be the same height. The *difference* between the heights of the two columns is equal to the pressure of the gas.

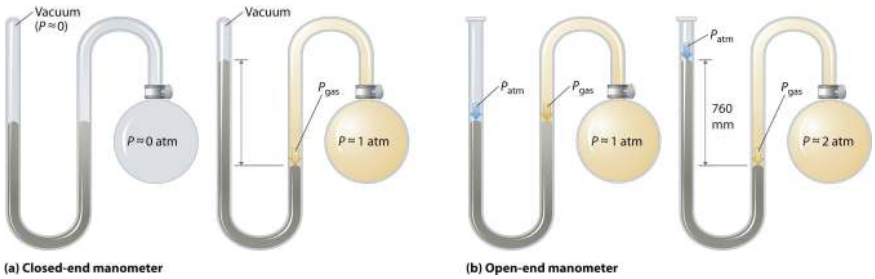


Figure 4.1.1*: The Two Types of Manometer. (a) In a closed-end manometer, the space above the mercury column on the left (the reference arm) is essentially a vacuum (P ≈ 0), and the difference in the heights of the two columns gives the pressure of the gas contained in the bulb directly. (b) In an open-end manometer, the left (reference) arm is open to the atmosphere (P ≈ 1 atm), and the difference in the heights of the two columns gives the difference between barometric pressure and the pressure of the gas in the bulb.*

If the tube is open to the atmosphere instead of closed, as in the open-end manometer shown in part (b) in Figure **4.1.1** , then the two columns of mercury have the same height only if the gas in the bulb has a pressure equal to the barometric pressure. If the gas in the bulb has a *higher* pressure, the mercury in the open tube will be forced up by the gas pushing down on the mercury in the other arm of the U-shaped tube. The pressure of the gas in the bulb is therefore the sum of the barometric pressure (measured with a barometer) and the difference in the heights of the two columns. If the gas in the bulb has a pressure *less* than that of the atmosphere, then the height of the mercury will be greater in the arm attached to the bulb. In this case, the pressure of the gas in the bulb is the barometric pressure minus the difference in the heights of the two columns.

Barometers and manometers are hydrostatic pressure gauges, involving the use of a column of liquid. Mechanical gauges that do not use liquids generally contain some surface (tube, diaphragm, wire, or semiconductor) that changes shape in response to a pressure change. There are also pressure gauges that respond to an extrinsic property of the gas sample, such as thermal conductivity or the extent of ionization.

Temperature

Many people confuse temperature with heat. **Temperature** is a measure of how hot or cold an object is relative to another object (its thermal energy content), whereas **heat** is the flow of thermal energy between objects with different temperatures.

Three different scales are commonly used to measure temperature: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K). Thermometers measure temperature by using materials that expand or contract when heated or cooled. Mercury or alcohol thermometers, for example, have a reservoir of liquid that expands when heated and contracts when cooled, so the liquid column lengthens or shortens as the temperature of the liquid changes.

The Fahrenheit Scale

The Fahrenheit temperature scale was developed in 1717 by the German physicist Gabriel Fahrenheit, who designated the temperature of a bath of ice melting in a solution of salt as the zero point on his scale. Such a solution was commonly used in the 18th century to carry out low-temperature reactions in the laboratory. The scale was measured in increments of 12; its upper end, designated as 96°, was based on the armpit temperature of a healthy person—in this case, Fahrenheit's wife. Later, the number of increments shown on a thermometer increased as measurements became more precise. The upper point is based on the boiling point of water, designated as 212° to maintain the original magnitude of a Fahrenheit degree, whereas the melting point of ice is designated as 32°.

The Celsius Scale

The Celsius scale was developed in 1742 by the Swedish astronomer Anders Celsius. It is based on the melting and boiling points of water under normal atmospheric conditions. The current scale is an inverted form of the original scale, which was divided into 100 increments. Because of these 100 divisions, the Celsius scale is also called the *centigrade scale*.

The Kelvin Scale

Lord Kelvin, working in Scotland, developed the Kelvin scale in 1848. His scale uses molecular energy to define the extremes of hot and cold. Absolute zero, or 0 K, corresponds to the point at which molecular energy is at a minimum. Absolute zero is the lowest temperature possible. The Kelvin scale is preferred in scientific work, although the Celsius scale is also commonly used. Temperatures measured on the Kelvin scale are reported simply as K, not °K.

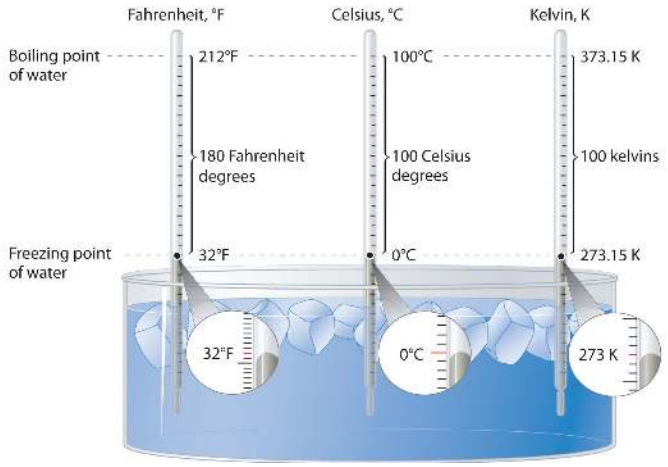


Figure 4.1.2: A Comparison of the Fahrenheit, Celsius, and Kelvin Temperature Scales. Because the difference between the freezing point of water and the boiling point of water is 100° on both the Celsius and Kelvin scales, the size of a degree Celsius (°C) and a kelvin (K) are precisely the same. In contrast, both a degree Celsius and a kelvin are 9/5 the size of a degree Fahrenheit (°F).

Converting between Scales

The kelvin is the same size as the Celsius degree, so measurements are easily converted from one to the other. The freezing point of water is 0°C = 273.15 K; the boiling point of water is 100°C = 373.15 K. The Kelvin and Celsius scales are related as follows:

$$T \text{ (in °C)} + 273.15 = T \text{ (in K)}$$

$$T \text{ (in K)} - 273.15 = T \text{ (in °C)}$$

Degrees on the Fahrenheit scale, however, are based on an English tradition of using 12 divisions, just as 1 ft = 12 in. The relationship between degrees Fahrenheit and degrees Celsius is as follows:where the coefficient for degrees Fahrenheit is exact. (Some calculators have a function that allows you to convert directly between °F and °C.) There is only one temperature for which the numerical value is the same on both the Fahrenheit and Celsius scales: −40°C = −40°F. The relationship between the scales are as follows:

°C = (5/9)*(°F-32)

°F = (9/5)*(°C)+32

The Equation of State for Perfect Gases

An equation of state is an equation that relates the variables which are required to fully describe a state of matter. One example of an equation of state is *V = f(p,T, n),* which states that volume of a sample of matter is a function of the pressure, temperature, and the number of particles in this sample. The exact expression for this relationship, the perfect gas law, will now be derived. (A gas sample in which there are no interactions among the particles is a **perfect gas**. A gas sample in which all of the interactions are identical is an **ideal gas**. Thus, all perfect gases are ideal gases, but not all ideal gases are perfect gases.)

Deriving the Perfect Gas Law

The relationship between a single quantity (such as V) and all of the other variables (p, T, and n) was obtained by combining the following three expressions into a single equation that describes all the relationships simultaneously:

- **Boyle's law**

$$V \propto \frac{1}{P} \text{ @ constant n and T} \tag{4.1.10}$$

- **Charles's law**

$$V \propto T \text{ @ constant n and P} \tag{4.1.11}$$

- **Avogadro's principle**

$$V \propto n \text{ @ constant T and P} \tag{4.1.12}$$

Combining these three expressions gives

$$V \propto \frac{nT}{P} \tag{4.1.13}$$

which shows that the volume of a gas is proportional to the number of moles and the temperature and inversely proportional to the pressure. This expression can also be written as

$$V = \text{Cons.} \left(\frac{nT}{P}\right) \tag{4.1.14}$$

By convention, the proportionality constant in Equation 4.1.14 is called the gas constant, which is represented by the letter R. Inserting R into Equation 4.1.14 gives

$$V = \frac{nRT}{P} \tag{4.1.15}$$

Clearing the fractions by multiplying both sides of Equation 4.1.15 by P gives

$$PV = nRT \tag{4.1.16}$$

The value of R can be found by multiplying Boltzmann's constant (N_A) by Avogadro's constant (k),

$$R = N_A k \tag{4.1.17}$$

Values of R in several common units are shown in the following table:

Table 1A.1: Values of R in Several Common Units

Value of R	Units
8.3145	$\frac{J}{K \cdot mole}$
0.082057	$\frac{dm^3 \cdot atm}{K \cdot mole}$
0.083145	$\frac{dm^3 \cdot bar}{K \cdot mole}$
8.3145	$\frac{m^3 \cdot Pa}{K \cdot mole}$
1.9872	$\frac{cal}{K \cdot mole}$

The Relationship between Pressure and Volume: Boyle's Law

As the pressure on a gas increases, the volume of the gas decreases because the gas particles are forced closer together. Conversely, as the pressure on a gas decreases, the gas volume increases because the gas particles can now move farther apart. Weather balloons get larger as they rise through the atmosphere to regions of lower pressure because the volume of the gas has increased; that is, the atmospheric gas exerts less pressure on the surface of the balloon, so the interior gas expands until the internal and external pressures are equal.

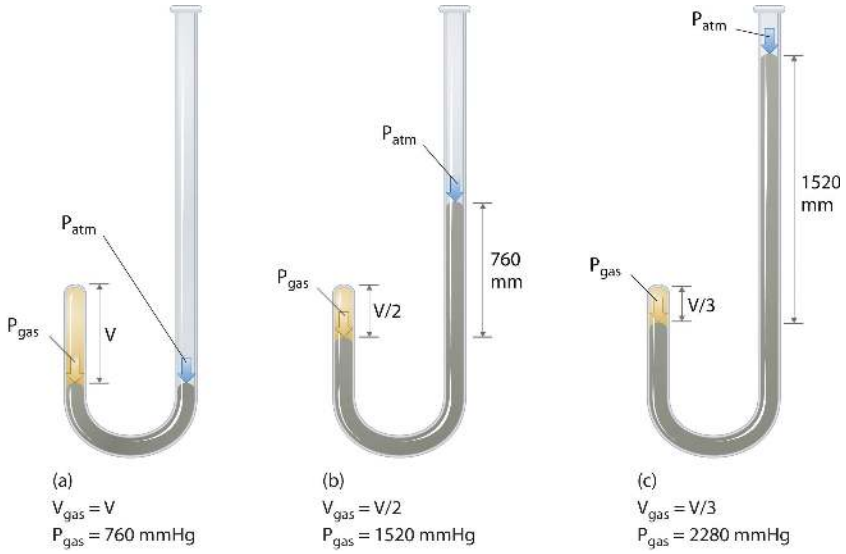


Figure 4.1.3: *Boyle's Experiment Using a J-Shaped Tube to Determine the Relationship between Gas Pressure and Volume. (a) Initially the gas is at a pressure of 1 atm = 760 mmHg (the mercury is at the same height in both the arm containing the sample and the arm open to the atmosphere); its volume is V. (b) If enough mercury is added to the right side to give a difference in height of 760 mmHg between the two arms, the pressure of the gas is 760 mmHg (atmospheric pressure) + 760 mmHg = 1520 mmHg and the volume is V/2. (c) If an additional 760 mmHg is added to the column on the right, the total pressure on the gas increases to 2280 mmHg, and the volume of the gas decreases to V/3.*

The Irish chemist Robert Boyle (1627–1691) carried out some of the earliest experiments that determined the quantitative relationship between the pressure and the volume of a gas. Boyle used a J-shaped tube partially filled with mercury, as shown in Figure **4.1.3**. In these experiments, a small amount of a gas or air is trapped above the mercury column, and its volume is measured at atmospheric pressure and constant temperature. More mercury is then poured into the open arm to increase the pressure on the gas sample. The pressure on the gas is atmospheric pressure plus the difference in the heights of the mercury columns, and the resulting volume is measured. This process is repeated until either there is no more room in the open arm or the volume of the gas is too small to be measured accurately. Data such as those from one of Boyle's own experiments may be plotted in several ways Figure **4.1.4**. A simple plot of V versus P gives a curve called a hyperbola and reveals an inverse relationship between pressure and

volume: as the pressure is doubled, the volume decreases by a factor of two. This relationship between the two quantities is described as follows:

$$PV = \text{constant} \tag{4.1.18}$$

Dividing both sides by p gives an equation illustrating the inverse relationship between P and V:

$$V = \frac{\text{const.}}{P} = const.\left(\frac{1}{P}\right) \tag{4.1.19}$$

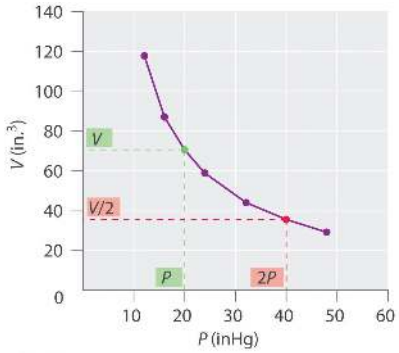
or

$$V \propto \frac{1}{P} \tag{4.1.20}$$

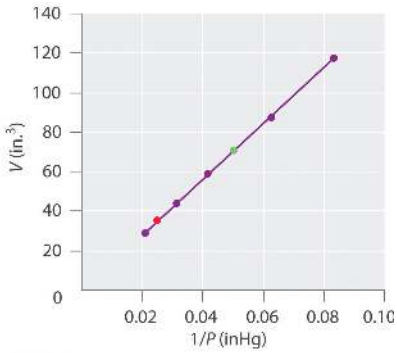
where the ∝ symbol is read “is proportional to.” A plot of V versus $1/P$ is thus a straight line whose slope is equal to the constant in Equations 4.1.18 and 4.1.19. Dividing both sides of Equation 4.1.18 by V instead of P gives a similar relationship between P and $1/V$. The numerical value of the constant depends on the amount of gas used in the experiment and on the temperature at which the experiments are carried out. This relationship between pressure and volume is known as Boyle's Law, after its discoverer, and can be stated as follows: *At constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure.* This law in practice is shown in Figure 4.1.4.

P (inHg)	V (in.^{3})	PV
12.0	117.5	1410
16.0	87.2	1400
20.0	70.7	1410
24.0	58.8	1410
32.0	44.2	1410
40.0	35.3	1410
48.0	29.1	1400

(a) Data from Boyle’s experiment



(b) Volume vs. pressure



(c) Volume vs. 1/pressure

Figure 4.1.4: *Plots of Boyle’s Data. (a) Here are actual data from a typical experiment conducted by Boyle. Boyle used non-SI units to measure the volume (in.^{3} rather than cm^3) and the pressure (in. Hg rather than mmHg). (b) This plot of pressure versus volume at constant temperature (known as an **isotherm**) is a hyperbola. Because PV is a constant, decreasing the pressure by a factor of two results in a twofold increase in volume and vice versa. (c) An **isotherm** of volume versus 1/pressure for the same data shows the inverse linear relationship between the two quantities, as expressed by the equation V = constant/P.*

The Relationship between Temperature and Volume: Charles's Law

The first experiments to quantify the relationship between the temperature and the volume of a gas were carried out in 1783 by an avid balloonist, the French chemist Jacques Alexandre César Charles (1746–1823). Charles’s initial experiments showed that a plot of the volume of a given sample of gas versus temperature (in degrees Celsius) at constant pressure is a straight line. Similar but more precise studies were carried out by another balloon enthusiast, the Frenchman Joseph-Louis Gay-Lussac (1778–1850), who showed that a plot of V versus T was a straight line that could be extrapolated to a point at zero volume, a theoretical condition now known to correspond to −273.15°C (Figure 4.1.5).A sample of gas cannot really have a volume of zero because any sample of matter must have some volume. Furthermore, at 1 atm pressure all gases liquefy at temperatures well above −273.15°C. Note from part (a) in Figure 4.1.5 that the slope of the plot of V versus T varies for the same gas at different pressures but that the intercept remains constant at −273.15°C. Similarly, as shown in part (b) in Figure 4.1.5, plots of V versus T for different amounts of varied gases are straight lines with different slopes but the same intercept on the T axis.

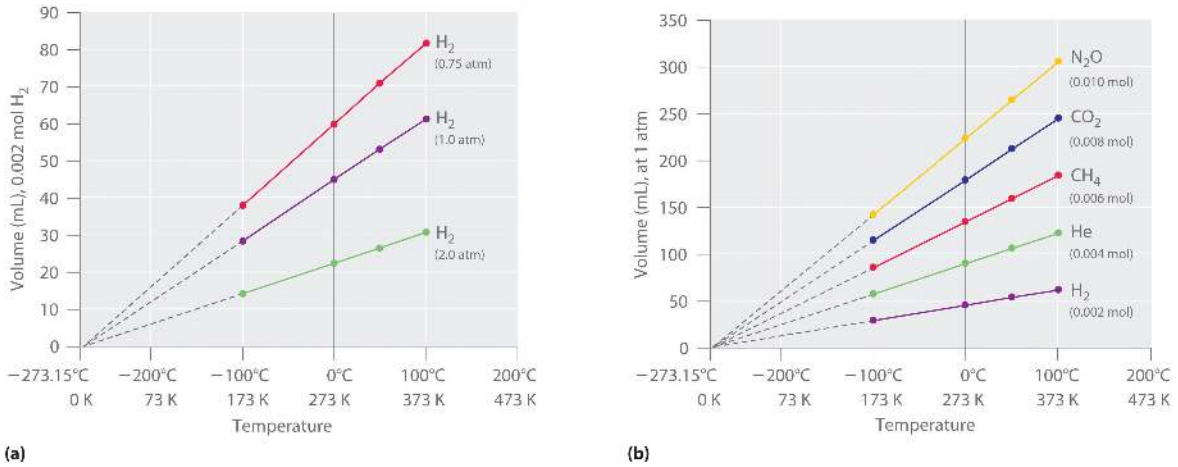


Figure 4.1.5*: The Relationship between Volume and Temperature at Constant Pressure. (a) In these plots of volume versus temperature at constant pressure (called* ***isobars****) for equal-sized samples of H_2 at three different pressures, the solid lines show the experimentally measured data down to −100°C, and the broken lines show the extrapolation of the data to V = 0. The temperature scale is given in both degrees Celsius and kelvins. Although the slopes of the lines decrease with increasing pressure, all of the lines extrapolate to the same temperature at V = 0 (−273.15°C = 0 K). (b) In these* ***isobars*** *for different amounts of selected gases at 1 atm pressure, all the plots extrapolate to a value of V = 0 at −273.15°C, regardless of the identity or the amount of the gas.*

The significance of the invariant T intercept in plots of V versus T was recognized in 1848 by the British physicist William Thomson (1824–1907), later named Lord Kelvin. He postulated that −273.15°C was the lowest possible temperature that could theoretically be achieved, for which he coined the term absolute zero (0 K).

We can state Charles's and Gay-Lussac's findings in simple terms: At constant pressure, the volume of a fixed amount of gas is directly proportional to its absolute temperature (in kelvins). This relationship, illustrated in part (b) in Figure **4.1.5** is often referred to as Charles's law and is stated mathematically as

$$V = \text{const.}\, T \tag{4.1.21}$$

or

$$V \propto T \tag{4.1.22}$$

with *temperature expressed in kelvins*, not *in degrees Celsius*. Charles's law is valid for virtually all gases at temperatures well above their boiling points.

The Relationship between Amount and Volume: Avogadro's Law

We can demonstrate the relationship between the volume and the amount of a gas by filling a balloon; as we add more gas, the balloon gets larger. The specific quantitative relationship was discovered by the Italian chemist Amedeo Avogadro, who recognized the importance of Gay-Lussac's work on combining volumes of gases. In 1811, Avogadro postulated that, at the same temperature and pressure, equal volumes of gases contain the same number of gaseous particles (Figure **4.1.6**). This is the historic "Avogadro's hypothesis."

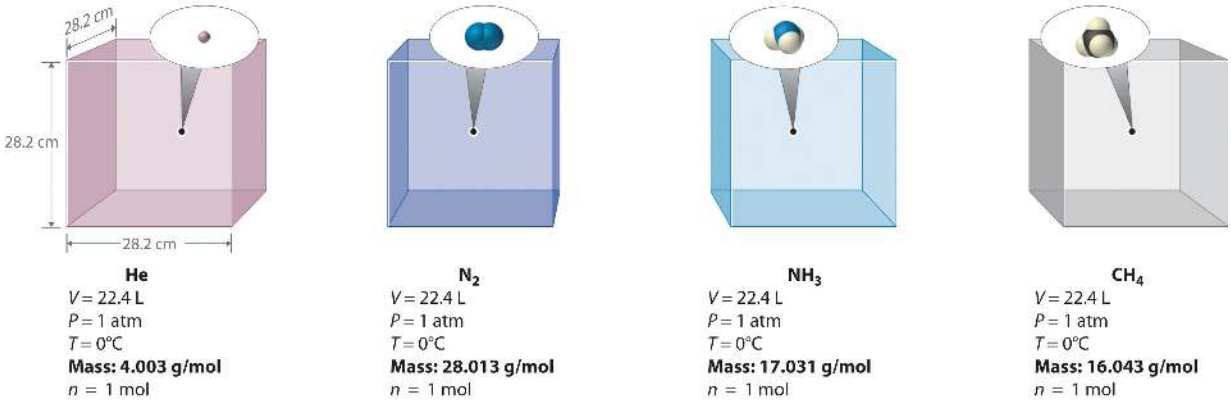


Figure 4.1.6: *Avogadro's Hypothesis. Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the mass of each gas sample is different even though all contain 1 mol of gas.*

A logical corollary to Avogadro's hypothesis (sometimes called Avogadro's law) describes the relationship between the volume and the amount of a gas: *At constant temperature and pressure, the volume of a sample of gas is directly proportional to the number of moles of gas in the sample.* Stated mathematically,

$$V = \text{const.}\, n \tag{4.1.23}$$

or

$$V \propto n \tag{4.1.24}$$

This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures.



Figure 4.1.7: *The Empirically Determined Relationships among Pressure, Volume, Temperature, and Amount of a Gas. The thermometer and pressure gauge indicate the temperature and the pressure qualitatively, the level in the flask indicates the volume, and the number of particles in each flask indicates relative amounts.*

A perfect gas is defined as a hypothetical gaseous substance whose behavior is independent of attractive and repulsive forces and can be completely described by the perfect gas law. In reality, there is no such thing as an perfect gas, but an perfect gas is a useful conceptual model that allows us to understand how gases respond to changing conditions. As we shall see, under many conditions, most real gases exhibit behavior that closely approximates that of a perfect gas. The perfect gas law can therefore be used to predict

the behavior of real gases under most conditions. The perfect gas law does not work well at very low temperatures or very high pressures, where deviations from perfect behavior are most commonly observed.

Applying the Perfect Gas Law

The perfect gas law allows us to calculate the value of the fourth variable for a gaseous sample if we know the values of any three of the four variables (*P*, *V*, *T*, and *n*). It also allows us to predict the *final state* of a sample of a gas (i.e., its final temperature, pressure, volume, and amount) following any changes in conditions if the parameters (*P*, *V*, *T*, and *n*) are specified for an *initial state*. Some applications are illustrated in the following examples. The approach used throughout is always to start with the same equation—the perfect gas law—and then determine which quantities are given and which need to be calculated. Let's begin with simple cases in which we are given three of the four parameters needed for a complete physical description of a gaseous sample.

Example 4.1.2

The balloon that Charles used for his initial flight in 1783 was destroyed, but we can estimate that its volume was 31,150 L (1100 ft^3), given the dimensions recorded at the time. If the temperature at ground level was 86°F (30°C) and the atmospheric pressure was 745 mmHg, how many moles of hydrogen gas were needed to fill the balloon?

Strategy:

A. Solve the perfect gas law for the unknown quantity, in this case *n*.
B. Make sure that all quantities are given in units that are compatible with the units of the gas constant. If necessary, convert them to the appropriate units, insert them into the equation you have derived, and then calculate the number of moles of hydrogen gas needed.

Solution:

A We are given values for *P*, *T*, and *V* and asked to calculate *n*. If we solve the ideal gas law (Equation 4.1.16) for *n*, we obtain

$$n = \frac{PV}{RT} \tag{4.1.25}$$

B *P* and *T* are given in units that are not compatible with the units of the gas constant [*R* = 0.08206 (L•atm)/(K•mol)]. We must therefore convert the temperature to kelvins and the pressure to atmospheres:

$$T = 273 + 30 = 303\text{K} \tag{4.1.26}$$

$$745\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{mmHg}} = 0.980\ \text{atm} \tag{4.1.27}$$

Substituting these values into the expression we derived for *n*, we obtain

$$n = \frac{PV}{RT} = \frac{0.980\ \text{atm} \times 31150\ \text{L}}{0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 303\ \text{K}} = 1.23 \times 10^3\ \text{mol} \tag{4.1.28}$$

Exercise 4.1.3

Suppose that an "empty" aerosol spray-paint can has a volume of 0.406 L and contains 0.025 mol of a propellant gas such as CO_2. What is the pressure of the gas at 25°C?

Answer: 1.5 atm

General Gas Equation

When one sample of gas is described under two different conditions, the ideal gas equation must be applied twice - to an initial condition and a final condition. This is:

$$\begin{matrix} \text{Initial condition } (i) & \text{Final condition} (f) \\ P_i V_i = n_i R T_i & P_f V_f = n_f R T_f \end{matrix} \tag{4.1.29}$$

Both equations can be rearranged to give:

$$R = \frac{P_i V_i}{n_i T_i} \qquad R = \frac{P_f V_f}{n_f T_f} \tag{4.1.30}$$

The two equations are equal to each other since each is equal to the same constant R. Therefore, we have:

$$\frac{P_i V_i}{n_i T_i} = \frac{P_f V_f}{n_f T_f} \tag{4.1.31}$$

The equation is called the **general gas equation,** or the **combined gas law**. The equation is particularly useful when one or two of the gas properties are held constant between the two conditions. In such cases, the equation can be simplified by eliminating these constant gas properties.

Example 4.1.3

Suppose that Charles had changed his plans and carried out his initial flight not in August but on a cold day in January, when the temperature at ground level was −10°C (14°F). How large a balloon would he have needed to contain the same amount of hydrogen gas at the same pressure as in Example **4.1.2**?

Strategy:

A. Use the results from Example **4.1.2** for August as the initial conditions and then calculate the *change in volume* due to the change in temperature from 30°C to −10°C. Begin by constructing a table showing the initial and final conditions.
B. Simplify the general gas equation by eliminating the quantities that are held constant between the initial and final conditions, in this case P and n.
C. Solve for the unknown parameter.

Solution:

A To see exactly which parameters have changed and which are constant, prepare a table of the initial and final conditions:

Initial (August)	Final (January)
$T_i = 30$°C = 303 K	$T_f =$−10°C = 263 K
$P_i =$0.980 atm	$P_f =$0.980 atm
$n_i =$1.23 × 103 mol	$n_f =$1.23 × 103 mol
$V_i = 31150$ L	$V_f =$?

B Both n and P are the same in both cases ($n_i = n_f, P_i = P_f$). Therefore, Equation can be simplified to:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f} \tag{4.1.32}$$

This is the relationship first noted by Charles.

C Solving the equation for V_f, we get:

$$V_f = V_i \times \frac{T_f}{T_i} = 31150\ \text{L} \times \frac{263\ \text{K}}{303\ \text{K}} = 2.70 \times 10^4\ \text{L} \tag{4.1.33}$$

It is important to check your answer to be sure that it makes sense, just in case you have accidentally inverted a quantity or multiplied rather than divided. In this case, the temperature of the gas decreases. Because we know that gas volume decreases with decreasing temperature, the final volume must be less than the initial volume, so the answer makes sense. We could have calculated the new volume by plugging all the given numbers into the perfect gas law, but it is generally much easier and faster to focus on only the quantities that change.

Exercise 4.1.4

Suppose that a fire extinguisher, filled with CO_2 to a pressure of 20.0 atm at 21°C at the factory, is accidentally left in the sun in a closed automobile in Tucson, Arizona, in July. The interior temperature of the car rises to 160°F (71.1°C). What is the internal pressure in the fire extinguisher?

Answer: 23.4 atm

In Example **4.1.3** , two of the four parameters (*P*, *V*, *T*, and *n*) were fixed while one was allowed to vary, and we were interested in the effect on the value of the fourth. In fact, we often encounter cases where two of the variables *P*, *V*, and *T* are allowed to vary for a given sample of gas (hence *n* is constant), and we are interested in the change in the value of the third under the new conditions.

Standard Conditions for Comparing Gas Samples

Scientists have chosen several sets of conditions to use as references:

Standard Ambient Temperature and Pressure (**SATP**) 25.0°C (298.15 K) and $1\ \text{bar} = 100\ \text{kPa} = 10^5\ \text{Pa}$ pressure,

$$\textbf{SATP:} \qquad T = 298.15\ \text{K and } P = 1\ \text{bar} = 10^5\ \text{Pa} \tag{4.1.34}$$

Standard Temperature and Pressure (**STP**) 0.0°C (273.15 K) and 1 atm pressure,

$$\textbf{STP:} \qquad T = 273.15\ \text{K and } P = 1\ \text{atm} \tag{4.1.35}$$

We can calculate the volume of 1.000 mol of an ideal gas under standard conditions using the variant of the perfect gas law given in Equation 4.1.15:

$$V = \frac{nRT}{P} \tag{1.1.15}$$

Thus the volume of 1 mol of an ideal gas is **24.79 L at SATP** and **22.41 L at STP**, approximately equivalent to the volume of three basketballs. The molar volumes of several real gases at 0°C and 1 atm are given in Table 1A.2, which shows that the deviations from ideal gas behavior are quite small. Thus the ideal gas law does a good job of approximating the behavior of real gases at 0°C and 1 atm.

Table 1A.2: Molar Volumes of Selected Gases at 0°C and 1 atm

Gas	Molar Volume (L)
NH_3	22.079
CO_2	22.260
Ar	22.397
O_2	22.397
N_2	22.402
H_2	22.433
He	22.434

P, V, T Surfaces

The ideal gas law is derived from empirical relationships among the pressure, the volume, the temperature, and the number of moles of a gas; it can be used to calculate any of the four properties if the other three are known. All of the empirical gas relationships are special cases of the ideal gas law in which two of the four parameters are held constant. The ideal gas law allows us to calculate the value of the fourth quantity (*P*, *V*, *T*, or *n*) needed to describe a gaseous sample when the others are known and also predict the value of these quantities following a change in conditions if the original conditions (values of *P*, *V*, *T*, and *n*) are known. The blue surface in the figure below shows some of the possible P, V, and T combinations for a fixed sample of a perfect gas. This sample of perfect gas can only exist in states that correspond to specific points on the surface shown.

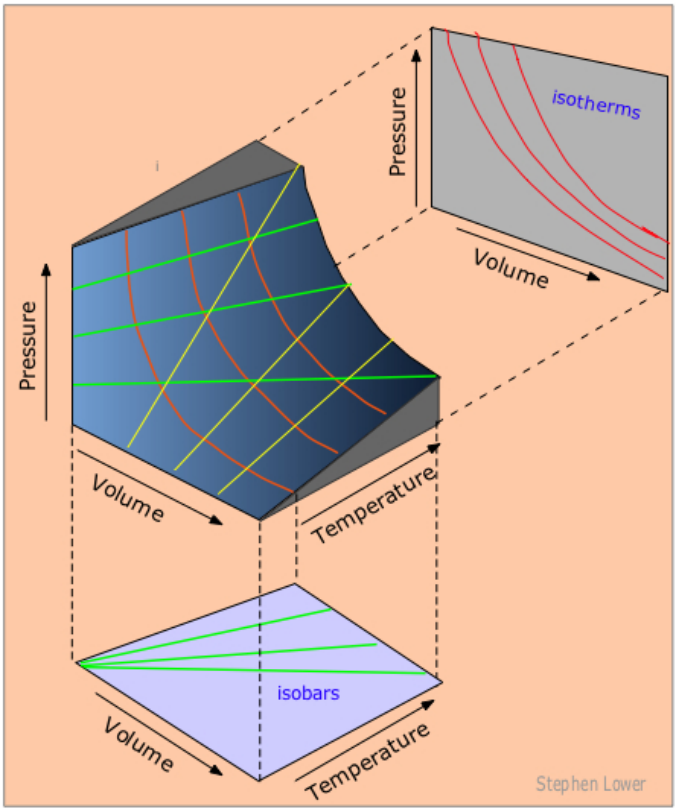


Figure 4.1.8: *A P,V,T Surface of a Fixed Sample of Perfect Gas. The central figure shows possible P, V, and T combinations for a fixed sample of a perfect gas. The graph below shows three possible* ***isobars*** *(constant pressure). The graph on the upper right shows three possible* ***isotherms*** *(constant temperature). The yellow lines on the P, V, T surface represent* ***isochores****, plots of pressure versus temperature at constant volume.*

http://www.chem1.com/acad/webtext/gas/gas_2.html#4A (Creative Commons Attribution-Share Alike 3.0 License)

Mixtures of Perfect Gases

The perfect gas law *assumes* that all gases behave identically and that their behavior is independent of attractive and repulsive forces. If volume and temperature are held constant, the perfect gas equation can be rearranged to show that the pressure of a sample of gas is directly proportional to the number of moles of gas present:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{const.} \tag{4.1.36}$$

Nothing in the equation depends on the *nature* of the gas—only the amount.

With this assumption, let's suppose we have a mixture of two perfect gases that are present in equal amounts. What is the total pressure of the mixture? Because the pressure depends on only the total number of particles of gas present, the total pressure of the mixture will simply be twice the pressure of either component. More generally, the total pressure exerted by a mixture of gases at a given temperature and volume is the sum of the pressures exerted by each gas alone. Furthermore, if we know the volume, the temperature, and the number of moles of each gas in a mixture, then we can calculate the pressure exerted by each gas individually, which is its partial pressure, the pressure the gas would exert if it were the only one present (at the same temperature and volume).

To summarize, ***the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases***. This law was first discovered by John Dalton, the father of the atomic theory of matter. It is now known as *Dalton's law of partial pressures*.

We can write it mathematically as

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots = \sum_{i=1}^{n} P_i \tag{4.1.37}$$

where P_{tot} is the total pressure and the other terms are the partial pressures of the individual gases (up to n component gases).

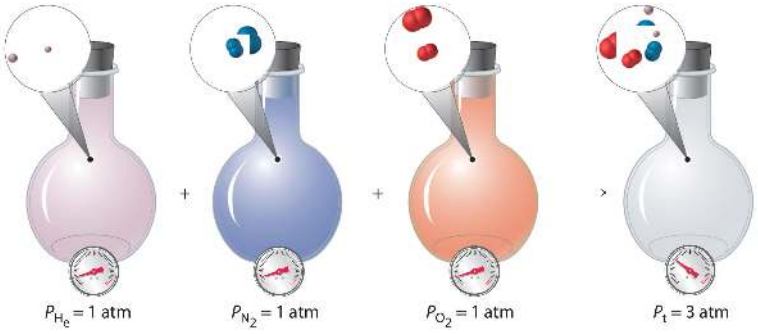


Figure 4.1.9: *Dalton's Law. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.*

For a mixture of two perfect gases, A and B, we can write an expression for the total pressure:

$$P_{tot} = P_A + P_B = n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) = (n_A + n_B)\left(\frac{RT}{V}\right) \tag{4.1.38}$$

More generally, for a mixture of n component gases, the total pressure is given by

$$P_{tot} = (P_1 + P_2 + P_3 + \cdots + P_n)\left(\frac{RT}{V}\right) \tag{4.1.39}$$

$$P_{tot} = \sum_{i=1}^{n} n_i\left(\frac{RT}{V}\right) \tag{4.1.40}$$

Equation 4.1.40 restates Equation 4.1.37 in a more general form and makes it explicitly clear that, at constant temperature and volume, the pressure exerted by a gas depends on only the total number of moles of gas present, whether the gas is a single chemical species or a mixture of dozens or even hundreds of gaseous species. For Equation 4.1.40 to be valid, the identity of the particles present cannot have an effect. Thus a perfect gas must be one whose properties are not affected by either the size of the particles or their intermolecular interactions because both will vary from one gas to another. The calculation of total and partial pressures for mixtures of gases is illustrated in Example 4.1.4.

Example 4.1.4: The Bends

Deep-sea divers must use special gas mixtures in their tanks, rather than compressed air, to avoid serious problems, most notably a condition called "the bends." At depths of about 350 ft, divers are subject to a pressure of approximately 10 atm. A typical gas cylinder used for such depths contains 51.2 g of O_2 and 326.4 g of He and has a volume of 10.0 L. What is the partial pressure of each gas at 20.00°C, and what is the total pressure in the cylinder at this temperature?

Strategy:

A. Calculate the number of moles of He and O_2 present.
B. Use the perfect gas law to calculate the partial pressure of each gas. Then add together the partial pressures to obtain the total pressure of the gaseous mixture.

Solution:

A The number of moles of He is

$$n_{\text{He}} = \frac{326.4\ \text{g}}{4.003\ \text{g/mol}} = 81.54\ \text{mol} \tag{4.1.41}$$

The number of moles of O_2 is

$$n_{O_2} = \frac{51.2\ \text{g}}{32.00\ \text{g/mol}} = 1.60\ \text{mol} \tag{4.1.42}$$

B We can now use the perfect gas law to calculate the partial pressure of each:

$$P_{He} = \frac{n_{He}RT}{V} = \frac{81.54\ \text{mol} \times 0.08206\ \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15\ \text{K}}{10.0\ \text{L}} = 196.2\ \text{atm} \tag{4.1.43}$$

$$P_{O_2} = \frac{n_{O_2}RT}{V} = \frac{1.60\ \text{mol} \times 0.08206\ \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15\ \text{K}}{10.0\ \text{L}} = 3.85\ \text{atm} \tag{4.1.44}$$

The total pressure is the sum of the two partial pressures:

$$P_{tot} = P_{He} + P_{O_2} = (196.2 + 3.85)\ \text{atm} = 200.1\ \text{atm} \tag{4.1.45}$$

Exercise 4.1.5

A cylinder of compressed natural gas has a volume of 20.0 L and contains 1813 g of methane and 336 g of ethane. Calculate the partial pressure of each gas at 22.0°C and the total pressure in the cylinder.

Answer

$P_{CH_4} = 137\ atm$; $P_{C_2H_6} = 13.4\ atm$; $P_{tot} = 151\ atm$

Mole Fractions of Gas Mixtures

The composition of a gas mixture can be described by the mole fractions of the gases present. The mole fraction (X) of any component of a mixture is the ratio of the number of moles of that component to the total number of moles of all the species present in the mixture (n_{tot}):

$$x_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{4.1.46}$$

The mole fraction is a dimensionless quantity between 0 and 1. If $x_A = 1.0$, then the sample is pure A, not a mixture. If $x_A = 0$, then no A is present in the mixture. The sum of the mole fractions of all the components present must equal 1.

To see how mole fractions can help us understand the properties of gas mixtures, let's evaluate the ratio of the pressure of a gas A to the total pressure of a gas mixture that contains A. We can use the perfect gas law to describe the pressures of both gas A and the mixture: $P_A = n_ART/V$ and $P_{tot} = n_tRT/V$. The ratio of the two is thus

$$\frac{P_A}{P_{tot}} = \frac{n_ART/V}{n_{tot}RT/V} = \frac{n_A}{n_{tot}} = x_A \tag{4.1.47}$$

Rearranging this equation gives

$$P_A = x_AP_{tot} \tag{4.1.48}$$

That is, the partial pressure of any gas in a mixture is the total pressure multiplied by the mole fraction of that gas. This conclusion is a direct result of the perfect gas law, which assumes that all gas particles behave ideally. Consequently, the pressure of a gas in a mixture depends on only the percentage of particles in the mixture that are of that type, not their specific physical or chemical properties. By volume, Earth's atmosphere is about 78% N_2, 21% O_2, and 0.9% Ar, with trace amounts of gases such as CO_2, H_2O, and others. This means that 78% of the particles present in the atmosphere are N_2; hence the mole fraction of N_2 is 78%/100% = 0.78. Similarly, the mole fractions of O_2 and Ar are 0.21 and 0.009, respectively. Using Equation 4.1.48, we therefore know that the partial pressure of N_2 is 0.78 atm (assuming an atmospheric pressure of exactly 760 mmHg) and, similarly, the partial pressures of O_2 and Ar are 0.21 and 0.009 atm, respectively.

Example 4.1.5: Exhaling Composition

We have just calculated the partial pressures of the major gases in the air we inhale. Experiments that measure the composition of the air we *exhale* yield different results, however. The following table gives the measured pressures of the major gases in both inhaled and exhaled air. Calculate the mole fractions of the gases in exhaled air.

	Inhaled Air / mmHg	Exhaled Air / mmHg
P_{N_2}	597	568
P_{O_2}	158	116
P_{H_2O}	0.3	28
P_{CO_2}	5	48
P_{Ar}	8	8
P_{tot}	767	767

Strategy:

Calculate the mole fraction of each gas using Equation 4.1.48.

Solution:

The mole fraction of any gas A is given by

$$x_A = \frac{P_A}{P_{tot}} \tag{4.1.49}$$

where P_A is the partial pressure of A and P_{tot} is the total pressure. For example, the mole fraction of CO_2 is given as:

$$x_{CO_2} = \frac{48 \text{ mmHg}}{767 \text{ mmHg}} = 0.063 \tag{4.1.50}$$

The following table gives the values of x_A for the gases in the exhaled air.

Gas	Mole Fraction
N_2	0.741
O_2	0.151
H_2O	0.037
CO_2	0.063
Ar	0.010

Exercise 4.1.6

Venus is an inhospitable place, with a surface temperature of 560°C and a surface pressure of 90 atm. The atmosphere consists of about 96% CO_2 and 3% N_2, with trace amounts of other gases, including water, sulfur dioxide, and sulfuric acid. Calculate the partial pressures of CO_2 and N_2.

Answer

$P_{CO_2} = 86$ atm; $P_{N_2} = 2.7$ atm

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4.2: Real Gases (Deviations From Ideal Behavior)

The postulates of the kinetic molecular theory of gases ignore both the volume occupied by the molecules of a gas and all interactions between molecules, whether attractive or repulsive. In reality, however, all gases have nonzero molecular volumes. Furthermore, the molecules of real gases interact with one another in ways that depend on the structure of the molecules and therefore differ for each gaseous substance. In this section, we consider the properties of real gases and how and why they differ from the predictions of the perfect (ideal) gas law. We also examine liquefaction, a key property of real gases that is not predicted by the kinetic molecular theory of gases.

The perfect gas law is an example of an Equation of state. One way to visualize any Equation of state is to plot the so-called *isotherms*, which are graphs of P vs. V at fixed values of T. For the ideal-gas Equation of state $P = nRT/V$, some of the isotherms are shown in Figure 4.2.1.

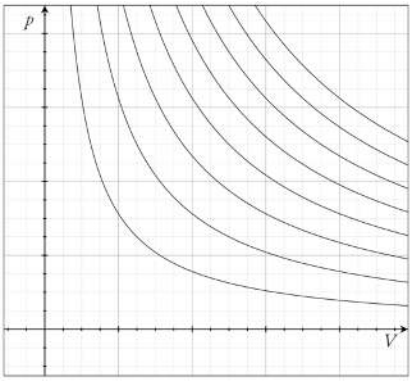


Figure* 4.2.1: Pressure vs. volume for different temperatures (isotherms) of the ideal-gas Equation of state.*
Image citation: https://commons.wikimedia.org/wiki/F..._isotherms.png

What is important to note here, is that an ideal gas can exist *only* as a gas. It is not possible for an ideal gas to condense into some kind of “ideal liquid”. In other words, a phase transition from gas to liquid can be modeled only if interparticle interactions are properly accounted for.

The Compressibility of a Gas

Note that the ideal-gas Equation of state can be written in the form

$$\frac{PV}{nRT} = \frac{P\bar{V}}{RT} = \frac{P}{\rho RT} = 1 \tag{4.2.1}$$

where $\bar{V} = V/n$ is called the molar volume (and is also known as V_m). Unlike V, which increases as the number of moles increases (an example of what is called an *extensive* quantity in thermodynamics), $\bar{V}$ does not exhibit this dependence and, therefore, is called *intensive*. The quantity

$$Z = \frac{PV}{nRT} = \frac{P\bar{V}}{RT} = \frac{P}{\rho RT} \tag{4.2.2}$$

is called the *compressibility* of the gas. In an ideal gas, if we “compress” the gas by increasing P , the density ρ must increase as well so as to keep $Z = 1$. For a real gas, Z, therefore, gives us a measure of how much the gas deviates from ideal-gas behavior.

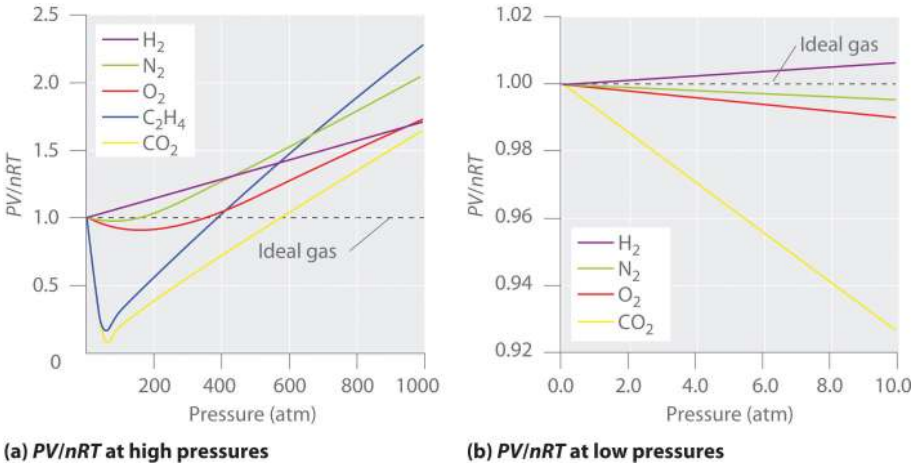


***Figure* 4.2.2:** *Two graphs of the compressibility factor (Z) vs. pressure at 273 K. The graph on the left shows real gases at high pressure. The graph on the right shows real gases at low pressure.*

Figure **4.2.2** shows a plot of Z vs. P for several real gases and for an ideal gas. The plot on the left shows the non-ideality of real gases at high pressures. There are large negative deviations observed for C_2H_4 and CO_2 because they liquefy at relatively low pressures. The plot on the right shows that for sufficiently low pressures (hence, low densities), each real gas approaches ideal-gas behavior, as expected.

Real gases also tend to approach ideal gas behavior more closely at higher temperatures, as shown in Figure **4.2.3** for N_2. Why do real gases behave so differently from ideal gases at high pressures and low temperatures? Under these conditions, the two basic assumptions behind the ideal gas law—namely, that gas molecules have negligible volume and that intermolecular interactions are negligible—are no longer valid.

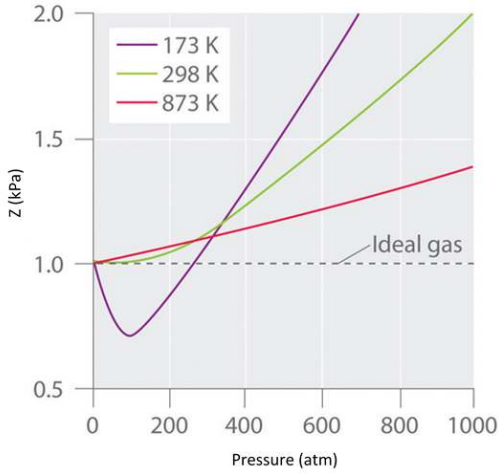


***Figure* 4.2.3:** *The Effect of Temperature on the Behavior of Real Gases. A plot of Z versus P for nitrogen gas at three temperatures shows that the approximation to ideal gas behavior becomes better as the temperature increases.*

Because the molecules of an ideal gas are assumed to have zero volume, the volume available to them for motion is always the same as the volume of the container. In contrast, the molecules of a real gas have small but measurable volumes. At low pressures, the gaseous molecules are relatively far apart, but as the pressure of the gas increases, the intermolecular distances become smaller and smaller (Figure **4.2.4**). As a result, the volume occupied by the molecules becomes significant compared with the volume of the container. Consequently, the total volume occupied by the gas is greater than the volume predicted by the ideal gas law. Thus at very high pressures, the experimentally measured value of Z is greater than the value predicted by the ideal gas law.

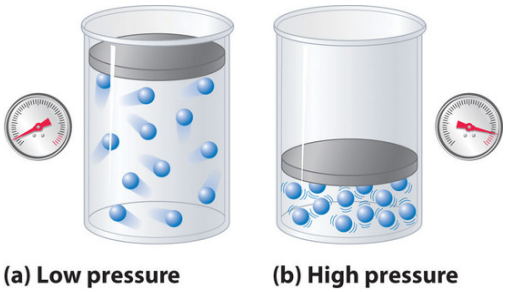


***Figure* 4.2.4:** *The Effect of Nonzero Volume of Gas Particles on the Behavior of Gases at Low and High Pressures. (a) At low pressures, the volume occupied by the molecules themselves is small compared with the volume of the container. (b) At high pressures, the molecules occupy a large portion of the volume of the container, resulting in significantly decreased space in which the molecules can move.*

Moreover, all molecules are attracted to one another by a combination of forces. These forces become particularly important for gases at low temperatures and high pressures, where intermolecular distances are shorter. Attractions between molecules reduce the number of collisions with the container wall, an effect that becomes more pronounced as the number of attractive interactions increases. Because the average distance between molecules decreases, the pressure exerted by the gas on the container wall decreases, and the observed pressure is *less* than expected (Figure **4.2.4**). Thus as shown in Figure **4.2.3**, at low temperatures, the value of Z is lower than predicted for an ideal gas, an effect that becomes particularly evident for complex gases and for simple gases at low temperatures. At very high pressures, the effect of nonzero molecular volume predominates. The competition between these effects is responsible for the minimum observed in the Z versus P plot for many gases.

> *Nonzero molecular volume makes the actual volume greater than predicted at high pressures; intermolecular attractions make the pressure less than predicted.*

At high temperatures, the molecules have sufficient kinetic energy to overcome intermolecular attractive forces, and the effects of nonzero molecular volume predominate. Conversely, as the temperature is lowered, the kinetic energy of the gas molecules decreases. Eventually, a point is reached where the molecules can no longer overcome the intermolecular attractive forces, and the gas liquefies (condenses to a liquid). Figure **4.2.5** shows isotherms for isopentane, which look similar to the isotherms of a perfect gas above 215 K, because the sample remains a gas at all pressures and volumes. At temperatures below 215, the isotherms begin to show deviations from ideality. For instance, at 185 K, the sample is entirely in the gas phase when the container size is 20 mL. As the volume of the container is decreased, however, the gas eventually begins to condense; in this case at a pressure of around 32 atm and a volume of about 7 mL. The pressure remains constant as the volume is decreased, because the gas can continue to condense, but once all the gas has condensed (at a volume of about 3 mL), the pressure shoots up rapidly because the sample is entirely liquid, and cannot be compressed further.

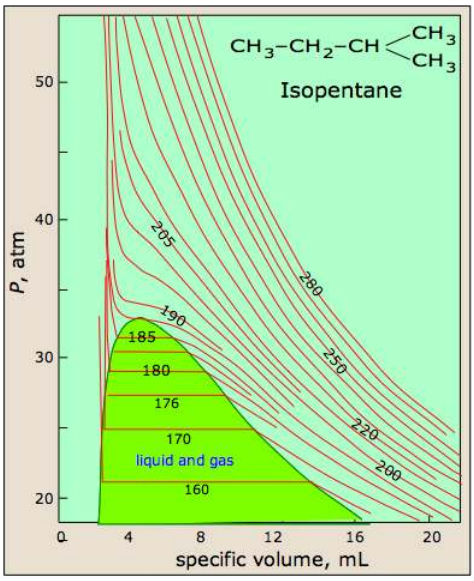


Figure* 4.2.5*: *Isotherms of isopentane, a real gas. Image citation:*http://www.chem1.com/acad/webtext/gas/gas_6.html

The Virial Equation of State

Because the perfect gas law is an imperfect description of a real gas, we can combine the perfect gas law and the compressibility factors of real gases to develop an equation to describe the isotherms of a real gas. This Equation is known as the *Virial Equation of state*, which expresses the deviation from ideality in terms of a power series in the density.

$$\frac{P}{RT} = \rho + B\rho^2 + C\rho^3 + \ldots \tag{4.2.3}$$

- B is the second virial coefficient,
- C is called the third virial coefficient, etc.

The second virial coefficient represents the initial departure from ideal-gas behavior, and describes the contribution of the pair-wise potential to the pressure of the gas. The third virial coefficient depends on interactions between three molecules. The j^{th} virial coefficient can be calculated in terms of the interaction of j molecules in a volume V. The second and third virial coefficients give most of the deviation from ideal $\frac{P}{\rho RT}$ up to 100 atm. It is important to note that value of the virial coefficients are temperature dependent.

Because

$$\rho = \frac{n}{V} = \frac{1}{\bar{V}} \tag{4.2.4}$$

and the virial Equation can be rearranged to

$$P\bar{V} = RT\left(1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \cdots\right) \tag{4.2.5}$$

Recall that

$$\frac{P\bar{V}}{RT} = Z \tag{4.2.6}$$

and it is easy to see that because

$$P\bar{V} = ZRT \tag{4.2.7}$$

then

$$Z = 1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \cdots \tag{4.2.8}$$

Example 4.2.1: Virial Equation of state

Calculate the pressure exerted by 0.275 moles of N_2 gas in a 0.500 L flask at 273 K using the first two terms of the series in Equation 4.2.5. The value of B for N_2 at 273 K is -10.5 $\frac{cm^3}{mole}$.

Strategy:

a) Convert all terms to the correct units: V = 0.500 L = 0.500 dm^3 = 5.00 x 10^{-4} m^3

$$B = -10.5\frac{cm^3}{mole} = -1.05 \times 10^{-5}\frac{m^3}{mole} \tag{4.2.9}$$

b) Calculate $\bar{V}$

$$\bar{V} = \frac{V}{n} = \frac{5.00 \times 10^{-4} m^3}{0.275\, moles} = 1.82 \times 10^{-3}\frac{m^3}{mole} \tag{4.2.10}$$

c) Solve for P

$$P = \frac{RT}{\bar{V}}\left(1 + \frac{B}{\bar{V}}\right) \tag{4.2.11}$$

$$P = \frac{8.3145\frac{J}{mole \cdot K}\, x\, 273K}{1.82x10^{-3}\frac{m^3}{moles}}\, x \left(1 - \frac{-1.05x10^{-5}\frac{m^3}{moles}}{1.82x10^{-3}\frac{m^3}{moles}}\right) \tag{4.2.12}$$

$$P = 1240\, kPa \tag{4.2.13}$$

For a perfect gas, the pressure would be 1250 kPa.

Exercise 4.2.1

Calculate the pressure exerted by 0.350 moles of CO_2 gas in a 0.500 L flask at 273 K. The value of B for CO_2 at 273 K is -149.7 $\frac{cm^3}{mole}$.

Answer: 1420 kPa

The virial Equation of state is a model that attempts to describe the properties of a real gas. If it were a perfect model, the virial Equation would give results identical to those of the perfect gas law as the pressure of a gas sample approached zero. For the virial Equation to collapse to the perfect gas law, all of the virial coefficients would need to have a value of zero at the same temperature. This is an unlikely occurrence, but because the second term in the virial Equation, $B = \frac{B}{\bar{V}}$ is the largest term in the Equation ($\frac{1}{\bar{V}} \ll \frac{1}{\bar{V}^2} \ll \frac{1}{\bar{V}^3} \ll \cdots$), we can focus on the temperature at which B is zero. This temperature is known as the **Boyle temperature**, T_B, and it is the temperature at which the repulsive forces between the gas molecules exactly balance the attractive forces between the gas molecules.

Note

Equation 4.2.5 can be rewritten as

$$P = RT\left(1 + \frac{B}{RT}P + \frac{C}{(RT)^2}P^2 + \cdots\right) \tag{4.2.14}$$

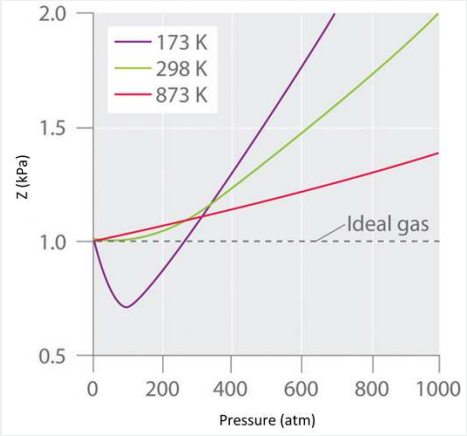
in which case

$$Z = 1 + \frac{B}{RT}P + \frac{C}{(RT)^2}P^2 + \cdots \tag{4.2.15}$$

Then

$$\frac{dZ}{dP} \rightarrow \frac{B}{RT} \; as \; P \rightarrow 0 \tag{4.2.16}$$

At the Boyle temperature, B = 0, and the slope of the graph of the compression factor versus the pressure is zero at P = 0. Compared to other temperatures, the slope of the plot of Z versus P at the Boyle temperature begins to approach zero at relatively higher pressures, and so the real gas closely approximates a perfect gas over a wider range of pressures. A second look at Figure **4.2.3** for N_2, shows us that the T_B is near 298 K. (In fact it is roughly 327 K.)



As we have seen, the Boyle temperature, T_B, is an intensive property of a real gas. A second defining temperature of a real gas is the critical temperature, T_C, the temperature at and above which the gas phase can not be condensed into the liquid phase, no matter how great the pressure becomes. In Figure **4.2.5** for isopentane, the isotherm for the critical temperature of 187ºC shows that the compound is not following ideal behavior, yet it does not condense into a liquid. The critical point, defined by the critical temperature, T_C, the critical pressure, P_C, and the critical molar volume, V_C, Is the point at which the interface defining the gas phase and the liquid phase disappears. Although the phase above the critical point is technically a gas, it has a much higher density than a typical gas, and it has much greater solvating properties than a gas. Thus, the phase beyond the critical point is usually called a supercritical fluid.

The van der Waals Equation

The Dutch physicist Johannes van der Waals (1837–1923; Nobel Prize in Physics, 1910) modified the ideal gas law to describe the behavior of real gases by explicitly including the effects of molecular size and intermolecular forces. In his description of gas behavior, the so-called *van der Waals* Equation,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \tag{4.2.17}$$

which can also be written as

$$\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT \tag{4.2.18}$$

a and *b* are empirical constants that are different for each gas. The values of a and b are listed in Table **4.2.1** for several common gases.

Table **4.2.1**:: van der Waals Constants for Some Common Gases (see Table A8 for more complete list)

Gas	a ($L^2 \cdot atm/mol^2$)	b (L/mol)
He	0.03410	0.0238
Ne	0.205	0.0167
Ar	1.337	0.032
H_2	0.2420	0.0265
N_2	1.352	0.0387
O_2	1.364	0.0319
Cl_2	6.260	0.0542
NH_3	4.170	0.0371
CH_4	2.273	0.0430
CO_2	3.610	0.0429

The pressure term in Equation 4.2.17: $P+(an^2/V^2)$—corrects for intermolecular attractive forces that tend to reduce the pressure from that predicted by the ideal gas law. Here, n^2/V^2 represents the concentration of the gas (n/V) squared because it takes two particles to engage in the pairwise intermolecular interactions of the type shown in Figure **4.2.6**. The volume term: $V-nb$—corrects for the volume occupied by the gaseous molecules, and thus takes into account repulsive forces among the molecules.

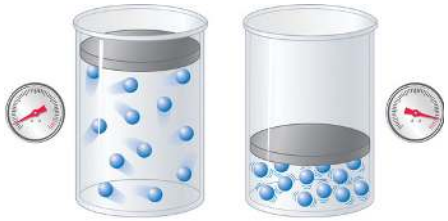


***Figure* 4.2.6:** *The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls. (a) At low pressures, there are relatively few attractive intermolecular interactions to lessen the impact of the molecule striking the wall of the container, and the pressure is close to that predicted by the ideal gas law. (b) At high pressures, with the average intermolecular distance relatively small, the effect of intermolecular interactions is to lessen the impact of a given molecule striking the container wall, resulting in a lower pressure than predicted by the ideal gas law.*

The correction for volume is negative, but the correction for pressure is positive to reflect the effect of each factor on V and P, respectively. Because nonzero molecular volumes produce a measured volume that is *larger* than that predicted by the ideal gas law, we must subtract the molecular volumes to obtain the actual volume available. Conversely, attractive intermolecular forces produce a pressure that is *less* than that expected based on the ideal gas law, so the an^2/V^2 term must be added to the measured pressure to correct for these effects.

Example 4.2.2

You are in charge of the manufacture of cylinders of compressed gas at a small company. Your company president would like to offer a 4.00 L cylinder containing 500 g of chlorine in the new catalog. The cylinders you have on hand have a rupture pressure of 40 atm. Use both the ideal gas law and the van der Waals Equation to calculate the pressure in a cylinder at 25°C. Is this cylinder likely to be safe against sudden rupture (which would be disastrous and certainly result in lawsuits because chlorine gas is highly toxic)?

Given: volume of cylinder, mass of compound, pressure, and temperature

Asked for: safety

Strategy:

A Use the molar mass of chlorine to calculate the amount of chlorine in the cylinder. Then calculate the pressure of the gas using the ideal gas law.

B Obtain *a* and *b* values for Cl_2 from Table **4.2.1**. Use the van der Waals relationship (Equation 4.2.17) to solve for the pressure of the gas. Based on the value obtained, predict whether the cylinder is likely to be safe against sudden rupture.

Solution:

A We begin by calculating the amount of chlorine in the cylinder using the molar mass of chlorine (70.906 g/mol):

$$n = \frac{m}{M} = \frac{500\ \text{g}}{70.906\ \text{g/mol}} = 7.052\ \text{mol} \tag{4.2.19}$$

Using the ideal gas law and the temperature in kelvins (298 K), we calculate the pressure:

$$P = \frac{nRT}{V} = \frac{7.052\ \text{mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L}} = 43.1\ \text{atm} \tag{4.2.20}$$

If chlorine behaves like an ideal gas, you have a real problem!

B Now let's use the van der Waals Equation with the *a* and *b* values for Cl_2 from Table **4.2.1**. Solving for *P* gives

$$\begin{aligned} P &= \frac{nRT}{V - nb} - \frac{an^2}{V^2} \\ &= \frac{7.052\ \text{mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L} - 7.052\ \text{mol} \times 0.0542 \frac{\text{L}}{\text{mol}}} - \frac{6.260 \frac{\text{L}^2\text{atm}}{\text{mol}^2} \times (7.052\ \text{mol})^2}{(4.00\ \text{L})^2} \\ &= 28.2\ \text{atm} \end{aligned} \tag{4.2.21}$$

This pressure is well within the safety limits of the cylinder. The ideal gas law predicts a pressure 15 atm higher than that of the van der Waals Equation.

Exercise 4.2.2

A 10.0 L cylinder contains 500 g of methane. Calculate its pressure to two significant figures at 27°C using the

a. ideal gas law.
b. van der Waals Equation.

Answer: a. 77 atm; b. 67 atm

Three Features of the van der Waals Equation

1. Best Conditions: The van der Waals equation works best at high temperatures and large molar volumes. At high temperatures, the $\frac{RT}{\bar{V} - b}$ term will be much greater than the $\frac{a}{\bar{V}^2}$ term. At large molar volumes, $\bar{V} - b$ will be essentially equal to $\bar{V}$. Under these conditions, the van der Waals equation collapses to the perfect gas law.

2. van der Waals Loops: At temperatures below the critical temperature, oscillations in the calculated isotherms occur when both terms in the equation have similar magnitudes. This similarity in magnitudes occurs when the repulsive forces and attractive forces are similar in magnitude. These oscillations are often replaced by horizontal lines (see Figure **4.2.3**) in a process called the Maxwell construction, which allows us to see the conditions under which gas and liquid are in equilibrium.

3. van der Waals coefficients and Critical Constants: The critical isotherm can be used to calculate the critical constants because the critical isotherm has an inflection point with zero slope at the critical point. From the first derivative of the van der Waals equation we see that:

$$\frac{dP}{d\bar{V}} = -\frac{RT}{\left(\bar{V} - b\right)^2} + \frac{2a}{\bar{V}^3} = 0 \tag{4.2.22}$$

The second derivative gives us:

$$\frac{d^2P}{d\bar{V}^2} = \frac{2RT}{\left(\bar{V}-b\right)^3} - \frac{6a}{\bar{V}^4} = 0 \tag{4.2.23}$$

These two equations can be rearranged to

$$RT = \frac{2a(\bar{V}-b)^2}{\bar{V}^3} \tag{4.2.24}$$

and

$$RT = \frac{3a(\bar{V}-b)^3}{\bar{V}^4} \tag{4.2.25}$$

Setting Equations 4.2.24 and 4.2.25 equal to one another, and simplifying gives

$$\bar{V}_C = 3b \tag{4.2.26}$$

Substituting this value back into Equation 4.2.24 results in

$$T_C = \frac{8a}{27Rb} \tag{4.2.27}$$

Substituting these values for $\bar{V}_C$ and T_C into Equation 4.2.18 allows us to determine that

$$P_C = \frac{a}{27b^2} \tag{4.2.28}$$

With these relationships, it is possible to show that there is a critical compression factor for all gases:

$$Z_C = \frac{P_C\bar{V}_C}{RT_C} = \frac{3}{8} \tag{4.2.29}$$

Although the value of Z_C for most gases varies from 0.375, the actual values are relatively close to this theoretical constant.

The Principle of Corresponding States

An additional assumption about real gases made by van der Waals was that all gases at corresponding states should behave similarly. The corresponding state that van der Waals choose to use is called the reduced state, which is based on the deviation of the conditions of a substance from its own critical conditions. Thus, the reduced properties for a gas are:

$$T_r = \frac{T}{T_C} \tag{4.2.30}$$

$$P_r = \frac{P}{P_C} \tag{4.2.31}$$

$$V_r = \frac{V_m}{V_C} \tag{4.2.32}$$

If any substance is at its critical point, then $T_r = P_r = V_r = 1$. van der Waals assumed that the values of these reduced properties should be the same for all real gases when existing under the same reduced conditions. In other words, all real gases at the same reduced temperature and the same reduced pressure should occupy the same reduced volume.

Example 4.2.3A: Reduced Properties

Calculate the reduced temperature and reduced pressure for a sample of helium at a temperature of 30.5 K and a pressure of 5.52 atm. The T_C of He is 5.2 K and the P_C of He is 2.26 atm.

Strategy:

Use Equations 4.2.30, 4.2.31, and 4.2.32 to calculate the reduced parameters.

Solution

$$T_r = \frac{30.5\,K}{5.2\,K} = 5.87 \tag{4.2.33}$$

and

$$P_r = \frac{5.52\,atm}{2.26\,atm} = 2.44 \tag{4.2.34}$$

Example 4.2.3*B*:

Calculate the required pressure and temperature for a sample of O_2 to be in a corresponding state with the He sample in Example **4.2.3*A***. The T_C of O_2 is 154.8 K and the P_C of O_2 is 50.14 atm.

Strategy:

Use Equations 4.2.30, 4.2.31, and 4.2.32 to calculate the reduced parameters.

Solution

$$T = (5.87)(154.8\,K) = 909K \tag{4.2.35}$$

and

$$P = (2.44)(50.14\,atm) = 122.3\,atm \tag{4.2.36}$$

Exercise 4.2.3

Calculate the required pressure and temperature for a sample of CO_2 to be in a corresponding state with the two samples in Example 1.3.3. The T_C of CO_2 is 304.2 K and the P_C of CO_2 is 72.9 atm.

Answer

$T = 1786\,K$ and $P = 178\,atm$

The basis for principle of corresponding states can be shown by substituting reduced properties into the van der Waals Equation 4.2.18:

$$P_r \cdot P_C = \frac{R \cdot T_r \cdot T_C}{V_r \cdot V_C - b} - \frac{a}{V_r^2 \cdot V_C^2} \tag{4.2.37}$$

We then substitute in the values of V_C, T_C, and P_C in terms of the constants a and b as defined in Equations 4.2.26, 4.2.27, and 4.2.28:

$$\frac{aP_r}{27b^2} = \left(\frac{\frac{R8aT_r}{27Rb}}{3bV_r - b} \right) - \frac{a}{9b^2V_r^2} \tag{4.2.38}$$

Solving for P_r, we get

$$P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2} \tag{4.2.39}$$

Equation 4.2.39 contains no substance-dependent terms, and so theoretically describes any and all gases. In practice, the equation and the principle of corresponding states works best for non-polar, spherical molecules.

The most important aspect of the principle of corresponding states and equation $ref1.3.29$ is that they enable us to compare properties of many gases on a single graph. One example is the plot of the value of the compressibility factor, Z_C, versus the reduced pressure, \(P_r)\ at various reduced temperatures, with curves that are followed quite closely by many substances:

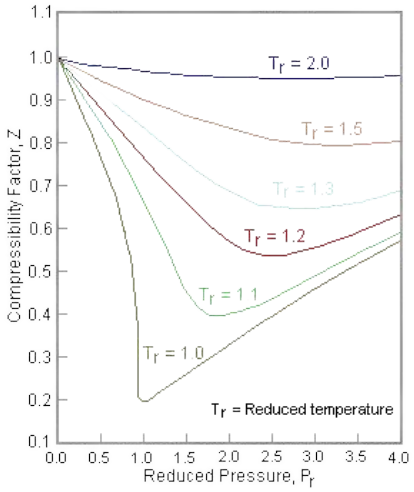


***Figure* 4.2.7:** *The compression factor of a typical real gas plotted using reduced variables. Many real gases, especially those with non-polar, spherical molecules are described well by these* plots. *(Public domain; Milton Beychok)*

Summary

The van der Waals equation is one of several equations of state that describe gases more accurately than the perfect gas law, but less accurately than the virial equation. Two other common equations of state are the Berthelot equation and the Dieterici equation. The equation that you choose to describe a gas depends on the substance that your are studying and the required accuracy of your results.

Contributors and Attributions

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4.3: van der Waals and Redlich-Kwong Equations of State

The ideal gas law is valid for low pressures, where the finite volume of particles and intermolecular attractions do not have a large impact. At higher pressures, we must account for these factors. The van der Waals and Redlich-Kwong equations of states are equations of state that attempt to account for real gas behavior by modifying the ideal gas law with two additional parameters.

4.3.1: The Van der Waals Equation of State

The van der Waals Equation of State is an equation relating the density of gases and liquids to the pressure, volume, and temperature conditions (i.e., it is a thermodynamic equation of state). It can be viewed as an adjustment to the ideal gas law that takes into account the non-zero volume of gas molecules and inter-particle attraction using correction terms a and b. It was derived in 1873 by Johannes Diderik van der Waals, who received the Nobel Prize in 1910 for this work. The van der Waals equation of state is:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \tag{4.3.1}$$

Equation 4.3.1 can also be rewritten as

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

If the correction terms a and b go to zero, the equation reduces to the ideal gas equation of state:

$$PV = nRT$$

Let's first look first at the correction term b, which represents the volumes of the particles and assumes a hard-wall potential, $u_o(r)$. This potential energy term describes a system of hard sphere “billiard balls” of diameter σ. Figure 16.2.1 shows two of these billiard ball type particles at the point of contact (i.e, the distance of closest approach). At this point, they undergo a collision and separate, so they cannot be closer than that distance.

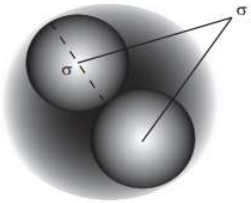


Figure 16.2.1 : Two hard spheres of diameter σ at closest contact. The distance between their centers is also σ. A sphere of radius σ just containing the two particles is shown in cross-section.

The distance between their centers is also σ. Because of this distance of closest approach, the total volume available to the particles is not the volume of the container, V, but some volume less than V. This reduction in volume can be calculated. Figure 16.2.1 shows a shaded sphere that just contains the pair of billiard ball particles. The volume of this sphere is the volume excluded from any two particles. The radius of the sphere is σ and the excluded volume for the two particles is $4\pi\sigma^3/3$, which is the volume of the shaded sphere. From this, we see that the excluded volume for any *one* particle is just half of this or $\frac{2}{3}\pi\sigma^3$. The excluded volume for a mole of such particles is the parameter b:

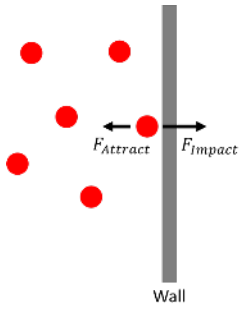
$$b = \frac{2}{3}\pi\sigma^3 N_0$$

Given n moles of gas, the total excluded volume is then nb, so that the total *available* volume is $V - nb$.

Let's turn our attention the a, which represents the intermolecular attractions of the particles. Molecular attractions tend to make the P exerted by the gas less than that predicted by the ideal gas law at low pressures. P is force over area:

$$P = \frac{F}{A}$$

Pressure is proportion to the net force on the wall of the container:



The net force is the force of the molecules impacting the container wall minus the intermolecular attraction of the molecules:

$$\bar{F}_{Net} = \bar{F}_{Impact} - \bar{F}_{Attract}$$

Therefore, the pressure will be less for the real gas than the ideal gas. We can add a correction term to pressure to account for intermolecular attractions:

$$P_{VDW} = P_{Real} + a\,(?)$$

V does influence the amount of intermolecular attraction because P is reduced as V is increased:

$$P \propto \frac{1}{V}$$

And pressure is proportional to the number of attractive interactions:

# of molecular interactions $\propto P^2$

# of molecular interactions $\propto \frac{1}{V^2}$

We now have an expression for the van der Waals P:

$$P = P_{Real} + \frac{an^2}{V^2}$$

The constants a and b depend on the substance. Some typical values are:[1]

Molecule	a $\left(\frac{L^2 \cdot bar}{mol^2}\right)$	b $\left(\frac{L}{mole}\right)$
H_2O	5.536	0.03049
N_2	1.43	0.03913
CH_4	2.283	0.04278
C_2H_6	5.562	0.0638

1. *R. C. Weast (1972). Handbook of Chemistry and Physics 53rd Edition. Chemical Rubber Pub.*

4.3.2: Redlich-Kwong Equation of State

The van der Waals Equation of State had to wait almost 100 years before a real, successful improvement was introduced to it. This progress occurred once researchers committed themselves to finding the empirical temperature dependency of the attraction parameter a proposed by van der Waals. In contrast, very little attention has been paid to modifying the parameter b for co-volume. It makes a lot of sense that b would not be modified by temperature, because it represents the *volume* of the molecules, which should not be affected by their kinetic energy (measured in terms of temperature). The very first noteworthy successful modification to the attraction parameter came with the publication of the equation of state of Redlich-Kwong in 1949.

The Redlich–Kwong equation of state is an empirical, algebraic equation that relates temperature, pressure, and volume of gases. It is generally more accurate than the van der Waals and the ideal gas equations of state at temperatures above the critical temperature. It was formulated by Otto Redlich and Joseph Neng Shun Kwong in 1949, who showed that a simple two-parameter

equation of state could well reflect reality in many situations. Redlich and Kwong revised the van der Waals Equation of State (Equation 4.3.1) and proposed the following expressions:

$$\left(P+\frac{a}{\sqrt{T}\bar{V}(\bar{V}+b)}\right)(\bar{V}-b)=RT \tag{4.3.2}$$

The fundamental change they introduced was to the functional form of $\partial P_{\text{attraction}}$. Additionally, they introduced the co-volume b into the denominator of this functional form. The important concept here is that the attraction parameter a of van der Waals needed to be made a function of temperature to do a better job of quantitatively matching experimental data. This was a realization that van der Waals had suggested, but no actual functional dependency had been introduced until the Redlich-Kwong equation.

We know what follows at this point. To come up with an expression for a and b of Equation 4.3.2, we apply the criticality conditions to this equation of state. As we recall, imposing the criticality conditions allows us to relate the coefficients a and b to the critical properties (P_c, T_c) of the substance. Once we have done that, we obtain the definition of a and b for the Redlich-Kwong equation of state:

$$a=0.42780\frac{R^2T_c^{2.5}}{P_c} \tag{4.3.3}$$

$$b=0.086640\frac{RT_c}{P_c} \tag{4.3.4}$$

The Redlich-Kwong equation of state radically improved, in a quantitative sense, the predictions of the van der Waals equation of state. We now recall that van der Waals-type equations are cubic because they are cubic polynomials in molar volume and compressibility factor. It comes as no surprise then, that we can transform Equation 4.3.2 into:

$$\bar{v}^3-\left(\frac{RT}{P}\right)\bar{v}^2+\frac{1}{P}\left(\frac{1}{T^{0.5}}-bRT-Pb^2\right)\bar{v}-\frac{ab}{PT^{0.5}}=0 \tag{4.3.5}$$

and, by defining the following parameters:

$$A=\frac{aP}{R^2T^{2.5}} \tag{4.3.6}$$

$$B=\frac{bP}{RT} \tag{4.3.7}$$

and introducing the compressibility factor definition:

$$Z=\frac{P\bar{v}}{RT}$$

we get:

$$Z^3-Z^2+(A-B-B^2)Z-AB=0 \tag{4.3.8}$$

We may also verify the two-parameter corresponding state theory by introducing Equations 4.3.3, 4.3.4, and 4.3.5 into Equation 4.3.8:

$$Z^3-Z^2+\frac{P_r}{T_r}\left(\frac{0.42748}{T_r^{1.5}}-0.08664-0.007506\frac{P_r}{T_r}\right)Z-0.03704\frac{P_r^2}{T_r^{3.5}}=0 \tag{4.3.9}$$

Where:

$$P_r=\frac{P}{P_c}$$

$$T_r=\frac{T}{T_c}$$

P_r and T_r are the pressure and temperature at the reduced state. See Section 16.4 for more information on reduced states. In Equation 4.3.9, we can observe the same thing that we saw with the van der Waals equation of state: gases at corresponding states

have the same properties. Equation 4.3.9 is particularly clear about it: any two different gases at the same P_r, T_r condition have the same compressibility factor.

Just as any other cubic equation of state, Equations 4.3.2 through 4.3.9, as they stand, are to be applied to pure substances. For mixtures, however, we apply *the same equation*, but we impose certain mixing rules to obtain a and b, which are functions of the properties of the pure components. Strictly speaking, we create a new "pseudo" pure substance that has the average properties of the mixture. Redlich-Kwong preserved the same mixing rules that van der Waals proposed for his eqution of state:

$$a_m = \sum_i \sum_j y_i y_j a_{ij}$$

with

$$a_{ij} = \sqrt{a_i a_j}$$

and

$$b_m = \sum_i y_i b_i$$

Naturally, Redlich and Kwong did not have the last word on possible improvements to the van der Waals equation of state. The Redlich-Kwong equation of state, as shown here, is no longer used in practical applications. Research continued and brought with it new attempts to improve the Redlich-Kwong equation of state. After more than two decades, a modified Redlich-Kwong equation of state with very good potential was developed.

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4.4: The Law of Corresponding States

Johannes Diderik van der Waals modified the ideal gas law to better describe the behavior of real gases by introducing corrections to account for the finite size of molecules and the intermolecular forces between them, leading to the well-known van der Waals equation.

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \tag{4.4.1}$$

This expression for the van der Waal gas involves two phenomenological constants, a and b. Van der Waals postulated that all real gases at corresponding states should behave similarly and he focused on applying Equation 4.4.1 at the critical point of difference gases—the unique temperature, pressure, and volume at which the distinction between liquid and gas disappears.

The corresponding state that van der Waals chose to use is called the **reduced state**, which is based on the deviation of the conditions of a substance from its own critical conditions. We can define reduced quantities:

$$P_r = \frac{P}{P_c}$$
$$V_r = \frac{V}{V_c}$$
$$T_r = \frac{T}{T_c}$$

By substitution into Equation 4.4.1, the Van der Waal equations can be expressed differently

$$\left(P_r + \frac{3}{\bar{V}_r^2}\right)\left(\bar{V}_r - \frac{1}{3}\right) = \frac{8}{3}T_r \tag{4.4.2}$$

Equation 4.4.2 means the critical parameters for a gas can be expressed in terms of a and b parameters:

$$V_c = 3b$$
$$P_c = \frac{a}{27b^2}$$
$$T_c = \frac{8a}{27bR}$$

Hence, when gases are expressed in terms of their **reduced variables**, the van der Waals equation takes on a universal form (Equation 4.4.2) that applies to all gases, regardless of their chemical identity. This discovery led van der Waals to formulate the **Law of Corresponding State**s, which states that different gases at the same reduced temperature and reduced pressure will exhibit similar thermodynamic behavior. This principle provided a unifying framework for understanding real-gas behavior and laid the foundation for generalized equations of state and compressibility charts used in modern thermodynamics.

Although the actual pressures and volumes may differ, two gases are said to be in corresponding states if their reduced pressure, volume, and temperature are the same. What it says is that the behavior of all gases (and liquids!!) is pretty much the same, except for a scaling factor that is related to the critical point of the substance. The compressibility value (Z) of 3/8 at the critical point for the van der Waals equation is actually not in such good agreement with measurement. This is why the more complicated Redlich-Kwong and Peng-Robertson expressions are better, although the idea is the same. Hence, all one needs to know to describe any fluid's behavior is its critical point. For example, argon behaves much the same at 300 K as ethane does at 600 K because these temperatures correspond to twice their respective critical temperatures (150.72 K and 305.4 K, respectively) so $T_r = 2.0$.

4.4.1: Compressibility

The Compressibility provides a useful way to compare the behavior of real gases with that predicted by the ideal gas law, and it connects directly to the critical ratios first introduced by van der Waals.

$$Z = \frac{PV}{RT}$$

Over the past 150 years, researchers have collected extensive experimental data on a wide variety of fluids, allowing the Law of Corresponding States to be tested and validated. When the pressure, temperature, and volume of different fluids are expressed in terms of their reduced values, their measurements can be superimposed on the same compressibility chart (Figure **4.4.1**). This overlap shows that most "normal" fluids, despite having different molecular structures, follow a common pattern of behavior when scaled by their critical properties.

We can rewrite the universal expression for compressibility Z using reduced variables and plot measured values of Z versus the reduced pressure, P_r (Figure **4.4.1**). As you can see, very different gases/liquids like nitrogen and water can be made to coincide if their properties are plotted relative to there critical points rather than in absolute terms. The compressibility factor Z can also be cast into the form of corresponding states showing that Z also can be expressed as a universal function of V_r and T_r or any other two reduced quantities:

$$Z = \frac{\bar{V}_r}{\bar{V}_r - \frac{1}{3}} - \frac{9}{8\bar{V}_r T_r}$$

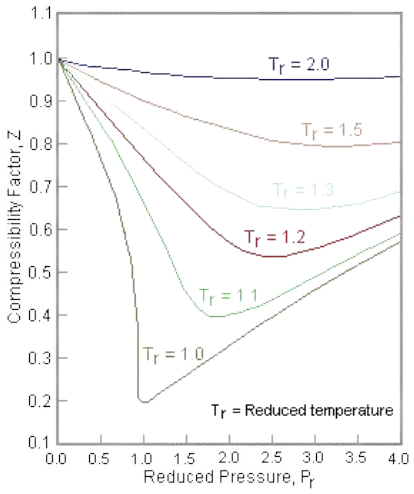


Figure **4.4.1**: Example of a generalized compressibility factor graph (Public domain; Milton Beychok)

These charts show that most "normal" fluids, such as simple hydrocarbons, noble gases, and diatomic molecules, conform closely to the predictions of the Law of Corresponding States. Deviations occur mainly in more complex or strongly associating fluids—such as water, ammonia, or hydrogen fluoride—where strong polarity or hydrogen bonding introduces additional interactions not accounted for by van der Waals' simple model. Nevertheless, the overall success of the law demonstrates its power: by scaling thermodynamic variables to the critical constants, we can describe the behavior of a wide variety of substances with a single framework. This insight not only validated van der Waals' pioneering theory but also provided a foundation for modern equations of state and practical tools in chemical engineering and physical chemistry.

Van der Waals did not stop here. He went on to describe the root cause of condensation of gases into liquids at lower temperatures: the attractive interactions between the molecules.

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4.5: The Repulsive Term in the Lennard-Jones Potential

Proposed by Sir John Edward Lennard-Jones, the Lennard-Jones potential describes the potential energy of interaction between two non-bonding atoms or molecules based on their distance of separation. The potential equation accounts for the difference between attractive forces (dipole-dipole, dipole-induced dipole, and London interactions) and repulsive forces.

4.5.1: Introduction

Imagine two rubber balls separated by a large distance. Both objects are far enough apart that they are not interacting. The two balls can be brought closer together with minimal energy, allowing interaction. The balls can continuously be brought closer together until they are touching. At this point, it becomes difficult to further decrease the distance between the two balls. To bring the balls any closer together, increasing amounts of energy must be added. This is because eventually, as the balls begin to invade each other's space, they repel each other; the force of repulsion is far greater than the force of attraction.

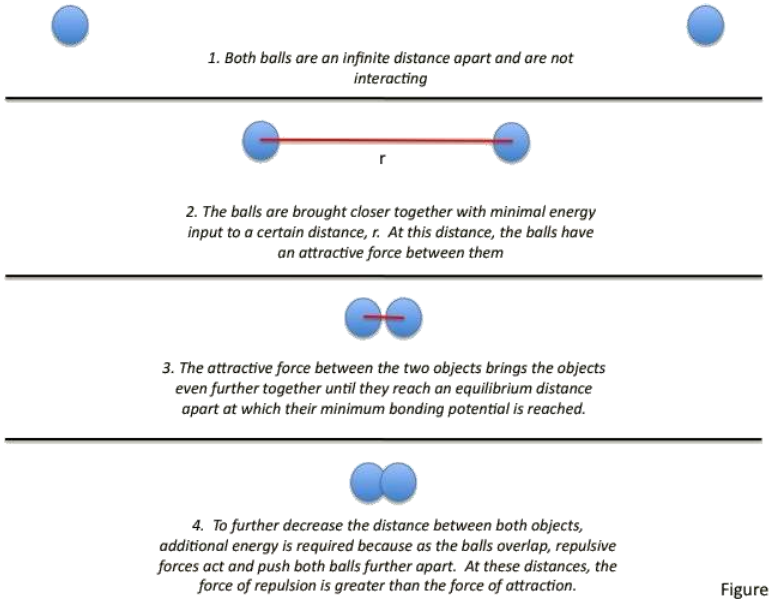


Figure A

This scenario is similar to that which takes place in neutral atoms and molecules and is often described by the **Lennard-Jones potential**.

4.5.2: The Lennard-Jones Potential

The Lennard-Jones model consists of two 'parts'; a steep repulsive term, and smoother attractive term, representing the London dispersion forces. Apart from being an important model in itself, the Lennard-Jones potential frequently forms one of 'building blocks' of many force fields. It is worth mentioning that the 12-6 Lennard-Jones model is not the most faithful representation of the potential energy surface, but rather its use is widespread due to its computational expediency. The Lennard-Jones Potential is given by the following equation:

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{4.5.1}$$

or is sometimes expressed as:

$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}} \tag{4.5.2}$$

where

- V is the intermolecular potential between the two atoms or molecules.
- ϵ is the well depth and a measure of how strongly the two particles attract each other.

- σ is the distance at which the intermolecular potential between the two particles is zero (Figure 4.5.1). σ gives a measurement of how close two nonbonding particles can get and is thus referred to as the *van der Waals radius*. It is equal to one-half of the internuclear distance between nonbonding particles.
- r is the distance of separation between both particles (measured from the center of one particle to the center of the other particle).
- $A = 4\epsilon\sigma^{12}$, $B = 4\epsilon\sigma^{6}$
- Minimum value of $\Phi_{12}(r)$ at $r = r_{min}$.

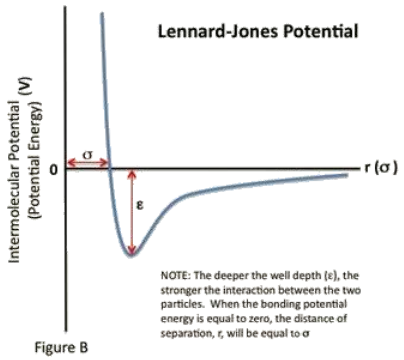


Figure 4.5.1: The Lennard-Jones potential describes both the attraction and repulsion between nonionic particles. The first part of the equation, the short-ranged $\sigma/r)^{12}$ term describes the repulsive forces between particles while the latter part of the equation and the longer-ranged σ/r^{6} term denotes the attraction.

Example 4.5.1: The van der Waals Radius

The ϵ and σ values for Xenon (Xe) are found to be 1.77 kJ/mol and 4.10 Angstroms, respectively. Determine the van der Waals radius for the Xenon atom.

Solution

Recall that the van der Waals radius is equal to one-half of the internuclear distance between nonbonding particles. Because σ gives a measure of how close two non-bonding particles can be, the van der Waals radius for Xenon (Xe) is given by:

$$r = \sigma/2 = 4.10 \text{ Angstroms}/2 = 2.05 \text{ Angstroms}$$

4.5.2.1: Bonding Potential

The Lennard-Jones potential is a function of the distance between the centers of two particles. When two non-bonding particles are an infinite distance apart, the possibility of them coming together and interacting is minimal. For simplicity's sake, their bonding potential energy is considered zero. However, as the distance of separation decreases, the probability of interaction increases. The particles come closer together until they reach a region of separation where the two particles become bound; their bonding potential energy decreases from zero to a negative quantity. While the particles are bound, the distance between their centers continue to decrease until the particles reach an equilibrium, specified by the separation distance at which the minimum potential energy is reached.

If the two bound particles are further pressed together, past their equilibrium distance, repulsion begins to occur: the particles are so close together that their electrons are forced to occupy each other's orbitals. Repulsion occurs as each particle attempts to retain the space in their respective orbitals. Despite the repulsive force between both particles, their bonding potential energy increases rapidly as the distance of separation decreases.

Example 4.5.2

Calculate the intermolecular potential between two Argon (Ar) atoms separated by a distance of 4.0 Angstroms (use ϵ=0.997 kJ/mol and σ=3.40 Angstroms).

Solution

To solve for the intermolecular potential between the two Argon atoms, we use equation 2.1 where V is the intermolecular potential between two non-bonding particles.

$$V = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

The data given are:

- $\epsilon = 0.997\ \text{kJ/mol}$,
- $\sigma = 3.40\ \text{Angstroms}$, and
- the distance of separation, $r = 4.0\ \text{Angstroms}$.

We plug these values into Equation 4.5.1 and solve as follows:

$$\begin{aligned} V &= 4(0.997\ \text{kJ/mol})\left[\left(\frac{3.40\ \text{Angstroms}}{4.0\ \text{Angstroms}}\right)^{12} - \left(\frac{3.40\ \text{Angstroms}}{4.0\ \text{Angstroms}}\right)^{6}\right] \\ &= 3.988(0.14 - 0.38) \\ &= 3.988(-0.24) \\ &= -0.96 kJ/mol \end{aligned}$$

4.5.2.2: Stability and Force of Interactions

Like the bonding potential energy, the stability of an arrangement of atoms is a function of the Lennard-Jones separation distance. As the separation distance decreases below equilibrium, the potential energy becomes increasingly positive (indicating a repulsive force). Such a large potential energy is energetically unfavorable, as it indicates an overlapping of atomic orbitals. However, at long separation distances, the potential energy is negative and approaches zero as the separation distance increases to infinity (indicating an attractive force). This indicates that at long-range distances, the pair of atoms or molecules experiences a small stabilizing force. Lastly, as the separation between the two particles reaches a distance slightly greater than σ, the potential energy reaches a minimum value (indicating zero force). At this point, the pair of particles is most stable and will remain in that orientation until an external force is exerted upon it.

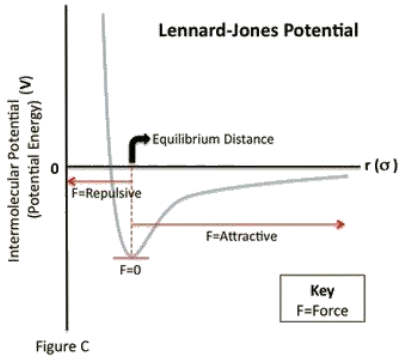


Figure C

Example 4.5.3

Two molecules, separated by a distance of 3.0 angstroms, are found to have a σ value of 4.10 angstroms. By decreasing the separation distance between both molecules to 2.0 angstroms, the intermolecular potential between the molecules becomes more negative. Do these molecules follow the Lennard-Jones potential? Why or why not?

Solution

Recall that σ is the distance at which the bonding potential between two particles is zero. On a graph of the Lennard-Jones potential, then, this value gives the x-intersection of the graph. According to the Lennard-Jones potential, any value of r greater than σ should yield a negative bonding potential and any value of r smaller than σ should yield a positive bonding potential. In this scenario, as the separation between the two molecules decreases from 3.0 angstroms to 2.0 angstroms, the bonding potential is becomes more negative. In essence however, because the starting separation (3.0 angstroms) is already less than σ

(4.0 angstroms), decreasing the separation even further (2.0 angstroms) should result in a more positive bonding potential. Therefore, these molecules do not follow the Lennard-Jones potential.

? Exercise 4.5.1

The second part of the Lennard-Jones equation is $(\sigma/r)^6$ and denotes attraction. Name at least three types of intermolecular interactions that represent attraction.

Answer

From section 2.1, dipole-dipole, dipole-induced dipole, and London interactions are all attractive forces.

? Exercise 4.5.2

At what separation distance in the Lennard-Jones potential does a species have a repulsive force acting on it? An attractive force? No force?

Answer

See Figure C. A species will have a repulsive force acting on it when r is less than the equilibrium distance between the particles. A species will have an attractive force acting on it when r is greater than the equilibrium distance between the particles. Lastly, when r is equal to t↑he equilibrium distance between both particles, the species will have no force acting upon it.

4.5.3: References

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CHAPTER OVERVIEW

5: Boltzmann

5.1: The Boltzmann Factor is used to Approximate the Fraction of Particles in a Large System
5.2: The Boltzmann Distribution represents a Thermally Equilibrated Distribution
5.3: The Average Ensemble Energy is Equal to the Observed Energy of a System
5.4: Heat Capacity at Constant Volume is the Change in Internal Energy with Temperature
5.5: Partition Functions can be Decomposed into Partition Functions of Each Degree of Freedom
5.6: Translational Partition Functions of Monotonic Gases
5.7: Most Atoms are in the Ground Electronic State
5.8: The Energy of a Diatomic/Polyatomic Molecule Can Be Approximated as a Sum of Separate Terms
5.9: Most Molecules are in the Ground Vibrational State
5.10: Most Molecules are Rotationally Excited at Ordinary Temperatures
5.11: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number

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5.1: The Boltzmann Factor is used to Approximate the Fraction of Particles in a Large System

Statistical Mechanics provides the connection between microscopic motion of individual atoms of matter and macroscopically observable properties such as temperature, pressure, entropy, free energy, heat capacity, chemical potential, viscosity, spectra, reaction rates, etc.

5.1.0.1: The Microscopic Laws of Motion

Consider a system of N classical particles. The particles are confined to a particular region of space by a container of volume V. In classical mechanics, the state of each particle is specified by giving its position and its velocity, i.e., by telling where it is and where it is going. The position of particle i is simply a vector of three coordinates $r_i = (x_i, y_i, z_i)$, and its velocity $\mathbf{v}_i$ is also a vector $(v_{x_i}, v_{y_i}, v_{z_i})$ of the three velocity components. Thus, if we specify, at any instant in time, these six numbers, we know everything there is to know about the state of particle i.

The particles in our system have a finite kinetic energy and are therefore in constant motion, driven by the forces they exert on each other (and any external forces which may be present). At a given instant in time t, the Cartesian positions of the particles are $\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t)$, and the velocities at t are related to the positions by differentiation:

$$\mathbf{v}_i(t) = \frac{d\mathbf{r}_i}{dt} = \dot{\mathbf{r}}_i \tag{5.1.1}$$

In order to determine the positions and velocities as function of time, we need the classical laws of motion, particularly, Newton's second law. Newton's second law states that the particles move under the action of the forces the particles exert on each other and under any forces present due to external fields. Let these forces be denoted $\mathbf{F}_1, \mathbf{F}_2, \ldots, \mathbf{F}_N$. Note that these forces are functions of the particle positions:

$$\mathbf{F}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{5.1.2}$$

which is known as a force field (because it is a function of positions). Given these forces, the time evolution of the positions of the particles is then given by Newton's second law of motion:

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

where $\mathbf{F}_1, \ldots, \mathbf{F}_N$ are the forces on each of the N particles due to all the other particles in the system. The notation $\ddot{\mathbf{r}}_i = d^2\mathbf{r}_i/dt^2$.

N Newton's equations of motion constitute a set of $3N$ coupled second order differential equations. In order to solve these, it is necessary to specify a set of appropriate initial conditions on the coordinates and their first time derivatives, $\{\mathbf{r}_1(0), \ldots, \mathbf{r}_N(0), \dot{\mathbf{r}}_1(0), \ldots, \dot{\mathbf{r}}_N(0)\}$. Then, the solution of Newton's equations gives the complete set of coordinates and velocities for all time t.

5.1.1: The Ensemble Concept (Heuristic Definition)

For a typical macroscopic system, the total number of particles is $N \sim 10^{23}$. Since an essentially infinite amount of precision is needed in order to specify the initial conditions (due to exponentially rapid growth of errors in this specification), the amount of information required to specify a trajectory is essentially infinite. Even if we content ourselves with quadrupole precision, however, the amount of memory needed to hold just one phase space point would be about 128 bytes $= 2^7 \sim 10^2$ bytes for each number or $10^2 \times 6 \times 10^{23} \sim 10^{17}$ gigabytes which is also 10^2 yottabytes! The largest computers we have today have perhaps 10^6 gigabytes of memory, so we are off by 11 orders of magnitude just to specify 1 classical state.

Fortunately, we do not need all of this detail. There are enormous numbers of microscopic states that give rise to the same macroscopic observable. Let us again return to the connection between temperature and kinetic energy:

$$\frac{3}{2}NkT = \sum_{i=1}^{N} \frac{1}{2} m_i \mathbf{v}_i^2 \tag{5.1.3}$$

which can be solved to give:

$$T = \frac{2}{3k}\left(\frac{1}{N}\sum_{i=1}^{N}\frac{1}{2}m_i v_i^2\right) \tag{5.1.4}$$

Here we see that T is related to the average kinetic energy of all of the particles. We can imagine many ways of choosing the particle velocities so that we obtain the same average. One is to take a set of velocities and simply assign them in different ways to the N particles, which can be done in $N!$ ways. Apart from this, there will be many different choices of the velocities, themselves, all of which give the same average.

Since, from the point of view of macroscopic properties, precise microscopic details are largely unimportant, we might imagine employing a construct known as the *ensemble concept* in which a large number of systems with different microscopic characteristics but similar macroscopic characteristics is used to "wash out" the microscopic details via an averaging procedure. This is an idea developed by individuals such as Gibbs, Maxwell, and Boltzmann.

Consider a large number of systems each described by the same set of microscopic forces and sharing a common set of macroscopic thermodynamic variables (e.g. the same total energy, number of moles, and volume). Each system is assumed to evolve under the microscopic laws of motion from a different initial condition so that the time evolution of each system will be different from all the others. Such a collection of systems is called an *ensemble*. The ensemble concept then states that macroscopic observables can be calculated by performing averages over the systems in the ensemble. For many properties, such as temperature and pressure, which are time-independent, the fact that the systems are evolving in time will not affect their values, and we may perform averages at a particular instant in time.

The questions that naturally arise are:

1. How do we construct an ensemble?
2. How do we perform averages over an ensemble?
3. How do we determine which thermodynamic properties characterize an ensemble?
4. How many different types of ensembles can we construct, and what distinguishes them?

These questions will be addresses in the sections ahead.

5.1.2: Thermal energy

A confined monatomic gas can be seen as a box with a whole bunch of atoms in it. Each of these particles can be in one of the states given by the last formula. If all of them have large n values there is obviously a lot of kinetic energy in the system. The lowest energy is when all atoms have 1,1,1 as quantum numbers. Boltzmann realized that this should relate to temperature. When we add energy to the system (by heating it up without changing the volume of the box), the temperature goes up. At higher temperatures we would expect higher quantum numbers, and at lower T, lower ones. But how exactly are the atoms distributed over the various states?

This is a good example of a problem involving a discrete probability distribution. The probability that a certain level (e.g., $n = (n_1, n_2, n_3)$ with energy E_i) is occupied should be a function of temperature: $P_i(T)$. Boltzmann postulated that you could look at temperature as a form of energy. The thermal energy of a system is directly proportional to an absolute temperature.

$$E_{thermal} = kT$$

The proportionality constant k (or k_B) is named after him: the Boltzmann constant. It plays a central role in all statistical thermodynamics. The Boltzmann factor is used to approximate the fraction of particles in a large system. The Boltzmann factor is given by:

$$e^{-\beta E_i} \tag{5.1.5}$$

where:

- E_i is the energy in the state i,
- T is the kelvin temperature, and
- k is Boltzmann constant.

As the following section demonstrates, the term β in Equation 5.1.5 is expressed as:

$$\beta = \frac{1}{kT}$$

The rates of many physical processes are also determined by the Boltzmann factor. For a random particle, its thermal energy of a particle is a small multiple of the energy kT. An increase in temperature results in more particles crossing the energy barrier characteristic of activation processes. If this is to occur, particles need to carry sufficient energy. This energy is needed for the particles to successfully cross the energy barrier and is usually called activation energy. The fraction of molecules that have sufficient energy to escape the original material surface is approximately proportional to the Boltzmann factor.

5.1.3: References

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5.1.4: Problems

1. How are temperature and the average energy per particle for a system related?
2. What does the Boltzmann factor tell you? Why is it important?
3. When is it possible for particles to get extra energy?
4. Give three examples of activation processes.
5. What do "separate arrangements" mean? What are the differences between these arrangements?

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5.2: The Boltzmann Distribution represents a Thermally Equilibrated Distribution

Consider a N-particle ensemble. The particles are not necessarily indistinguishable and possibly have mutual potential energy. Since this is a large system, there are many different ways to arrange its particles and yet yield the same thermodynamic state. Only one arrangement can occur at a time. The sum of the probabilities of each separate arrangement equals the total number of separate arrangements. Then the probability of a system is:

$$p_N = W_N p_i$$

where p_N is the probability of the system, W_N is the total number of different possible arrangements of the N particles in the system, and p_i is the probability of each separate arrangement. Heisenberg's uncertainty principle states that it is impossible to simultaneously know the momentum and the position of an object with complete precision. In agreement with the uncertainty principle, the total possible number of combinations can be defined as the total number of distinguishable rearrangements of the N particles.

The most practical ensemble is the canonical ensemble with N, V, and T fixed. We can imagine a collection of boxes with equal volumes and number of particles with the entire collection kept in thermal equilibrium. Based on the Boltzmann factor, we know that for a system that has states with energies e_1, e_2, e_3..., the probability p_j that the system will be in the state j with energy E_j is exponentially proportional to the energy of state j. The partition functions of the state places a very important role in calculating the properties of a system, for example, it can be used to calculate the probability, as well as the energy, heat capacity, and pressure.

5.2.1: The Boltzmann Distribution

We are ultimately interested in the probability that a given distribution will occur. The reason for this is that we must have this information in order to obtain useful thermodynamic averages. Let's consider an ensemble of A systems. We will define a_j as the number of systems in the ensemble that are in the quantum state j. For example, a_1 represents the number of systems in the quantum state 1. The total number of possible microstates is:

$$W(a_1, a_2, ...) = \frac{A!}{a_1! a_2! ...}$$

The overall probability that P_j that a system is in the jth quantum state is obtained by averaging a_j/A over all the allowed distributions. Thus, P_j is given by:

$$P_j = \frac{\langle a_j \rangle}{A}$$
$$= \frac{1}{A} \frac{\sum_a W(a) a_j(a)}{\sum_a W(a)}$$

where the angle brackets indicate an ensemble average. Using this definition we can calculate any average property (i.e. any thermodynamic property):

$$\langle M \rangle = \sum_j M_j P_j \tag{5.2.1}$$

The method of the most probable distribution is based on the idea that the average over P_j is **identical** to the most probable distribution. Physically, this results from the fact that we have so many particles in a typical system that the fluctuations from the mean are extremely (immeasurably) small. The equivalence of the average probability of an occupation number and the most probable distribution is expressed as follows:

$$P_j = \frac{\langle a_j \rangle}{A} = \frac{a_j}{A}$$

The probability function is subject to the following constraints:

- Constraint 1: Conservation of energy requires:

$$E_{total} = \sum_j a_j e_j \tag{5.2.2}$$

where e_j is the energy of the jth quantum state.

- Constraint 2: Conservation of mass requires:

$$A = \sum_j a_j \tag{5.2.3}$$

which says only that the total number of all of the systems in the ensemble is A.

As we will learn in later chapters, the system will tend towards the distribution of a_j that maximizes the total number of microstates. This can be expressed as:

$$\sum_j \left(\frac{\partial \ln W}{\partial a_j} \right) = 0$$

Our constraints becomes:

$$\sum_j e_j da_j = 0$$

$$\sum_j da_j = 0$$

The method of Lagrange multipliers (named after Joseph Louis Lagrange is a strategy for finding the local maxima and minima of a function subject to equality constraints. Using the method of LaGrange undetermined multipliers we have:

$$\sum_j \left[\left(\frac{\partial \ln W}{\partial a_j} \right) da_j + \alpha da_j - \beta e_j da_j \right] = 0$$

We can use Stirling's approximation:

$$\ln x! \approx x \ln x – x$$

to evaluate:

$$\left(\frac{\partial \ln W}{\partial a_j} \right)$$

to get:

$$\left(\frac{\partial A!}{\partial a_j} \right) - \sum_i \left(\frac{\partial \ln a_i}{\partial a_j} \right) = 0$$

as outlined below.

5.2.2: Application of Stirling's Approximation

First step is to note that:

$$\ln W = \ln A! - \sum_j \ln a_j ! a \approx A \ln A – A - \sum_j a_j \ln a_j - \sum_j a_j$$

Since (from Equation 5.2.3):

$$A = \sum_j a_j$$

these two cancel to give:

$$\ln W = A \ln A - \sum_j a_j \ln a_j$$

The derivative is:

$$\left(\frac{\partial \ln W}{\partial a_j}\right) = \frac{\partial A \ln A}{\partial a_j} - \sum_i \frac{\partial a_i \ln a_i}{\partial a_j}$$

Therefore we have:

$$\left(\frac{\partial A \ln A}{\partial a_j}\right) = \frac{\partial A}{\partial a_j}\ln A - \frac{\partial A}{\partial a_j} = \ln A - 1$$

$$\left(\frac{\partial a_i \ln a_i}{\partial a_j}\right) = \frac{\partial a_i}{\partial a_j}\ln a_i - \frac{\partial a_i}{\partial a_j} = \ln a_j + 1$$

These latter derivatives result from the fact that:

$$\left(\frac{\partial a_i}{\partial a_i}\right) = 1$$

$$\left(\frac{\partial a_j}{\partial a_i}\right) = 0$$

The simple expression that results from these manipulations is:

$$-\ln\left(\frac{a_j}{A}\right) + \alpha - \beta e_j = 0$$

The most probable distribution is:

$$\frac{a_j}{A} = e^{\alpha}\sum_j e^{-\beta e_j} \tag{5.2.4}$$

Now we need to find the undetermined multipliers α and β.

The left hand side of Equation 5.2.4 is 1. Thus, we have:

$$P_j = \frac{a_j}{A} = \frac{e^{-\beta e_j}}{\sum_j e^{-\beta e_j}}$$

This determines α and defines the Boltzmann distribution. We will show that β from the optimization procedure of method of Lagrange multipliers is:

$$\beta = \frac{1}{kT}$$

This identification will show the importance of temperature in the Boltzmann distribution. The distribution represents a thermally equilibrated most probable distribution over all energy levels (Figure 17.2.1).

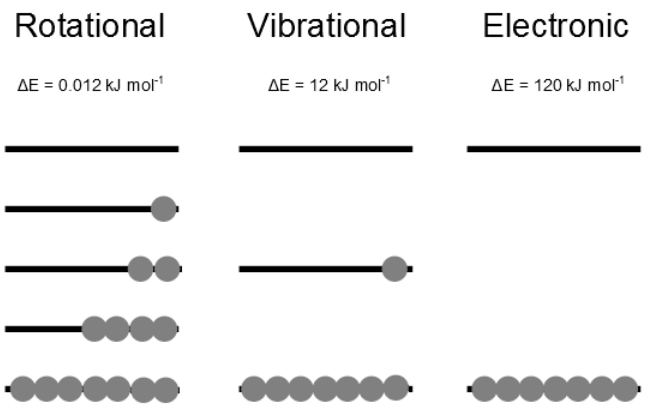


Figure 17.2.1 : At lower temperatures, the lower energy states are more greatly populated. At higher temperatures, there are more higher energy states populated, but each is populated less. k_BT 2.5 $kJ\ mol^{-1}$ at 300 K. (CC SA-BY 3.0; Mysterioso via Wikiversity).

Boltzmann Distribution

The Boltzmann distribution represents a thermally equilibrated **most probable** distribution over all energy levels. There is always a **higher** population in a state of lower energy than in one of higher energy.

Once we know the probability distribution for energy, we can calculate thermodynamic properties like the energy, entropy, free energies and heat capacities, which are all average quantities (Equation 5.2.1). To calculate P_j, we need the energy levels of a system (i.e., $\{e_i\}$). The energy ("levels") of a system can be built up from the quantum energy levels

> *It must always be remembered that no matter how large the energy spacing is, there is always a non-zero probability of the upper level being populated. The only exception is a system that is at absolute zero. This situation is however hypothetical as absolute zero can be approached but not reached.*

5.2.3: Partition Function

The sum over all factors $e^{-\beta e_j}$ is given a name. It is called the molecular partition function, q:

$$q = \sum_j e^{-\beta e_j}$$

The molecular partition function q gives an indication of the average number of states that are thermally accessible to a molecule at the temperature of the system. The partition function is a sum over states (of course with the Boltzmann factor β multiplying the energy in the exponent) and is a number. Larger the value of q, larger the number of states which are available for the molecular system to occupy (Figure 17.2.2).

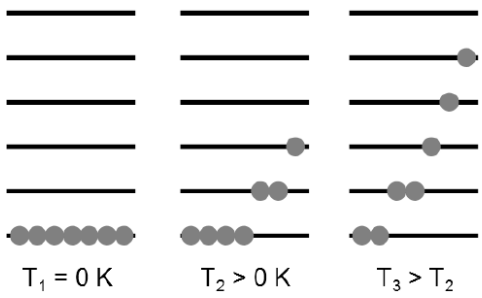


Figure 17.2.2 : At lower temperatures, the lower energy states are more greatly populated. At higher temperatures, there are more higher energy states populated, but each is populated less. (CC SA-BY 3.0; Mysterioso via Wikiversity).

We distinguish here between the partition function of the ensemble, Q and that of an individual molecule, q. Since Q represents a sum over all states accessible to the system it can written as:

$$Q(N,V,T) = \sum_{i,j,k\ldots} e^{-\beta(e_i+e_j+e_k\ldots)}$$

where the indices i, j, k represent energy levels of **different** particles.

Regardless of the type of particle the molecular partition function, q represents the energy levels of one individual molecule. We can rewrite the above sum as:

$$Q = q_i q_j q_k \ldots$$

or:

$$Q = q^N$$

for N particles. Note that q_i means a sum over states or energy levels accessible to molecule i and q_j means the same for molecule j. The molecular partition function, q counts the energy levels accessible to molecule i only. Q counts not only the states of all of the

molecules, but all of the possible combinations of occupations of those states. However, if the particles are not distinguishable then we will have counted $N!$ states too many. The factor of $N!$ is exactly how many times we can swap the indices in $Q(N,V,T)$ and get the same value (again provided that the particles are not distinguishable). See this video for more information.

5.2.4: References

1. Hakala, R.W. (1967). Simple justification of the form of Boltzmann's distribution law. *Journal of Chemical Education. 44(11), 657.* **doi:** 10.1021/ed044p657
2. Grigorenko, I, Garcia, M.E. (2002). Calculation of the partition function using quantum genetic algorithms. Physica A: Satistical Mechanics and its Applications. 313. 463-470. Retrieved from http://www.sciencedirect.com/science...78437102009883

5.2.5: Problems

1. Complete the justification of Boltzmann's distribution law by computing the proportionality constant a.
2. A system contains two energy levels E_1, E_2. Using Boltzmann statistics, express the average energy of the system in terms of E_1, E_2.
3. Consider a system contains N energy levels. Redo problem #2.
4. Use the property of exponential function, derive equation (17.9).
5. What are the uses of partition functions?

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5.3: The Average Ensemble Energy is Equal to the Observed Energy of a System

We will be restricting ourselves to the canonical ensemble (constant temperature and constant pressure). Consider a collection of N molecules. The probability of finding a molecule with energy E_i is equal to the fraction of the molecules with energy E_i. That is, in a collection of N molecules, the probability of the molecules having energy E_i:

$$P_i = \frac{n_i}{N}$$

This is the directly obtained from the Boltzmann distribution, where the fraction of molecules n_i/N having energy E_i is:

$$P_i = \frac{n_i}{N} = \frac{e^{-E_i/kT}}{Q} \tag{5.3.1}$$

The average energy is obtained by multiplying E_i with its probability and summing over all i:

$$\langle E \rangle = \sum_i E_i P_i \tag{5.3.2}$$

Equation 5.3.2 is the standard average over a distribution commonly found in quantum mechanics as expectation values. The quantum mechanical version of this Equation is

$$\langle \psi \left| \hat{H} \right| \psi \rangle$$

where Ψ^2 is the distribution function that the Hamiltonian operator (e.g., energy) is averaged over; this equation is also the starting point in the Variational method approximation.

Equation 5.3.2 can be solved by plugging in the Boltzmann distribution (Equation 5.3.1):

$$\langle E \rangle = \sum_i \frac{E_i e^{-E_i/kT}}{Q} \tag{5.3.3}$$

Where Q is the partition function:

$$Q = \sum_i e^{-\frac{E_i}{kT}}$$

We can take the derivative of $\ln Q$ with respect to temperature, T:

$$\left(\frac{\partial \ln Q}{\partial T}\right) = \frac{1}{kT^2} \sum_i \frac{E_i e^{-E_i/kT}}{Q} \tag{5.3.4}$$

Comparing Equation 5.3.3 with 5.3.4, we obtain:

$$\langle E \rangle = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)$$

It is common to write these equations in terms of β, where:

$$\beta = \frac{1}{kT}$$

The partition function becomes:

$$Q = \sum_i e^{-\beta E_i}$$

We can take the derivative of $\ln Q$ with respect to β:

$$\left(\frac{\partial \ln Q}{\partial \beta}\right) = -\sum_i \frac{E_i e^{-\beta E_i}}{Q}$$

And obtain:

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)$$

Replacing $1/kT$ with β often simplifies the math and is easier to use.

> It is not uncommon to find the notation changes: Z instead of Q and $\bar{E}$ instead of $\langle E \rangle$.

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5.4: Heat Capacity at Constant Volume is the Change in Internal Energy with Temperature

The heat capacity at constant volume (C_V) is defined to be the change in internal energy with respect to temperature:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} \tag{5.4.1}$$

Since:

$$E = -\frac{\partial \ln Q(N,V,\beta)}{\partial \beta} \tag{5.4.2}$$

We see that:

$$\begin{aligned} C_V &= \frac{\partial U}{\partial T} \\ &= \frac{\partial U}{\partial \beta}\frac{\partial \beta}{\partial T} \\ &= \frac{1}{kT^2}\frac{\partial^2}{\partial \beta^2}\ln Q(N,V,\beta) \\ &= k\beta^2\frac{\partial^2}{\partial \beta^2}\ln Q(N,V,\beta) \end{aligned} \tag{5.4.3}$$

where k is the Boltzmann constant. Energy can be stored in materials/gases via populating the specific degrees of freedom that exist in the sample. Understanding how this occurs requires the usage of Quantum Mechanics.

Dulong-Petit Law on the Heat Capacities of Solids

Pierre Louis Dulong and Alexis Thèrèse Petit conducted experiments in 1819 on three dimensional solid crystals to determine the heat capacities of a variety of these solids (Heat capacity is the solids ability to absorb and retain heat). Dulong and Petit discovered that all investigated solids had a heat capacity of approximately 2.49 x 10^4 J kilomole^{-1} K^{-1} at around 298 K or room temperature. The result from their experiment was explained by considering every atom inside the solid as an oscillator with six degrees of freedom (an oscillator can be thought of as a spring connecting all the atoms in the solid lattice). These springs extend into three dimensional space. The more energy that is added to the solid the more these springs vibrate. Each atom has an energy of $\frac{1}{2}kT$, where k is the Boltzmann constant and T is the absolute temperature. Thus,

$$C_V = \frac{6R}{2} = 3R \qquad \text{(Dulong-Petit Law)}$$

The number 6 in this equation is the number of degrees of freedom for the molecule. Petit and Dulong suggested that these results supported their foundation for the heat capacity of solids. The explanation for Petit and Dulong's experiment was not sufficient when it was discovered that heat capacity decreased as temperature approached absolute zero. The degrees of freedom do not slow down or cease to move when the solid reaches a sufficiently cold temperature. An additional model was proposed to explain this deviance. Two main theories were developed to explain this puzzling deviance in the heat capacity experiments. The first was constructed by Einstein and the second was authored by Debye.

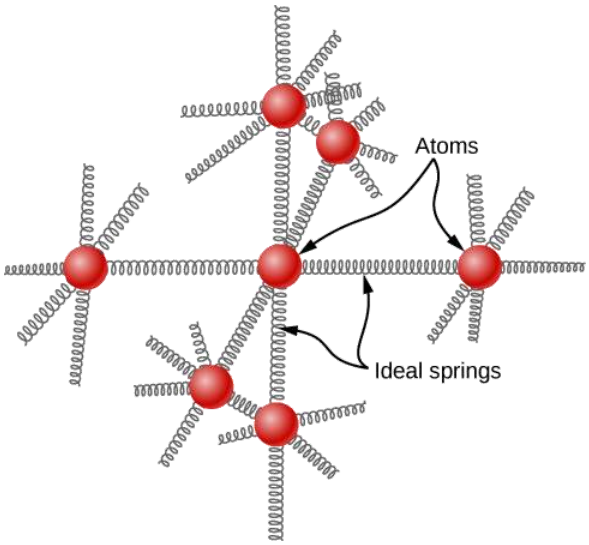


Figure 17.4.1 : In a simple model of a solid element, each atom is attached to others by six springs, two for each possible motion: x, y, and z. Each of the three motions corresponds to two degrees of freedom, one for kinetic energy and one for potential energy. (CC BY-SA 4.0; OpenStax).

Einstein's Theory on the Heat Capacities of Solids

Einstein assumed three things when he investigated the heat capacity of solids. First, he assumed that each solid was composed of a lattice structure consisting of N atoms. Each atom was treated as moving independently in three dimensions within the lattice (3 degrees of freedom). This meant that the entire lattice's vibrational motion could be described by a total of $3N$ motions, or degrees of freedom. Secondly, he assumed that the atoms inside the solid lattice did not interact with each other and thirdly, all of the atoms inside the solid vibrated at the same frequency. The third point highlights the main difference in Einstein's and Debye's two models.

Einstein's first point is accurate because the experimental data supported his hypothesis, however his second point is not because if atoms inside a solid could not interact, sound could not propagate through it. For example, a tuning fork's atoms, when struck, interact with one another to create sound which travels through air to the listener's ear. Atoms also interact in a solid when they are heated. Take for example a frying pan. If the pan is heated on one side, the heat transfers throughout the metal effectively warming the entire pan. Molecules that make up the frying pan interact to transfer heat. Much in the same way the oscillators in a solid interact when energy is added to the system. The extent of these interactions lead to the physically observed heat capacity.

The heat capacity of a solid at a constant volume is

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\ &= 3Nk\left(\frac{\theta_E}{T}\right)^2 \\ &= \frac{\exp\left(\frac{\theta_E}{T}\right)}{\left(\exp\frac{\theta_E}{T}-1\right)^2} \end{aligned}$$

where

- $\theta_E = \frac{h\nu}{k}$ is the **Einstein temperature**,
- h is Planck's constant,
- k is Boltzmann's constant, and
- ν is the oscillator frequency of the atoms inside the solid.

The Einstein temperature's accessibility of the vibrational energy inside of a solid molecule determines the heat capacity of that solid. The greater the accessibility the greater the heat capacity. If the vibrational energy is easily accessible the collisions in the molecule have a greater probability of exciting the atom into an upper vibrational level. This is displayed below.

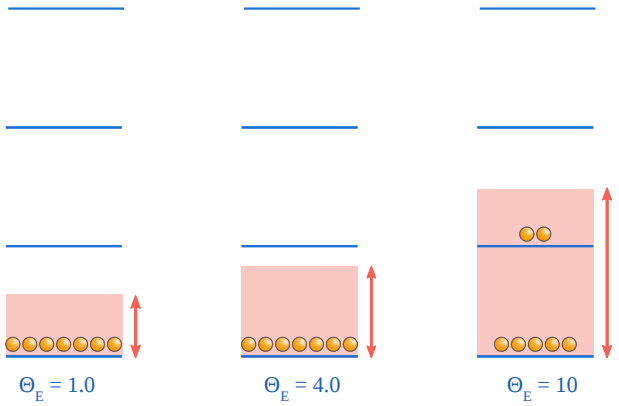


Figure 17.4.2 : This Figure illustrates the effect of the Einstein temperature on the likelihood of an oscillator absorbing energy from a collision and transferring that energy into stored heat or heat capacity. As the Einstein temperature increases, the greater the probability of an oscillator being excited to the next vibrational state. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

So the Einstein temperature specifically indicates the probability that a molecule has in its degrees of freedom to store energy in its atomic oscillators (or bonds). Comparing the Einstein temperature to the traditional classical values of Heat capacity will illustrate the differences the specific strengths (high temperature) and weaknesses (low temperature) of the Einstein model.

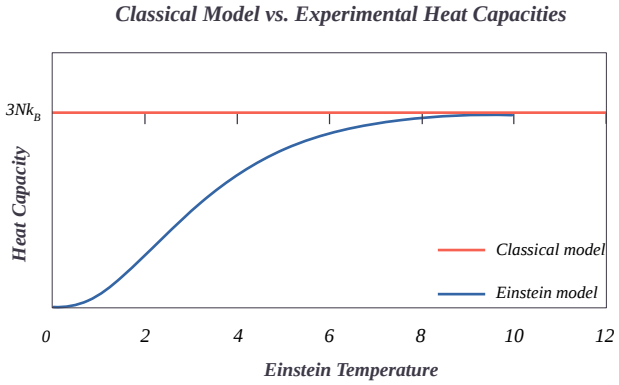


Figure 17.4.3 :This graph shows the accuracy of the of the Einstein temperature at low temperatures. The classical model is effective at temperatures above 10 Einstein Temperatures. (Cc BY-NC; Ümit Kaya via LibreTexts)

Thus, in the high temperature limit ($\frac{\theta_E}{T} \ll 1$) (i.e., the temperature is very large compared to the Einstein temperature) then

$$C_V \approx 3Nk = 3nR. \tag{5.4.4}$$

Einstein's model reveals the accuracy of the Petit and Dulong model and models high temperatures accurately. However, just as Petit and Dulong's model decreased in accuracy as the temperature decreased, so followed Einstein's.

When examining the extremely low temperature limit: $\frac{\theta_E}{T} \gg 1$, it can be seen:

$$C_V = 3Nk\left(\frac{\theta_E}{T}\right)^2 e^{\frac{-\theta_E}{T}} \tag{5.4.5}$$

As temperature (T) goes to zero, the exponential portion of the above equation goes to zero and therefore C_V also approaches zero. This supports the experimental values as temperature approaches zero the heat capacity of the solid likewise decreases to zero.

Einstein's theory also explains solids that exhibit a low heat capacity even at relatively high temperatures. An example of such a solid is diamond. The heat capacity of diamond approaches $3Nk$ as temperature greatly increases. Einstein's model supports this through the definition of an Einstein temperature. As the Einstein temperature increases, ν must increase likewise. This is the

equivalent of each atom possessing more energy and therefore vibrating more rapidly within the solid itself. The oscillator frequency, ν, can be written as:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}} \tag{5.4.6}$$

where κ is the force constant and μ is the reduced mass. This formula better predicts solids with high force constants or low reduced masses. This corrects deviations from the Petit and Dulong model.

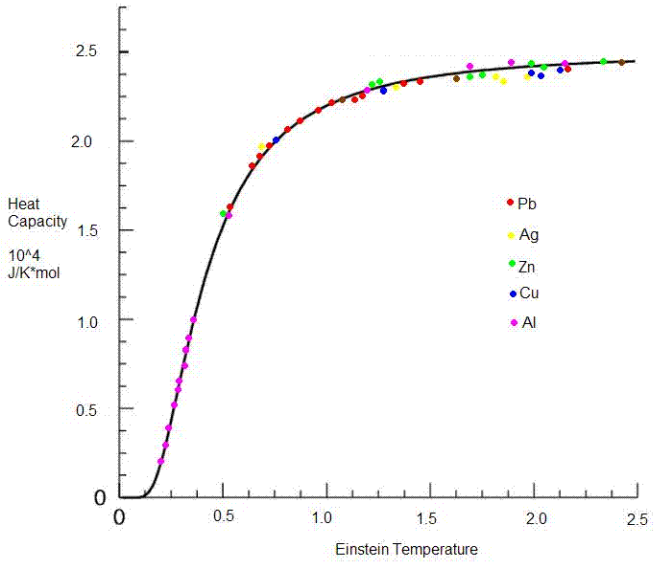


Figure 17.4.4 . This graph indicates the heat capacity of several solid metals as a function of the Einstein temperature: $\theta_E = \frac{h\nu}{k_B}$.

Essentially the Einstein temperature allows for the heat capacity equation and the vibrational frequencies in the solid to change as the temperature changes. This effectively adjusts for the deviations seen in the Petit/Dulong model. As the temperature increases or decreases, the Einstein temperature increases or decreases likewise to mirror the actual physical activity within the solid.

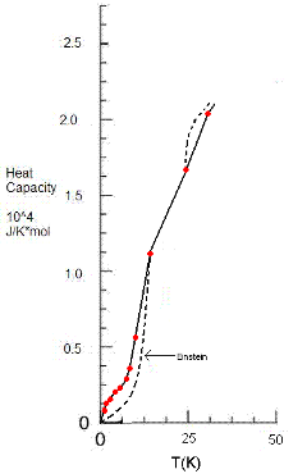


Figure 17.4.5 . This plot shows the heat capacity of lead compared to the expected values calculated from Einstein's model.

Einstein's model predicts relatively low temperatures well. However, when decreasing from approximately 15 K, Einstein's model deviates from experimental values. Also, this can be observed, although not as dramatically, for temperatures from 25 K to 30 K. Clearly a term or correction is still missing from Einstein's model to increase its accuracy.

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5.5: Partition Functions can be Decomposed into Partition Functions of Each Degree of Freedom

From the previous sections, the partition function for a system of N indistinguishable and independent molecules is:

$$Q(N,V,\beta) = \frac{\sum_i e^{-\beta E_i}}{N!} \tag{5.5.1}$$

And the average energy of the system is:

$$\langle E \rangle = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right) \tag{5.5.2}$$

We can combine these two equations to obtain:

$$\begin{aligned} \langle E \rangle &= kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \\ &= NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \\ &= N \sum_i \epsilon_i \frac{e^{-\epsilon_i / kT}}{q(V,T)} \end{aligned} \tag{5.5.3}$$

The average energy is equal to:

$$\langle E \rangle = N \langle \epsilon \rangle \tag{5.5.4}$$

where $\langle \epsilon \rangle$ is the average energy of a single particle. If we compare Equation 5.5.2 with Equation 5.5.2, we can see:

$$\langle \epsilon \rangle = \sum_i \epsilon_i \frac{e^{-\epsilon_i / kT}}{q(V,T)}$$

The probability that a particle is in state i, π_i, is given by:

$$\langle \epsilon \rangle = \frac{e^{-\epsilon_i / kT}}{q(V,T)} = \frac{e^{-\epsilon_i / kT}}{\sum_i e^{-\epsilon_i / kT}}$$

The energy of a particle is a sum of the energy of each degree of freedom for that particle. In the case of a molecule, the energy is:

$$\epsilon = \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{elec}}$$

The molecular partition function is the product of the degree of freedom partition functions:

$$q(V,T) = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$$

The partition function for each degree of freedom follows the same is related to the Boltzmann distribution. For example, the vibrational partition function is:

$$q_{\text{vib}} = \sum_i e^{-\epsilon_i / kT}$$

The average energy of each degree of freedom follows the same pattern as before. For example, the average vibrational energy is:

$$\langle \epsilon_{\text{vib}} \rangle = kT^2 \frac{\partial \ln q_{\text{vib}}}{\partial t} = -\frac{\partial \ln q_{\text{vib}}}{\partial \beta}$$

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5.6: Translational Partition Functions of Monotonic Gases

Let us consider the translational partition function of a monatomic gas particle confined to a cubic box of length L. The particle inside the box has translational energy levels given by:

$$E_{\text{trans}} = \frac{h^2\left(n_x^2 + n_y^2 + n_z^2\right)}{8mL^2}$$

where n_x, n_y and n_z are the quantum numbers in the three directions. The translational partition function is given by:

$$q_{\text{trans}} = \sum_i e^{-\epsilon_i/kT}$$

which is the product of translational partition functions in the three dimensions. We can write the translation partition function as the product of the translation partition function for each direction:

$$q_{\text{trans}} = q_x q_y q_z \tag{5.6.1}$$

$$= \sum_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \sum_{n_y=1}^{\infty} e^{-\epsilon_y/kT} \sum_{n_z=1}^{\infty} e^{-\epsilon_z/kT} \tag{5.6.2}$$

Since the levels are very closely spaced (continuous), we can replace each sum in Equation 5.6.2 with an integral. For example:

$$q_x = \sum_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \tag{5.6.3}$$

$$\approx \int_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \tag{5.6.4}$$

and after substituting the energy for the relevant dimension:

$$\epsilon_x = \frac{h^2 n_x^2}{8mL^2}$$

we can extend the lower limit of integration in the approximation of Equation 5.6.4:

$$q_x = \int_1^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2kT}} \approx \int_0^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2kT}}$$

We then use the following solved Gaussian integral:

$$\int_o^{\infty} e^{-an^2} dn = \sqrt{\frac{\pi}{4a}}$$

with the following substitution:

$$a = \frac{h^2}{8mL^2kT}$$

we get:

$$q_x = \frac{1}{2}\sqrt{\frac{\pi}{a}} = \frac{1}{2}\sqrt{\frac{\pi 8mkT}{h^2}}L$$

or more commonly presented as:

$$q_x = \frac{L}{\Lambda}$$

where Λ is the **de Broglie wavelength** and is given by

$$\Lambda = \frac{h}{\sqrt{2\pi 8mkT}}$$

Multiplying the expressions for q_x, q_y and q_z (Equation 5.6.1) and using V as the volume of the box L^3, we arrive at:

$$q_{trans} = \left(\frac{\sqrt{2\pi 8mkT}}{h} \right)^{3/2} V = \frac{V}{\Lambda^3} \tag{5.6.5}$$

This is usually a very large number (10^{20}) for volumes of 1 cm^3 for small molecular masses. This means that such a large number of translational states are accessible and available for occupation by the molecules of a gas. This result is very similar to the result of the classical kinetic gas theory that said that the observed energy of an ideal gas is:

$$U = \frac{3}{2} nRT$$

We postulate therefore that the observed energy of a macroscopic system should equal the statistical average over the partition function as shown above. In other words: if you know the particles your system is composed of and their energy states you can use statistics to calculate what you should observe on the whole ensemble.

Example

Calculate the translational partition function of an I_2 molecule at 300K. Assume V to be 1 liter.

Solution

Mass of I_2 is $2 \times 127 \times 1.6606 \times 10^{-27} kg$

$$\begin{aligned} 2\pi mkT &= 2 \times 3.1415 \times (2 \times 127 \times 1.6606 \times 10^{-27}\, kg) \times 1.3807 \times 10^{-23}\, J/K \times 300K \\ &= 1.0969 \times 10^{-44}\, J\, kg \end{aligned}$$

$$\begin{aligned} \Lambda &= \frac{h}{\sqrt{2\pi mkT}} \\ &= \frac{6.6262 \times 10^{-34}\, J\, s}{\sqrt{1.0969 \times 10^{-44}\, J\, kg}} = 6.326 \times 10^{-12}\, m \end{aligned}$$

The via Equation 5.6.5

$$q_{trans} = \frac{V}{\Lambda^3} = \frac{1000 \times 10^{-6} m^3}{(6.326 \times 10^{-12}\, m)^3} = 3.95 \times 10^{30}$$

This means that 3.95×10^{30} quantum states are thermally accessible to the molecular system

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5.7: Most Atoms are in the Ground Electronic State

Writing the electronic energies as $E_1, E_2, E_3, ...$ with corresponding degeneracies $g_1, g_2, g_3, ...$ The electronic partition function is then given by the following summation:

$$q_{el}(T) = g_1 e^{-E_1/kT} + g_2 e^{-E_2/kT} + g_3 e^{-E_3/kT} + ... \tag{5.7.1}$$

Usually, the differences in electronic energies are significantly greater than thermal energy kT:

$$kT \ll E_1 < E_2 < E_3$$

If we treat the lowest energy electronic state E_1 as the reference value of zero of energy, the electronic partition function (Equation 5.7.1) can be approximated as:

$$q_{elec}(T) = g_1 + g_2 e^{-E_2/kT} + g_3 e^{-E_3/kT} + ... \tag{5.7.2}$$

Typically electronic states are tens of thousands of wave numbers above the ground state. For example, the first excited electronic state of nitric oxide (NO) is ~40,000 cm^{-1}. Using this value:

$$\frac{E_2}{kT} = \frac{40000 \text{ cm}^{-1}}{kT} = \frac{10^4 \text{ K}}{T}$$

That means, that even at 1,000 K, the value of the second term in {\reference{3.24}} is:

$$g_2 e^{-10} = g_2 4.5 \times 10^{-5}$$

The result is that the higher electronic states are not accessible under ordinary temperatures. There are some cases, however, where the first excited state lies much closer to the ground state, but these are the exception rather than the rule.

Example 18.2.1

Find the electronic partition of H_2 at 300 K.

Solution

The lowest electronic energy level of H_2 is near $-32\ eV$ and the next level is about $5\ eV$ higher. Taking -32 eV as the zero (or reference value of energy), then

$$q_{el} = e_0 + e^{-5eV/kT} + ...$$

At 300 K, T = 0.02\; eV and

$$q_{el} = 1 + e^{-200} + ...$$
$$\approx 1.0$$

Where all terms other than the first are essentially 0. This implies that $q_{el} = 1$.

The physical meaning of the result from Example 18.2.1 is that only the ground electronic state is generally thermally accessible at room temperature.

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5.8: The Energy of a Diatomic/Polyatomic Molecule Can Be Approximated as a Sum of Separate Terms

A monatomic gas has three degrees of freedom per molecule, all of them translational:

1. movement in x-direction
2. movement in y-direction
3. movement in z-direction

A polyatomic gas, including diatomic molecules, has other levels that you can 'stuff' energy into. Polyatomic molecules can rotate and vibrate, and if enough energy is available you could also excite the electrons involved in the σ and π bonds. A reasonable approximation of the partition function of the molecule would become:

$$q_{\text{tot}}(V,T) = q_{\text{trans}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}}$$

The partition function of a molecular idea gas is then:

$$Q(N,V,T) = \frac{(q_{\text{trans}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}})^N}{N!}$$

The total energy of the molecule is then the sum of the translation, vibrational, rotational, and electronic energies:

$$E_{tot} = E_{\text{trans}} E_{\text{vib}} E_{\text{rot}} E_{\text{elec}}$$

We will only scratch the surface of the additional degrees of freedom and their partition functions.

5.8.1: Electronic

At room temperature the system is usually in its ground electronic state. This means that the **electronic partition function** $q_{\text{elec}} = 1$. Usually we do not have to worry about these degrees of freedom. If we do, there are usually just a few levels to worry about. This includes their **degeneracy g**. If there is a single state at a certain energy ($g = 1$), two states ($g = 2$), or more states, we must multiply the Boltzmann factor by this degeneracy number.

If there are more than one state to worry about, we could follow the same procedure as we did for the translational states:

1. Define the energy states and their degeneracies
2. Compose the partition function q for the molecule and Q for the gas
3. Use the (β or T) derivative of $\ln Q$ to determine $\langle E \rangle$
4. Use the T derivative of $U \approx \langle E \rangle$ to find the contribution to the heat capacity

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5.9: Most Molecules are in the Ground Vibrational State

The vibrational energy levels of a diatomic are given by:

$$E_v = (v + 1/2)h\nu$$

where is ν the vibrational frequency and v is the vibrational quantum number. In this case, it is easy to sum the geometric series shown below:

$$\begin{aligned} q_{\text{vib}} &= \sum_{v=0}^{\infty} e^{-(v+1/2)h\nu/kT} \\ &= e^{-h\nu/2kT}\left(1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \ldots\right) \end{aligned}$$

or rewritten as:

$$q_{\text{vib}} = e^{-h\nu/2kT}\left(1 + x + x^2 + x^3 + \ldots\right) \tag{5.9.1}$$

where $x = e^{-h\nu/kT}$. Given the following power series expansion:

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + \ldots.$$

Equation 5.9.1 can be rewritten as:

$$q_{\text{vib}} = e^{-h\nu/2kT}\left(\frac{1}{1-x}\right)$$

or:

$$q_{\text{vib}} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} \tag{5.9.2}$$

If the zero of energy scale is at $h\nu/2kT$, then Equation 5.9.2 can be rewritten as:

$$q_{\text{vib}} \approx \frac{1}{1 - e^{-h\nu/kT}} \tag{5.9.3}$$

A vibrational temperature Θ_{vib} may be defined as:

$$\Theta_{\text{vib}} = \frac{hc\tilde{\nu}}{k}$$

where $\tilde{\nu}$ is the vibrational frequency in cm^{-1}. Θ_{vib} is a good way to express the *stiffness* of the vibrating bond in units of the Boltzmann constant. Because the stiffness obviously depends on what bond your are talking about, this is a good way to do the same thing we did for the critical temperature of the non-ideal gases.

Table **5.9.1** : Representative molecular data for a few diatomics

Molecule	g	Bond Length (pm)	ω (cm^{-1})	Θ_{vib} (K)	$\tilde{B}$ (cm^{-1})	Θ_{rot} (K)	Force constant k (dynes/cm)	D_0 (kcal/mol)
H_2	1	0.7474	4400	6332	60.9	87.6	5.749	103.2
D_2	1	0.7415	3118	4487	30.45	43.8	5.77	104.6
N_2	1	1.097	2358	3393	2.001	2.99	22.94	225.1
O_2	3	1.207	1580	2274	1.446	2.08	11.76	118.0
Cl_2	1	1.987	560	805	0.244	0.351	3.2	57.0
CO	1	1.128	2170	3122	1.931	2.78	19.03	255.8
NO	2	1.15	190	2719	1.695	2.45	15.7	150.0
HCl	1	1.275	2938	4227	10.44	15.02	4.9	102.2
HI	1	1.609	2270	3266	6.46	9.06	3.0	70.5
Na_2	1	3.096	159	229	0.154	0.221	0.17	17.3
K_2	1	3.979	92.3	133	0.0561	0.081	0.10	11.8

Example 18.4.1

The vibrational frequency of of I_2 is $214.57\ cm^{-1}$. Calculate the vibrational partition function of I_2 at 300 K.

Solution:

$$\frac{h\nu}{kT} = \frac{214.57}{209.7} = 1.0232$$

so

$$e^{-h\nu/kT} = 0.3595$$

and

$$q_{vib} = \frac{1}{1 - 0.3595} = 1.561$$

This implies, as before, that very few vibrational states are accessible and much less than rotation states and many orders less than translation states.

5.9.1: Vibrational Heat Capacity

The vibrational energy is given by the above expression and the molar heat capacity at constant volume, $\bar{C}_V$ is given by:

$$\bar{C}_V = \left(\frac{\partial E}{\partial T}\right)_V$$

We have:

$$\frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta} \tag{5.9.4}$$

$$= \frac{-1}{kT^2}\frac{\partial}{\partial \beta} \tag{5.9.5}$$

$$= (-k\beta^2)\left(\frac{\partial}{\partial \beta}\right) \tag{5.9.6}$$

Therefore:

$$\bar{C}_V = (-k\beta^2)\left(\frac{\partial \varepsilon_{\text{vib}}}{\partial \beta}\right)$$

and when the vibrational partition function (Equation 5.9.3) is introduced:

$$q_{\text{vib}} = -k\beta^2 \frac{\left[(1-e^{-hc\nu/kT})(-hc\tilde{\nu}) - e^{-hc\nu/kT}(+hc\tilde{\nu})\right] e^{-hc\nu/kT}}{(1-e^{-hc\nu/kT})^2} h\nu\tilde{\nu} \tag{5.9.7}$$

$$= k\left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{\left(1-e^{-\Theta_{\text{vib}}/T}\right)^2} \tag{5.9.8}$$

For large T, the $\bar{C}_V$ becomes:

$$N_A k = R$$

and for small T, $\bar{C}_V$ goes to zero as demonstrated in Figure 18.4.1 .

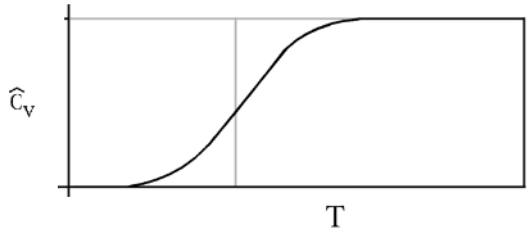


Figure 18.4.1 : Vibrational heat capacity of a diatomic

The vibrational heat capacity is shown as function of the reduced temperature T/Θ to get a general picture valid for all diatomic gases. Compare the parameters on Table 18.4.1 to see on what different absolute scales we have to think for different gases. Clearly the vibrational contribution to the heat capacity *depends on temperature*. For many molecules (especially light ones), the vibrational contribution only kicks in at quite high temperatures.

The value of Θ_{vib} is determined mostly by

1. the strength of a bond (the stronger the higher Θ_{vib})
2. the (effective) mass of the molecule (the lighter the higher Θ_{vib})

Molecules with low Θ_{vib} often dissociate at lower temperatures, although the *harmonic* oscillator model is not sufficient to describe that phenomenon.

5.9.2: Vibrational Populations

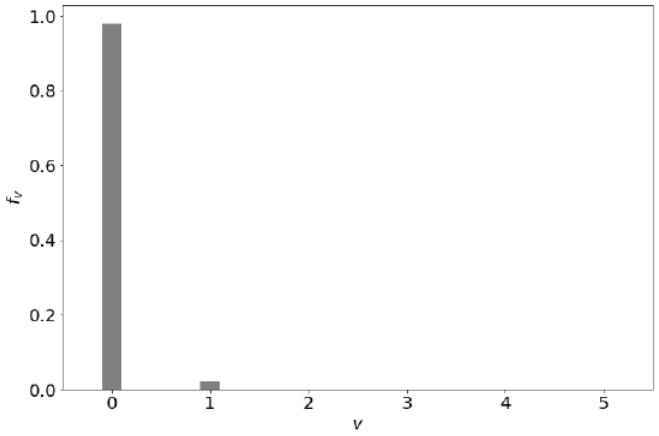
We can calculate the fraction of molecules in each vibrational state. The fraction of molecules in the vth vibrational state is given by:

$$f_v = \frac{e^{-h\nu(v+\frac{1}{2})/kT}}{q_{\text{vib}}}$$

Substituting in Equation 5.9.2, we get:

$$\begin{aligned} f_v &= \left(1-e^{-h\nu/kT}\right) e^{-h\nu v/kT} \\ &= \left(1-e^{-\Theta_{\text{vib}}/T}\right) e^{-\Theta_{\text{vib}} v/T} \end{aligned} \tag{5.9.9}$$

We can plot the fraction molecules in each vibrational state.



The vibrational population of Cl_2 at 300 K. Most of the molecules are in the ground vibrational state, $v = 0$.

From the figure, we can see that most of the Cl_2 molecules are in the ground vibrational state at room temperature (300 K). This is true for most molecules. Only molecules with very weak bonds and low vibrational temperatures will populate a significant fraction of molecules in excited vibrational states.

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5.10: Most Molecules are Rotationally Excited at Ordinary Temperatures

The rotational quantum number is J and the energy of the rotations is:

$$E(J) = \tilde{B}J(J+1)$$

Where $\tilde{B}$ is in units of cm^{-1} and is equivalent to:

$$\frac{h}{8\pi^2 Ic}$$

Where c is the speed of light in units of cm^{-1}. However, with the exception of the ground state (i.e., $J = 0$), multiple eigenstates exist for a given value of J. This is a form of **degeneracy**, (g), and the number of levels per energy goes as 1, 3, 5, 7, 9 etc or:

$$g(J) = 2J + 1$$

Therefore, the summation to find the partition function $q_{rot}(T)$ contains an extra factor $g = 2J + 1$. This factor is mathematically very handy, because it is the derivative of:

$$g(J) = J(J+1)$$

This makes it possible to change variables to $X = J(J+1)$ and the integration becomes very easy. Notice that just like in the translation partition function, we approximate the summation with an integral. However, because we are dealing with far fewer levels, this is less justified in the rotational case. How justified it is depends on the gas and the temperature we consider. Roughly speaking we should be at a temperature $T >> \Theta_{rot}$.

? Exercise 18.5.1

Look at table 18.2. When do we need to actually work out the (discrete) summation instead of making a (continuous) integration out of it?

Answer

Only for the lightest gases like $\mathbf{He}$ and $\mathbf{H_2}$ do we need to worry and then only at pretty low cryogenic circumstances. At room temperature, we can take the rotational levels as a continuous set and use an integral. Notice that the vibrational Θ values are much larger! At $T = 300\,\mathrm{K}$, usually only a single level is occupied and we are in the discrete limit. On the surface of the sun that would be a different matter of course.

The rotational constant B is directly linked to the moment of inertia:

$$I = \mu r^2$$

Where μ is the reduced mass of the molecule:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

and r is the bond length. Again we can scale the behavior of different systems to one and the same picture by introducing a characteristic temperature:

$$\Theta_{rot} = \frac{hb}{k} = \frac{\hbar^2}{2Ik_b}$$

As we did for the translations, we can calculate the moment $\langle\epsilon\rangle$. For vibrations we get a relatively complicated function of temperature. However, for rotations, the moment is simply equal to NkT and this means that the rotational contribution to the molar C_v of a diatomic is simply R. As the vibrational and electronic contributions to the heat capacity are typically negligible at room temperature, we get:

- monatomic gas

$$C_v = C_v^{trans} = \frac{3}{2}nR$$

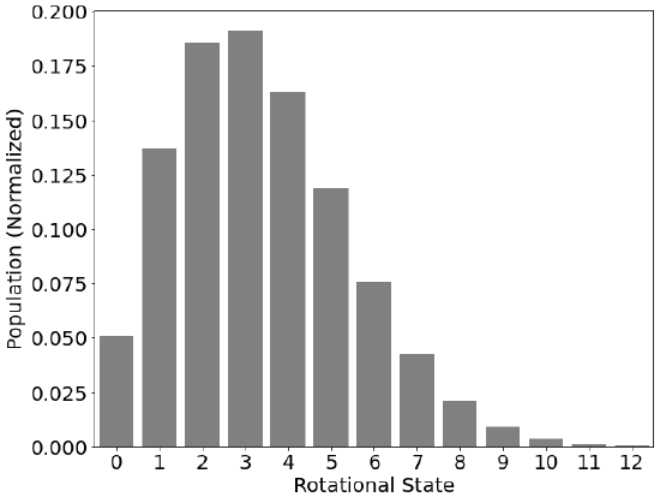
- diatomic

$$C_v = C_v^{trans} + C_v^{rot} \tag{5.10.1}$$

$$= \frac{3}{2}nR + nR \tag{5.10.2}$$

$$= \frac{5}{2}nR \tag{5.10.3}$$

Rotational energies are less than vibrational and electronic energies and, at room temperature, many rotational states will be populated.



The normalized rotational population of HCl at room temperature.

5.10: Most Molecules are Rotationally Excited at Ordinary Temperatures is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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5.11: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number

The rotational energy levels of a **diatomic molecule** are given by:

$$E_{\text{rot}}(J) = \tilde{B}J(J+1) \tag{5.11.1}$$

where:

$$\tilde{B} = \frac{h}{8\pi^2 Ic}$$

Here, $\tilde{B}$ is the rotational constant expressed in cm^{-1}. The rotational energy levels are given by:

$$E_j = \frac{J(J+1)h^2}{8\pi I}$$

where I is the moment of inertia of the molecule given by μr^2 for a diatomic, and μ is the reduced mass, and r the bond length (assuming rigid rotor approximation). The energies can be also expressed in terms of the rotational temperature, Θ_{rot}, defined as:

$$\Theta_{\text{rot}} = \frac{r^2}{8\pi^2 Ik} \tag{5.11.2}$$

The interpretation of θ_{rot} is as an estimate of the temperature at which thermal energy ($\approx kT$) is comparable to the spacing between rotational energy levels. At about this temperature the population of excited rotational levels becomes important. See Table 1.

Table 1: Select Rotational Temperatures. In each case the value refers to the most common isotopic species.

Molecule	H_2	N_2	O_2	F_2	HF	HCl	CO_2	HBr	CO
Θ_{rot}	87.6	2.88	2.08	1.27	30.2	15.2	0.561	12.2	2.78

In the summation for the expression for rotational partition function (q_{rot}), Equation 5.11.3, we can do an explicit summation:

$$q_{\text{rot}} = \sum_{j=0} (2J+1)e^{-E_J/kT} \tag{5.11.3}$$

if only a finite number of terms contribute. The factor $(2J+1)$ for each term in the expansion accounts for the degeneracy of a rotational state J. For each allowed energy E_J from Equation 5.11.1 there are $(2J+1)$ eigenstates. The Boltzmann factor must be multiplied by $(2J+1)$ to properly account for the degeneracy these states:

$$(2J+1)e^{-E_J/kT}$$

If the rotational energy levels are lying very close to one another, we can integrate similar to what we did for q_{trans} previously to get:

$$q_{\text{rot}} = \int_0^\infty (2J+1)R^{-\tilde{B}J(J+1)/kT}dJ$$

This integration can easily be done by substituting $x = J(J+1)$ and $dx = (2J+1)dJ$:

$$q_{\text{rot}} = \frac{kT}{\tilde{B}} \tag{5.11.4}$$

For a homonuclear diatomic molecule, rotating the molecule by 180° brings the molecule into a configuration which is *indistinguishable* from the original configuration. This leads to an overcounting of the accessible states. To correct for this, we divide the partition function by σ, which is called the **symmetry number** and is equal to the distinct number of ways by which a molecule can be brought into identical configurations by rotations. The rotational partition function becomes:

$$q_{\text{rot}} = \frac{kT}{\tilde{B}\sigma} \tag{5.11.5}$$

or commonly expressed in terms of Θ_{rot}:

$$q_{rot} = \frac{T}{\Theta_{rot}\sigma} \tag{5.11.6}$$

Example 18.6.1

What is the rotational partition function of H_2 at 300 K?

Solution

The value of $\tilde{B}$ for H_2 is 60.864 cm^{-1}. The value of kT in cm^{-1} can be obtained by dividing it by hc, i.e., which is $kT/hc = 209.7\ cm^{-1}$ at 300 K. $\sigma = 2$ for a homonuclear molecule. Therefore from Equation 5.11.5,

$$\begin{aligned} q_{rot} &= \frac{kT}{\tilde{B}\sigma} \\ &= \frac{209.7\ cm^{-1}}{(2)(60.864\ cm^{-1})} \\ &= 1.723 \end{aligned}$$

Since the rotational frequency of H_2 is quite large, only the first few rotational states are accessible at 300 K

Contributors and Attributions

- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf

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CHAPTER OVERVIEW

6: The First Law

A physical chemistry Textmap organized around the textbook by Atkins and De Paula

Physical Chemistry

Template:HideTOC

6.1: Internal Energy

6.2: Enthalpy

6.3: Thermochemistry

6.4: State Functions and Exact Differentials

6.5: Adiabatic Changes

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6.1: Internal Energy

Defining the System

Chemists are interested in systems containing matter—that which has mass and occupies physical space. Classical thermodynamics looks at *macroscopic* aspects of matter. It deals with the properties of aggregates of vast numbers of microscopic particles (molecules, atoms, and ions). The macroscopic viewpoint, in fact, treats matter as a *continuous* material medium rather than as the collection of discrete microscopic particles we know are actually present. Although this e-book is an exposition of classical thermodynamics, at times it will point out connections between macroscopic properties and molecular structure and behavior.

A thermodynamic **system** is any three-dimensional region of physical space on which we wish to focus our attention. Usually we consider only one system at a time and call it simply “the system.” The rest of the physical universe constitutes the **surroundings** of the system.

The **boundary** is the closed three-dimensional surface that encloses the system and separates it from the surroundings. The boundary may (and usually does) coincide with real physical surfaces: the interface between two phases, the inner or outer surface of the wall of a flask or other vessel, and so on. Alternatively, part or all of the boundary may be an imagined intangible surface in space, unrelated to any physical structure. The size and shape of the system, as defined by its boundary, may change in time. In short, our choice of the three-dimensional region that constitutes the system is arbitrary—but it is essential that we know exactly what this choice is.

We usually think of the system as a part of the physical universe that we are able to influence only indirectly through its interaction with the surroundings, and the surroundings as the part of the universe that we are able to directly manipulate with various physical devices under our control. That is, we (the experimenters) are part of the surroundings, not the system.

For some purposes we may wish to treat the system as being divided into *subsystems*, or to treat the combination of two or more systems as a *supersystem*.

If over the course of time matter is transferred in either direction across the boundary, the system is **open**. If no matter is transferred into or out of the system, the system is **closed**. If the system is open, matter may pass through a stationary boundary, or the boundary may move through matter that is fixed in space.

Note

One difficulty in describing energy exchange is the fact that heat is not an object; it is the process of energy transfer because of a temperature difference. However, it often difficult to word statements so that heat does not sound like an entity. So, although it is preferable to write that that a system has "heated up", you will often read that a system "gained heat" or "gained energy in the form of heat".

Both open and closed systems can transfer energy in either direction across the boundary if the boundary allows such an energy transfer. A boundary that allows **heat** exchanges is called **diathermal** or **diathermic**. An **adiabatic** (Greek: *impassable*) boundary, on the other hand, is a boundary that does not allow heat transfer. We can, in principle, ensure that the boundary is adiabatic by surrounding the system with an adiabatic wall—one with perfect thermal insulation and a perfect radiation shield. An **isolated** system is one that exchanges no matter, heat, or work with the surroundings, so that the mass and total energy of the system remain constant over time. A closed system with an adiabatic boundary, constrained to do no work and to have no work done on it, is an isolated system.

In chemistry, systems can undergo changes in heat because of changes in the number and types of bonds, as well as changes in the type and effectiveness of intermolecular forces. Any process that results in the heating of the system is called an **exothermic** process. These processes occur when the energy released by the formation of new bonds and intermolecular forces is greater than the energy taken in by the breaking of existing bonds and intermolecular forces. When a system undergoes an exothermic process, its temperature will increase. If held in an adiabatic container, the system will maintain this increased temperature indefinitely. If held in a diathermic container, the system will lose heat to the surroundings until the temperatures are once again in thermal equilibrium.

Any process that results in the cooling of the system is called an **endothermic** process. These processes occur when the energy released by the formation of new bonds and intermolecular forces is less than the energy taken in by the breaking of existing bonds and intermolecular forces. When a system undergoes an endothermic process, its temperature will decrease. If held in an adiabatic container, the system will maintain this decreased temperature indefinitely. If held in a diathermic container, the system will gain heat from the surroundings until the temperatures are once again in thermal equilibrium.

The constraints required to prevent work usually involve forces between the system and surroundings. In that sense a system may interact with the surroundings even though it is isolated. For instance, a gas contained within rigid, thermally-insulated walls is an isolated system. However, the gas exerts a force on each wall, and the walls exert an equal and opposite force on the gas. An isolated system may also experience a constant external field, such as a gravitational field.

Heat

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of “hot” or “cold.” When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is “hot.” When the atoms and molecules are moving slowly, they have lower KE, and we say that the object is “cold” (Figure **6.1.1**). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

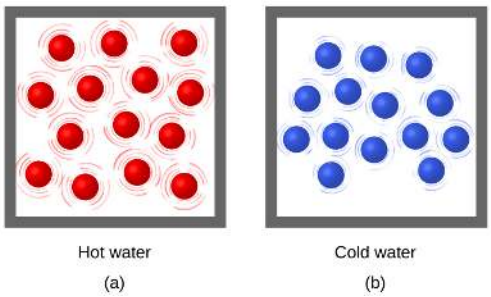


Figure **6.1.1**: *(a) The molecules in a sample of water at a higher temperature move more rapidly than (b) those in a sample of water at a lower temperature.*

Work

Work is the purposeful, or organized, transfer of energy associated with the non-random motion of atoms and molecules. On a macroscopic scale, we describe work as the result of a force moving an object. In other words, the energy is expended in an organized, coordinated fashion to make an object move. This same concept can be applied on the molecular level to describe the coordinated movement of molecules and atoms as work.

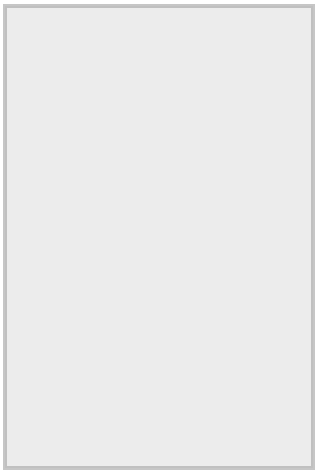


Figure 6.1.2: *Pressure·Volume Work by Gas Particles. Using a frictionless piston, if the external pressure is less than P_{int} (a), the gas molecules with an upward component to their motion will collide with the piston, collectively forcing the piston to move upward. The final volume (V_f) will be greater than V_i. Alternatively, if the external pressure is greater than P_{int} (b), the piston will perform work on the gas particles as it causes them to collectively gain a downward component to their motion.The final volume (V_f) will be less than V_i.*

Internal Energy

The First Law, Part 1

The state of a system is a complete description of a system at a given time, including its temperature and pressure, the amount of matter it contains, its chemical composition, and the physical state of the matter. A state function is a property of a system whose magnitude depends on only the present state of the system, not its previous history. Temperature, pressure, volume, and potential energy are all state functions. The temperature of an oven, for example, is independent of however many steps it may have taken for it to reach that temperature. Similarly, the pressure in a tire is independent of how often air is pumped into the tire for it to reach that pressure, as is the final volume of air in the tire. Heat and work, on the other hand, are not state functions because they are *path dependent*. For example, a car sitting on the top level of a parking garage has the same potential energy whether it was lifted by a crane, set there by a helicopter, driven up, or pushed up by a group of students (Figure **6.1.3**). The amount of work expended to get it there, however, can differ greatly depending on the path chosen. If the students decided to carry the car to the top of the ramp, they would perform a great deal more work than if they simply pushed the car up the ramp (unless, of course, they neglected to release the parking brake, in which case the work expended would increase substantially!). The potential energy of the car is the same, however, no matter which path they choose.



Figure 6.1.3: *Elevation as an Example of a State Function. The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top. In contrast, the distance traveled and the work needed to reach the top do depend on which path is taken. Elevation is a state function, but distance and work are not state functions.*

The relationship between the energy change of a system and that of its surroundings is given by the first law of thermodynamics, which states that the energy of the universe is constant. We can express this law mathematically as follows:

$$U_{univ} = \Delta U_{sys} + \Delta U_{surr} = 0 \tag{6.1.1}$$

$$\Delta U_{sys} = -\Delta U_{surr} \tag{6.1.2}$$

where the subscripts univ, sys, and surr refer to the universe, the system, and the surroundings, respectively. Thus ΔU_{sys}, the change in internal energy of a system, is identical in magnitude but opposite in sign to the change in energy of its surroundings.

(ΔU_{sys}) is independent of the path taken and is therefore a state function. Thus ΔU_{sys} also can be expressed as:

$$\Delta U_{sys} = U_{final} - U_{initial} \tag{6.1.3}$$

Because we focus almost exclusively on the changes in the energy of a system, we will not use “sys” as a subscript unless we need to distinguish explicitly between a system and its surroundings. It should also be noted that ΔU_{sys} is an extensive property that changes with the amount of substance present. A related, intensive property is the molar internal energy, U_m, defined as

$$U_m = \frac{U}{n} \tag{6.1.4}$$

Contributions to Internal Energy

Internal energy can be explained on a molecular level by taking into account the various terms that can contribute to this total energy. This accounting process is easiest to carry out for a perfect gas sample because the particles do not interact with each other. The internal energy of a perfect gas can thus be approximated by adding the contributions of the zero-point energy, the translational energy, rotational energy, vibrational energy, and electronic energy. The translational and rotational energy contributions involve the most straightforward calculations because for these terms, each degree of freedom contributes $\frac{1}{2}RT$ to the molar internal energy according to the equipartion theorem. Thus, the translational contribution for all particles is $\frac{3}{2}RT$ for movement in the x, y and z directions. The rotational contribution depends on the number of atoms in the particle. Single atoms have no rotational degrees of freedom. Linear molecules have 2 degrees of freedom (along the two axes perpendicular to the bond axis. Polyatomic, nonlinear molecules all have three degrees of rotational freedom.

It is important to note that the internal energy of a sample of a perfect gas is independent of the volume occupied by the gas particles. There are no intermolecular attractions between the particles, so there is no difference in potential energy if the particles are very close together in a small container, or very far apart in a large container.

The internal energy of real gases, liquids, and solids cannot be so simply described because the particles do experience intermolecular forces of attraction, and thus there is a contribution of their potential energy to the total internal energy. It is still true, however, that as the temperature increases the internal energy increases because the likelihood of having higher-energy translational and rotational energy levels increases.

The First Law, Part 2

Because heat and work are the only two ways in which energy can be transferred between a system and its surroundings, any change in the internal energy of the system is the sum of the heat transferred (q) and the work done (w):

$$\Delta U_{sys} = q + w \tag{6.1.5}$$

Assuming the universe is an isolated system, the second law can be reworded as:

Definition

The internal energy of an isolated system is constant. Thus, q = 0 and w = 0 for an isolated system, just as the definition demands.

For a closed system, energy can be transferred into and out of the system. By convention, the q and w terms in Equation 6.1.5 are assigned negative values if energy leaves the system (an exothermic process, or work is done **by** the system), and assigned positive values if energy enters the system (an endothermic process, or work is done **on** the system.)

Example 6.1.1:

Suppose that 150 kJ of work are used to compress a spring, and that 25 kJ of heat are given off by the spring during this compression. What is the change in internal energy of the spring during the process?

Strategy: Use $\Delta U_{sys} = q + w$ to solve for ΔU_{sys} with the understanding that work is done on the system (+ w) and heat is lost from the system (- q).

Answer: ΔU_{sys} = 150 kJ - 25 kJ = + 125 kJ.

Exercise 6.1.1

Suppose that 100 kJ of work is done by a motor, but that it also gives off 10 kJ of heat while carrying out this work. What is the change in internal energy of the motor during the process?

Answer: ΔU_{sys} = -100 kJ - 10 kJ = - 110 kJ.

Expansion/Compression Work

Work in general is defined as a product of a force **F** and a path element **ds**. Both are vectors and work is computed by integrating over their product

$$w = \int \mathbf{F} \cdot \mathbf{ds} \tag{6.1.6}$$

Moving an object against the force of friction is but one example of work.

$$w_{friction} = \int \mathbf{F}_{friction} \cdot \mathbf{ds} \tag{6.1.7}$$

We could also think of *electrical* work. In that case we would be moving a charge *e* (e.g. the negative charge of an electron) against an electrical (vector) field **E**. The work would be:

$$w_{electical} = \int e\mathbf{E} \cdot \mathbf{ds} \tag{6.1.8}$$

Other examples are the stretching of a rubber band against the elastic force or moving a magnet in a magnetic field etc, etc.

In the case of a cylinder filled with a perfect gas, we can introduce the area of the piston A and forget about the vectorial nature. The movement of the piston is constrained to one direction, the one in which we apply an external pressure, P_{ex}. Recall that P is force (F) per area (A). We can also assume that the molecules of the gas rapidly equilibrate to the applied pressure and make it into an all-sided phenomenon.

$$w_{volume} = \int \left(\frac{F}{\cancel{A}}\right)(\cancel{A}\, ds) = \int P_{ex}\, dV \tag{6.1.9}$$

This particular form of work is called ***volume work*** and will play an important role in the development of our theory. Notice however that volume work is only ***one form*** of work.

conventions

It is important to create a sign convention at this point: positive heat and positive work are always what you put in into the system. If the system happens to give off heat or to do work, these events get a minus sign.

In other words: ***you pay the bill***.

To comply with this convention we need to rewrite volume work (Equation 6.1.9) as

$$w_{volume} = -\int \left(\frac{F}{\cancel{A}}\right)(\cancel{A}\, ds) = -\int P_{ex}\, dV \tag{6.1.10}$$

Hence, to decrease the volume of the gas (ΔV is negative), we must do work on the gas. This is a gain of energy by the system, so the sign of the work is positive. If the volume of the gas increases, work must be done by the gas to move the piston. This is a loss of energy from the system, and so the sign of the work is negative.

Irreversible Expansion/Contraction against a Constant Pressure

When a system is far from equilibrium, an infinitesimal change in any variable will be insignificant because at least one variable in the system will be undergoing a relatively large change as the system drives toward equilibrium. Because the system is far from equilibrium, the significant change(s) that occur as the system attains equilibrium are considered **irreversible changes**, not only because they are not easily undone, but also because to undo them would drive the system away from equilibrium. Such a situation

occurs when starting materials in a chemical reaction are mixed together, when a very hot object is set next to a cold object, and when a 50 kilogram mass is placed on a piston that was in equilibrium with a gas sample that was at one atmosphere pressure.

If a gas expands against a constant pressure (atmospheric pressure or a constant mass set on the piston), Equation 6.1.10 can be simplified to

$$w = -P_{ex} \int dV = -P_{ex}(V_{final} - V_{initial}) = -P_{ex}\Delta V \tag{6.1.11}$$

Because integrals can be interpreted as an area under a curve, the value of w is equal to the area under the constant pressure line, $P = P_{ex}$ between $V_{initial}$ and V_{final}. Figure 6.1.4 shows a PV graph (known as an **indicator graph**)of a constant pressure expansion.

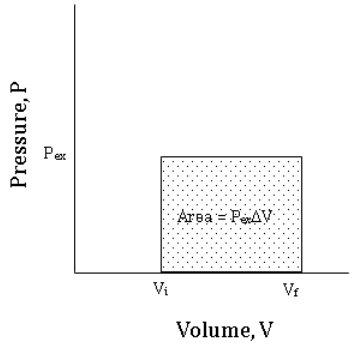


Figure* 6.1.4*: *An indicator graph for a constant pressure expansion*

This type of indicator graph could be obtained by adding energy to a gas sample, held in a cylinder by a piston that is exerting a constant pressure. The cylinder would need to have diathermal walls, and must be surrounded by a constant temperature bath. The initial state of this expansion is not stable, because the pressure of the gas, P_{gas}, must be quite different than the external pressure, P_{ex}. If you want the gas to undergo an expansion, $P_{gas} > P_{ex}$. If you want the gas to undergo a compression, $P_{gas} < P_{ex}$. For both processes, the piston must be held in place initially until you are ready to start the process. It is also true that in both compression and expansion, the process will continue until $P_{gas} = P_{ex}$. For the isothermal expansion, the energy needed for the expansion work will be delivered into the system by the surrounding constant temperature bath. For the isothermal compression, the heat created when the work is done on the system will be dissipated into the surrounding constant temperature bath.

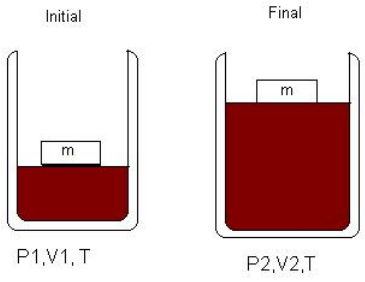


Figure* 6.1.5*: *An system undergoing a constant pressure expansion. The mass exerting the pressure is a fixed value, so P_{ex} is constant.*

If the gas expands with no opposing force, then P_{ex} must be 0 and thus w must be 0. This special case of expansion is called free expansion, and occurs whenever a gas expands into a vacuum.

Example 6.1.2:

Suppose 3.00 moles of an perfect gas held in a 4.00 L container at 20.0 bar undergoes an irreversible, isothermal expansion against a constant external pressure of 5.00 bar. How much work was done by the gas?

Strategy: You need to use Equation 6.1.11 to solve the Equation. You know P_{ex} and V_i, so you must first find the V_f of the gas. To do so, you need to find the T of the gas, using PV=nRT.

Answer:

$$T = \frac{P_i \cdot V_i}{nR} = \frac{(20.0bar)(4.00L)}{(3.00moles)(0.08314\frac{bar \cdot L}{mole \cdot K})} = 321K$$

$$V_f = \frac{nRT}{P_f} = \frac{(3.00moles)(0.08314\frac{bar \cdot L}{mole \cdot K})(321K)}{5.00bar} = 16.0L$$

$$w_{irreversible} = -P_{ex}\Delta V = -5.00bar\, x\, \frac{10^5 Pa}{bar}\, x\, (16.0L - 4.00L)\, x\, \frac{10^{-3}m^3}{L} = -6.00x10^3 J$$

Exercise 6.1.2

A. Suppose 2.50 moles of an perfect gas held in a 2.00 L container at 10.0 bar undergoes an irreversible, isothermal expansion against a constant external pressure of 2.00 bar. How much work was done by the gas?

B. Suppose 2.50 moles of an perfect gas held in a 2.00 L container at 10.0 bar undergoes three, separate irreversible, isothermal expansions. The first step involves an expansion against a P_{ex} of 6.00 bar. The second step involves an expansion against a P_{ex} of 3.00 bar. The third step involves an expansion against a P_{ex} of 2.00 bar. How much total work was done by the gas over the three combined steps?

Answer: A. -1.60 x 10^3 J B. -2.47 x 10^3 J

Notice that the final state in part B is the same as the final state in part A. However, the work done by the gas increased when the number of irreversible steps increased.

Example 6.1.3

A sample of an ideal gas in the cylinder of an engine is compressed from 400 mL to 50.0 mL during the compression stroke against a constant pressure of 8.00 atm. At the same time, 140 J of energy is transferred from the gas to the surroundings as heat. What is the total change in the internal energy (ΔU) of the gas in joules?

Given: initial volume, final volume, external pressure, and quantity of energy transferred as heat

Asked for: total change in internal energy

Strategy:

A. Determine the sign of q to use in Equation 6.1.5.
B. From Equation 6.1.11 calculate w from the values given. Substitute this value into Equation 6.1.5 to calculate ΔU.

Solution

A. From Equation 6.1.5, we know that ΔU = q + w. We are given the magnitude of q (140 J) and need only determine its sign. Because energy is transferred from the system (the gas) to the surroundings, q is negative by convention.

B Because the gas is being compressed, we know that work is being done on the system, so w must be positive. From Equation 6.1.11,

$$w = -P_{\text{ext}}\Delta V = -8.00\ \text{atm}(0.0500\ \text{L} - 0.400\ \text{L})\left(\frac{101.3\ \text{J}}{\text{L} \cdot \text{atm}}\right) = 284\ \text{J}$$

Thus

$$\Delta U = q + w = -140\ \text{J} + 284\ \text{J} = 144\ \text{J}$$

In this case, although work is done on the gas, increasing its internal energy, heat flows from the system to the surroundings, decreasing its internal energy by 144 J. The work done and the heat transferred can have opposite signs.

Exercise 6.1.3

A sample of an ideal gas is allowed to expand from an initial volume of 0.200 L to a final volume of 3.50 L against a constant external pressure of 0.995 atm. At the same time, 117 J of heat is transferred from the surroundings to the gas. What is the total change in the internal energy (ΔU) of the gas in joules?

Answer:

−216 J

Reversible Expansion/Contraction

When a system is at equilibrium, an infinitesimal change in any variable will cause the system to change infinitesimally to attain a new equilibrium. From this new equilibrium, a further infinitesimal change would cause the system to change infinitesimally once again to attain a new equilibrium, which could, in fact, be the original equilibrium state. Because the system is always at or infinitesimally close to equilibrium, all of the infinitesimal changes are considered **reversible changes** because any given change can be undone by one or more further infinitesimal changes. Such a situation can occur for a reaction at chemical equilibrium, for an object in thermal equilibrium with its surroundings, and for a gas held in a cylinder by a piston in mechanical equilibrium with the external pressure. A perfectly reversible process, also known as a **quasi-static** process, would never actually finish, yet we can use the concept to determine the limiting result for many thermodynamic processes.

As was just noted, we can approximate a reversible expansion with a gas sample held in a cylinder by a piston. If the pressure of the gas is equal to the external pressure on the piston, the system is in mechanical equilibrium with the surroundings. If the pressures are equal, then $P_{ex} = P_{gas}$, and Equation 6.1.10 can be expressed as

$$w = -\int P_{gas}\, dV \tag{6.1.12}$$

Isothermal Reversible Expansion/Contraction

Suppose we have a sample of a perfect gas held under pressure in a cylinder by a piston that can be moved in infinitesimally small increments by a motor. The cylinder has diathermal walls, and is submerged in a constant temperature bath. As will be shown in an upcoming section of this chapter, if there is no change in temperature for a perfect gas, there can be no change in internal energy. Thus, for an isothermal process carried out on/by an perfect gas:

$$\Delta U = 0 = q + w \tag{6.1.13}$$

Inside the cylinder is a coil that adds heat to the gas sample. The constant temperature bath keeps the gas sample at a constant temperature, so the added heat cannot raise the temperature of the gas. If the temperature of the gas does not change, there is no change in internal energy. If there is no change in internal energy, even though heat is being added, then the gas must be using all the heat being added to the gas to do work on the surroundings. In other words:

$$w_{done\ by\ gas} = -q_{added\ to\ gas} \tag{6.1.14}$$

The work that the gas is doing on the surroundings is to push against the piston to expand the volume of the contained gas. If the coil adds heat to the gas in infinitesimal increments, then the volume of the gas will increase by infinitesimal increments as it pushes against the P_{ex}. However, as the volume expands, the P_{gas} will decrease infinitesimally. To maintain (or remain extremely close to) the mechanical equilibrium between P_{gas} and P_{ex}, the motor will need to reduce the pressure exerted by the piston. When the pressure exerted by the piston is reduced, P_{gas} will once again equal P_{ex}, and both pressures will be infinitesimally less than they were before the coil added the infinitesimal increment of heat to the gas. We thus have a process that meets the requirements for a reversible expansion. If we carry out the heating process to the extent that we change the volume of a gas by a significant amount, we can can assume that the process actually occurred by way of an infinite number of reversible expansions in which the gas pressure always equaled the external pressure. The total work for such a process can be calculated if we express P as a function of V:

$$P = \frac{nRT}{V} \tag{6.1.15}$$

and then substitute into Equation 6.1.12 to obtain

$$w = -\int \frac{nRT}{V}\,dV = -nRT\int \frac{dV}{V} = -nRT\ln\frac{V_f}{V_i} \tag{6.1.16}$$

Because V_f is larger than V_i, the work will be negative, as is expected when work is done **by** the system.

(The exact same result could be obtained by reducing the pressure exerted by the piston by infinitesimal amounts. After each incremental reduction in P_{ex}, the gas would respond by expanding doing work against the piston until its volume increased to the point at which P_{gas} was equal to the new, lower P_{ex}. The heater coil would need to respond by transferring the appropriate amount of heat into the gas to maintain a constant temperature.)

Figure 6.1.5 is an indicator diagram for this reversible process, starting at the high pressure, low volume state, and ending at the low pressure, high volume state.

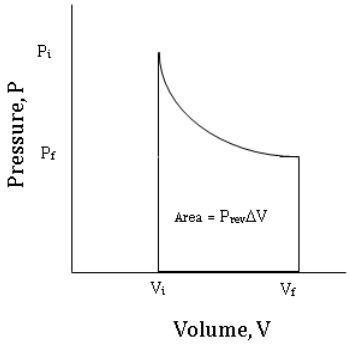
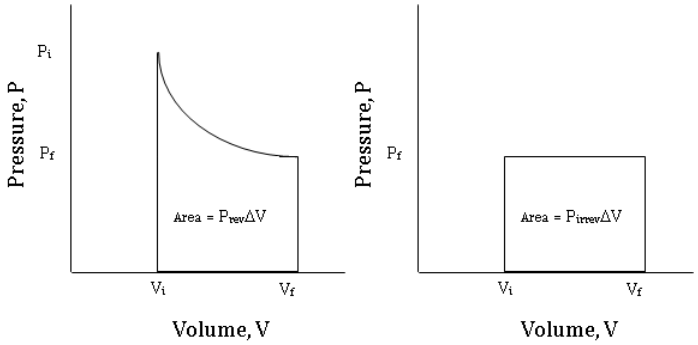


Figure 6.1.6 compares the indicator diagram for the reversible expansion from V_i to V_f to the indicator diagram of an irreversible expansion from V_i to V_f against a constant pressure equal to the final P_{ex} attained by the reversible process.



It is easy to see that the area under the curve of the reversible expansion is greater than the area under the curve of the constant pressure, irreversible expansion. This extra area represents the extra work that can be done by the system is the process is carried out reversibly rather than irreversibly. The fact that reversible processes provide maximum work will be expanded upon in Chapter 3, section A.

Note

In this example we are claiming that the heat added to the gas by the coil was never able to raise the temperature of the gas, but instead was used by the gas to do work. We are also claiming that the system was always at mechanical equilibrium, with P = P_{ex}, even though each infinitesimal change could happen only if $P \neq P_{ex}$. These are impossible parameters to meet, but by assuming them, we can calculate the maximum work that could be done by the process.

Example 6.1.4:

Suppose 3.00 moles of an perfect gas held in a 4.00 L container at 20.0 bar undergoes a **reversible**, isothermal expansion to a final pressure of 5.00 bar. How much work was done by the gas?

Strategy: As in Example 2.1.2, you need to calculate the temperature and final volume of the gas sample. You then use Equation 6.1.16 to find the work done by the gas.

Answer: $T = \frac{P_i \cdot V_i}{nR} = \frac{(20.0bar)(4.00L)}{(3.00moles)(0.08314\frac{bar \cdot L}{mole \cdot K})} = 321K$

$$V_f = \frac{nRT}{P_f} = \frac{(3.00moles)(0.08314\frac{bar \cdot L}{mole \cdot K})(321K)}{5.00bar} = 16.0L$$

$$w = -nRT\ln\frac{V_f}{V_i} = -(3.00moles\ x\ 8.314\frac{J}{mole \cdot K}\ x\ 321K\ x\ \ln\frac{16.0L}{4.00L} = -1.11x10^4J$$

Notice that the reversible process does about twice as much work as the one-step irreversible process!

Exercise 6.1.4

Suppose 2.50 moles of an perfect gas held in a 2.00 L container at 10.0 bar undergoes an irreversible, isothermal expansion against a constant external pressure of 2.00 bar. How much work was done by the gas?

Answer: -3.22 x 10^3 J

Heat Transfer

Some systems can do no work. If the system is a gas, this would mean that the container in which the gas is held has a constant volume. Because no work can be done, the only way in which the system can change internal energy is to gain or lose heat. For such a system, the first law would be

$$\Delta U = q_V \tag{6.1.17}$$

where the subscript "V" indicates that the system is at constant volume.

Calorimetry

Calorimetry is the experimental measurement of heat changes. The basic premise of a calorimetry experiment is that the first law will always be followed; heat can be neither created nor destroyed:

$$q_{system} = -q_{surroundings} \tag{6.1.18}$$

Constant Volume Calorimetry, also know as bomb calorimetry, is used to measure the q_V for many exothermic processes, such as combustion reactions. A bomb calorimeter structure consists of the following:

- Steel inner container ("bomb") which contains the reactants
- Water bath in which the bomb is submerged
- Thermometer
- A motorized stirrer
- Wire for ignition

All of these components are contained within the double-walled outer part of the calorimeter (Figure 1). Since the process takes place at constant volume, the reaction vessel must be constructed to withstand the high pressure resulting from the combustion process, which amounts to a confined explosion. The vessel is usually called a “bomb”, and the technique is known as ***bomb calorimetry***.

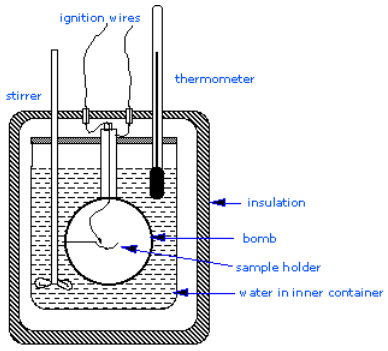


***Figure 1**: A simplified bomb calorimeter*

In an adiabatic, constant-volume calorimeter, the entire experiment is sealed or isolated from the rest of the room so that no heat will enter or leave the calorimeter "universe". Under these conditions, the change in heat of the reaction will be equal, but opposite, to the change in heat of the surroundings, which is limited to the water and other components of the calorimeter.

$$q_{reaction} = -q_{calorimeter} \tag{6.1.19}$$

The value of $q_{calorimeter}$ actually depends on two terms

$$q_{calorimeter} = q_{water} + q_{bomb} \tag{6.1.20}$$

but if the same amount of water is used for every experiment, then Equation 6.1.19 is valid for all experiments.

Once the initial temperature of the calorimeter water has been measured, the heated wire inside the bomb is used to start the reaction. The temperature inside the calorimeter rises due to the conversion from chemical energy to thermal energy that occurs through the combustion reaction. To ensure complete combustion, the experiment is carried out in the presence of oxygen above atmospheric pressure. After combustion the final temperature of the calorimeter water is measured. However, the heat given off by the reaction not only heated the calorimeter water; it also heated the calorimeter apparatus, itself. Thus, it is necessary to determine the **calorimeter constant**, C, which is the fixed amount of energy needed to raise the temperature of the calorimeter apparatus 1 kelvin.

$$C = \frac{q_{calorimeter}}{\Delta T} \tag{6.1.21}$$

The value of C is usually determined by one of two methods. A chemical reaction with a known heat output can be carried out in the calorimeter. You know the value of $q_{reaction}$ and thus the value of $q_{calorimeter}$ for the known amount of water in your calorimeter. You also know the ΔT for the reaction, so you can calculate the value of C.

The second method involves adding heat to the calorimeter apparatus by means of an electrical heater. If you pass a constant electrical current (I) through a heater with a known voltage drop ($\Delta\phi$) for a known amount of time (t), you can calculate the heat added to the calorimeter apparatus by the fact that heat = (current)(time)(potential difference):

$$q = \Delta\phi \cdot I \cdot t \tag{6.1.22}$$

Example 6.1.5:

The temperature of a calorimeter rises 6.00 K when a 12.0 V power supply is used to pass a 17.0 amp current through a heating coil for 200. seconds. What is the value of C for the calorimeter?

Strategy:

Step 1: Use Equation 6.1.19 to calculate $q_{reaction}$ (because the heater is the source of added heat). Remember that $1\ Volt = 1\frac{Joule}{Coulomb} = 1\frac{J}{C}$ and that $1\,ampere = 1\frac{Coulomb}{second} = 1\frac{C}{s}$.

Step 2: Use Equation 6.1.21 to calculate C.

Answer:

Step 1: $q_{reaction} = \Delta\phi \cdot I \cdot t = (12.0\frac{J}{C})(17.0\frac{C}{s})(200.s)(\frac{1\,kJ}{1000\,J}) = 40.8\,kJ$

Step 2: $C = \frac{40.8\,kJ}{6.00\,K} = 6.80\frac{kJ}{K}$

Exercise 6.1.5

The temperature of a calorimeter rises 8.00 K when a 12.0 V power supply is used to pass a 20.0 amp current through a heating coil for 150. seconds. What is the value of C for the calorimeter?

Answer: 4.50 $\frac{kJ}{K}$

Other Calorimeters

There are many other types of calorimeters other than bomb calorimeters including **isobaric calorimeters** (example: a coffee cup open to the atmosphere), **adiabatic flame calorimeters** (a constant-pressure calorimeter used for combustion reactions), **differential scanning calorimeters** (DSC, a calorimeter which compares the amount of energy needed to keep the temperature of a sample and the temperature of a standard reference material the same as energy is added to both substances), and **isothermal titration calorimeters** (a calorimeter similar to a DSC, but which moderates the energy needed to maintain equal temperatures of a reference and a chemical reaction as precisely measured volumes of a reagent are added to the reaction mixture.)

Heat Capacity

As noted earlier, the internal energy of a system increases as the temperature of the system increases. If we are working with a pure substance that is kept at a constant volume, we can obtain both an intensive and extensive property of the substance from a plot of the internal energy versus the temperature. The slope of the tangent line to the U vs T curve at any temperature is known as the **heat capacity** at constant volume C_v for that substance:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{6.1.23}$$

This is a partial derivative because the internal energy of a system will typically vary with both volume and temperature, but we are holding the volume constant and allowing only the temperature to change.

Because C_V tells us the amount of heat needed to change the temperature of a sample of a substance at constant volume, we can also say that an infinitesimal change in internal energy is equal to an infinitesimal change in temperature multiplied by the heat capacity at constant volume

$$dU = C_V\,dT \tag{6.1.24}$$

If the heat capacity at constant volume of the substance does not change a great deal as the temperature changes, then the slope of the U versus T graph will be fairly constant. In this case

$$\Delta U = \int C_V\,dT = C_V \cdot (T_2 - T_1) = C_V \cdot \Delta T \tag{6.1.25}$$

As noted in Equation 6.1.17,

$$\Delta U = q_V \tag{2.1.17}$$

so that

$$q_V = C_V \cdot \Delta T \tag{6.1.26}$$

Equation 6.1.26 shows us that we can experimentally determine the constant volume heat capacity of a substance fairly easily by measuring the change in temperature of a substance as heat is added to it.

The value of C_V is an extensive property because it tells us how much heat is need to change the temperature of that specific sample of the pure substance. We can determine the intensive property of this pure substance, the molar heat capacity at constant volume, $C_{V,m}$, if we divide the experimentally obtained C_V by the number of moles of the substance used in the experiment:

$$C_{V,m} = \frac{C_V}{n} \tag{6.1.27}$$

We can also calculate a second intensive property, the specific heat capacity, $C_{V,s}$, which is the heat capacity per mass of sample:

$$C_{V,s} = \frac{C_V}{mass} \tag{6.1.28}$$

Example 6.1.6:

When 18.9 kJ is transferred to a gas sample in a constant-volume adiabatic container with a calorimeter constant of 2.22 $\frac{kJ}{K}$, the temperature of the gas (and calorimeter) increases by 8.06 K.

A. What is the heat capacity of the sample?

B. If the sample has a mass of 0.500 kilograms, what is the specific heat capacity of the substance?

C. If the sample is krypton, what is the molar heat capacity at constant volume of krypton?

Strategy:

A. Use a modified version of Equation 6.1.18,

$$q_{added} = -(q_{calorimeter} + q_{V\ gas}) \tag{6.1.29}$$

and substitute in Equations 6.1.21 and 6.1.26 to obtain

$$q_{added} = -(C_{calorimeter}\Delta T + C_{V\ gas}\Delta T) \tag{6.1.30}$$

Then solve for $C_{V\ gas}$.

B. Use Equation 6.1.28 to find the specific heat capacity.

C. Determine the number of moles of krypton present and then use Equation 6.1.27 to find the molar heat capacity at constant volume.

Answer:

A. $-18,900J = -[(2,220\frac{J}{K})(8.06K) + (C_{V\ gas})(8.06K)]$

$$\frac{18,900J - 17,893J}{8.06K} = C_{V\ gas}$$

$$125\frac{J}{K} = C_{V\ gas}$$

B. $C_{V,s\ gas} = \frac{C_{V\ gas}}{mass} = \frac{125\frac{J}{K}}{0.500kg} = 250.\frac{J}{kg \cdot K}$

C. $molesKr = \frac{gramsKr}{83.8\frac{grams}{mole}} = \frac{500.grams}{83.8\frac{grams}{mole}} = 5.97moles$

$$C_{V,m\ gas} = \frac{C_{V\ gas}}{moles} = \frac{125\frac{J}{K}}{5.97moles} = 20.9\frac{J}{mole \cdot K}$$

Exercise 6.1.6

When 20.3 kJ is transferred to a 253 gram gas sample in a constant-volume adiabatic container with a calorimeter constant of 4.30 $\frac{kJ}{K}$, the temperature of the gas (and calorimeter) increases by 4.50 K. What is the specific heat capacity of the substance?

Answer: $C_{V,s} = 834\frac{J}{kg \cdot K}$

Note

It should be noted that the temperature of a pure substance does not change during phase changes. The heat being added is breaking up the electrostatic interactions that hold the particles together. With $\Delta T = 0$, Equation 6.1.26 tells us that the C_V at phase changes must approach infinity:

$$C_V = \frac{q_V}{\Delta T} = \frac{q_V}{0} \tag{6.1.31}$$

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6.2: Enthalpy

Enthalpy

A Definition

In the previous section, we discussed several different process conditions, focusing first on isothermal expansions and contractions, and then on adiabatic, constant-volume calorimetry. In this section we will focus on constant pressure processes so that we can study the thermodynamic property enthalpy, H. Recall the definition of internal energy

$$U = q + w \tag{6.2.1}$$

Under constant volume conditions, the system could do no work, so

$$U = q_V \tag{6.2.2}$$

If the volume of the system is allowed to change, however, the system can do work as it expands against the external pressure, w will have a negative, non-zero value, and

$$U < q \tag{6.2.3}$$

Equation 6.2.1 can be rewritten as

$$U = q + (-PV) \tag{6.2.4}$$

where $w = -PV$ is always be negative if the system is constrained to do only expansion work.

Enthalpy (H) is defined as the sum of the internal energy (U) and the product of pressure and volume (PV):

$$H = U + PV \tag{6.2.5}$$

Enthalpy is a state function which depends entirely on the state functions V, P and U. It is not possible to measure absolute enthalpy, but the change in enthalpy (ΔH) for a process between initial and final states can be measured experimentally:

$$\Delta H = \Delta U + \Delta PV \tag{6.2.6}$$

If temperature and pressure remain constant through the process and the work is limited to pressure-volume work, then the enthalpy change is given by the equation:

$$\Delta H = \Delta U + P\Delta V \tag{6.2.7}$$

Note

Equation 6.2.7 can be derived starting with the basic premise of an infinitesimal change to the system:

$$H + dH = (U + dU) + (P + dP)(V + dV) \tag{6.2.8}$$

$$H + dH = U + dU + PV + VdP + PdV + dPdV \tag{6.2.9}$$

The VdP term is 0 because the process is carried out at constant pressure. The $dPdV$ term is so small (the product of two infinitesimal changes) that it can be approximated as 0. Thus Equation 6.2.9 becomes

$$H + dH = U + dU + PV + PdV \tag{6.2.10}$$

By the definition of Equation 6.2.5, $H = U + PV$, thus

$$H + dH = H + dU + PdV \tag{6.2.11}$$

which becomes

$$dH = dU + PdV \tag{6.2.12}$$

If the system undergoes a change from a fixed initial condition to a fixed final condition, then

$$\int dH = \int dU + P\int dV \tag{6.2.13}$$

resulting in

$$\Delta H = \Delta U + P\Delta V \tag{6.2.14}$$

Per the definition of the first law,

$$\Delta U = q + w \tag{6.2.15}$$

Because the constant-pressure work will always be expansion work against the surroundings, $w = -P\Delta V$, and

$$\Delta H = q_P + (-P\Delta V) + P\Delta V \tag{6.2.16}$$

We now can see that the change in enthalpy is the change in heat at constant pressure:

$$\Delta H = q_P \tag{6.2.17}$$

Example 6.2.1: Enthalpy Change Accompanying a Change in State

When a liquid vaporizes, the temperature remains constant because the liquid absorbs heat from its surroundings to replace the energy taken in by the vaporizing molecules as the intermolecular forces are broken. This heat required to vaporize the liquid is called enthalpy of vaporization (or heat of vaporization).

Suppose that a sample of methanol is heated to its boiling point at a constant pressure of 1.00 atm. An electric current of 0.750 amps from a 12.0 Volt power supply is passed through a coil for 250 seconds to add heat to the liquid. If 1.88 grams of methanol is converted to vapor by this process, what is the ΔH for this specific process, what is the ΔH_m for methanol?

Strategy: Use the Equation $q = I \cdot t \cdot \Delta\phi$ to calculate the energy used to vaporize the liquid, which is ΔH, and then divide by the number of moles to determine the molar enthalpy of vaporization.

Answer

$$q_P = \Delta H = (0.750\frac{C}{s})(250s)(12.0\frac{J}{C}) = 2250J$$

$$\Delta H_m = \left(\frac{2250\,J}{1.88\,grams}\right)\left(\frac{32.0\,grams}{1.00\,mole}\right)\left(\frac{1.00\,kJ}{1000\,J}\right) = 38.3\frac{kJ}{mole}$$

Exercise 6.2.1

Suppose that a sample of water is heated to its boiling point at a constant pressure of 1.00 atm. An electric current of 0.850 amps from a 12.0 Volt power supply is passed through a coil for 150 seconds to add heat to the liquid. If 1.88 grams of water is converted to vapor by this process, what is the ΔH for this specific process, what is the ΔH_m for methanol?

Answer: ΔH = 1530 J, ΔH_m = 40.7 $\frac{kJ}{mole}$

Constant Pressure Calorimetry

It is relatively easy to measure an enthalpy change for a chemical or physical change that occurs at constant pressure. Often an insulated container such as a Styrofoam™ cup can be used as the reaction vessel, with the atmosphere exerting the constant pressure. This type of calorimeter is called an **isobaric** calorimeter. A bomb calorimeter can be used to find ΔH for reactions involving solids and liquids because the molar volumes of solids and liquids are relatively small, leading to $\Delta H \approx \Delta U$. ΔH may differ greatly from ΔU for processes involving gases because of the large molar volumes of gases. For a reaction that involves a change in the number of moles of perfect gases Δn_g, under isothermal conditions,

$$\Delta H = \Delta U + \Delta n_g RT \tag{6.2.18}$$

Example 6.2.2: ΔH *vs.* ΔU

A) Solids

Calculate the difference between the ΔH_m and the ΔU_m for the conversion of graphite to diamond when the pressure is 1.0 bar. The density of graphite is 2.15 $\frac{grams}{cm^3}$ and the density of diamond is 3.51 $\frac{grams}{cm^3}$.

Strategy: You will need to use Equation 6.2.7 to solve this problem, with the understanding that ΔV_m can be found by dividing the molar mass M by the density ρ.

First, rearrange the Equation $\Delta H_m = \Delta U_m + P\Delta V_m$ to $\Delta H_m - \Delta U_m = P\Delta V_m$.

Next, realize that $\Delta V_m = V_{m,\,diamond} - V_{m,\,graphite}$

and therefore $\Delta V_m = \frac{M_{carbon}}{\rho_{diamond}} - \frac{M_{carbon}}{\rho_{graphite}}$

Answer: $\Delta H_m - \Delta U_m = P\left(\frac{M_{carbon}}{\rho_{diamond}} - \frac{M_{carbon}}{\rho_{graphite}}\right) = PM\left(\frac{1}{\rho_{diamond}} - \frac{1}{\rho_{graphite}}\right)$

$$\Delta H_m - \Delta U_m = (1.0x10^5 Pa)x(12.01\frac{grams}{mole})x\left(\frac{1.00cm^3}{3.51grams} - \frac{1.00cm^3}{2.15gram}\right)x\left(\frac{1.00\,m^3}{1.00x10^6\,cm^3}\right)x\left(\frac{1.00J)}{1.00Pa\cdot m^3}\right)$$

$$= -0.22\frac{J}{mole}$$

This is a small fraction of ΔH_m for the process, which is +1.9 kJ.

B) Gases

Calculate the difference between the ΔH_m and the ΔU_m for the reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$ at 298 K.

Strategy: Use Equation 6.2.18 to solve for $\Delta H_m - \Delta U_m = \Delta n_g RT$

Answer: $\Delta H_m - \Delta U_m = (-1mole)\,x\,0.008314\frac{kJ}{mole\cdot K}\,x\,(298K) = -2.48kJ$

Notice that the difference between ΔH and ΔU is much greater for a reaction involving the change in the number of moles of gases than it is for a phase change involving different solid forms of an element.

Exercise 6.2.2

A. Calculate the difference between the ΔH_m and the ΔU_m for the conversion of white phosphorus to black phosphorus when the pressure is 1.0 bar. The density of white phosphorus is 1.82 $\frac{grams}{cm^3}$ and the density of black phosphorus is 2.69 $\frac{grams}{cm^3}$.

Answer: $-0.55\frac{J}{mole}$

B. Calculate the difference between the ΔH_m and the ΔU_m for the reaction NH_3 (g) + HCl(g) $\rightleftharpoons$ NH_4Cl(s) at 298 K.

Answer: -4.96 kJ

The Relationship between Enthalpy and Temperature

It is often assumed that the enthalpy of a substance or a reaction is constant over a small range of temperatures. While this assumption is true, it is possible to calculate how much the enthalpy changes as the temperature changes. The manner in which the enthalpy varies as the temperature changes depends on whether the process is carried out under constant pressure or constant volume conditions.

ΔH vs. ΔT at Constant Pressure

The enthalpy of most systems increases as the temperature increases, and so a plot of enthalpy versus temperature results in a graph with a positive slope at any point. Each instantaneous slope is defined as the **heat capacity at constant pressure**, C_P. In other words,

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{6.2.19}$$

As with the described in the derivation of the heat capacity at constant volume, C_V, Equation 6.2.19 is a partial derivative because the enthalpy of a system will typically vary with both pressure and temperature, but we are holding the pressure constant and allowing only the temperature to change.

Because C_P tells us the amount of heat needed to change the temperature of a sample of a substance at constant pressure, we can also say that an infinitesimal change in enthalpy is equal to an infinitesimal change in temperature multiplied by the heat capacity at constant pressure

$$dH = C_P\,dT \tag{6.2.20}$$

If the heat capacity of the substance does not change a great deal over the temperature range of interest, then the slope of the H versus T graph will be fairly constant. In this case

$$\Delta H = \int C_P\,dT = C_P \cdot (T_2 - T_1) = C_P \cdot \Delta T \tag{6.2.21}$$

As noted in Equation 6.2.17,

$$\Delta H = q_P \tag{2.2.17}$$

so that

$$q_P = C_P \cdot \Delta T \tag{6.2.22}$$

Equation 6.2.22 shows us that we can experimentally determine the constant pressure heat capacity of a substance fairly easily by measuring the change in temperature of a substance as heat is added to it under constant pressure conditions.

The value of C_P is an extensive property because it tells us how much heat is needed to change the temperature of that specific sample of the pure substance. We can determine the intensive property of this pure substance, the molar heat capacity at constant pressure, $C_{P,m}$, if we divide the experimentally obtained C_P by the number of moles of the substance used in the experiment:

$$C_{P,m} = \frac{C_P}{n} \tag{6.2.23}$$

We can also calculate a second intensive property, the specific heat capacity, $C_{P,s}$, which is the heat capacity per mass of sample:

$$C_{P,s} = \frac{C_P}{mass} \tag{6.2.24}$$

The value of C_P does actually change as the temperature changes. If it is necessary to estimate this change in value of C_P with a change in temperature, the following equation can be used:

$$C_{P,m} = a + bT + \frac{c}{T^2} \tag{6.2.25}$$

where the values of a, b, and c are temperature-independent and can be found in reference tables.

Example 6.2.3:

What is the change in molar enthalpy of CO_2 when it is heated from 20° C to 75° C? For CO_2 a = 44.22 J·mole^{-1}·K^{-1}, b = 8.79 x 10^{-3} J·mole^{-1}·K^{-2}, and c = -8.62 x 10^5 J·mole^{-1}·K.

Strategy: Because C_P changes as the temperature changes, we must use Equation 6.2.21:

$$\Delta H = \int C_P\,dT = C_P \cdot (T_2 - T_1) = C_P \cdot \Delta T$$

determine the integral and evaluate the result over the range of temperatures.

Answer: $\Delta H_m = \int \left(a + bT + \frac{c}{T^2}\right) dT = H_m(T_2) - H_m(T_1) = a(T_2 - T_1) + \frac{1}{2}b(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$H_m\ (348K) - H_m\ (293K) = 44.22\frac{J}{mole \cdot K}(348K - 293K) + \frac{1}{2}\left(0.00879\frac{J}{mole \cdot K^2}\right)[(348K)^2 - (293K)^2] - \left(-862,000\frac{J \cdot K}{mole}\right)\left(\frac{1}{348K} - \frac{1}{293K}\right) = 2120\frac{J}{mole} = 2.12\frac{kJ}{mole}$

Exercise 6.2.3

What is the change in molar enthalpy of CO_2 when it is heated from 10° C to 125° C? For CO_2 a = 44.22 J·mole^{-1}·K^{-1}, b = 8.79 x 10^{-3} J·mole^{-1}·K^{-2}, and c = -8.62 x 10^5 J·mole^{-1}·K.

Answer: $4.55\frac{kJ}{mole}$

C_P vs. C_V

If the system of interest expands when heated under constant pressure conditions (as most systems do), then the system is doing work on the surroundings. In this case, less energy is acting to heat the system, and the temperature of the system increases less than it would if the system were held to a constant volume. A smaller increase in temperature indicates a higher heat capacity. Thus, in most cases, the constant pressure heat capacity is greater than the constant volume heat capacity,

$$C_P > C_V \tag{6.2.26}$$

For perfect gases

$$C_P - C_V = nR \tag{6.2.27}$$

Contributors and Attributions

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6.3: Thermochemistry

In this section, we will discuss the use of experimentally-determined enthalpy changes to predict the enthalpy changes in chemical reactions and physical changes that are of interest to us. As noted in previous sections, any process that releases energy is called an **exothermic** process. For example, when methane or propane is oxidized by O_2, the heat released causes the gas to expand, releasing heat and light, and doing work at the same time. If the process is carried out at constant pressure, this loss of energy represents a decrease in enthalpy ($\Delta H < 0$). An **endothermic** process absorbs energy, and in all cases, the energy is supplied from another source so that the enthalpy of the system increases ($\Delta H > 0$).

Standard Enthalpy Changes

In order to make the tabulated enthalpy data useful for scientific and engineering applications, there is a general agreement to report the enthalpy changes for a mole of a process at a set of standard conditions. For the vast majority of calculations, the accepted standard states, all at 1 bar pressure are:

- solids: pure solid
- liquids: pure liquid
- gases: pure gas
- solutes: 1 molal concentration $\frac{1\,mole\,solute}{kg\,solvent}$

There is no specific temperature associated with standard conditions. You must specify the temperature for the process of interest. For example, the standard state for water at 298 K is pure liquid water at 1 bar and 298 K. The standard state for water at 398 K is pure gas at 1 bar and 398 K. The conventional temperature for standard state enthalpy values that are found in reference tables is 298.15 K, but there are certainly tables of enthalpy values for different temperatures.

The **standard enthalpy change** for a process, ΔH^o, is defined as the change in enthalpy when the pure, separate reactants, in their standard states, change to the pure, separate products, in their standard states, at a specified temperature. This definition holds for physical changes and for chemical reactions.

> The **standard enthalpy change** for a process, ΔH^o, has the units of $\frac{kJ}{mole\,process}$, where a process is a physical change or a chemical reaction. This is often a confusing concept because the word "process" is often left out of the units. As will become clear later, the presence or absence of the word "process" depends on the context of the statement or question.

The following are examples of **thermochemical equations**, each of which is a combination of a process and its corresponding change in standard enthalpy:

$$H_2O(l) \rightarrow H_2O(g)\ \Delta H^o = 44.016\,kJ$$

$$H_2O(l) \rightarrow H_2O(g)\ \Delta H^o = 40.656\,kJ\,(373K)$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)\ \Delta H^o = -571.66\,kJ$$

The reactions might more clearly be written as

$$44.016\,kJ + H_2O(l) \rightarrow H_2O(g)$$

$$40.656\,kJ + H_2O(l) \rightarrow H_2O(g)\,@(373K)$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) + 571.66\,kJ$$

Physical Changes

When a pure liquid vaporizes, or when a solid changes from one polymorph to another, a change in state occurs. These changes in state involve changes in enthalpy that are classified as **enthalpies of transition**. It is common practice to list **standard enthalpies of transition** as the enthalpy change per 1 mole of particles undergoing the transition at 1 bar pressure. For example, the standard enthalpy of fusion (ΔH^o_{fus}) for 1 mole of benzene at 278.6 K is written as

$$C_6H_6(s) \rightarrow C_6H_6(l)$$

with

$$\Delta H^o_{fus} = 10.59 \frac{kJ}{mole} (278.6K)$$

Chemical Changes

A chemical change can be thought of as a process in which bonds between atoms in existing substances are broken and these atoms rearrange and/or reorganize to form the new bonds of different substances. To describe the enthalpy change of such a process it is common practice to list the **standard enthalpy of reaction**, ΔH^o_r which has the units of $\frac{kJ}{mole\,reaction}$.

$$3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$$

with

$$\Delta H^o_r = -92.22 \frac{kJ}{mole}$$

is interpreted as 92.22 kJ of heat are given off per every 3 moles of H_2 consumed, every 1 mole of N_2 consumed, and every 2 moles of NH_3 produced.

A Few Rules

At 298 K, the combustion of 1.0 mole hydrogen with 0.5 moles of oxygen to form 1.0 mole of H_2O releases 285.8 kJ of energy. We represent the reaction:

$$\mathrm{H_{2(g)} + \frac{1}{2}O_2 \rightarrow H_2O_{(l)}}, \quad \Delta H^o_r = -285.8\,\mathrm{kJ/mole}$$

For the reverse reaction, 285.8 kJ/mol is required, thus the sign for ΔH^o_r changes

$$\mathrm{H_2O_{(l)} \rightarrow H_{2(g)} + \frac{1}{2}O_2}, \quad \Delta H^o_r = +285.8\,\mathrm{kJ/mole}$$

It is also true that the amount of energy released in a chemical reaction is related to the amount of reactants. For example, when the amount of reactants is doubled, so is the amount of energy released.

$$\mathrm{2H_{2(g)} + O_2 \rightarrow 2H_2O_{(l)}}, \quad \Delta H^o_r = -571.66\,\mathrm{kJ/mole}$$

Example 6.3.1: Standard Enthalpy of Reaction

The standard enthalpy for the combustion of methane is -890. kJ per mole,

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g) \quad \Delta H^o_r = -890.\,kJ$$

Calculate the standard enthalpy change when 3.50 moles of oxygen are consumed during the conversion of methane to the gaseous products at 298 K.

Solution

When 2.00 moles of O_2, at 298 K and 1.00 bar, reacts with CH_4 according to the given equation, the standard enthalpy change is 890. kJ. Thus, the standard change of enthalpy when 3.50 moles of O_2 are used is

$$\Delta H^o_r = 3.50\,moles\,O_2 \times \frac{890.\,kJ}{2.00\,mole\,O_2} = -1560\,kJ.$$

Exercise 6.3.1

Calculate the standard change in enthalpy when 75.0 grams of Al are completely used up in the following reaction:

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3 + 850kJ$$

Answer: ΔH^o_r = -1180 kJ

Standard Heats of Formation

Another way to look at ΔH^o_r is to state that

$$\Delta H_r^o = \sum_{products} vH_m^o - \sum_{reactants} vH_m^o \tag{6.3.1}$$

where v is the stoichiometric coefficient of each substance with the units of $\frac{moles\ substance}{moles\ reaction}$.

Equation 6.3.1 is of no use for practical applications because the values of absolute H_m^o are unknown. This inconvenience can be overcome by creating a self-consistent system in which definitions that are demonstrably incorrect can nevertheless be used to calculate ΔH_m^o values known as **standard enthalpies of formation**, ΔH_f^o. By definition, the ΔH_f^o of a substance is the enthalpy change the accompanies the formation of exactly 1 mole of the substance when the starting materials are the pure elements in their most stable form at the given set of conditions. The demonstrably incorrect aspect is that the ΔH_f^o of pure elements in their most stable allotrope under the given conditions is defined to be 0 $\frac{kJ}{mole}$, a tactic that will be explained later. A similar definition, instituted to allow for the determination of ΔH_f^o for ions in aqueous solutions, is that ΔH_f^o = 0 kJ for the hydrogen ion, H^+ (aq).

For example, at 298 K, the combustion of 1.0 mole hydrogen with 0.5 moles of oxygen to form 1.0 mole of H_2O releases 286 kJ of energy. We represent the reaction:

$$\mathrm{H_{2(g)} + \frac{1}{2}O_2 \rightarrow H_2O_{(l)}}, \quad \Delta H_f^o = -286\ \mathrm{kJ/mol}$$

The following table shows several reactions that fit into the category of standard enthalpy of formation reactions:

$$\mathrm{Mg_{(s)} + \frac{1}{8}S_{8(s)} \rightarrow MgS_{(s)}} \qquad \Delta H_f^\circ = -598\ \mathrm{kJ/mol} \tag{6.3.2}$$

$$\mathrm{P_{(s)} + \frac{3}{2}Cl_{2(g)} \rightarrow PCl_{3(g)}} \qquad \Delta H_f^\circ = -320\ \mathrm{kJ/mol} \tag{6.3.3}$$

$$\mathrm{P_{(s)} + \frac{5}{2}Cl_{2(g)} \rightarrow PCl_{5(g)}} \qquad \Delta H_f^\circ = -440\ \mathrm{kJ/mol} \tag{6.3.4}$$

$$\mathrm{H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}} \qquad \Delta H_f^\circ = -286\ \mathrm{kJ/mol} \tag{6.3.5}$$

$$\mathrm{\frac{1}{2}N_{2(g)} + O_{2(g)} \rightarrow NO_{2(g)}} \qquad \Delta H_f^\circ = +34\ \mathrm{kJ/mol} \tag{6.3.6}$$

$$\mathrm{Cu_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CuO_{(s)}} \qquad \Delta H_f^\circ = -157\ \mathrm{kJ/mol} \tag{6.3.7}$$

$$\mathrm{Mg_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow MgO_{(s)}} \qquad \Delta H_f^\circ = -602\ \mathrm{kJ/mol} \tag{6.3.8}$$

$$\mathrm{C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}} \qquad \Delta H_f^\circ = -394\ \mathrm{kJ/mol} \tag{6.3.9}$$

$$\mathrm{C_{(graphite)} + 4H_{2(g)} \rightarrow CH_{4(g)}} \qquad \Delta H_f^\circ = -75\ \mathrm{kJ/mol} \tag{6.3.10}$$

In all the above equations of reaction, the right hand side has only one product and its coefficient is 1. To obtain a balanced equation, it is often necessary to use fractional coefficients for the pure element reactants, which is allowed because all of the reactions are taking place on the molar scale. (Thermodynamics is a study of **macroscopic** systems.) Because all standard enthalpy of formation reactions are, by definition, the formation of 1 mole of a pure substance from its component elements in their most stable form under the reaction conditions, we often do not write out the entire equation, but instead simply write

$$\Delta H_f^o\ MgS(s) = -598\ \frac{kJ}{mole\ MgS}$$

Note

The use of ΔH_f^o values to calculate ΔH_r^o values is made possible by assuming that any chemical reaction can be broken down into two distinct , hypothetical steps:

Step 1) All of the reactants decompose ("unform") to produce the pure elements of which they are composed.

Step 2) All of the pure elements created in Step 1 react to form the products of the overall reaction.

If these hypothetical steps are assumed to occur, it is perfectly legitimate (although absolutely incorrect) to assign all of the pure elements a ΔH_f^o = 0 kJ. For example, even though we know that 436 kJ is released when 2 moles of H atoms react to form 1 mole of H_2 , we can proceed with the erroneous assumption that the ΔH_f^o of H_2 = 0 kJ because the ΔH_f^o of every hydrogen-containing compound will incorporate this erroneous value of ΔH_f^0 of H_2. Thus, the ΔH_f^o of H_2O incorporates not only the enthalpy change associated with the formation of the bonds in H_2O, but also the enthalpy change associated with the breaking of bonds in H_2 and in O_2.

When calculating both the change in enthalpy for Step 1 and the change in enthalpy for Step 2 of any reaction, the incorrect assignment of a value of 0 kJ will be canceled out as we first "unform" reactants and then form products. (Two wrongs make a right in this case!) The following calculation will show this point:

Calculate the ΔH_r^o for the reaction $CH_4\,(g) + 2\,O_2\,(g) \rightarrow 2\,H_2O\,(g) + CO_2\,(g)$, given the data: $\Delta H_f^o\ H_2O$ = -286 $\frac{kJ}{mole}$; $\Delta H_f^o\ CO_2$ = -394 $\frac{kJ}{mole}$; $\Delta H_f^o\ CH_4$ = -75 $\frac{kJ}{mole}$.

Step 1: Unforming reactants $CH_4\,(g) + 2\,O_2\,(g) \rightarrow C\,(graphite) + 2H_2\,(g) + 2\,O_2\,(g)$

Step 2: Forming products $C\,(graphite) + 2H_2\,(g) + 2\,O_2\,(g) \rightarrow 2\,H_2O\,(g) + CO_2\,(g)$

It is not possible to obtain a thermodynamically precise value of \(\Delta H^o_f)\ for a substance by adding up the contribution of each of the bonds in the substance. For instance, the \(\Delta H^o_f)\ for CH_4 can not be precisely approximated by adding up the energy released by the formation of 4 C - H bonds. The attempts fails because the ΔH of a C - H bond differs from compound to compound, and even within a compound. (For instance, the energy needed to break the first C - H bond in CH_4 is different from the energy needed to break the second C - H bond in the remaining CH_3 particle.) Molecular modeling with computers has improved the approximated bond energies, but experimentation is still the most reliable technique to determine precise values for \(\Delta H^o_f)\.

Given the concept of ΔH_f^o, it is possible to re-write equation 6.3.1 as

$$\Delta H_r^o = \sum_{products} v\Delta H_f^o - \sum_{reactants} v\Delta H_f^o \tag{6.3.11}$$

in which we use the standard enthalpies of formation to calculate the standard enthalpy of reaction.

To demonstrate the use of tabulated ΔH^o_f values, we will use them to calculate ΔH_{rxn} for the combustion of glucose:

$$C_6H_{12}O_6\,(s) + O_2\,(g) \rightarrow CO_2\,(g) + 6H_2O\,(l) \tag{6.3.12}$$

Using Equation 6.3.11, we write

$$\begin{aligned}&\Delta H_r^o \\ &= \left\{6\Delta H_f^o\,[CO_2\,(g)] + 6\Delta H_f^o\,[H_2O\,(g)]\right\} - \left\{6\Delta H_f^o\,[C_6H_{12}O_6\,(s)] + 6\Delta H_f^o\,[O_2\,(g)]\right\}\end{aligned} \tag{6.3.13}$$

The relevant ΔH^o_f values are $\Delta H^o_f\,[CO_2(g)]$ = -393.5 kJ/mol, $\Delta H^o_f\,[H_2O(l)]$ = -285.8 kJ/mol, and $\Delta H^o_f\,[C_6H_{12}O_6(s)]$ = -1273.3 kJ/mol. Because O_2(g) is a pure element in its standard state, $\Delta H^o_f\,[O_2(g)]$ = 0 kJ/mol. Inserting these values into Equation 6.3.13 and changing the subscript to indicate that this is a combustion reaction, we obtain

$$\begin{aligned}\Delta H_{comb}^o &= [6\,(-393.5\ kJ/mol) + 6\,(-285.8\ kJ/mol)] \\ &-[-1273.3 + 6\,(0\ kJ\ mol)] = -2802.5\ kJ/mol\end{aligned} \tag{6.3.14}$$

As illustrated in Figure 6.3.1, we can use Equation 6.3.11 to calculate ΔH^o_f for glucose because enthalpy is a state function. The figure shows two pathways from reactants (middle left) to products (bottom). The more direct pathway is the downward green arrow labeled ΔH^o_{comb} The alternative hypothetical pathway consists of four separate reactions that convert the reactants *to the elements* in their standard states (upward purple arrow at left) and then convert the elements into the desired products (downward purple arrows at right). The reactions that convert the reactants to the elements are the reverse of the equations that define the ΔH^o_f values of the reactants. Consequently, the enthalpy changes are

$$\begin{aligned}\Delta H_1^o &= \Delta H_f^o\,[glucose\,(s)] = -1\ \cancel{mol\ glucose}\left(\frac{1273.3\ kJ}{1\ \cancel{mol\ glucose}}\right) = +1273.3\ kJ \\ \Delta H_2^o &= 6\Delta H_f^o\,[O_2\,(g)] = 6\ \cancel{mol\ O_2}\left(\frac{0\ kJ}{1\ \cancel{mol\ O_2}}\right) = 0\ kJ\end{aligned} \tag{6.3.15}$$

(Recall that when we reverse a reaction, we must also reverse the sign of the accompanying enthalpy change.) The overall enthalpy change for conversion of the reactants (1 mol of glucose and 6 mol of O_2) to the elements is therefore +1273.3 kJ.

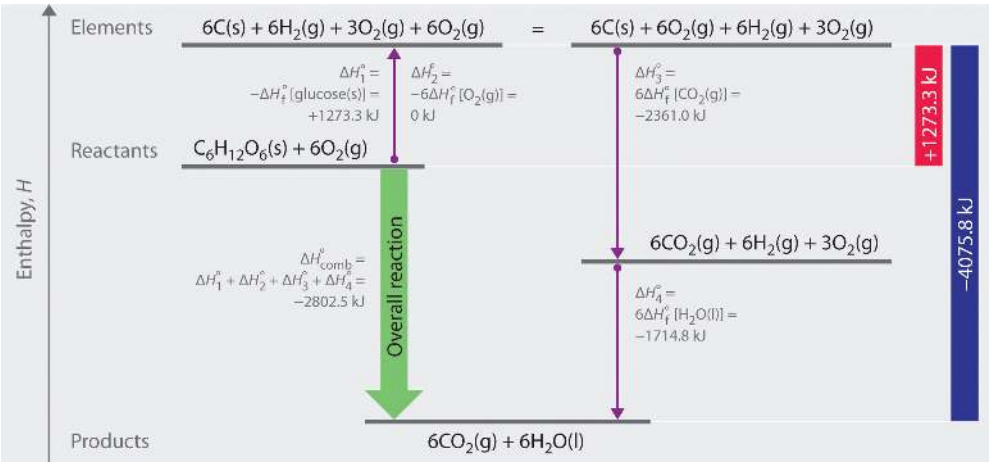


Figure* 6.3.1*: *A Thermochemical Cycle for the Combustion of Glucose. Two hypothetical pathways are shown from the reactants to the products. The green arrow labeled ΔH^o_{comb} indicates the combustion reaction. Alternatively, we could first convert the reactants to the elements via the reverse of the equations that define their standard enthalpies of formation (the upward arrow, labeled ΔH^o_1 and ΔH^o_2). Then we could convert the elements to the products via the equations used to define their standard enthalpies of formation (the downward arrows, labeled ΔH^o_3 and ΔH^o_4). Because enthalpy is a state function, ΔH^o_{comb} is equal to the sum of the enthalpy changes $\Delta H^o_1 + \Delta H^o_2 + \Delta H^o_3 + \Delta H^o_4$.*

The reactions that convert the elements to final products (downward purple arrows in Figure 2.3.1) are identical to those used to define the ΔH^o_f values of the products. Consequently, the enthalpy changes are

$$\Delta H^o_3 = \Delta H^o_f [CO_2\,(g)] = 6\ \cancel{mol\ CO_2}\left(\frac{393.5\ kJ}{1\ \cancel{mol\ CO_2}}\right) = -2361.0\ kJ$$
$$\Delta H^o_4 = 6\Delta H^o_f [H_2O\,(l)] = 6\ \cancel{mol\ H_2O}\left(\frac{-285.8\ kJ}{1\ \cancel{mol\ H_2O}}\right) = -1714.8\ kJ \tag{6.3.16}$$

The overall enthalpy change for the conversion of the elements to products (6 mol of carbon dioxide and 6 mol of liquid water) is therefore −4075.8 kJ. Because enthalpy is a state function, the difference in enthalpy between an initial state and a final state can be computed using *any* pathway that connects the two. Thus the enthalpy change for the combustion of glucose to carbon dioxide and water is the sum of the enthalpy changes for the conversion of glucose and oxygen to the elements (+1273.3 kJ) and for the conversion of the elements to carbon dioxide and water (−4075.8 kJ):

$$\Delta H^o_{comb} = +1273.3\ kJ + (-4075.8\ kJ) = -2802.5\ kJ \tag{6.3.17}$$

This is the same result we obtained using the "products minus reactants" rule (Equation 6.3.11) and ΔH^o_f values. The two results must be the same because Equation 6.3.17 is just a more compact way of describing the thermochemical cycle shown in Figure 6.3.1.

Example 6.3.2

Long-chain fatty acids such as palmitic acid [$CH_3(CH_2)_{14}CO_2H$] are one of the two major sources of energy in our diet (ΔH^o_f =−891.5 kJ/mol). Use the appropriate data to calculate ΔH^o_r for the combustion of 1 mole of palmitic acid.

Given: compound and ΔH^o_f values

Asked for: ΔH^o_r per mole

Strategy:

A. After writing the balanced chemical equation for the reaction, use Equation 6.3.11 and the ΔH^o_f values for H_2O(l) and CO_2 (g) to calculate ΔH^o_r, the energy released by the combustion of 1 mol of palmitic acid.

Solution:

A To determine the energy released by the combustion of palmitic acid, we need to calculate its ΔH^o_r. As always, the first requirement is a balanced chemical equation:

$$C_{16}H_{32}O_{2(s)} + 23O_{2(g)} \rightarrow 16CO_{2(g)} + 16H_2O_{(l)} \tag{6.3.18}$$

Using Equation 6.3.11 with ΔH^o_f values (and omitting the physical states of the reactants and products to save space) gives

$$\Delta H^o_r = \sum m\Delta H^o{}_f\,(products) - \sum n\Delta H^o{}_f\,(reactants)$$

$$= [16\,(-393.5\ kJ/mol\ CO_2) + 16\,(-285.8\ kJ/mol\ H_2O\,)]$$

$$-\,[-891.5\ kJ/mol\ C_{16}H_{32}O_2 + 23\,(0\ kJ/mol\ O_2\,)]$$

$$= -9977.3\ kJ/mol$$

This is the energy released by the combustion of 1 mol of palmitic acid.

Exercise 6.3.2

Calculate ΔH^o_r for the *water–gas shift reaction*, which is used industrially on an enormous scale to obtain H_2(g):

$$\underset{water-gas\ shift\ reaction}{CO\,(g) + H_2O\,(g) \rightarrow CO_2\,(g) + H_2\,(g)}$$

Answer:

−41.2 kJ/mol

Hess's Law

Hess's Law of Constant Heat Summation (or just **Hess's Law**) states that regardless of the multiple stages or steps of a reaction, the total enthalpy change for the reaction is the sum of all changes. This law is a manifestation of enthalpy as a state function, which allows us to calculate the overall change in enthalpy by simply summing up the changes for each step of the way, until the desired product is formed. All steps have to proceed under the same reaction conditions and the equations for the individual steps must balance out. The principle underlying Hess's law does not just apply to enthalpy and can be used to calculate other state functions like changes in Gibbs' free energy and entropy.

Definition: Hess's Law

The heat of any reaction ΔH°_r for a specific reaction is equal to the sum of the heats of reaction for any set of reactions which in sum are equivalent to the overall reaction:

Application

Hydrogen gas, which is of potential interest nationally as a clean fuel, can be generated by the reaction of carbon (coal) and water:

$$C_{(s)} + 2H_2O_{(g)} \rightarrow CO_{2\,(g)} + 2H_{2\,(g)} \tag{6.3.19}$$

Calorimetry reveals that this reaction requires the input of 90.1 kJ of heat for every mole of $C_{(s)}$ consumed. By convention, when heat is absorbed during a reaction, we consider the quantity of heat to be a positive number: in chemical terms, $q > 0$ for an endothermic reaction. When heat is evolved, the reaction is exothermic and $q < 0$ by convention.

It is interesting to ask where this input energy goes when the reaction occurs. One way to answer this question is to consider the fact that the reaction converts one fuel, $C_{(s)}$, into another, $H_{2(g)}$. To compare the energy available in each fuel, we can measure the heat evolved in the combustion of each fuel with one mole of oxygen gas. We observe that

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \tag{6.3.20}$$



produces $393.5\ kJ$ for one mole of carbon burned; hence $q = -393.5\ kJ$. The reaction

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \tag{6.3.21}$$

produces 483.6 kJ for two moles of hydrogen gas burned, so q=-483.6 kJ. It is evident that more energy is available from combustion of the hydrogen fuel than from combustion of the carbon fuel, so it is not surprising that conversion of the carbon fuel to hydrogen fuel requires the input of energy. Of considerable importance is the observation that the heat input in equation 6.3.19, 90.1 kJ, is exactly equal to the difference between the heat evolved, -393.5 kJ, in the combustion of carbon and the heat evolved, -483.6 kJ, in the combustion of hydrogen. This is not a coincidence: if we take the combustion of carbon and add to it the reverse of the combustion of hydrogen, we get

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

$$2H_2O_{(g)} \rightarrow 2H_{2(g)} + O_{2(g)}$$

$$C_{(s)} + O_{2(g)} + 2H_2O_{(g)} \rightarrow CO_{2(g)} + 2H_{2(g)} + O_{2(g)} \tag{6.3.22}$$

Canceling the $O_{2(g)}$ from both sides, since it is net neither a reactant nor product, equation 6.3.22 is equivalent to equation 6.3.19. Thus, taking the combustion of carbon and "subtracting" the combustion of hydrogen (or more accurately, adding the reverse of the combustion of hydrogen) yields equation 6.3.19. And, the heat of the combustion of carbon minus the heat of the combustion of hydrogen equals the heat of equation 6.3.19. By studying many chemical reactions in this way, we discover that this result, known as Hess's Law, is general.

Why it works

A pictorial view of Hess's Law as applied to the heat of equation 6.3.19 is illustrative. In figure 2.3.1, the reactants C(s) + 2 H_2O(g) are placed together in a box, representing the state of the materials involved in the reaction prior to the reaction. The products CO_2(g) + 2 H_2(g) are placed together in a second box representing the state of the materials involved after the reaction. The reaction arrow connecting these boxes is labeled with the heat of this reaction. Now we take these same materials and place them in a third box containing C(s), O_2(g), and 2 H_2(g). This box is connected to the reactant and product boxes with reaction arrows, labeled by the heats of reaction in equation 6.3.20 and equation 6.3.21.

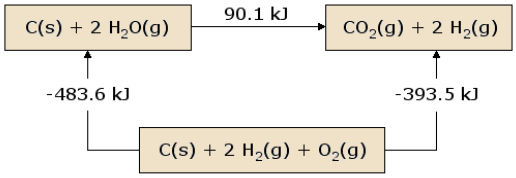


***Figure 1**: A Pictorial View of Hess's Law.*

This picture of Hess's Law reveals that the heat of reaction along the "path" directly connecting the reactant state to the product state is exactly equal to the total heat of reaction along the alternative "path" connecting reactants to products via the intermediate state containing $C_{(s)}$, $O_{2(g)}$, and 2 $H_{2(g)}$. A consequence of our observation of Hess's Law is therefore that the net heat evolved or absorbed during a reaction is independent of the path connecting the reactant to product (this statement is again subject to our restriction that all reactions in the alternative path must occur under constant pressure conditions).

Extensive tables of ΔH°r values have been compiled that allow us to calculate the heat of reaction for any reaction of interest, even including hypothetical reactions which may be difficult to perform or impossibly slow to react. The following reactions are examples of such $\Delta H°_r$ reactions:

$$2H_{(g)} \rightarrow H_{2(g)} \qquad \Delta H^\circ = -436\ \text{kJ/mol} \qquad (6.3.23)$$
$$2O_{(g)} \rightarrow O_{2(g)} \qquad \Delta H^\circ = -498\ \text{kJ/mol} \qquad (6.3.24)$$
$$H_2O_{(l)} \rightarrow H_2O_{(g)} \qquad \Delta H^\circ = 44\ \text{kJ/mol at 298 K} \qquad (6.3.25)$$
$$H_2O_{(l)} \rightarrow H_2O_{(g)} \qquad \Delta H = 41\ \text{kJ/mol at 373 K, non-standard condition} \qquad (6.3.26)$$
$$Mg_{(s)} + S_{(s)} \rightarrow MgS_{(s)} \qquad \Delta H^\circ = -598\ \text{kJ/mol} \qquad (6.3.27)$$
$$2H_{(g)} + O_{(g)} \rightarrow H_2O_{(g)} \qquad \Delta H^\circ = -847\ \text{kJ/mol} \qquad (6.3.28)$$
$$Cu_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CuO_{(s)} \qquad \Delta H^\circ = -157\ \text{kJ/mol} \qquad (6.3.29)$$
$$\frac{1}{2}N_{2(g)} + O_{2(g)} \rightarrow NO_{2(g)} \qquad \Delta H^\circ = 34\ \text{kJ/mol} \qquad (6.3.30)$$
$$Mg_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow MgO_{(s)} \qquad \Delta H^\circ = -602\ \text{kJ/mol} \qquad (6.3.31)$$
$$2P_{(s)} + 3Cl_{2(g)} \rightarrow 2PCl_{3(s)} \qquad \Delta H^\circ = -640\ \text{kJ/mol} \qquad (6.3.32)$$
$$2P_{(s)} + 5Cl_{2(g)} \rightarrow 2PCl_{5(s)} \qquad \Delta H^\circ = -880\ \text{kJ/mol} \qquad (6.3.33)$$
$$C_{(\text{graphite})} + 2O_{(g)} \rightarrow CO_{2(g)} \qquad \Delta H^\circ = -643\ \text{kJ/mol} \qquad (6.3.34)$$
$$C_{(\text{graphite})} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H^\circ = -394\ \text{kJ/mol} \qquad (6.3.35)$$
$$C_{(\text{graphite})} + 2H_{2(g)} \rightarrow CH_{4(g)} \qquad \Delta H^\circ = -75\ \text{kJ/mol} \qquad (6.3.36)$$
$$2Al_{(s)} + Fe_2O_{3(s)} \rightarrow Al_2O_{3(s)} + 2Fe_{(s)} \qquad \Delta H^\circ = -850\ \text{kJ/mol} \qquad (6.3.37)$$

Example 6.3.3: Solving for Standard Enthalpy of Reaction Using Hess's Law

QUESTION

Calculate the standard enthalpy of combustion of the transition of C(s, graphite) → C(s, diamond), **given**

$$C\,(s, \text{graphite}) + O_2 \longrightarrow CO_2 \quad \Delta H_r^o = -393.5 kJ/mol \qquad (6.3.38)$$
$$CO_2 \longrightarrow C_{(s,\text{diamond})} + O_2 \quad \Delta H_r^o = +395.41 kJ/mol \qquad (6.3.39)$$

Solution

1. Find appropriate reactions and their standard enthalpy reaction
2. Flip reactions and/or multiply reactions, if necessary, so that the combination of reactions results in the desired overall reaction
3. Change the sign and/or magnitude of the ΔH_r^o values of the combined reactions, based on how the combined reactions were manipulated in Step 2
4. Sum up the individual steps and sum up the individual ΔH_r^o values to obtain the ΔH_r^o value of the desired reaction.

Answer

In this case, there is no need to flip an equation around because it is possible to cancel out terms as the reactions are given. What is left is canceling out the O_2 and the CO_2 species, writing the overall reaction and then summing the two reaction enthalpies together.

C(s, graphite) + ~~O_2~~ → ~~CO_2~~

~~CO_2~~ → C(s, diamond) + ~~O_2~~

$$C_{(s,graphite)} \rightarrow C_{(s,diamond)}$$

Adding the enthalpies gives (-393.5 kJ/mol + 395.41 kJ/mol) = +1.91 kJ/mol. Since the \(\Delta H^o_r\) is positive, the reaction is **endothermic**.

Exercise 6.3.3: Steam Reforming

Steam reforming is a method for producing hydrogen, carbon monoxide, or other useful products from hydrocarbon fuels such as natural gas. Use Hess's Law to calculate the following enthalpy of reaction of the major process of steam reforming:

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)} \qquad (6.3.40)$$

Given the separate reactions of carbon dioxide and hydrogen gas and methane decomposition;

$$CO_{(g)} + H_{2(g)} \rightarrow C_{(graphite)} + H_2O_{(g)} \quad \Delta H^\circ = -131.3\ kJ \tag{6.3.41}$$

$$C_{(graphite)} + 2H_{2(g)} \rightarrow CH_{4(g)} \quad \Delta H^\circ = -74.8\ kJ \tag{6.3.42}$$

$$CH_{4(g)} + H_2O \rightarrow CO + 3H_2 \quad \Delta H^\circ = +74.8\ kJ + 131.3\ kJ \tag{6.3.43}$$

Answer

$CH_{4(g)} + H_2O \rightarrow CO + 3H_2 \quad \Delta H_r^\circ = 201.1\ kJ$

Hence, it is not surprising that this reforming reactions takes place at high temperatures.

The Temperature Dependence of ΔH_r^o

For educational purposes most textbooks list thermodynamic values such as ΔH_f^o and ΔH_r^o for processes occurring at 298 K. It is obvious that not all reactions occur at this temperature. More advanced texts and reference books may have tables of thermodynamic data at temperatures other than 298 K, but they do not have values for all temperatures. Kirchhoff's Law can be used to accurately estimate the standard enthalpy of reaction at an elevated temperature if the standard enthalpy of reaction and the constant pressure heat capacity are known.

Kirchhoff's law is

$$\Delta H_r^o(T_2) = \Delta H_r^o(T_1) + \int \Delta_r C_P^o \, dT \tag{6.3.44}$$

where $T_2 > T_1$, the C_P values of the products and reactants do not change much over the temperature range from T_1 to T_2, and $\Delta_r C_P^o$ is the difference between the constant pressure molar heat capacities of the products and reactants, weighted by their stoichiometric coefficients:

$$\Delta_r C_{P,m}^o = \sum_{products} vC_{P,m}^o - \sum_{reactants} vC_{P,m}^o \tag{6.3.45}$$

where v is the stoichiometric coefficient of each substance.

If $\Delta_r C_{P,m}^o$ remains constant over the temperature range, then equation 6.3.44 becomes

$$\Delta H_r^o(T_2) = \Delta H_r^o(T_1) + (T_2 - T_1)\Delta_r C_{P,m}^o \tag{6.3.46}$$

Example 6.3.4:

The ΔH_f^o for H_2O (l) at 298 K is -286 $\frac{kJ}{mole}$. Estimate the value of ΔH_f^o for H_2O (l) at 350 K. The constant pressure molar heat capacities of the reactants and products are: H_2O (l) = 75.29 $\frac{J}{K \cdot mole}$; H_2 (g) = 28.84 $\frac{J}{K \cdot mole}$; O_2 (g) = 29.37 $\frac{J}{K \cdot mole}$. It is assumed that these values do not change over the given temperature range.

Given: ΔH_f^o H_2O (l) at 298 and $C_{P,m}^o$ values for the reactants and products.

Asked for: ΔH_f^o H_2O (l) at 350 K

Strategy: Use equation 6.3.45 to determine the $\Delta_r C_{P,m}^o$ for the reaction, then substitute this value into equation 6.3.46.

Solution: The reaction is $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

Thus, $\Delta_r C_{P,m}^o = C_{P,m}^o(H_2O, l) - \left(C_{P,m}^o(H_2, g) + \frac{1}{2}C_{P,m}^o(O_2, g)\right)$

and $\Delta_r C_{P,m}^o = 75.29\frac{J}{K \cdot mole} - \left(28.84\frac{J}{K \cdot mole} + \frac{1}{2}29.37\frac{J}{K \cdot mole}\right) = 31.77\frac{J}{K \cdot mole} = 0.03177\frac{kJ}{K \cdot mole}$

Then, $\Delta H_f^o(H_2O(l), 350K) = -286\frac{kJ}{mole} + (350K - 298K)\left(0.03177\frac{J}{K \cdot mole}\right) = -284\frac{kJ}{mole}$

This is not a large change, but it may be significant depending what you are trying to measure.

Exercise 6.3.4

The ΔH_f^o for H_2O (g) at 298 K is -241.8 $\frac{kJ}{mole}$. Estimate the value of ΔH_f^o for H_2O (l) at 400 K. The constant pressure molar heat capacities of the reactants and products are: H_2O (g) = 33.58 $\frac{J}{K \cdot mole}$; H_2 (g) = 28.84 $\frac{J}{K \cdot mole}$; O_2 (g) = 29.37 $\frac{J}{K \cdot mole}$. It is assumed that these values do not change over the given temperature range.

Answer: -242.8 kJ/mole

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6.4: State Functions and Exact Differentials

Exact and Inexact Differentials

To study a system undergoing a change, we usually apply the principles of calculus; that is, we think of the overall change as occurring in a series of infinitesimally small steps. We must then ask ourselves if matters which small steps we take as we change the system.

If we can take any random assortment of small steps to make our change, and yet always get the same net change in the specific property we are studying, then that property is considered a state function. For a state function, each infinitesimal step that we add together by the process of integration is called an **exact differential**. When integrated, the sum of exact differentials is a value that is independent of path, depending only on the initial and final states. The change in internal energy is a state function, so the small steps involved in the change are exact differentials. In mathematical symbols, we can describe the change as

$$\int_i^f dU = \Delta U = U_f - U_i \tag{6.4.1}$$

If the net change in the specific property we are studying depends on the specific path of small steps that we take, then that property is considered a path function. For a path function, each infinitesimal step that we add together by the process of integration is called an **inexact differential**. When integrated, the sum of inexact differentials is a value that is dependent of path, so the path between the initial and final states must be specified. The change in work is a path function, so the small steps involved in the change are inexact differentials. In mathematical symbols, we can describe the change as

$$\int_{i,path}^f dw = w \tag{6.4.2}$$

It is important to note that we do not use the symbol Δw because w is not a state function, and the work that accompanies the change cannot be found from the simple calculation of $w_f - w_1$.

Often we come to recognize or remember which properties are state functions and which are path functions. However, to help us identify which is which during calculations, it is useful to remember that a change in a state function can be symbolized by Δ, and that inexact differentials are often symbolized by using a "d" with a bar across the vertical line, đ.

Properties of Perfect Gases

In this section, we will look at a closed system (no matter can enter or leave, but energy can enter or leave) containing a sample of a perfect gas. The gas is described by the perfect gas law (PV = nRT), and because the system is closed, the only variables are V, T, and P. The internal energy of the gas can thus be described in terms of any two of these variables (because stating two of the variables automatically fixes the value of the third variable.)

The Internal Pressure, π_T

Internal pressure, π_T, results from the interactions of the particles in a gas sample. An equation for internal pressure can be derived from the expression of internal energy as a function of volume and temperature:

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \tag{6.4.3}$$

As was shown in Topic 2.1, $\left(\frac{\partial U}{\partial T}\right)_V$ is equal to the constant-volume heat capacity, C_V. The first partial differential of Equation 6.4.3, the internal pressure, is a measure of the change of internal energy of a sample as the volume changes under conditions of constant temperature. Thus,

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T \tag{6.4.4}$$

Equation 6.4.3 can be rewritten as

$$dU = \pi_T\, dV + C_V\, dT \tag{6.4.5}$$

If the gas is a perfect gas, there are no interactions among the particles in the sample and thus $\pi_T = 0$. In this case, the internal energy does not change as the space between the particles changes, and so internal energy is independent of the volume of the gas sample. For real gases, π_T may be greater than or less than 0, depending on whether attractive forces or repulsive forces among the particles dominate. If attractive forces in the gas sample are dominant, then $\pi_T > 0$, because as the particles are moved farther and farther apart, their potential energy increases. If repulsive forces in the sample are dominant, then $\pi_T < 0$, because the potential energy of the system decreases as the particles move farther apart.

The Expansion Coefficient, α

The expansion coefficient α is defined as the change in volume of a gas sample that occurs as the temperature increases under conditions of constant pressure. An expression for the expansion coefficient can be derived from Equation 6.4.4 by first dividing both sides by dT:

$$\left(\frac{dU}{dT}\right) = \pi_T \left(\frac{dV}{dT}\right) + C_V \tag{6.4.6}$$

Under conditions of constant pressure, the equation becomes

$$\left(\frac{\partial U}{\partial T}\right)_P = \pi_T \left(\frac{\partial V}{\partial T}\right)_P + C_V \tag{6.4.7}$$

The expansion coefficient is related to the partial derivative $\left(\frac{\partial V}{\partial T}\right)_P$, and is defined as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{6.4.8}$$

The magnitude of α is directly proportional to the extent of expansion of the gas sample as the temperature increases.

The Isothermal Compressibility, κ_T

The isothermal compressibility κ_T is a measure of the decrease in volume of a sample of gas that occurs as a result of an increase in pressure under conditions of constant temperature. The mathematical expression is

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{6.4.9}$$

The negative sign is necessary to ensure that κ_T has a positive value because dV is always a negative value when the pressure is increased.

Example 6.4.1:

Determine the value of κ_T for an ideal gas.

Given: Equation 6.4.9 and the relationship $V = \frac{nRT}{P}$ for a perfect gas.

Solution:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial \frac{nRT}{P}}{\partial P}\right)_T = -\frac{1}{V}x\left(-\frac{nRT}{P^2}\right) = \frac{1}{V}x\frac{V}{P} = \frac{1}{P}$$

Exercise 6.4.1

Determine the value of α for an ideal gas.

Answer: $\frac{1}{T}$

The Relationship between C_V and C_P for a Perfect Gas

It is possible to derive a relationship between C_V and C_P for a perfect gas. We start with the previously derived relationships

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{6.4.10}$$

and

$$C_V = \left(\frac{\partial U}{\partial T}\right)_P \tag{6.4.11}$$

Thus,

$$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_P \tag{6.4.12}$$

If we recall that

$$H = U + PV = U + nRT \tag{6.4.13}$$

then

$$C_P - C_V = \left(\frac{\partial (U+nRT)}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_P = nR \tag{6.4.14}$$

The Relationship between C_V and C_P for a Real Gas

It is also possible to use α and κ_T to derive a relationship between C_V and C_P for a real gas. We again start with the previously derived relationships

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{2.4.10}$$

and

$$H = U + PV \tag{2.4.13}$$

then

$$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - C_V \tag{6.4.15}$$

and

$$C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_P + \left(\frac{\partial (PV)}{\partial T}\right)_P - C_V \tag{6.4.16}$$

By substituting the definition of α (Eqution 6.4.8) into Equation 6.4.7 and rearranging, we get

$$\left(\frac{\partial U}{\partial T}\right)_P - C_V = \alpha \pi_T V \tag{6.4.17}$$

Substituting Equation 6.4.17 into Equation 6.4.16 results in

$$C_P - C_V = \left(\frac{\partial (PV)}{\partial T}\right)_P + \alpha \pi_T V \tag{6.4.18}$$

Again employing the definition of α it can be shown that

$$\left(\frac{\partial (PV)}{\partial T}\right)_P = P\left(\frac{\partial V}{\partial T}\right)_P = \alpha PV \tag{6.4.19}$$

which leads to

$$C_P - C_V = \alpha PV + \alpha \pi_T V \tag{6.4.20}$$

The term αPV represents the work done by the system to push back the atmosphere. The term $\alpha \pi_T V$ represents the work required to break up the intermolecular forces of attraction among the particles of the sample.

It can be shown, using the second law of thermodynamics, that

$$\pi_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{6.4.21}$$

Substitution of Equation 6.4.21 into Equation 6.4.20 leads to

$$C_P - C_V = \alpha TV\left(\frac{\partial P}{\partial T}\right)_V \tag{6.4.22}$$

The partial derivative can be replaced by the following tactic

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \tag{6.4.23}$$

If $\left(\frac{\partial(P)}{\partial T}\right)_V$ is at constant volume, then dV = 0 and Equation 6.4.23 becomes

$$\left(\frac{\partial V}{\partial T}\right)_P dT = -\left(\frac{\partial V}{\partial P}\right)_T dP \tag{6.4.24}$$

Dividing by dT gives

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V \tag{6.4.25}$$

which rearranges to be

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{6.4.26}$$

Referring to Equations 6.4.8 and 6.4.9, it can be shown that

$$\frac{\alpha}{\kappa_T} = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{6.4.27}$$

Thus, Equation 6.4.22 becomes

$$C_P - C_V = \alpha TV\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha^2 TV}{\kappa_T} \tag{6.4.28}$$

This equation applies to all substances and phases. It collapses to equal nR for perfect gases, for which $\alpha = \frac{1}{T}$ and $\kappa_T = \frac{1}{P}$

$$C_P - C_V = \frac{PV}{T} = nR \tag{6.4.29}$$

The Joule-Thompson Effect

In 1852, working with William Thomson (who would later become Lord Kelvin), Joule conducted an experiment in which they pumped gas at a steady rate through a lead pipe that was cinched to create a construction. On the upstream side of the constriction, the gas was at a higher pressure than on the downstream side of the constriction. Also, the temperature of the gas was carefully monitored on either side of the construction. The cooling that they observed as the gas expanded from a high pressure region to a lower pressure region was extremely important and lead to a common design of modern refrigerators.

Not all gases undergo a cooling effect upon expansion. Some gases, such as hydrogen and helium, will experience a warming effect upon expansion under conditions near room temperature and pressure. The direction of temperature change can be determined by measuring the Joule-Thomson coefficient, μ_{JT}. This coefficient has the definition

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial p}\right)_H \tag{6.4.30}$$

Note: The derivation of μ_{JT}

Referring to equation 6.4.13, H = U +PV, we can say that

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP, \ + \left(\frac{\partial H}{\partial T}\right)_P dT \tag{6.4.31}$$

Because the process is carried out at a constant enthalpy, dH =0. Thus

$$0 = \left(\frac{\partial H}{\partial P}\right)_T dP, \ + \left(\frac{\partial H}{\partial T}\right)_P dT \tag{6.4.32}$$

and

$$\left(\frac{\partial H}{\partial P}\right)_T dP = -\left(\frac{\partial H}{\partial T}\right)_P dT \tag{6.4.33}$$

The partial derivative on the right side of equation 6.4.33 is C_P, so that

$$\left(\frac{\partial H}{\partial P}\right)_T dP = -C_P dT \tag{6.4.34}$$

Dividing both sides by dP results in

$$\left(\frac{\partial H}{\partial P}\right)_T = -C_P \left(\frac{\partial T}{\partial P}\right)_H \tag{6.4.35}$$

As defined in equation 6.4.30, the partial derivative on the right side of equation 6.4.35 is μ_{JT}:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H \tag{2.4.30}$$

Thus for a closed system of constant composition under isenthalpic conditions,

$$dH = -\mu_{JT} C_P dP + C_P dT \tag{6.4.36}$$

The following schematic shows how the Joule-Thomson coefficient can be measured by observing the temperature drop or increase a gas undergoes for a given pressure drop (Figure 2.4.1). The apparatus is thermally insulated so that no heat can be transferred in or out, making the expansion adiabatic.

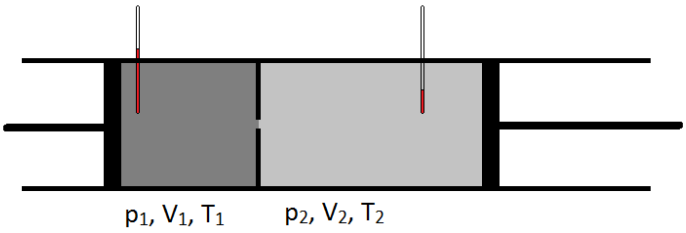


Figure 2.4.1

Note: Why is the Process Isenthalpic?

The Joule-Thomson experiment is carried out adiabatically, so q = 0 and δU = w. The gas sample on the left is compressed isothermally under the constant pressure, P_1. The volume of this gas changes from V_1 to 0. Thus the work done on this gas is

$$w_1 = -P_1(0 - V_1) = P_1 V_1 \tag{6.4.37}$$

The gas on the right side of the equation expands isothermally (but possibly at a different constant temperature as the gas on the left) against the constant pressure, P_2. The volume of this gas changes from 0 to V_2. Thus the work done on this gas is

$$w_2 = -P_2(V_2 - 0) = -P_2 V_2 \tag{6.4.38}$$

The total work done on the system of gases is

$$w_1 + w_2 = P_1V_1 - P_2V_2 \tag{6.4.39}$$

Thus,

$$\delta U = U_2 - U_1 = w_1 + w_2 = P_1V_1 - P_2V_2 \tag{6.4.40}$$

which can be rearranged to the form

$$U_2 + P_2V_2 = U_1 + P_1V_1 \tag{6.4.41}$$

According to equation 6.4.13, H = U + PV, so that equation 6.4.41 can be simplified to

$$H_2 = H_1 \tag{6.4.42}$$

In practice, the value of μ_{JT} is difficult to obtain. Instead, the isothermal Joule-Thomson coefficient, μ_T, is obtained using an apparatus in which a gas at high pressure is passed through a porous plug into a lower pressure container. Because the gas will cool as it undergoes the pressure drop, heat is added to the gas after it has passed through the plug so that the gas remains at the same temperature on both sides of the pressure drop. μ_T is the slope of the plot of enthalpy versus pressure at constant temperature:

$$\mu_T = \left(\frac{\partial H}{\partial P}\right)_T \tag{6.4.43}$$

The value of μ_T is converted to μ_{JT} using the equation

$$\mu_T = -C_P\mu_{JT} \tag{6.4.44}$$

The typical behavior of the Joule-Thomson coefficient for a real gas can be summarized in Figure 2.4.2. At the combinations of T and p for which $\mu_{JT} > 0$ (inside the shaded region), the sample will **cool upon expansion**. At those p and T conditions outside of the shaded region, where $\mu_{JT} < 0$, the gas will undergo a **temperature increase upon expansion**. Along the boundary, a gas will undergo neither a temperature increase not decrease upon expansion. For a given pressure, there are typically two temperatures at which m_{JT} changes sign. These are the upper and lower inversion temperatures.

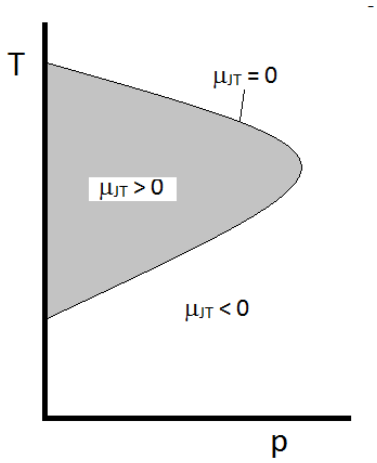


Figure 2.4.2:

Using the tools of mathematics, it is possible to express the Joule-Thomson coefficient in terms of measurable properties. Consider enthalpy as a function of pressure and temperature: $H(p,T)$. This suggests that the total differential dH can be expressed

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT \tag{6.4.45}$$

It will be shown later (again, once we develop the *Maxwell Relations*) that

$$\left(\frac{\partial H}{\partial p}\right)_T dp = -T\left(\frac{\partial V}{\partial T}\right)_p + V \tag{6.4.46}$$

A simple substitution shows

$$\left(\frac{\partial H}{\partial p}\right)_T dp = -TV\alpha + V = V(1 - T\alpha) \tag{6.4.47}$$

So

$$dH = V(1 - T\alpha)dP + C_p dT \tag{6.4.48}$$

For an ideal gas, $\alpha = 1/T$, so

$$dH = V(1 - T\cancelto{0}{\frac{1}{T}})dP + C_p dT \tag{6.4.49}$$

which causes the first term to vanish. So for constant enthalpy expansion ($dH = 0$), there can be no change in temperature ($dT = 0$). This will mean that real gases show non-zero values for μ_{JT} only because they deviate from ideal behavior!

Example 6.4.2:

Derive an expression for μ_{JT} in terms of α, C_p, V, and T.

Solution

Using the total differential for $H(p,T)$ (Equation 6.4.45):

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT \tag{6.4.50}$$

Dividing by dp and constraining to constant H:

$$\left.\frac{dH}{dp}\right|_H = \left(\frac{\partial H}{\partial p}\right)_T \left.\frac{dp}{dp}\right|_H + \left(\frac{\partial H}{\partial T}\right)_p \left.\frac{dT}{dp}\right|_H \tag{6.4.51}$$

Noting that

$$\left.\frac{dH}{dp}\right|_H = 0 \tag{6.4.52}$$

$$\left.\frac{dp}{dp}\right|_H = 1 \tag{6.4.53}$$

and

$$\left.\frac{dT}{dp}\right|_H = \left(\frac{\partial T}{\partial p}\right)_H \tag{6.4.54}$$

so

$$0 = \left(\frac{\partial H}{\partial p}\right)_T + \left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H \tag{6.4.55}$$

We can then use the following substitutions:

$$\left(\frac{\partial H}{\partial p}\right)_T = V(1 - T\alpha) \tag{6.4.56}$$

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p \tag{6.4.57}$$

$$\left(\frac{\partial T}{\partial p}\right)_H - \mu_{JT} \tag{6.4.58}$$

To get

$$0 = V(1 - T\alpha) + C_p \mu_{JT} \tag{6.4.59}$$

And solving for μ_{JT} gives

$$\mu_{JT} = \frac{V}{C_p}(T\alpha - 1) \tag{6.4.60}$$

A Molecular Explanation

When gas particles are allowed to expand into a volume of lower pressure, they are (obviously) likely to move father apart from each other than they originally were. If the pressure and temperature conditions are such that attractive intermolecular forces are dominant among the particles of the expanding gas sample, then the potential energy of these particles must be increased as they separate from each other. If the process is carried out under adiabatic conditions, the only source of energy is the kinetic energy of the particles themselves. Thus, as they move farther apart, their kinetic energy decreases, and therefore their temperature drops. When cooling occurs during expansion, we know that $\mu_{JT} > 0$.

It is also possible that the pressure and temperature conditions are such that repulsive intermolecular forces are dominant among the particles of the expanding gas sample, in which case the potential energy of these particles will be decreased as they separate from each other. If the process is carried out under adiabatic conditions, the only process by which the molecules can lose potential energy is to increase their own kinetic energy. Thus, as they move farther apart, their kinetic energy increases, and therefore their temperature increases. When heating occurs during expansion, we know that $\mu_{JT} < 0$.

References

1. Chang, Raymond. Physical Chemistry for the Biosciences. Sausalito, CA: University Science, 2005.

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6.5: Adiabatic Changes

The following discussions apply to a sample of ideal gas in an isolated system (an adiabatic, or thermally insulated system) that undergoes a reversible, adiabatic expansion or compression against a constant external pressure. Because there is no heat exchange during these volume changes, the internal energy will decrease during an expansion and increase during a compression. These internal energy changes occur because the gas molecules lose kinetic energy as they do work to move the piston, or gain kinetic energy as work is done on the by the piston.

Changes in Temperature

In this example, we want to find the change in temperature of a gas sample as it undergoes a reversible adiabatic expansion. This expansion will lead to a decrease in temperature and an increase in volume. It would be difficult to monitor the point-by-point changes in temperature as the volume slowly increases. However, because ΔU is a state function, we can separate the overall process into two theoretical steps:

- Step 1: an isothermal expansion from V_1 to V_2
- Step 2: a decrease in temperature at constant volume.

In Topic 2A we noted that the internal energy of an ideal gas is independent of the volume of its container. Because of this fact, the isothermal expansion in Step 1 will not affect the internal energy of the gas. Thus, the change in internal energy during the adiabatic expansion can be assigned to Step 2, the change in temperature at constant volume. Once again using a concept developed in Topic 2A, we know that at constant volume

$$\Delta U = C_V \, \Delta T = C_V \, (T_2 - T_1) \tag{6.5.1}$$

As noted above, in an adiabatic process $\Delta U = w_{ad}$ so that

$$w_{ad} = C_V \, \Delta T \tag{6.5.2}$$

This relationship makes sense because the energy needed to carry out the work of the expansion must come from the gas particles, which will lose energy as they do work, resulting in a drop in the temperature of the system.We assume that the value of C_V is independent of temperature.

To determine the relationship between the volume change and the temperature change, we can start with the premise that the work done by an ideal gas as it expands adiabatically against an external pressure, P, is

$$dw = -PdV \tag{6.5.3}$$

For an adiabatic change $dU = dw$ and for an ideal gas $dU = C_V dT$, thus in this case

$$dU = C_V dT = dw = -PdV \tag{6.5.4}$$

and

$$C_V dT = -PdV \tag{6.5.5}$$

Because we are using an ideal gas, $P = \frac{nRT}{V}$, thus

$$\frac{C_V dT}{T} = -\frac{nRdV}{V} \tag{6.5.6}$$

The limits of integration are set by the initial conditions (T_1, V_1) and final conditions (T_2, V_2):

$$C_V = \int \frac{dT}{T} = -nR \int \frac{dV}{V} \tag{6.5.7}$$

resulting in

$$C_V \ln \frac{T_2}{T1} = -nR \frac{V_2}{V_1} \tag{6.5.8}$$

which can be rearranged to

$$\frac{C_V}{nR}\ln\frac{T_2}{T_1}=\ln\frac{V_1}{V_2} \tag{6.5.9}$$

To solve for T_2, we need to define $\frac{C_V}{nR}=c$ so that

$$\ln\left(\frac{T_2}{T_1}\right)^c=\ln\frac{V_1}{V_2} \tag{6.5.10}$$

This equation allows us to assume that

$$\left(\frac{T_2}{T_1}\right)^c=\frac{V_1}{V_2} \tag{6.5.11}$$

and so

$$T_2=T_1\left(\frac{V_1}{V_2}\right)^{1/c} \tag{6.5.12}$$

Example 6.5.1:

Calculate the final temperature, the work done, and the change in internal energy when 0.0500 moles of He at 25.0°C undergoes a reversible adiabatic expansion from 250. L to 750. L. The constant volume molar heat capacity of He at 25°C is 12.48 $\frac{J}{mole\cdot K}$.

Asked For: T_f, w_{ad}, and ΔU

Solution: If $C_V=12.48\frac{J}{mole\cdot K}$, then c = $\frac{12.48\frac{J}{mole\cdot K}}{/}8.314\frac{J}{mole\cdot K}$ = 1.501.

Use equation 6.5.12 to find that $T_2=298.15\,K\times\left(\frac{250.\,L}{750.\,L}\right)^{1/1.501}=143\,K$.

Use equation 6.5.2 to find that $w_{ad}=(0.0500\,moles\,He)\times\left(12.48\frac{J}{mole\cdot K}\right)\times(143K-298K)=-96.7\,J$.

According to the definition of an adiabatic process, $\Delta U=w_{ad}$. Therefore, ΔU = -96.7 J.

Exercise 6.5.1

Calculate the final temperature, the work done, and the change in internal energy when 0.0400 moles of CO at 25.0°C undergoes a reversible adiabatic expansion from 200. L to 800. L. The constant volume molar heat capacity of CO at 25°C is 20.16 $\frac{J}{mole\cdot K}$.

Answers: T_f = 168 K; w_{ad} = -105 J; ΔU = - 105 J

Changes in Pressure

In this example, we want to find the change in pressure of a gas sample as it undergoes a reversible adiabatic expansion. This expansion will lead to a decrease in pressure and an increase in volume. Because we are working with an ideal gas

$$\frac{P_1V_1}{P_2V_2}=\frac{T_1}{T_2} \tag{6.5.13}$$

Substituting in a rearranged version of Equation 6.5.12, we get

$$\frac{P_1V_1}{P_2V_2}=\left(\frac{V_2}{V_1}\right)^{\frac{1}{c}} \tag{6.5.14}$$

which rearranges to

$$\frac{P_1}{P_2}\left(\frac{V_1}{V_2}\right)^{\frac{1}{c}+1}=1 \tag{6.5.15}$$

In Topic 2B, it was stated that $C_{P,m} - C_{V,m} = R$. This relationship can be used to develop the term, γ:

$$\frac{1}{c} + 1 = \frac{1+c}{c} = \frac{R + C_{V,m}}{C_{V,m}} = \frac{C_{P,m}}{C_{V,m}} = \gamma \tag{6.5.16}$$

Thus, Equation 6.5.15 can be written as

$$\frac{P_1}{P_2}\left(\frac{V_1}{V_2}\right)^{\gamma} = 1 \tag{6.5.17}$$

Solving for P_2, we get

$$P_2 = P_1 \times \left(\frac{V_1}{V_2}\right)^{\gamma} \tag{6.5.18}$$

recall that:

- for a monatomic ideal gas, $C_{V,m} = \frac{3}{2}R$ and $C_{P,m} = \frac{5}{2}R$, so $\gamma = \frac{5}{3}$.
- for nonlinear, polyatomic molecules, which can rotate as well as translate, $C_{V,m} = 3R$ and $C_{P,m} = 4R$, so $\gamma = \frac{4}{3}$.

Example 6.5.2:

Calculate the final pressure when a sample of He at 250. kPa undergoes a reversible adiabatic expansion from 2.00 L to 4.00 L.

Solution: Use equation 6.5.18 and the fact that $\gamma = \frac{5}{3}$ for He to find that $P_f = (250kPa)\left(\frac{2.00\,L}{4.00\,L}\right)^{5/3} = 78.7kPa$.

Exercise 6.5.2

Calculate the final pressure when a sample of Xe at 100. kPa undergoes a reversible adiabatic expansion from 1.00 L to 5.00 L.

Answer $P_f = 6.84kPa$.

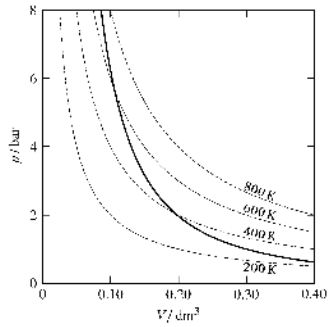


Figure 2.5.1 *An adiabat (solid curve) and four isotherms (dashed curves) for an ideal gas ($n = 0.0120\,mole$, ($CV_m = 1.5R$). Image by Howard DeVoe.*

The solid curve in Fig. 2.5.1 shows how the pressure of an ideal gas varies with volume during a reversible adiabatic expansion or compression. This curve is an *adiabat*. The dashed curves in the figure are *isotherms* showing how pressure changes with volume at constant temperature according to the equation of state $p = nRT/V$. In the direction of increasing V (expansion), the adiabat crosses isotherms of progressively lower temperatures. This cooling effect, of course, is due to the loss of energy by the gas as it does work on the surroundings without a compensating flow of heat into the system.

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CHAPTER OVERVIEW

7: Entropy and The Second Law of Thermodynamics

7.1: Energy Does not Determine Spontaneity

7.2: The Second Law of Thermodynamics

7.3: We Must Always Devise a Reversible Process to Calculate Entropy Changes

7.4: The Famous Equation of Statistical Thermodynamics is S=k ln W

7.5: Entropy Can Be Expressed in Terms of a Partition Function

7.6: The Statistical Definition of Entropy is Analogous to the Thermodynamic Definition

7.7: Thermodynamics Provides Insight into the Conversion of Heat into Work

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7.1: Energy Does not Determine Spontaneity

There are many spontaneous events in nature. If you open the valve in both cases a spontaneous event occurs. In the first case the gas fills the evacuated chamber, in the second the gases will mix. The state functions U and H do not give us a clue what will happen. You might think that only those events are spontaneous that produce heat.

Not so:

- If you dissolve KNO_3 in water, it does so spontaneously, but the solution gets ***cold***.
- If you dissolve KOH in water, it does so spontaneously, but the solution gets ***hot***.

Clearly the first law is not enough to describe nature.

7.1.1: Two items left on our wish list

The development of the new state function entropy has brought us much closer to a complete understanding of how heat and work are related:

1. the spontaneity problem

   we now have a criterion for spontaneity for isolated systems

2. the asymmetry between work->heat (dissipation) and heat->work (power generation)

   at least we can use the new state law to predict the limitations on the latter.

Two problems remain:

1. we would like a spontaneity criterion *for all systems* (not just isolated ones)
2. we have a new state function S, but what is it?

7.1.2: Entropy on a microscopic scale

Let us start with the latter. Yes we can use S to explain the odd paradox between w and q both being forms energy on the one hand, but the conversion being easier in one direction than the other, but we have introduced the concept *entropy* purely as a phenomenon on iis own. Scientifically there is nothing wrong with such a phenomenological theory except that experience tells us that if you can understand the phenomenon itself better your theory becomes more powerful.

To understand entropy better we need to leave the macroscopic world and look at what happens on a molecular level and do statistics over many molecules. First, let us do a bit more statistics of the kind we will need.

7.1.2.1: Permutations

If we have n distinguishable objects, say playing cards we can arrange them in a large number of ways. For the first object in our series we have n choices, for number two we have $n-1$ choices (the first one being spoken for) etc. This means that in total we have

$$W = n(n-1)(n-2)\ldots.4.3.2.1 = n! \text{ choices.}$$

The quantity W is usually called the number of realizations in thermodynamics.

The above is true if the objects are all distinguishable. If they fall in groups within which they are not distinguishable we have to correct for all the swaps within these groups that do not produce a distinguishably new arrangement. This means that W becomes $\frac{n!}{a!b!c!\ldots z!}$ where a,b, c to z stands for the size of the groups. (Obviously $a+b+c+..+z=n$)

In thermodynamincs our 'group of objects' is typically an ensemble of systems, think of size N_{av} and so the factorial become horribly large. This makes it necessary to work with logarithms. Fortunately there is a good approximation (by Stirling) for a logarithmic factorial:

$$\ln N! \approx N \ln N - N$$

Causality vs. Correlation

In Europe nosey little children who are curious to find out where their newborn little brother or sister came from, often get told that the stork brought it during the night. When you look at the number of breeding pairs of this beautiful bird in e.g. Germany since 1960 you see a long decline to about 1980 when the bird almost got extinct. After that the numbers go up again due to breeding programs mostly. The human birth rate in the country follows a pretty much identical curve and the correlation between the two is very high (>0.98 or so). (Dr H. Sies in Nature (volume 332 page 495; 1988). Does this prove that storks indeed bring babies?



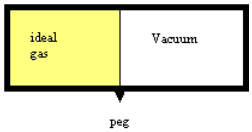
An adult White Stork. from Wikipedia (credit: Frank Vassen).

Answer:

No, it does ***not*** show causality, just a correlation due a common underlying factor. In this case that is the choices made by the German people. First they concentrated on working real hard and having few children to get themselves out of the poverty WWII had left behind and neglected the environment, then they turned to protect the environment and opened the doors to immigration of people, mostly from Muslim countries like Turkey or Morocco, that usually have larger families. The lesson from this is that you can only conclude causality ***if*** you are sure that there are no other intervening factors.

7.1.3: Changing the size of the box with the particles in it

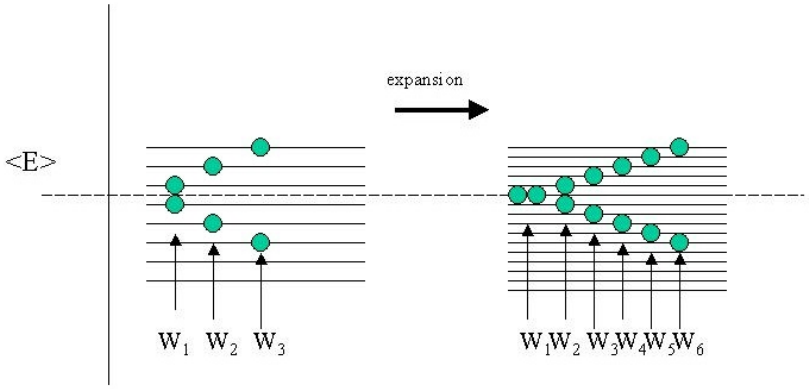
The expansion of an ideal gas against vacuum is really a wonderful *model experiment*, because *nothing else happens* but a spontaneous expansion and a change in entropy. No energy change, no heat, no work, no change in mass, no interactions, nothing. In fact, it does not even matter whether we consider it an isolated process or not. We might as well do so.



Physicists and Physical Chemists love to find such experiments that allows them to retrace *causality*. All this means that if we look at what happens at the atomic level, we should be able to retrace the ***cause*** of the entropy change. As we have seen before, the available energy states of particles in a box depend on the size of the box.

$$E_{kin} = \frac{h^2}{8ma^2}\left[n_1^2 + n_2^2 + n_2^2\right]$$

Clearly if the side (a and therefore the volume of the box changes, the energy spacing between the states will become smaller. Therefore during our expansion against vacuum, the energy states inside the box are changing. Because U does not change the *average* energy $\langle E \rangle$ is constant. Of course this average is taken over a great number of molecules (*systems*) in the gas (the *ensemble*), but let's look at just two of them and for simplicity let us assume that the energy of the states are equidistant (rather than quadratic in the quantum numbers n).



As you can see there is more than one way to skin a cat, or in this case to *realize* the same average $\langle E \rangle$ of the complete ensemble (of only two particles admittedly). Before expansion I have shown three realizations W_1, W_2, W_3 that add up to the same $\langle E \rangle$. After expansion however, there are more energy states available and the schematic figure shows twice as many realizations W in the same energy interval.

Boltzmann was the first to postulate that this is what is at the root of the entropy function, not so much the (total) energy itself (that stays the same!), but the number of ways the energy can be distributed in the ensemble. Note that because the ensemble average (or total) energy is identical, we could also say that the various realizations W represent the degree of *degeneracy* Ω of the ensemble.

Boltzmann considered a much larger (*canonical*) ensemble consisting of a great number of identical *systems* (e.g. molecules, but it could also be planets or so). If each of our systems already has a large number of energy states the systems can all have the same (total) energy but distributed in rather different ways. This means that two systems within the ensemble can either have the same distribution or a different one. Thus we can divide the ensemble A in subgroups a_j having the same energy distribution and calculate the number of ways to distribute energy in the ensemble A as

$$W = \frac{A!}{a1!a2!\ldots}.$$

Boltzmann postulated that entropy was directly related to the number of realizations W, that is the number of ways the same energy can be distributed in the ensemble. This leads immediately to the concept of order versus disorder, e.g, if the number of realizations is $W = 1$, all systems must be in the same state (W=A! / A!0!0!0!…) which is a very orderly arrangement of energies.

If we were to add two ensembles to each other the total number of possible arrangements W_{tot} becomes the product W_1W_2 but the entropies should be additive. As logarithms transform products into additions Boltzmann assumed that the relation between W and S should be logarithmic and wrote:

$$S = k \ln W$$

Again, if we consider a very ordered state, e.g. where all systems are in the ground state the number of realizations A!/A!= 1 so that the entropy is zero. If we have a very messy system where the number of ways to distribute energy over the many many different states is very large S becomes very large. Thus entropy is very large.

This immediately gives us the driving force for the expansion of a gas into vacuum or the mixing of two gases. We simply get more energy states to play with, this increases W. This means an increase in S. This leads to a spontaneous process.

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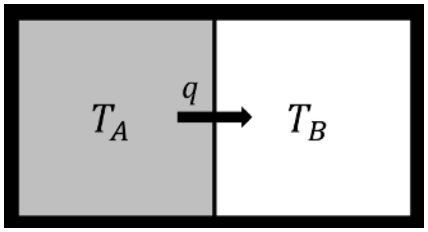
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7.2: The Second Law of Thermodynamics

7.2.1: Spontaneity of an isolated system

> An **isolated system** is a little more than just adiabatic. In the latter heat cannot get in or out. In an isolated system *nothing* gets in or out, neither heat nor mass nor even any radiation, such as light. The isolated system is like a little universe all to itself.

Let us consider a zero law process. We have two identical blocks of metal, say aluminum. They are each at thermal equilibrium, but at different temperatures. They are brought into contact with each other but isolated from the rest of the universe.



- ***Zeroth law***: *Heat will flow from hot to cold*
- ***First law***: *There is no change in total energy*

so:

$$dU_A = -dU_B$$

There is also no work so:

$$dU_A = \delta q_A + 0$$

Because U is a state function this makes q a state function as well, otherwise this equality does not hold. As there is only one term on the right there is only one path (along q). So we could write:

$$dU_A = dq_A$$

This implies that we do not need to worry about reversible and irreversible paths as there is only one path. Since:

$$dS = \frac{\delta q_{rev}}{T}$$

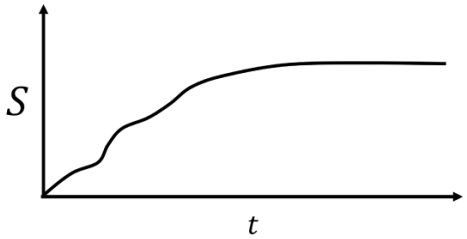
In this particular case:

$$TdS = \delta q_{rev} = dU$$

Thus we get:

$$dS = \frac{dU_A}{T_A} + \frac{dU_B}{T_B} = \frac{dU_A}{T_A} - \frac{dU_A}{T_B} = dU_A\left(\frac{1}{T_A} - \frac{1}{T_B}\right)$$

Clearly as long as the two temperatures are not the same dS is not zero and entropy is not conserved. Instead it is **increasing**. Over time, the temperatures will become the same (if the blocks are identical, the final temperature is the average of T_A and T_B) and the entropy will reach a maximum.



For our two identical blocks of metal (with same heat capacity, C_V), we can, in fact, derive that the entropy change:

$$\Delta S = C_V \ln \left[\frac{T_A^2 + T_B^2}{4 T_A T_B} \right].$$

This is indeed a positive quantity. In general, we can say for an isolated system:

$$dS \geq 0$$

Thus if we are dealing with a spontaneous (and isolated) process $dS > 0$ and ***entropy is being produced***. This gives us a ***criterion for spontaneity***.

7.2.2: Entropy exchange of an open system

In an isolated system dS represents the produced entropy dS_{prod} and this is a good criterion for spontaneity. Of course the requirement that the system is isolated is very restrictive and makes the criterion as good as useless... What happens in a system that can exchange heat with the rest of the universe? We do have entropy changes in that case, but part of them may have nothing to do with production, because we also have to consider the heat that is exchanged.

$$dS = dS_{prod} + dS_{exchange}$$

If the process is reversible (that is completely non-spontaneous) we are dealing with δq_{rev} so that $dS_{exchange} = \delta q_{rev}/T$, but that is also what dS_{tot} is equal to (by definition). This leaves no room for entropy production.

So we have:

Isolated: $dS = dS_{prod} + 0$

Reversible $dS = 0 + \delta q_{rev}/T$

Notice that this demonstrates that for non-isolated systems entropy change is *not* a good criterion for spontaneity at all... In the case the heat exchange is ***irreversible*** *part* of the entropy is entropy production by the system:

Irreversible: $dS = dS_{prod} + \delta q_{irrev}/T$

$dS > \delta q_{irrev}/T$ in this case.

Generalizing the isolated, irreversible and reversible cases we may say:

$$dS \geq \frac{\delta q}{T}$$

This is the ***Clausius inequality***.

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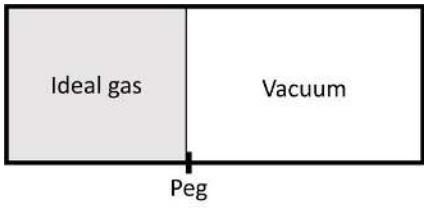
7.3: We Must Always Devise a Reversible Process to Calculate Entropy Changes

The second law of thermodynamics can be formulated in many ways, but in one way or another they are all related to the fact that the state function entropy, S, tends to increase over time in isolated systems. For a long time, people have looked at the entire universe as an example of an isolated system and concluded that its entropy must be steadily increasing until $\delta S_{universe}$ becomes zero. As we will see below, the second law has important consequences for the question of how we can use heat to do useful work.

> Of late, cosmologists like the late Richard Hawkins have begun to question the assumption that the entropy of the universe is steadily increasing. The key problem is the role that gravity and relativity play in creating black holes.

7.3.1: Vacuum Expansion

Let's compare two expansions from V_1 to V_2 for an ideal gas, both are isothermal. The first is an irreversible one, where we pull a peg an let the piston move against vacuum:



The second one is a reversible isothermal expansion from V_1 to V_2 (and P_1 to P_2) that we have examined before. In both cases, the is no change in internal energy since T does not change. During the irreversible expansion, however, there is also no volume work because the piston is expanding against a vacuum and the following integral:

$$\int -P_{ext} dV = 0$$

integrates to zero. The piston has nothing to perform work against until it slams into the right hand wall. At this point $V = V_2$ and then dV becomes zero. This is not true for the reversible isothermal expansion as the external pressure must always equal the internal pressure.

> *No energy and no work means no heat!*

Clearly the zero heat is irreversible heat ($q_{irr} = 0$) and this makes it hard to calculate the entropy of this spontaneous process. But then this process ends in the same final state as the reversible expansion from V_1 to V_2. We know that dU is still zero, but now $\delta w_{rev} = -\delta q_{rev}$ is nonzero. We calculated its value before:

$$q_{rev} = nRT \ln \left(\frac{V_2}{V_1} \right) \tag{7.3.1}$$

The Claussius definition of entropy change can be used to find ΔS (under constant temperature).

$$\Delta S = \frac{q_{rev}}{T} \tag{7.3.2}$$

Substituting Equation 7.3.1 into Equation 7.3.2 results in

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$$

As S is a state function this equation also holds for the irreversible expansion against vacuum.

> Always calculate the entropy difference between two points along a **reversible** path.

For the irreversible expansion into vacuum we see that

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= nR\ln\left(\frac{V_2}{V_1}\right) + 0 \\ &= nR\ln\left(\frac{V_2}{V_1}\right)\end{aligned}$$

For the reversible expansion, heat is transferred to the system while the system does work on the surroundings in order to keep the process isothermal:

$$\Delta S_{\text{sys}} = nR\ln\left(\frac{V_2}{V_1}\right)$$

The entropy change for the surrounding is the opposite of the system:

$$\Delta S_{\text{surr}} = -nR\ln\left(\frac{V_2}{V_1}\right)$$

This is because the amount of heat transferred to the system is the same as the heat transferred from the surroundings and this process is reversible so the system and surroundings are at the same temperature (equilibrium). Heat is related to entropy by the following equation:

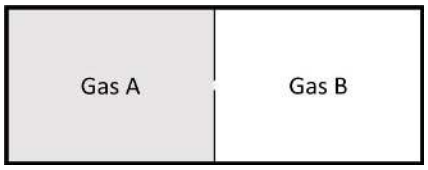
$$dS = \frac{\delta q}{T}$$

Therefore, the total entropy change for the reversible process is zero:

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= nR\ln\left(\frac{V_2}{V_1}\right) - nR\ln\left(\frac{V_2}{V_1}\right) \\ &= 0\end{aligned}$$

7.3.2: The Mixing of Two Gases

Consider two ideal gases at same pressure separated by a thin wall that is punctured. Both gases behave as if the other one is not there and again we get a spontaneous process, mixing in this case.



If the pressure is the same the number of moles of each gas should be proportional to the original volumes, V_A and V_B, and the total number of moles to the total volume V_{tot}.

For gas A we can write:

$$\Delta S_A = n_A R\ln\frac{V_{tot}}{V_A} = n_A R\ln\frac{n_{tot}}{n_A}$$

and similarly for gas B we can write:

$$\Delta S_B = n_B R\ln\frac{V_{tot}}{V_B} = n_B R\ln\frac{n_{tot}}{n_B}$$

The total entropy change is therefore the sum of constituent entropy changes:

$$\Delta S = \Delta S_A + \Delta S_B$$

and the entropy change total per mole of gas is:

$$\frac{\Delta S}{n_{tot}} = R\frac{\left[n_B\ln\frac{n_{tot}}{n_B} + n_A\ln\frac{n_{tot}}{n_A}\right]}{n_{tot}} \tag{7.3.3}$$

Equation 7.3.3 can be simplified using mole fractions:

$$\chi_A = \frac{n_A}{n_{tot}}$$

and the mathematical relationship of logarithms that:

$$\ln\left(\frac{x}{y}\right) = -\ln\left(\frac{y}{x}\right)$$

to:

$$\Delta\bar{S} = -R[\chi_A \ln \chi_A + \chi_B \ln \chi_B] \tag{7.3.4}$$

In the case of mixing of more than two gases, Equation 7.3.4 can be expressed as:

$$\Delta\bar{S} = -R\sum \chi_i \ln \chi_i \tag{7.3.5}$$

This entropy expressed in Equations 7.3.4 and 7.3.5 is known as the **entropy of mixing**; its existence is the major reason why there is such a thing as diffusion and mixing when gases, and also solutions (even solid ones), are brought into contact with each other.

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7.4: The Famous Equation of Statistical Thermodynamics is S=k ln W

A common interpretation of entropy is that it is somehow a measure of chaos or randomness. There is some utility in that concept. Given that entropy is a measure of the dispersal of energy in a system, the more chaotic a system is, the greater the dispersal of energy will be, and thus the greater the entropy will be. Ludwig Boltzmann (1844 – 1906) (O'Connor & Robertson, 1998) understood this concept well, and used it to derive a statistical approach to calculating entropy. Boltzmann proposed a method for calculating the entropy of a system based on the number of energetically equivalent ways a system can be constructed.

Boltzmann proposed an expression, which in its modern form is:

$$S = k_b \ln(W) \tag{7.4.1}$$

W is the number of available microstates in a macrostate (ensemble of systems) and can be taken as the quantitative measure of energy dispersal in a macrostate:

$$W = \frac{A!}{\prod_j a_j!}$$

Where a_j is the number of systems in the ensemble that are in state j and A represents the total number of systems in the ensemble:

$$A = \sum_j a_j$$

Equation 20.5.1 is a rather famous equation etched on Boltzmann's grave marker in commemoration of his profound contributions to the science of thermodynamics (Figure 7.4.1).



Figure 7.4.1: Ludwig Boltzmann (1844 - 1906)

Example 7.4.1:

Calculate the entropy of a carbon monoxide crystal, containing 1.00 mol of CO, and assuming that the molecules are randomly oriented in one of two equivalent orientations.

Solution:

Using the Boltzmann formula (Equation 7.4.1):

$$S = nK \ln(W)$$

And using $W = 2$, the calculation is straightforward.

$$S = \left(1.00\,mol \cot \frac{6.022 \times 10^{23}}{1\,mol}\right)(1.38 \times 10^{-23} J/K) \ln 2$$
$$= 5.76\,J/K$$

7.4.1: Contributors and Attributions

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- Jerry LaRue (Department of Chemistry and Biochemistry, Chapman University)

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7.5: Entropy Can Be Expressed in Terms of a Partition Function

We have seen that the partition function of a system gives us the key to calculate thermodynamic functions like energy or pressure as a moment of the energy distribution. We can extend this formulism to calculate the entropy of a system once its Q is known. We can start with Boltzmann's (statistical) definition of entropy:

$$S = k\ln(W) \tag{7.5.1}$$

with

$$W = \frac{A!}{\prod_j a_j!}$$

Combining these equations, we obtain:

$$S_{ensemble} = k\ln\frac{A!}{\prod_j a_j!}$$

Rearranging:

$$S_{ensemble} = k\ln A! - k\sum_j \ln a_j!$$

Using Sterling's approximation:

$$\begin{aligned} S_{ensemble} &= kA\ln A - kA - k\sum_j a_j \ln a_j + k\sum_j a_j \\ &= kA\ln A - k\sum_j a_j \ln a_j \end{aligned}$$

Since:

$$\sum_j a_j = A$$

The probability of finding the system in state a_j is:

$$p_j = \frac{a_j}{A}$$

Rearranging:

$$a_j = p_j A$$

Plugging in:

$$S_{ensemble} = kA\ln A - k\sum_j p_j A \ln p_j A$$

Rearranging:

$$S_{ensemble} = kA\ln A - k\sum_j p_j A\ln p_j - k\sum_j p_j A\ln A$$

If A is constant, then:

$$k\sum_j p_j A\ln A = kA\ln A\sum_j p_j$$

Since:

$$\textstyle\sum_j p_j = 1$$

We get:

$$S_{ensemble} = kA \ln A - k \sum_j p_j A \ln p_j - kA \ln A$$

The first and last term cancel out:

$$S_{ensemble} = -k \sum_j p_j A \ln p_j$$

We can divide by A to get the entropy of the system:

$$S_{system} = -k \sum_j p_j \ln p_j \tag{7.5.2}$$

If all the p_j are zero except for the for one, then the system is perfectly ordered and the entropy of the system is zero. The probability of being in state j is

$$p_j = \frac{e^{-\beta E_j}}{Q} \tag{7.5.3}$$

Plugging Equation 7.5.3 into Equation 7.5.2 results in

$$\begin{aligned} S &= -k \sum_j \frac{e^{-\beta E_j}}{Q} \ln \frac{e^{-\beta E_j}}{Q} \\ &= -k \sum_j \frac{e^{-\beta E_j}}{Q} (-\beta E_j - \ln Q) \\ &= -\beta k \sum_j \frac{E_j e^{-\beta E_j}}{Q} + \frac{k \ln Q}{Q} \sum_j e^{-\beta E_j} \end{aligned}$$

Making use of:

$$\beta k = \frac{1}{T}$$

And:

$$\sum \frac{e^{-\beta E_j}}{Q} = \sum p_j = 1$$

We obtain:

$$S = \frac{U}{T} + k \ln Q \tag{7.5.4}$$

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7.6: The Statistical Definition of Entropy is Analogous to the Thermodynamic Definition

The laws of thermodynamics can be understood in two ways: by looking at large-scale properties like temperature and pressure, or by examining how countless tiny atoms move and interact. Both perspectives lead to the same laws, even though the reasoning behind them is quite different.

We learned earlier that entropy, S, is related to the number of microstates, W, in an ensemble with A systems:

$$S_{ensemble} = k_B \ln W \tag{7.6.1}$$

and

$$W = \frac{A!}{\prod_j a_j!} \tag{7.6.2}$$

Combining Equations 7.6.1 and 7.6.2 to get:

$$\begin{aligned} S_{ensemble} &= k_B \ln \frac{A!}{\prod_j a_j!} \\ &= k_B \ln A! - k_B \sum_j \ln a_j! \end{aligned}$$

Using Sterling's approximation:

$$\ln A! \approx A \ln A - A$$

We obtain:

$$S_{ensemble} = k_B A \ln A - k_B A - k_B \sum_j a_j \ln a_j + k_B \sum a_j$$

Since:

$$A = \sum a_j$$

The expression simplifies to:

$$S_{ensemble} = k_B A \ln A - k_B \sum_j a_j \ln a_j$$

We can make use of the fact that the number of microstates in state j is equal to the total number of microstates multiplied by the probability of finding the system in state j, p_j:

$$a_j = p_j A$$

Plugging in, we obtain

$$\begin{aligned} S_{ensemble} &= k_B A \ln A - k_B \sum_j p_j A \ln p_j A \\ &= k_B A \ln A - k_B \sum_j p_j A \ln p_j - k_B \sum_j p_j A \ln A \end{aligned}$$

Since A is a constant and the sum of the probabilities of finding the system in state j is always 1:

$$\sum p_j = 1$$

The first and last term cancel out:

$$S_{ensemble} = -k_B A \sum_j p_j \ln p_j$$

We can use that the entropy of the system is the entropy of the ensemble divided by the number of systems:

$$S_{system} = S_{ensemble}/A$$

Dividing by A, we obtain:

$$S_{system} = -k_B \sum_j p_j \ln p_j$$

We can differentiate this equation and dropping the subscript:

$$dS = -k_B \sum_j (dp_j + \ln p_j dp_j)$$

Since $\sum_j p_j = 1$, the derivative $\sum_j dp_j = 0$:

$$dS = -k_B \sum_j \ln p_j dp_j$$

In short:

$$\sum_j \ln p_j dp_j = -\frac{\delta q_{rev}}{k_B T}$$

Plugging in:

$$dS = \frac{\delta q_{rev}}{T} \tag{7.6.3}$$

The thermodynamic definition of entropy comes from macroscopic observations. In classical thermodynamics, entropy is defined as the measure of energy dispersal in a system (Equation 7.6.3). It tells us how much heat is spread out or distributed in a system at temperature. This definition is practical and works well at the bulk level but does not say why entropy behaves this way.

The statistical definition of entropy in Equation 7.6.1, developed by Boltzmann, defines entropy in terms of the number of possible microstates that correspond to the same overall macroscopic state (macrostate). This shows that entropy measures the degree of microscopic disorder or multiplicity of arrangements consistent with what we see at the macroscopic level.

Both definitions describe the same underlying concept:

- The thermodynamic view says entropy measures the spread of energy in terms of heat and temperature.
- The statistical view says entropy measures the spread of possible microstates that energy can occupy.

They are equivalent because a system with more accessible microstates (higher disorder) will also tend to have greater energy dispersal, and thus higher entropy. In fact, the statistical definition explains why the thermodynamic definition works: macroscopic energy dispersal arises from the overwhelming number of microscopic ways energy can be arranged.

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7.7: Thermodynamics Provides Insight into the Conversion of Heat into Work

Heat and work are both forms of transferring energy, and under the right circumstance, one form may be transformed into the other. However, the second law of thermodynamics puts a limitation on this. To go from work to heat is called dissipation and there is no limitation on this at all. In fact it was through dissipation (by friction) that we discovered that heat and work were both forms of energy. There is, however, a limitation on converting heat to work.

7.7.1: The Carnot Cycle

Let's consider a circular, reversible path of an ideal gas on a PV diagram in Figure 7.7.1:

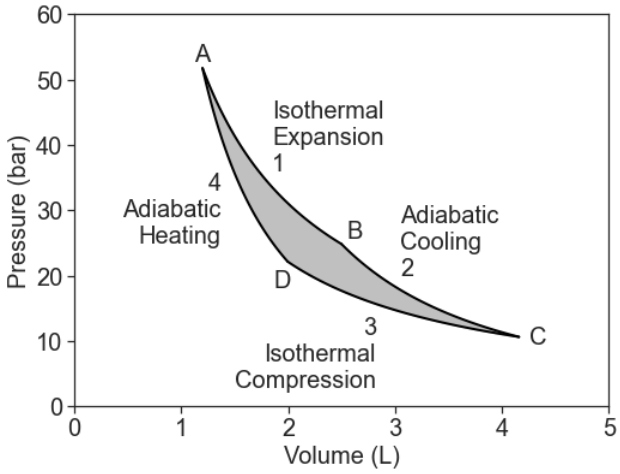


Figure 7.7.1: A circular, reversible path of a Carnot cycle as an ideal gas on a PV diagram. (CC BY 4.0; Jerry LaRue via LibreTexts)

This cycle forms the 4-stage Carnot cycle heat engine. A heat engine converts heat energy into work. The cycle consists of:

1. Isothermal expansion at the hot temperature, T_h:

$$\Delta U_1 = w_1 + q_h = 0$$

2. Adiabatic cooling from T_h to T_c:

$$\Delta U_2 = w_2$$

3. Isothermal compression at the cold temperature, T_c:

$$\Delta U_3 = w_3 + q_c = 0$$

4. Adiabatic heating from T_c to T_h:

$$\Delta U_4 = w_4$$

The total four-step process produces work because $w_{hot} > w_{cold}$. The work is the integral under the upper isotherm minus the one under the lower curve, i.e. the surface *area in between*.

Sadi Carnot

Sadi Carnot was a French engineer at the beginning of the 19th century. He considered a cyclic process involving a cylinder filled with gas. This cycle the Carnot cycle contributed greatly to the development of thermodynamics and the improvement of the steam engine. Carnot demonstrated that the cold temperature on the right is as important as the heat source on the left in defining the possible efficiency of a heat engine

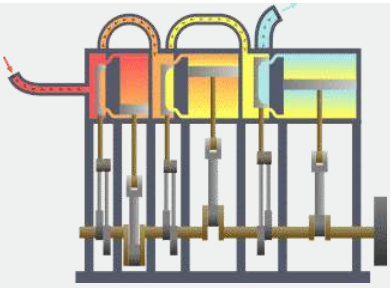


Figure **7.7.2**: Animation of a typical vertical triple-expansion engine. (CC SA-BY 2.5; Emoscopes)

7.7.2: Efficiency

Of course we spend good money on the fuel to start the cycle by heating things up. So how much work do we get for the heat we put in? In other words, we want to know how efficient our heat engine is. The efficiency, η of a heat engine is:

$$\eta = \frac{|w_{\text{cycle}}|}{q_h} = \frac{q_h + q_c}{q_h} = 1 + \frac{q_c}{q_h}$$

To get the work of the cycle, we can make use of internal energy as a state function. As the path is circular the circular integrals for U is zero:

$$\begin{aligned} \oint dU &= \Delta U_{\text{cycle}} \\ &= \sum \Delta U_i \\ &= w_1 + q_h + w_2 + w_3 + q_c + w_4 \\ &= 0 \end{aligned}$$

Rearranging:

$$\begin{aligned} q_h + q_c &= -w_1 - w_2 - w_3 - w_4 \\ &= -w_{\text{cycle}} \end{aligned}$$

An ideal engine would take $q_h \rightarrow q_c$ with 100% efficiency. The work of the cycle will be equivalent to the heat transfer. For ideal gases:

1. $w_1 = -RT_h \ln\left(\frac{V_B}{V_A}\right) = -q_h$
2. $dU = \delta w = \bar{C}_V dT \rightarrow w_2 = \bar{C}_V (T_c - T_h)$
3. $w_3 = -RT_c \ln\left(\frac{V_D}{V_C}\right) = -q_c$
4. $w_4 = \bar{C}_V (T_h - T_c)$

Finding an expression for w_{cycle}:

$$\begin{aligned} w_{\text{cycle}} &= -RT_h \ln\left(\frac{V_B}{V_A}\right) + \bar{C}_V (T_c - T_h) - RT_c \ln\left(\frac{V_D}{V_C}\right) + \bar{C}_V (T_h - T_c) \\ &= -RT_h \ln\left(\frac{V_B}{V_A}\right) - RT_c \ln\left(\frac{V_D}{V_C}\right) = -R(T_h - T_c) \ln\left(\frac{V_B}{V_A}\right) \end{aligned}$$

We have an expression for work, so we can evaluate the efficiency, η. The efficiency of the Carnot engine is:

$$\eta = \frac{|w_{\text{cycle}}|}{q_h} = \frac{R(T_h - T_c) \ln\left(\frac{V_B}{V_A}\right)}{RT_h \ln\left(\frac{V_B}{V_A}\right)} = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h}$$

Paths (2) and (4) are adiabats, so we can also use entropy, S, to get the same solution:

$$\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c} = 0$$

Therefore:

$$\frac{q_c}{q_h} = -\frac{T_c}{T_h}$$

And we get that:

$$\eta = 1 + \frac{q_c}{q_h} = 1 - \frac{T_c}{T_h} \tag{7.7.1}$$

As you see we can only get full efficiency if T_{cold} is 0 K, which is never (i.e., we always waste energy). Another implication is that if $T_c = T_h$ then **no work** can be obtained, no matter how much energy is available in the from of heat. Or in other words, if one dissipates work into heat isothermally, *none* of it can be retrieved. Equation 7.7.1 is not very forgiving at all. Just imaging that you have a heat source of say 400 K (a superheated pool of water, e.g. a geyser) and you are dumping in the river at room temperature 300 K. The best efficiency you'll ever get is:

$$\eta = 1 - \frac{300}{400} = 24\%$$

Sadly, you'd be dumping three quarters of your energy as heat in the river (and that is best case scenario as there are always more losses, e.g. due to friction). The arrow saying Q_C in Figure 7.7.3 should then be three times as fat as the one that says w.

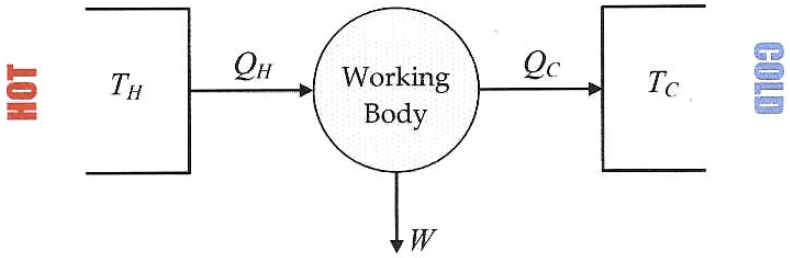


Figure 7.7.3: Carnot engine diagram (modern) - where an amount of heat Q_H flows from a high temperature $T_H$furnace through the fluid of the "working body" (working substance) and the remaining heat Q_C flows into the cold sink T_C, thus forcing the working substance to do mechanical work W on the surroundings, via cycles of contractions and expansions. (Public Domain; Eric Gaba)

7.7.3: Heat pumps

So getting our work from heat is hard and always less than 100% successful. The other way around should be easy. After all, we can dissipate work into heat freely even under isothermal conditions!

What happens if we let the heat engine run backwards? Consider reversing all the flows in the above diagram. Obviously we must *put in work* to make the cycle run in reverse. The heat will now flow from cold to hot, say from your cold garden into your nice and warm apartment. The amount of heat you get in your humble abode will be the sum of all the work (say 100 Joules) you dissipate *plus* the heat you pumped out of the garden (say 300 Joules). Thus if you are willing to pay for the energy you dissipate (100 Joules), you may well end up with a total of 400 Joules of heat in your apartment! Obviously if it is heat you after this is a better deal than just dissipating the work in your apartment (by burning some oil). Then you'd only get 100 J for your precious buck.

Dissipating it as electrical heating is even worse because you would

1. first burn (a lot more!) oil to generate heat
2. use this heat to produce electrical work at great expense because a lot of the heats gets dumped at the low temperature side (the river or so)
3. dissipate the work again in your apartment (without using it to pump any heat out of the garden)

Refrigerators are also heat pumps. They heat the kitchen by pumping heat from its innards to the kitchen. If I keep the door open, however, all it does is dissipate precious electrical work, because the pumped heat will flow back into its innards and spoil the milk.

7.7.4: Stirling Engine

Let's consider another type of heat engine, the Stirling engine. The Stirling engine uses a circular reversible path in an ideal PV diagram in Figure 7.7.4:

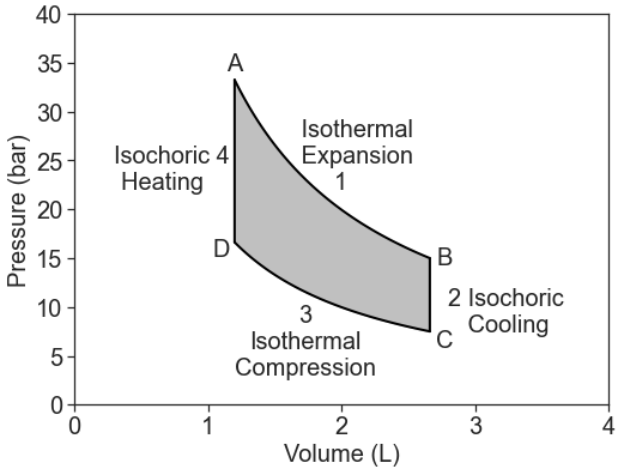


Figure **7.7.4**: an ideal PV diagram of the Stirling engine. (CC BY 4.0; Jerry LaRue via LibreTexts)

The path consists of four steps:

1. *Isothermal* expansion at the hot temperature T_h:

$$q_1 = q_h = -w$$

and we get work **out** (i.e., negative work):

$$w_h = -RT_h \ln\left(\frac{V_B}{V_A}\right)$$

2. *Isochoric* heating from T_c to T_h (with constant C_V):

$$q_2 = \frac{C_V}{\Delta T} \tag{7.7.2}$$

3. *Isothermal* compression at the cold temperature T_c:

$$q_3 = q_c = -w$$

and we must put work **in** (i.e., positive work):

$$w_c = -RT_c \ln\left(\frac{V_D}{V_C}\right) = RT_c \ln\left(\frac{V_B}{V_A}\right)$$

4. *Isochoric* cooling from T_h to T_c (with constant C_V):

$$q_4 = -\frac{C_V}{\Delta T} \tag{7.7.3}$$

Notice that this gray area *vanishes* if $T_h = T_c$. Obviously how cold the cold side is of great importance! The amount of work is also equal to the difference in the heat picked up at high temperature q_h and dumped at low temperature q_c. The isochoric heats cancel. The problem is that q_c is only zero if the cold temperature is 0 K. That means that we can never get all the heat we pick up at high temperatures to come out as work.

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CHAPTER OVERVIEW

8: The Third Law, Absolute Entropy, and the Gibbs Free Energy of Formation

8.1: Heat Capacity as a Function of Temperature

8.2: The Third Law

8.3: Absolute Entropy

8.4: Evaluating Entropy Changes Using Thermochemical Cycles

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8.1: Heat Capacity as a Function of Temperature

It is relatively easy to measure heat capacities as a function of temperature. If we measure the constant-pressure heat capacity of a pure substance over a wide temperature range, we typically observe a curve like that in Figure 1. The heat capacity is a smooth, continuous function of temperature except for a small number of discontinuities. These occur at temperatures where the substance undergoes phase changes. These can be changes from one solid phase to another, melting to convert a solid phase to the liquid, or vaporization to convert the liquid to the gas. The details of the curve are pressure dependent; for example, at a low pressure, we might observe sublimation of the material from a solid phase directly into its gas phase.

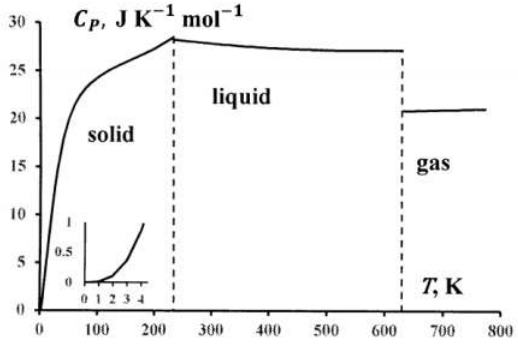


Figure 1. Heat capacity of mercury *versus* temperature

Another general feature of these curves is that the heat capacity of the solid substance decreases to zero as the absolute temperature decreases to zero; the curve meets the abscissa at the zero of temperature and does so asymptotically. That this is true for all substances seems like an odd sort of coincidence. Why should all solid substances exhibit essentially the same heat capacity (zero) at one temperature (absolute zero)?

As it turns out, this result has a straightforward molecular interpretation in the theory of statistical thermodynamics. In Section 22.6, we consider a theory of low-temperature heat capacity developed by Einstein. Einstein's theory explains all of the qualitative features that are observed when we measure heat capacities at low temperatures, but its predictions are not quantitatively exact. Debye extended the Einstein model and developed a theory that gives generally excellent quantitative predictions. The Debye theory predicts that, at temperatures near absolute zero, the heat capacity varies as the cube of temperature: $C_P = AT^3$, where A is a constant. If we have heat capacity data down to a temperature near absolute zero, we can estimate the value of A from the value of C_P at the lowest available temperature.

Anticipating results that we develop in Chapter 22, we can characterize the statistical interpretation as follows: When a system of molecules gives up heat to its surroundings, some of the molecules move from higher energy levels to lower ones. Statistical thermodynamics posits that the fraction of the molecules that are in the lowest energy level approaches one as the temperature goes to zero. If nearly all of the molecules are already in the lowest energy level, decreasing the temperature still further has a negligible effect on the energy and enthalpy of the system.

Given such heat capacity data, we can find the enthalpy or entropy change that occurs as we change the temperature of a quantity of the substance from some reference temperature to any other value. When we use pressure and temperature as the independent variables, we have

$$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$$

and

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

At constant pressure, we have

$$(dH)_P = C_P dT$$

so that

$$H(T) - H(T_{ref}) = \int_{T_{ref}}^{T} C_P dT$$

and

$$(dS)_P = \frac{C_P}{T} dT$$

so that

$$S(T) - S(T_{ref}) = \int_{T_{ref}}^{T} \frac{C_P}{T} dT$$

If phase transitions occur as the temperature goes from the reference temperature to the temperature of interest, these integrations must be carried out in steps. Also, we must include the enthalpy and entropy changes that occur during these phase changes.

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8.2: The Third Law

For entropy on the other hand, the fact that the heat capacity goes to zero as the temperature decreases has important consequences. Consider the change in the entropy of a pure substance whose heat capacity approaches some finite limiting value as its temperature decreases to absolute zero. For such a substance, C_P/T becomes arbitrarily large as the temperature decreases, and the entropy integral

$$\int_T^0 \frac{C_P}{T} dT$$

approaches minus infinity as the temperature approaches zero. For real substances, this does not occur. In the neighborhood of absolute zero, heat capacities decrease more rapidly than temperature. The entropy change approaches zero as the temperature approaches zero.

The idea that the entropy change for a pure substance goes to zero as the temperature goes to zero finds expression as the third law of thermodynamics. In 1923, Lewis and Randall[1] gave a statement of the third law that is particularly convenient in chemical applications:

> *If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, every substance has a positive finite entropy; but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances.*

Implicitly, the Lewis and Randall statement defines the entropy of any substance, at any temperature, T, to be the difference between the entropy of the constituent elements, at absolute zero, and the entropy of the substance at temperature T. Equivalently, we can say that it is the entropy change when the substance is formed at temperature T from its constituent elements at absolute zero. Arbitrarily, but very conveniently, the statement sets the entropy of an element to zero at absolute zero.

The distinction between perfect crystalline substances and less-than-perfect crystalline substances lies in the regularity of the arrangement of the molecules within the crystal lattice. In any lattice, each molecule of the substance is localized at a specific site in the lattice. In a perfect crystal, all of the molecules are in oriented the same way with respect to the lattice. Some substances form crystals in which the molecules are not all oriented the same way. This can happen when the molecule can fit into a lattice site of the same shape in more than one way. For example, in solid carbon monoxide, the individual molecules occupy well-defined lattice sites. If the carbon monoxide crystal were perfect, all of the molecules would point in the same direction, as diagrammed in Figure 2. Instead, they point randomly in either of two possible directions.

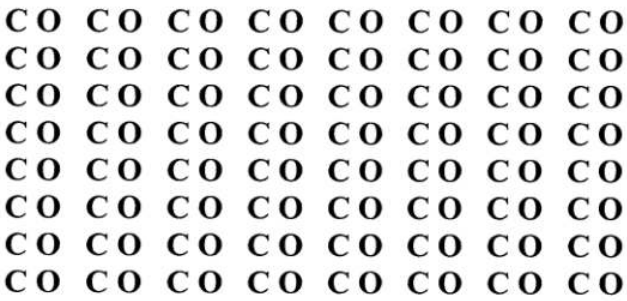


Figure 2. A two-dimensional representation of a perfect CO crystal.

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8.3: Absolute Entropy

By the Lewis and Randall statement of the third law, the entropy of a substance that forms a perfect crystal is identically equal to zero at absolute zero. Much as the ideal gas temperature scale has a natural zero at the temperature at which the volume extrapolates to zero, a perfect crystalline substance has a natural zero of entropy at this same temperature. We can choose a non-zero value for the absolute zero of temperature. The Centigrade scale is based on such a choice. However, for thermodynamic purposes, any such choice is much less convenient. Similarly, we could choose arbitrary values for the entropies of the elements at the absolute zero of temperature. The entropy of a perfect crystalline substance at absolute zero would then be the sum of the entropies of its constituent elements. (See problem 5.) However, choosing non-zero values proves to be much less convenient.

Given the entropy of a substance at absolute zero, its entropy at any higher temperature can be calculated from the entropy changes that occur as the substance is warmed to the new temperature. At the very lowest temperatures, this entropy change is calculated by integrating C_P/T, using Debye's theoretical relationship, $C_P = AT^3$; A is obtained from the value of C_P at the lowest temperature for which an experimental value of C_P is available. In temperature ranges where experimental heat capacity data are available, the entropy change is obtained by integration using these data.

Phase changes are isothermal and reversible. Where the substance undergoes phase changes, the contribution that the phase change makes to the entropy of the substance is equal to the enthalpy change for the phase change divided by the temperature at which it occurs.

At any given temperature, the entropy value that is obtained in this way is called the substance's ***absolute entropy*** or its ***third-law entropy***. When the entropy value is calculated for one mole of the substance in its standard state, the resulting absolute entropy is called the ***standard entropy***. The standard entropy is usually given the symbol S^o. It is usually included in compilations of thermodynamic data for chemical substances.

We write $S^o_A(T)$ to indicate the absolute entropy of substance A in its standard state at temperature T. $S^o_A(T)$ is the entropy of the substance in its standard state at absolute zero plus the entropy increase that occurs as the substance changes reversibly to its standard state at T. So long as substance A forms a perfect crystal at absolute zero, $S^o_A(T)$ is the difference between its molar entropy at T and its molar entropy at absolute zero—as calculated from heat capacity and phase-change enthalpy data.

If substance A does not form a perfect crystal at absolute zero, the true value of $S^o_A(T)$ exceeds the calculated value. The excess is the molar entropy of the imperfect crystal at absolute zero. We observe the discrepancy when measured values, at T, of entropies of reactions that involve A fail to agree with those calculated using the incorrect value of $S^o_A(T)$.

In Section 11.2 we note that many tables of thermochemical properties present "absolute enthalpy" data for chemical substances. An absolute enthalpy is the difference between the enthalpies of a substance at two different temperatures, but the reference temperature is not absolute zero. In Section 6.4 and Section 6.5, we introduce enthalpy standard states and the standard enthalpy of formation of substance A at temperature T, which we designate as $\Delta_f H^o_A(T)$. We define the standard enthalpy of formation of any element at any temperature to be zero. In Section 8.6, we find that the enthalpy difference between reactants in their standard states and products in their standard states is readily calculated from the standard enthalpies of formation of the participating substances. As illustrated in Figure 8-2, this calculation is successful because it utilizes an isothermal cycle which begins and ends in a common set of elements, all of which are at the same temperature.

We can also define the standard entropy of formation of any substance to be the difference between its standard entropy, $S^o_A(T)$, and those of its pure constituent elements in their standard states at the same temperature. This definition is embedded in the Lewis and Randall statement of the third law. For example, the standard entropy of formation of water at 400 K is the difference

$$\Delta_f S^o(H_2O,\ 400\ \text{K}) = \Delta S^o(H_2O,\ 400\text{K})$$

$$-\Delta S^o(H_2,\ 400\ \text{K}) - \frac{1}{2}\Delta S^o(O_2, 400\text{K})$$

Because of this definition, the standard entropy of formation of an element in its standard state is zero. We can calculate the standard entropy change for any reaction, $\Delta_r S^o(T)$, either as the difference between the standard entropies of formation (the $\Delta_f S^o(T)$ values) of the reactants and products or as the difference between their standard entropies (the $S^o_A(T)$ values). Either calculation is successful because it begins and ends with a common set of elements, all of which are at the same temperature. When

we compute $\Delta_r S^o(T)$ using values of $S^o_A(T)$ for the reactants and products the reference temperature for the elements is absolute zero. When we compute $\Delta_r S^o(T)$ using values of $\Delta_f S^o(T)$ for the reactants and products, the reference temperature is T.

Given $\Delta_f H^o(T)$ and $\Delta_f S^o(T)$, the standard Gibbs free energy of formation is immediately obtained from $\Delta_f G^o(T) = \Delta_f H^o(T) - T\Delta_f S^o(T)$. For any element at any temperature, we have $\Delta_f H^o = 0$ and $\Delta_f S^o = 0$; it follows that the standard Gibbs free energy of formation of an element in its standard state is zero. Tables of thermodynamic data usually give values for$\Delta_f H^o$, $\Delta_f G^o$, and S^o. (A set of standard entropies contains the same information as the corresponding set of entropies of formation. Entropies of formation are seldom tabulated. If $\Delta_f S^o$ is needed, it can be calculated either from $\Delta_f H^o$ and $\Delta_f G^o$ or from the absolute entropies of the substance and the elements from which it is formed.)

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8.4: Evaluating Entropy Changes Using Thermochemical Cycles

As for the standard enthalpy of reaction, we can obtain the standard entropy of reaction at a new temperature by evaluating entropy changes around a suitable thermochemical cycle. To do so, we need the standard entropy change at one temperature. We also need heat capacity data for all of the reactants and products. For the reaction

$$a\ A + b\ B \rightarrow c\ C + d\ D$$

we can evaluate the entropy change at a second temperature by summing the individual contributions to the change in entropy around the cycle in Figure 5. For this cycle, we have

$$\Delta_r S^o(T_2) = \Delta_r S^o(T_1) + c\int_{T_1}^{T_2} \frac{C_P(C)}{T}dT + d\int_{T_1}^{T_2} \frac{C_P(D)}{T}dT - a\int_{T_1}^{T_2} \frac{C_P(A)}{T}dT - b\int_{T_1}^{T_2} \frac{C_P(B)}{T}dT$$

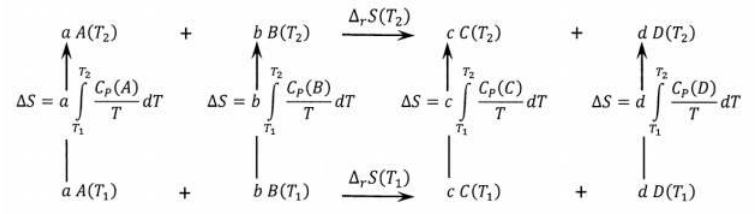


Figure 5. Cycle relating the entropy changes for a reaction at two temperatures.

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CHAPTER OVERVIEW

9: Helmholtz and Gibbs Energies

9.1: Helmholtz Energy

9.2: Gibbs Energy Determines the Direction of Spontaneity at Constant Pressure and Temperature

9.3: The Maxwell Relations

9.4: Thermodynamic Functions have Natural Variables

9.5: The Enthalpy of an Ideal Gas is Independent of Pressure

9.6: The Gibbs-Helmholtz Equation

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9.1: Helmholtz Energy

We have answered the question: what is entropy, but we still do not have a general criterion for spontaneity, just one that works in an isolated system. We will consider what happens when we hold volume and temperature constant. As discussed previously, the expression for the change in internal energy:

$$dU = TdS - PdV$$

is only valid for *reversible* changes. Let us consider a spontaneous change. If we assume constant volume, the $-PdV$ work term drops out. From the *Clausius inequality* $dS > \frac{\delta q}{T}$ we get:

$$dU \underset{\text{constant V}}{\leq} TdS$$

$$dU - TdS \underset{\text{constant V}}{\leq} 0$$

Consider a new state function, **Helmholtz energy**, **A**:

$$A \equiv U - TS$$

$$dA = dU - TdS - SdT \tag{9.1.1}$$

If we also set T constant, we see that Equation 9.1.1 becomes

$$dA = dU - TdS \underset{\text{constant V and T}}{\leq} 0$$

This means that the Helmholtz energy, A, is a ***decreasing quantity*** for spontaneous processes (regardless of isolation!) when T and V are held constant. A becomes constant once a reversible equilibrium is reached.

Example 22.1.1 : What A stands for

A good example is the case of the mixing of two gases. Let's assume isothermal conditions and keep the total volume constant. For this process, ΔU is zero (isothermal, ideal) but the

$$\Delta S_{molar} = -y_1 R \ln y_1 - y_2 R \ln y_2$$

This means that

$$\Delta A_{molar} = RT(y_1 \ln y_1 + y_2 \ln y_2).$$

This is a negative quantity because the mole ratios are smaller than unity. So yes this spontaneous process has a negative ΔA. If we look at $\Delta A = \Delta U - T\Delta S$ we should see that the latter term is the same thing as $-q_{rev}$ So we have :

$$\Delta A = \Delta U - q_{rev} = w_{rev}$$

This is however the *maximal work that a system is able to produce* and so the Helmholtz energy is a direct measure of how much work one can get out of a system. A is therefore often called the Helmholtz ***free*** energy. Interestingly this work **cannot** be volume work as volume is constant. so it stands for the maximal ***other*** work (e.g. electrical work) that can be obtained under the unlikely condition that volume is constant.

9.1.1: Natural variables of A

Because $A \equiv U - TS$ we can write

$$\begin{aligned} dA &= dU - TdS - SdT \\ &= TdS - PdV - TdS - SdT \\ &= -PdV - SdT \end{aligned}$$

The natural variables of A are volume V and temperature T.

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9.2: Gibbs Energy Determines the Direction of Spontaneity at Constant Pressure and Temperature

The Helmholtz energy A is developed for isochoric changes and as we have often said before it is much easier to deal with isobaric ones where $P =$ constant. We can therefore repeat the above treatment for the enthalpy and introduce another state function the Gibbs energy

$$\begin{aligned} G &\equiv H - TS \\ &= U + PV - TS \\ &= A + PV \end{aligned}$$

If we take both T and P constant we get

$$\begin{aligned} dU - TdS + PdV &\leq 0 \\ dG &\leq 0 \end{aligned}$$

G either decreases (spontaneously) or is constant (at equilibrium). Calculating the state function between two end points we get:

$$\Delta G = \Delta H - T\Delta S \leq 0 (T, P \text{ constant})$$

This quantity is key to the question of spontaneity under the conditions we usually work under. If for a process ΔG is positive it does not occur spontaneous and can only be made to occur if it is 'pumped', i.e. coupled with a process that has a negative ΔG. The latter is spontaneous.

> If $\Delta G = 0$ then the system is as ***equilibrium***.

9.2.1: Direction of the spontaneous change

Because the ΔS term contains the temperature T as coefficient the spontaneous direction of a process, e.g. a chemical reaction can **change** with temperature depending on the values of the enthalpy and the entropy change ΔH and ΔS. This is true for the melting process, e.g. for water below 0°C we get water=>ice, above this temperature ice melts to water, but it also goes for chemical reactions.

Example

Consider

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$$

$\Delta_r H$ at 298K / 1 bar is -176.2 kJ. The change in entropy is -0.285 kJ/K so that at 298K ΔG is -91.21 kJ. Clearly this is a reaction that will proceed to the depletion of whatever is the limiting reagent on the left.

However at 618 K this is a different story. Above this temperature ΔG is positive! (assuming enthalpy and entropy have remained the same, which is almost but not completely true) The reaction will not proceed. Instead the *reverse* reaction would proceed spontaneously. The salt on the right would decompose in the two gases -base and acid- on the left.

9.2.2: Meaning of the ΔG term

As we have seen, ΔA can be related to the maximal amount of work that a system can perform at constant V and T. We can hold an analogous argument for ΔG except that V is not constant so that we have to consider volume work (zero at constant volume) .

$$dG = d(U + PV - TS) = dU - TdS - SdT - PdV + VdP$$

As $dU = TdS + \delta w_{rev}$

$$dG = \delta w_{rev} - SdT + VdP + PdV$$

As the later term is $-\delta w_{volume}$

$$dG = \delta w_{rev} - SdT + VdP - \delta w_{volume}$$

At constant T and P the two middle terms drop out

$$dG = \delta w_{rev} - \delta w_{volume} = \delta w_{otherusefulwork}$$

Note

ΔG stands for the (maximal) reversible, isobaric isothermal non-PV work that a certain spontaneous change can perform. The volume work may not be zero, but is corrected for.

9.2.3: Natural variables of G

Because $G \equiv H - TS$, we can write

$$\begin{aligned} dG &= dH - TdS - SdT \\ &= TdS + VdP - TdS - SdT \\ &= VdP - SdT \end{aligned}$$

The natural variables of G are pressure P and temperature T. This is what makes this function the most useful of the four U, H, A, and G: these are the natural variables of most of your laboratory experiments!

9.2.4: Summary

We now have developed the basic set of concepts and functions that together form the framework of thermodynamics. Let's summarize four very basic state functions:

state function	natural variables
$dU = -PdV + TdS$	$U(V,S)$
$dH = +VdP + TdS$	$H(P,S)$
$dA = -PdV - SdT$	$A(V,T)$
$dG = +VdP - SdT$	$G(P,T)$

Note:

1. The replacement of δq by TdS was based on *reversible* heat. This means that in the irreversible case the expressions for dU and dH become inequalities
2. We only include *volume* work in the above expressions. If other work (elastic, electrical e.g.) is involved extra terms need to be added: $dU = TdS - PdV + xdX$ etc.

We are now ready to begin applying thermodynamics to a number of very diverse situations, but we will first develop some useful partial differential machinery.

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9.3: The Maxwell Relations

Modeling the dependence of the Gibbs and Helmholtz functions behave with varying temperature, pressure, and volume is fundamentally useful. But in order to do that, a little bit more development is necessary. To see the power and utility of these functions, it is useful to combine the First and Second Laws into a single mathematical statement. In order to do that, one notes that since

$$dS = \frac{dq}{T}$$

for a reversible change, it follows that

$$dq = TdS$$

And since

$$dw = TdS - pdV$$

for a reversible expansion in which only p-V works is done, it also follows that (since $dU = dq + dw$):

$$dU = TdS - pdV \tag{9.3.1}$$

This is an extraordinarily powerful result. This differential for dU can be used to simplify the differentials for H, A, and G. But even more useful are the constraints it places on the variables T, S, p, and V due to the mathematics of exact differentials!

9.3.1: Maxwell Relations

The above result suggests that the natural variables of internal energy are S and V (or the function can be considered as $U(S,V)$). So the total differential (dU) in Equation 9.3.1 can be expressed:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{9.3.2}$$

Also, by inspection (comparing the two expressions for dU in Equations 9.3.1 and 9.3.2) it is apparent that:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{9.3.3}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \tag{9.3.4}$$

But the value does not stop there! Since dU is an exact differential, the Euler relation must hold that

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V$$

By substituting Equations 9.3.3 and 9.3.4, we see that

$$\left[\frac{\partial}{\partial V}(T)_V\right]_S = \left[\frac{\partial}{\partial S}(-p)_S\right]_V$$

or

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

This is an example of a **Maxwell Relation**. These are very powerful relationship that allows one to substitute partial derivatives when one is more convenient (perhaps it can be expressed entirely in terms of α and/or κ_T for example.)

A similar result can be derived based on the definition of H.

$$H \equiv U + pV$$

Differentiating (and using the chain rule on $d(pV)$) yields

$$dH = dU + pdV + Vdp$$

Making the substitution using the combined first and second laws ($dU = TdS–pdV$) for a reversible change involving on expansion (p-V) work

$$dH = TdS–\cancel{pdV} + \cancel{pdV} + Vdp$$

This expression can be simplified by canceling the pdV terms.

$$dH = TdS + Vdp \tag{9.3.5}$$

And much as in the case of internal energy, this suggests that the natural variables of H are S and p. Or

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dV \tag{9.3.6}$$

Comparing Equations 9.3.5 and 9.3.6 show that

$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{9.3.7}$$

and

$$\left(\frac{\partial H}{\partial p}\right)_S = V \tag{9.3.8}$$

It is worth noting at this point that both Equation 9.3.3

$$\left(\frac{\partial U}{\partial S}\right)_V$$

and Equation 9.3.7

$$\left(\frac{\partial H}{\partial S}\right)_p$$

are equal to T. So they are equation to each other

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p$$

Moreover, the Euler Relation must also hold

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right)_p\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)_S\right]_p$$

so

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

This is the Maxwell relation on H. Maxwell relations can also be developed based on A and G. The results of those derivations are summarized in Table 9.3.1.

Table 9.3.1: Maxwell Relations

Function	Differential	Natural Variables	Maxwell Relation
U	$dU = TdS - pdV$	S, V	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
H	$dH = TdS + Vdp$	S, p	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
A	$dA = -pdV - SdT$	V, T	$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
G	$dG = Vdp - SdT$	p, T	$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

The Maxwell relations are extraordinarily useful in deriving the dependence of thermodynamic variables on the state variables of p, T, and V.

Example 9.3.1

Show that

$$\left(\frac{\partial V}{\partial T}\right)_p = T\frac{\alpha}{\kappa_T} - p$$

Solution

Start with the combined first and second laws:

$$dU = TdS - pdV$$

Divide both sides by dV and constraint to constant T:

$$\left.\frac{dU}{dV}\right|_T = \left.\frac{TdS}{dV}\right|_T - p\left.\frac{dV}{dV}\right|_T$$

Noting that

$$\left.\frac{dU}{dV}\right|_T = \left(\frac{\partial U}{\partial V}\right)_T$$

$$\left.\frac{TdS}{dV}\right|_T = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left.\frac{dV}{dV}\right|_T = 1$$

The result is

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

Now, employ the Maxwell relation on A (Table 6.2.1)

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

to get

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

and since

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

It is apparent that

$$\left(\frac{\partial V}{\partial T}\right)_p = T\frac{\alpha}{\kappa_T} - p$$

Note: How cool is that? This result was given without proof in Chapter 4, but can now be proven analytically using the Maxwell Relations!

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9.4: Thermodynamic Functions have Natural Variables

The fundamental thermodynamic equations follow from five primary thermodynamic definitions and describe internal energy, enthalpy, Helmholtz energy, and Gibbs energy in terms of their natural variables. Here they will be presented in their differential forms.

9.4.1: Introduction

The fundamental thermodynamic equations describe the thermodynamic quantities U, H, G, and A in terms of their natural variables. The term "natural variable" simply denotes a variable that is one of the convenient variables to describe U, H, G, or A. When considered as a whole, the four fundamental equations demonstrate how four important thermodynamic quantities depend on variables that can be controlled and measured experimentally. Thus, they are essentially equations of state, and using the fundamental equations, experimental data can be used to determine sought-after quantities like G or H.

9.4.2: First Law of Thermodynamics

The first law of thermodynamics is represented below in its differential form

$$dU = đq + đw$$

where

- U is the internal energy of the system,
- q is heat flow of the system, and
- w is the work of the system.

The "đ" symbol represent **inexact differentials** and indicates that both q and w are path functions. Recall that U is a state function. The first law states that internal energy changes occur only as a result of heat flow and work done.

It is assumed that w refers only to PV work, where

$$w = -\int pdV$$

The fundamental thermodynamic equation for internal energy follows directly from the first law and the principle of Clausius:

$$dU = đq + đw$$

$$dS = \frac{\delta q_{rev}}{T}$$

we have

$$dU = TdS + \delta w$$

Since only PV work is performed,

$$dU = TdS - pdV \tag{9.4.1}$$

The above equation is the fundamental equation for U with natural variables of entropy S and volume$V$.

9.4.2.1: Principle of Clausius

The *Principle of Clausius* states that the entropy change of a system is equal to the ratio of heat flow in a reversible process to the temperature at which the process occurs. Mathematically this is written as

$$dS = \frac{\delta q_{rev}}{T}$$

where

- S is the entropy of the system,
- q_{rev} is the heat flow of a reversible process, and
- T is the temperature in Kelvin.

9.4.3: Enthalpy

Mathematically, enthalpy is defined as

$$H = U + pV \tag{9.4.2}$$

where H is enthalpy of the system, p is pressure, and V is volume. The fundamental thermodynamic equation for enthalpy follows directly from it deffinition (Equation 9.4.2) and the fundamental equation for internal energy (Equation 9.4.1) :

$$\begin{aligned} dH &= dU + d(pV) \\ &= dU + pdV + VdP \\ dU &= TdS - pdV \\ dH &= TdS - pdV + pdV + Vdp \\ dH &= TdS + Vdp \end{aligned}$$

The above equation is the fundamental equation for H. The natural variables of enthalpy are S and p, entropy and pressure.

9.4.4: Gibbs Energy

The mathematical description of Gibbs energy is as follows

$$\begin{aligned} G &= U + pV - TS \\ &= H - TS \end{aligned} \tag{9.4.3}$$

where G is the Gibbs energy of the system. The fundamental thermodynamic equation for Gibbs Energy follows directly from its definition 9.4.3 and the fundamental equation for enthalpy 9.4.2:

$$\begin{aligned} dG &= dH - d(TS) \\ & dH - TdS - SdT \end{aligned}$$

Since

$$\begin{aligned} dH &= TdS + VdP \\ dG &= TdS + VdP - TdS - SdT \\ &= VdP - SdT \end{aligned} \tag{9.4.4}$$

The above equation is the fundamental equation for G. The natural variables of Gibbs energy are P and T.

9.4.5: Helmholtz Energy

Mathematically, Helmholtz energy is defined as

$$A = U - TS \tag{9.4.5}$$

where A is the Helmholtz energy of the system, which is often written as the symbol F. The fundamental thermodynamic equation for Helmholtz energy follows directly from its definition (Equation 9.4.5) and the fundamental equation for internal energy (Equation 9.4.1):

$$\begin{aligned} dA &= dU - d(TS) \\ &= dU - TdS - SdT \end{aligned}$$

Since

$$\begin{aligned} dU &= TdS - pdV \\ dA &= TdS - pdV - TdS - SdT \\ &= -pdV - SdT \end{aligned} \tag{9.4.6}$$

Equation 9.4.6 is the fundamental equation for A with natural variables of V and T. For the definitions to hold, it is assumed that **only** PV work is done and that **only reversible** processes are used. These assumptions are required for the first law and the principle of Clausius to remain valid. Also, these equations do not account include n, the number of moles, as a variable. When n is included, the equations appear different, but the essence of their meaning is captured without including the n-dependence.

9.4.6: Chemical Potential

The fundamental equations derived above were not dependent on changes in the amounts of species in the system. Below the n-dependent forms are presented[1,4].

$$dU = TdS - PdV + \sum_{i=1}^{N} \mu_i dn_i$$

$$dH = TdS + VdP + \sum_{i=1}^{N} \mu_i dn_i$$

$$dG = -SdT + Vdp + \sum_{i=1}^{N} \mu_i dn_i$$

$$dA = -SdT - PdV + \sum_{i=1}^{N} \mu_i dn_i$$

where μ_i is the chemical potential of species i and dn_i is the change in number of moles of substance i.

9.4.7: Importance/Relevance of Fundamental Equations

The differential fundamental equations describe U, H, G, and A in terms of their natural variables. The natural variables become useful in understanding not only how thermodynamic quantities are related to each other, but also in analyzing relationships between measurable quantities (i.e. P, V, T) in order to learn about the thermodynamics of a system. Below is a table summarizing the natural variables for U, H, G, and A:

Thermodynamic Quantity	Natural Variables
U (internal energy)	S, V
H (enthalpy)	S, P
G (Gibbs energy)	T, P
A (Helmholtz energy)	T, V

9.4.8: Maxwell Relations

The fundamental thermodynamic equations are the means by which the Maxwell relations are derived[1,4]. The Maxwell Relations can, in turn, be used to group thermodynamic functions and relations into more general "families"[2,3].

As we said dA is an **exact differential**. Let's write is out in its natural variables (Equation 9.4.6) and take a cross derivative. The dA expression in natural variables is

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$

The partial derivatives of A of first order can already be quite interesting we see e.g. in step 2 that the first partial of A versus V (at T constant) is the negative of the pressure.

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

Likewise we find the (isochoric) slope with temperature gives us the negative of the entropy. Thus entropy is one of the ***first order derivatives*** of A.

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

When we apply a cross derivative

$$\left(\frac{\partial^2 A}{\partial V \partial T}\right) = \left(\frac{\partial(-S)}{\partial V}\right)_T + \left(\frac{\partial(-P)}{\partial T}\right)_V$$

we get what is known as a ***Maxwell relation***:

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

? Exercise

What does Equation three mean for the heat capacity? answer

A similar treatment of dG (Equation 9.4.4 gives:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

and another Maxwell relation

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

? Exercise 9.4.1

If the assumptions made in the derivations above were not made, what would effect would that have? Try to think of examples were these assumptions would be violated. Could the definitions, principles, and laws used to derive the fundamental equations still be used? Why or why not?

Answer

If it was not assumed that PV-work was the only work done, then the work term in the second law of thermodynamics equation would include other terms (e.g. for electrical work, mechanical work). If reversible processes were not assumed, the Principle of Clausius could not be used. One example of such situations could the movement of charged particles towards a region of like charge (electrical work) or an irreversible process like combustion of hydrocarbons or friction.

? Exercise 9.4.2

For what kind of system does the number of moles not change? This said, do the fundamental equations without n-dependence apply to a wide range of processes and systems?

Answer

In general, a closed system of non-reacting components would fit this description. For example, the number of moles would not change for a closed system in which a gas is sealed (to prevent leaks) in a container and allowed to expand/is contracted.

? Exercise 9.4.3

Derive the Maxwell Relations.

Answer

See the Maxwell Relations section.

? Exercise 9.4.4

1. Derive the expression

$$\left(\frac{\partial H}{\partial P}\right)_{T,n} = -T\left(\frac{\partial V}{\partial T}\right)_{P,n} + V$$

Then apply this equation to an ideal gas. Does the result seem reasonable?

Answer

$(\frac{\partial H}{\partial P})_{T,n} = 0$ for an ideal gas. Since there are no interactions between ideal gas molecules, changing the pressure will not involve the formation or breaking of any intermolecular interactions or bonds.

? Exercise 9.4.5

Using the definition of Gibbs energy and the conditions observed at phase equilibria, derive the Clapeyron equation.

Answer

See the third outside link.

9.4.9: References

1. DOI: 10.1063/1.1749582
2. DOI: 10.1063/1.1749549
3. DOI:10.1103/PhysRev.3.273
4. *A Treatise on Physical Chemistry*, 3rd ed.; Taylor, H. S. and Glasstone, S., Eds.; D. Van Nostrand Company: New York, 1942; Vol. 1; p 454-485.

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9.5: The Enthalpy of an Ideal Gas is Independent of Pressure

How does pressure affect enthalpy H? As we showed above we have the following relations of first and second order for G

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = -V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

We also know that by definition:

$$G = H - TS \tag{9.5.1}$$

Consider an isothermal change in pressure, so taking the partial derivative of each side of Equation 9.5.1, we get:

$$\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \tag{9.5.2}$$

For an ideal gas

$$\frac{\partial V}{\partial T} = \frac{nR}{P}$$

so Equation 9.5.2 becomes

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{nR}{P}\right) = 0$$

As we can see for an ideal gas, there is no dependence of H on P.

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9.6: The Gibbs-Helmholtz Equation

9.6.0.1: Ideal gas

For a mole of ideal gas we can use the gas law to integrate volume over pressure and we get

$$\Delta G_{molar} = RT \ln\left(\frac{P_2}{P_1}\right)$$

It is customary to identify one of the pressures (P_1} with the *standard state* of **1 bar** and use the plimsoll to indicate the fact that we are referring to a standard state by writing:

$$G_{molar}(P) = G^o_{molar} + RT \ln\left(\frac{P}{1}\right) = G^o_{molar} + RT \ln[P]$$

The fact that we are making the function intensive (per mole) is usually indicated by putting a bar over the G symbol, although this is often omitted for $G^{\ominus}_{molar}$

9.6.0.1: Solids

For solids the volume does not change very much with pressure (the *isothermal compressibility* κ is small), so can assume it more or less constant:

$$G(P_{final}) = G(P_{initial}) + \int V dP(\text{from init to final})$$
$$\approx G(P_{initial}) + V \int dP(\text{from init to final}) = G(P_{initial}) + V\Delta P$$

9.6.1: The Gibbs-Helmholtz Expression

$$\frac{G}{T} = \frac{H}{T} - S$$

Take the derivative under constant pressure of each side to get

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2} + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P$$

We make use of the relationship between C_p and H and C_p and S

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2} + \frac{C_P}{T} - \frac{C_P}{T} \tag{9.6.1}$$
$$= -\frac{H}{T^2} \tag{9.6.2}$$

We said before that S is a first order derivative of G. As you can see from this derivation the enthalpy H is also a first order derivative, albeit not of G itself, but of G/T.

$$\left(\frac{\partial \Delta G/T}{\partial T}\right)_P = -\frac{\triangle H}{T^2}$$

The last step in the derivation simply takes the step before twice -say for the G and H at the begin and end of a *process*- and subtracts the two identical equations leading to a Δ symbol. In this differential form the Gibbs-Helmholtz equation can be applied to any process.

9.6.2: Gibbs Energy as a Function of Temperature

If heat capacities are know from 0 K we could determine both enthalpy and entropy by integration:

$$S(T) = S(0) + \int_0^T \frac{C_p}{T} dT$$

$$H(T) = H(0) + \int_0^T C_p \, dT$$

As we have seen we must be careful at phase transitions such as melting or vaporization. At these points the curves are *discontinuous* and the derivative C_p is undefined.

$$H(T) = H(0) + \int_0^{T_{fus}} C_p(T)_{solid} dT + \Delta H_{fus} + \int_{T_{fus}}^{T_{boil}} C_p(T)_{liquid} dT + \Delta H_{vap} + etc. \tag{9.6.3}$$

$$S(T) = S(0) + \int_0^{T_{fus}} \frac{C_p(T)_{solid}}{T} dT + \Delta S_{fus} + \int_{T_{fus}}^{T_{boil}} \frac{C_p(T)_{liquid}}{T} dT + \Delta S_{vap} + etc. \tag{9.6.4}$$

$$= S(0) + \int_0^{T_{fus}} \frac{C_p(T)_{solid}}{T} dT + \frac{\Delta H_{fus}}{T_{fus}} + \int_{T_{fus}}^{T_{boil}} \frac{C_p(T)_{liquid}}{T} dT + \frac{\Delta H_{vap}}{T_{boil}} + etc. \tag{9.6.5}$$

with $H(T = 0) = \textbf{undefined}$ and $S(T = 0) = 0$ from the third law of thermodynamics.

> We also discussed the fact that the third law allows us to define $S(0)$ as zero in most cases. For the enthalpy we cannot do that so that our curve is with respect to an undefined zero point. We really should plot $H(T) - H(0)$ and leave $H(0)$ undefined.

Because the Gibbs free energy $G = H - TS$ we can also construct a curve for G as a function of temperature, simply by combining the H and the S curves (Equations 9.6.3 and 9.6.5):

$$G(T) = H(T) - TS(T)$$

Interestingly, if we do so, the **discontinuties** at the phase transition points will **drop out** for G because at these points $\Delta_{trs}H = T_{trs}\Delta_{trs}S$. Therefore, G is **always** continuous.

The $H(0)$ problem does not disappear so that once again our curve is subject to an arbitrary offset in the y-direction. The best thing we can do is plot the quantity $G(T) - H(0)$ and leave the offset $H(0)$ undefined.

We have seen above that the derivative of G with temperature is $-S$. As entropy is always positive, this means that the G-curve is always *descending* with temperature. It also means that although the curve is *continuous* even at the phase transitions, the slope of the G curve is not, because the derivative $-S$ makes a jump there. Fig. 22.7 in the book shows an example of such a curve for benzene. Note the kinks in the curve at the mp and the boiling point.

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CHAPTER OVERVIEW

10: Phase Equilibria

Phase equilibria is the term used to describe with two or more phases co-exist (in equilibrium). The stability of phases can be predicted by the chemical potential, in that the most stable form of the substance will have the minimum chemical potential at the given temperature and pressure. A key tool in exploring phase equilibria is a phase diagram which is used to show conditions (pressure, temperature, volume, etc.) at which thermodynamically distinct phases (such as solid, liquid or gaseous states) occur and coexist at equilibrium.

10.1: A Phase Diagram Summarizes the Solid-Liquid-Gas Behavior of a Substance

10.2: Gibbs Energies and Phase Diagrams

10.3: The Chemical Potentials of a Pure Substance in Two Phases in Equilibrium

10.4: The Clausius-Clapeyron Equation

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10.1: A Phase Diagram Summarizes the Solid-Liquid-Gas Behavior of a Substance

A good map will take you to your destination with ease, provided you know how to read it. A map is an example of a *diagram*, a pictorial representation of a body of knowledge. In science they play a considerable role. Next to plots and tables *diagrams* are an important means of making information and/or theoretical knowledge accessible.

Constructing them takes quite a bit of thought. You want to represent as much of what you know and give as accurate a picture of it without conveying anything incorrect. If the drawing can be made to scale that makes it quite a bit more powerful, but this is not strictly necessary. A remark like *not to scale* or *schematically* does need to be given if applicable. A good caption or description is essential.

10.1.1: Thermodynamic Stability and Fluctuations

There are different kinds of equilibrium, besides the ***stable*** equilibrium that represents an absolute minimum in the G function. Of course G is potentially a function of a great number of variables, but let us look at a *diagram* in which G is shown as a function of only one unspecified variable. You could think of the density, the mole fraction of one of the components of a mixture or an applied electrical field or whatever, but the argument is general.

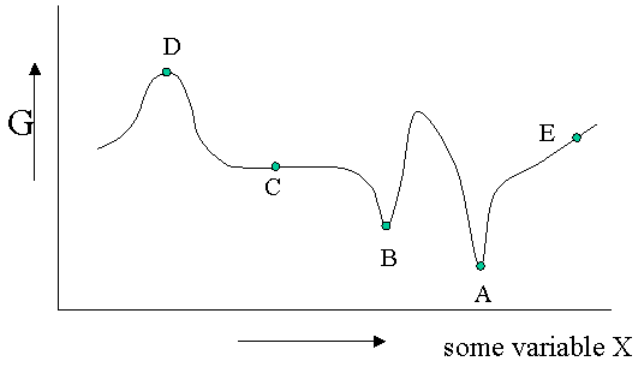


Figure 23.1.1 : A schematic G curve showing various Points of stability. Due to statistical fluctuations the value of G is not quite constant over time, because less likely realizations of the ensemble (having a slightly less favorable value of G) do occur from time to time. After all, the Boltzmann distribution is simply the most likely one, not the only one possible. The fluctuations have drastically different consequences depending on whether the system is in an unstable (E), labile (D) , indifferent (C), metastable (B) or stable (A) state. Notice that A and B just wobble around a bit. C fluctuates wildly in the value of X, while both E and D eventually vanish because the system transits to a more favorable state. For E this starts immediately, for D it starts once fluctuation has caused it to move from its peak sufficiently.

Figure 23.1.1 is helpful to point out that besides a stable equilibrium (A) there can also be an ***metastable*** equilibrium (B) or an ***indifferent*** equilibrium (C). The local derivatives of G (versus *all* variables of which we only show one) are zero in all three cases, which means that changes in the variables are *not spontaneous*. For a ***labile*** equilibrium (D) the opposite is true. Any small deviation will make the system role down hill. (Note that the second derivative has the opposite sign compared to cas A) and B)) A labile equilibrium is seldom or never observed except in a circus where artists delight in balancing objects on their heads (because you pay for it).. This usually requires continuous small corrections to maintain the precarious balance. All other points in our diagram represent state of ***instability*** because locally dG is not zero and a spontaneous process can take place.

The fact that $dG = 0$ in the equilibrium points does not mean small deviations from the minimum cannot happen at times. We have seen e.g. that the Boltzmann distribution was simply *the most likely* distribution. The most likely one is the one that has the highest number of realizations W. Another way of saying that is that it is the one with the highest entropy S. A slightly less likely distribution may occur from time to time by chance. It will have a little less entropy, but the same $\langle E \rangle$. That means it will have a slightly higher G ($G = H - TS$). From time to time therefore G will fluctuate a bit. Such fluctuations are very small for large systems, but they are of greater relative importance for small systems (like a nanoparticle). (Statistical averaging works best on large ensembles.)

The fluctuations in G mean that small fluctuations in its variables like density etc. can also occur. They are usually kept in check, because dG is no longer zero when moving away from the equilibrium state. This drives the system back to the minimum

spontaneously. You could picture the system wobbling a bit around in its G-well. This holds for stable and metastable equilibria alike.

In the indifferent case (C) however the derivative is zero (or very close to zero) for a *range* of neighboring values of some variable. In contrast to A and B also the *second derivative* is zero. This means that there is little penalty to much larger deviations in the variable. If this variable is the density the system becomes milky and shows *opalescence* a strong scattering of light because the refractive index depends on the strongly fluctuating density. This is observed near critical points and is called *critical opalescence*.

10.1.2: Unary Phase Diagrams

A unary phase diagram summarizes the equilibrium states of a single pure substance. We will see that we can also look at mixtures of two components (binary diagrams) or more (ternary, quaternary, quinary, senary etc.). Usually a phase diagram only maps out stable equilibria, but occasionally metastable ones may be given too (e.g., with a dashed line).

10.1.2.0.1: Liquid-Vapor Equilibrium Curve

We have seen that the Gibbs function G depends strongly (logarithmically) on pressure for a gas, but only slightly (and linearly) for a liquid. The two curves intersect in a point representing the *equilibrium vapor pressure* of the liquid. At lower pressures the vapor is more stable, at higher ones the liquid. (For a solid the same holds as for the liquid). This means that except at the intersection point we only will observe one phase.

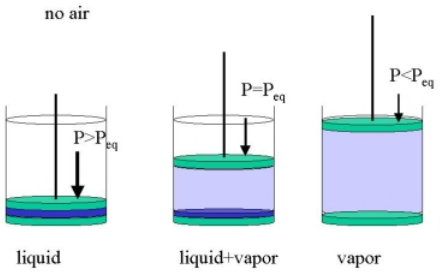


Figure 23.1.2 *: A cylinder with one substance*

It is important to stress that this holds *in the absence of other matter*, e.g., when we put only water into an evacuated cylinder (Figure 23.1.2). We may get three cases:

- we compress the cylinder until it only contains the liquid under hydrostatic pressure ($P > P_{eq}$)
- we expand the cylinder until all water has vaporized ($P < p_{eq}$)>
- we let part of the water evaporate, just enough so that the space above the liquid is filled with an equilibrium vapor pressure ($P = P_{eq}$)

At room temperature P_{eq} for water is only about 15 Torr. If we apply 1 bar -or let the atmosphere do the job- we will only have liquid water. If other gases are present, e.g., air, we must distinguish between the total pressure (e.g., 1 bar) and the equilibrium vapor pressure which will now be the *partial* pressure. In a cylinder with water and one bar of air just enough water will evaporate to establish equilibrium. The evaporation will be limited to the gas-liquid interface unless the partial pressure equals the total pressure. Then the liquid will *boil*.

> *(Do allow the volume to expand, though., why? If the volume is constant the pressure builds up and boiling will stop.*

If we consider the set of equilibrium pressures as a function of temperature and plot that in a P vs. T diagram we have one component of our phase diagram.

10.1.2.0.1: Gas-solid Equilibrium Curve

For solids the situation is similar as the $G(P)$ curve is once again an almost flat straight line. The intersection with the logarithmic curve for the gas will define an equilibrium pressure for gas-solid co-existence. Generally vapor pressures above solids are quite

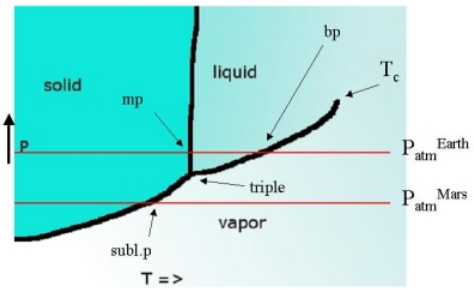
small, but not negligible. As for liquids we can construct a line representing the equilibrium pressures for sublimation as function of temperature and add it to the phase diagram.

10.1.2.0.1: Liquid-solid Equilibrium Curve

The $\mathbf{solid \rightleftharpoons liquid}$ equilibrium is known as **melting** or **freezing** is not very dependent on pressure. Usually melting points increase a little bit with pressure, although water is a peculiar exception. It expands upon freezing and the melting point goes down (a bit) with pressure. In our diagram this will represent an almost vertical line leaning a little forwards for most substances, but backwards for water and a few others.

10.1.2.1: Putting the Curve Together

The three lines come together in the *triple point*, the only point where all three phases are at equilibrium with each other. For water, its temperature is only 0.01 K different from the normal melting point (273.16 K) and its pressure is only 4.58 Torr. The intersection points with a line representing atmospheric pressure give the melting and boiling points at that pressure.



A typical unary diagram

If the triple point lies above the line that represents atmospheric pressure this implies that a liquid is never observed. On earth CO_2 is such a substance. The intersection of the solid-vapor equilibrium line with the 1 bar line represents a state where the solid will *'boil'* (evaporate from inside out). This is known as the *sublimation point*. The melting points at P=1 bar are known as the *standard melting point*, the only slightly different one at 760 Torr = 1 atm is called *normal melting point*. The same goes for boiling and sublimation points.

There is *nothing magical* about $\boldsymbol{P = 1\ bar}$. It just happens to be the pressure of our home planet. On a planet with higher atmospheric pressures $\boldsymbol{CO_2}$ may well be a liquid and on such a planet, all boiling points will be quite different (higher than on earth). The melting points will also differ, but only slightly so. On Mars where atmospheric pressure is much lower water can not occur in liquid form, much like carbon dioxide on earth - it sublimes.

We should also realize that in a *closed container* (glass ampoule, hermetically sealed DSC pan), we can observe melting points at only very slightly different temperature values, but we will ***not*** see a boiling effect. Why?

To see a boiling point the container must be open to the (*constant!*) 1 bar pressure of the earths atmosphere that ***defines*** it and causes the boiling phenomenon. If the ampoule is sealed it will generate its *own* (autogenous) pressure, depending on what you put in, how much of it in relation to the volume, how volatile it is and the temperature. The autogenous pressure does not interfere with the melting point much (the melting line is almost vertical), but as $\boldsymbol{P}$ changes with temperature you may never reach boiling conditions.

In DSC experiments it is possible to observe boiling points only if the pan has been carefully *perforated* with a hole of known size. It must be big enough that the pressure inside the pan does not build up above atmospheric, but small enough that it does not cause premature loss of mass during the run. The latter spoils the calculation of the intensive value (per mole, per gram) of the heat of vaporization.

The liquid evaporation line ends in a point that we have encountered before: the critical point $\boldsymbol{T_C}$. As temperature increases the liquid and vapor phases in equilibrium with each other start to resemble each other more and more and at $\boldsymbol{T_c}$ they coalesce. At

this point the liquid-gas equilibrium becomes indifferent with respect to density and large fluctuations occur leading to critical opalescence.

Notice that there is a relationship of dimensionality between the objects in the diagram and the number of phases present:

- 2 D planes: one phase
- 1 D curves: two phases
- 0 D point: three phases

As you see the sum is always three.

10.1.3: Number of moles

So far we have typically considered one substance at the time, but for chemists it is imperative to deal with more than one because we are typically changing one into the other in our reactions. This means that the number of moles n, that we often simply set equal to one now becomes an important variable in its own right. Besides we will actually have two (or more) of them: the number of moles of component one and the one for the other component. This makes n a much less trivial variable.

This is already the case at a simple melting point, say when ice melts, because we are dealing with changing quantities of ice and water:

$$n_{ice} + n_{water} = n_{total}$$

If all we do is turn water into ice or vice versa, we have $dn_{total} = 0$, so that:

$$dn_{ice} = -dn_{water}$$

To deal with changing n's, we need to expand our mathematical notation a bit.

10.1.3.1: Partial variables

So far we have simply divided our thermodynamic functions if they were extensive by the number of moles and arrived at intensive molar values:

$$G_{molar} = \frac{G}{n}$$

$$V_{molar} = \frac{V}{n}$$

We have written such intensive molar values by writing a bar over the symbol G or V. We should note that scaling the function this way departs from the assumption that the function G depends on the variable n as a straight line that passes through the origin.

If we have the same pure compound in two phases, like ice and water we can still apply this principle and write:

$$G^{ice}_{molar} = \frac{G^{ice}}{n^{ice}}$$

$$V^{ice}_{molar} = \frac{V^{ice}}{n^{ice}}$$

$$G^{water}_{molar} = \frac{G^{water}}{n^{water}}$$

$$V^{water}_{molar} = \frac{V^{water}}{n^{water}}$$

If we have a ***mixture*** of two substances present as n_1 and n_2 moles the dependency need not be linear on either if the two substances interact with each other. This is also true for function like the volume of a liquid mixture. In the presence of interactions volumes do *not* have to be linearly additive. We can define a partial molar value of e.g. for the volume:

$$V_{partialmolar,1} = \frac{\partial V}{\partial n_1}$$

at n_2 = constant

$$V_{partialmolar,2} = \frac{\partial V}{\partial n_2}$$

at n_1 = constant

The notation of putting a bar over the V symbol is used for these partial quantities as well. Partial molar volumes have been measured for many binary systems. They are functions of the composition (mole fraction) as well as the temperature and to a lesser extent the pressure.

The partial molar Gibbs free energy

The partial molar Gibbs free energy ($\left(\frac{\partial G}{\partial n_i}\right)_{P,T}$, all other n's) is denoted with μ and is called the thermodynamic potential.

When numbers of moles can change we can write the corresponding change in G as:

$$dG = -SdT + VdP + \sum_i^N \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_{j \neq i}} dn_i$$

$$dG = -SdT + VdP + \sum_i^N \mu_i dn_i$$

over N phases in the system. As you can see we are adding a set of conjugate variables $\mu_i n_i$ for each phase i. If we are considering a *pure* component (but in different modifications, like ice and steam), we can still write:

$$\mu_i = \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_{j \neq i}} = \frac{G_i}{n_i}$$

As soon as we are dealing with mixtures we really do have derivatives.

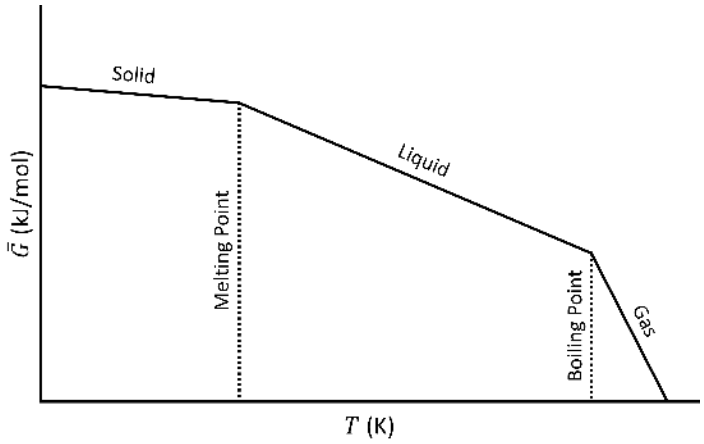
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10.2: Gibbs Energies and Phase Diagrams

10.2.1: First Order Transitions

The following plot shows the Gibbs energy as a function of temperature, including phase changes from solid to liquid (melting) and liquid to gas (boiling).



Gibbs energy ($\bar{G}$) as a function of temperature (T).

Although the G curve is continuous, its first order derivatives ($-S$) is discontinuous at the phase changes. This is why this transition it called a *first order transition*. We could say that:

- G is continuous but has a kink
- The first order derivatives (H,S,..) are discontinuous (have a jump)
- The second order derivatives (C_P, ..) have a singularity (go to ∞)

10.2.2: Second Order Transitions

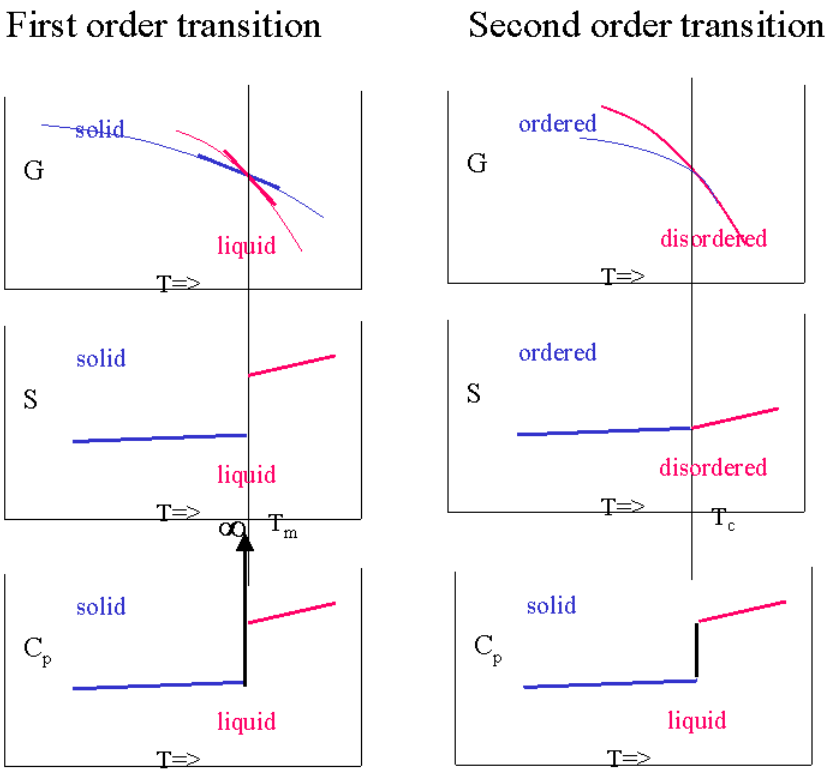
More subtle transitions where G is continuous, H and S are also continuous but have a kink and the discontinuity is only found in the second order derivatives (such as C_P) also exist. They are called *second order transitions*. In such a case:

- G is continuous and has no kink
- The first order derivatives (H,S,..) are continuous (but have a kink)
- The second order derivatives (C_P, ..) are discontinuous (have a jump)

Table 23.2.1: Properties of Phase Transitions

Transition Order	Function	1st Order	2nd Order
0	G,A	kink	smooth
1	H,S,V,..	jump	kink
2	CP,CV,α,κ	sing. ∞	jump

This classification goes back to Ehrenfest. Obviously it based on the question: what order derivative is the first to go discontinuous? Of course we could extend this principle and define *third order transitions* but there are reasons to be doubtful that such things exist. Another problem is that it is assumed that the order must be integer: 1,2, etc. Is it possible to have a transition of intermediate non-integer order, say 1.3? Although derivatives of fractional order are beyond the scope of the chemistry curriculum the mathematics does exist (Liouville).



Schematic comparison of G, S and C_P for 1st and 2nd order transitions

The Gibbs free energy is a particularly important function in the study of phases and phase transitions. The behavior of $G(N,P,T)$, particularly as a function of P and T, can signify a phase transition and can tell us some of the thermodynamic properties of different phases.

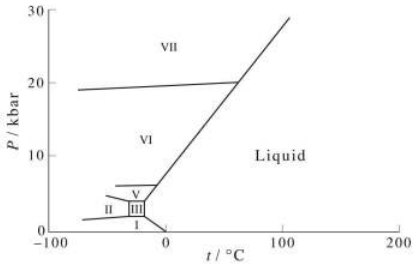


Figure 13.4: Some of the ice polymorphs.

Consider, first, the behavior of G vs. T between the solid and liquid phases of benzene: We immediately notice several things. First, although the free energy is continuous across the phase transition, its first derivative, $\partial G/\partial T$ is not: The slope of $G(T)$ in the solid region is different from the slope in the liquid region. When the first derivative of the free energy with respect to one of its dependent thermodynamic variables is discontinuous across a phase transition, this is an example of what is called a *first order phase transition*. The solid-liquid-gas phase transition of most substances is first order. When the free energy exhibits continuous first derivatives but discontinuous second derivatives, the phase transition is called *second order*. Examples of this type of phase transition are the order-disorder transition in paramagnetic materials.

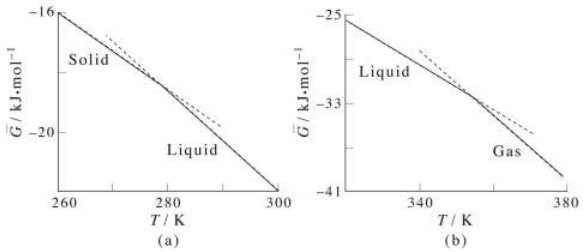


Figure 13.5: Behavior of the Gibbs free energy across the solid-liquid phase (left) and liquid-gas (right) transitions for benzene.

Now, recall that

$$S = -\frac{\partial G}{\partial T} \tag{10.2.1}$$

Consider the slopes in the solid and liquid parts of the graph:

$$\frac{\partial G^{(\text{solid})}}{\partial T} = -S^{(\text{solid})}, \quad \frac{\partial G^{(\text{liquid})}}{\partial T} = -S^{(\text{liquid})} \tag{10.2.2}$$

However, since

$$\frac{\partial G^{(\text{liquid})}}{\partial T} < \frac{\partial G^{(\text{solid})}}{\partial T} \tag{10.2.3}$$

(*note that the slopes are all negative, and the slope of the liquid line is more negative than that of the solid line*), it follows that $-S^{(\text{liquid})} < -S^{(\text{solid})}$ or $S^{(\text{liquid})} > S^{(\text{solid})}$. This is what we might expect considering that the liquid phase is higher in entropy than the solid phase. The same argument can be made with regards to the gaseous phase.

Similarly, if we consider the dependence of G on pressure, we obtain a curve like that shown in the figure below:

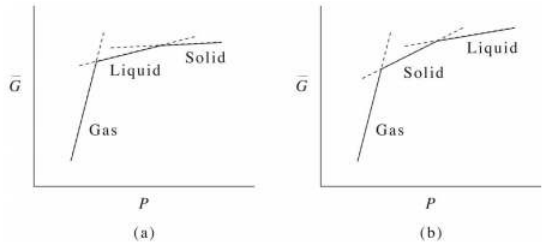


Figure 13.6: Dependence of the Gibbs free energy as a function of pressure for benzene (left) and water (right). For benzene, the temperature is above the triple point, whereas for water, it is set below triple point.

As noted previously, here again, we see that the first derivative of $\bar{G}(P)$ is discontinuous, signifying a first-order phase transition. Recalling that the average molar volume is

$$\bar{V} = \frac{\partial \bar{G}}{\partial P} \tag{10.2.4}$$

From the graph, we see that the slopes obey

$$\bar{V}^{(\text{gas})} \gg \bar{V}^{(\text{liquid})} > \bar{V}^{(\text{solid})} \tag{10.2.5}$$

as one might expect for a normal substance like benzene at a temperature above its triple point. Because the temperature is above the triple point, the free energy follows a continuous path (even though it is not everywhere differentiable) from gas to liquid to solid.

On the other hand, for water, we see something a bit different, namely, that

$$\bar{V}^{(\text{gas})} \gg \bar{V}^{(\text{solid})} > \bar{V}^{(\text{liquid})} \tag{10.2.6}$$

at a temperature below the triple point. This, again, indicates, the unusual property of water that its solid phase is less dense than its liquid phase in the coexistence region.

Interestingly, if we look at how the plot of $G(P)$ changes with T, we obtain a plot like that shown below: Below the triple point, it is easy to see from the benzene phase diagram that the system proceeds directly from solid to gas. There is a liquid curve on this plot that is completely disconnected from the gas-solid curve, suggesting that, below the triple point, the liquid state can exist metastably if at all. AT the triple point, the solid can transition into the liquid or gas phases depending on the value of the free energy. Near the critical temperature, we see the liquid-gas transition line, while the solid line is disconnected. Above the critical temperature, the system exists as a supercritical fluid, which is shown on the lower line, and this line now shows derivative discontinuity.

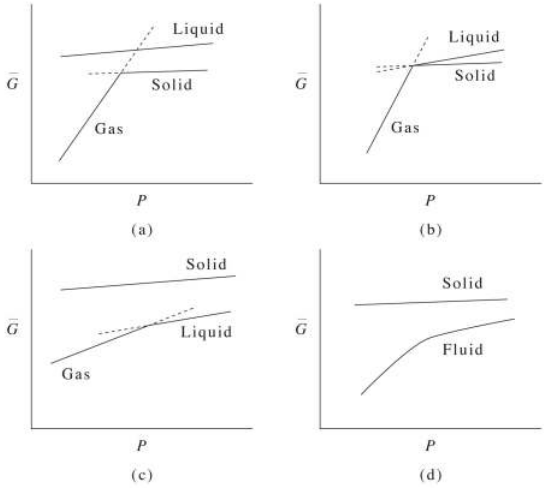


Figure 13.7: Behavior of the Gibbs free energy as a function of P across different phases at different temperatures for benzene. (a): Temperature is less than the triple point; (b): Temperature is equal to the triple point; (c): Temperature is just below the critical temperature; (d): Temperature is greater than the critical temperature.

10.2.3: Conjugate Variables

As discussed before there are many other forms of work possible, such as electrical work, magnetic work or elastic work. These they are commonly incorporated in the formalism of thermodynamics by adding other terms, e.g:

$$dG = -SdT + VdP + \mathcal{E}de + MdH + FdL + \gamma dA$$

1. $\mathcal{E}de$ stands for the electromotoric force $\mathcal{E}$ and de the amount of charge transported against it.
2. MdH stand for magnetization and (change in) magnetic field.
3. F stands for the elastic force of e.g. a rubber band dL for the length it is stretched
4. γ stands for the surface tension (e.g. of a soap bubble), A for its surafce area.

The terms always appear in a pair of what is known as conjugate variables. That is even clearer if we write out the state function rather than its differential form:

$$G = U + PV - TS + \mathcal{E}e + MH + FL + \gamma A + ...$$

The PV term can also be generalized -and needs to be so- for a viscous fluid to a stress-strain conjugate pair. It then involves a stress tensor. We will soon encounter another conjugate pair: μdn that deals with changes in composition (n) and the thermodynamic potential μ.

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10.3: The Chemical Potentials of a Pure Substance in Two Phases in Equilibrium

10.3.1: Chemical Potential of Two Phases in Equilibrium

Equilibrium between two phases, e.g. water ice (ice) and liquid water ($water$), is at constant T and P. Therefore:

$$dG = \cancel{-SdT + VdP} + \mu_{ice}dn_{ice} + \mu_{water}dn_{water}$$

There is a relationship between the amount of ice and water:

$$dn_{ice} = -dn_{water}$$

From this, we get:

$$0 = [\mu_{ice} - \mu_{water}]dn_{water} = \Delta\mu\ dn_{water}$$

As dn_{water} is not zero, this means that $\Delta\mu$ must be zero! This must hold true for any set of points where ice and water are in equilibrium. The statement is not just for liquid and solid water, but for any two phases in equilibrium. That is, any two phases in equilbrium will always have the same chemical potential.

10.3.2: The Clapeyron Equation

That is the almost vertical line in the diagram. Its points are not at the same P and T, but we can find out where they should be by considering the thermodynamic potential μ as a *function* of T and P:

$$d\mu = \left(\frac{\partial\mu}{\partial P}\right)_T dT + \left(\frac{\partial\mu}{\partial T}\right)_P dP$$

Because $\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} = \bar{G}$, it is not hard to identify the partial derivatives:

$$\left(\frac{\partial\mu}{\partial P}\right) = \left(\frac{\partial\bar{G}}{\partial P}\right) = \bar{V}$$

$$\left(\frac{\partial\mu}{\partial T}\right) = \left(\frac{\partial\bar{G}}{\partial T}\right) = -\bar{S}$$

This is true for both water and ice, or any two phases in equilibrium. As the $\Delta\mu = 0$, we can equate the $d\mu$ expressions for both water and ice:

$$\left(\frac{\partial\mu_{ice}}{\partial P}\right)_T dT + \left(\frac{\partial\mu_{ice}}{\partial T}\right)_P dP = \left(\frac{\partial\mu_{water}}{\partial P}\right)_T dT + \left(\frac{\partial\mu_{water}}{\partial T}\right)_P dP$$

Rearranging and identifying the partials gives:

$$\bar{V}_{ice}dP - \bar{S}_{ice}dT = \bar{V}_{water}dP - \bar{S}_{water}dT$$

Solving for dP/dT we get:

$$\frac{dP}{dT} = \frac{\Delta\bar{S}}{\Delta\bar{V}}$$

As $\Delta\bar{G} = \Delta\bar{H} - T\Delta\bar{S} = 0$, we have:

$$\Delta\bar{S} = \frac{\Delta\bar{H}}{T_m}$$

So:

$$\frac{dP}{dT} = \frac{\Delta\bar{H}}{T\Delta\bar{V}}$$

This expression should be valid for all points along a phase boundary, such as the melt line. In fact, it tells use that the phase boundary is **defined** by $\Delta\bar{H}/T\Delta\bar{V}$. For water and ice, we immediately see why the melt line runs a little to the left: exceptionally

$\Delta\bar{V}$ is negative for ice, because water is actually a little denser that ice.

The above expression(s) are named after ***Clapeyron.*** The values of $\Delta\bar{H}$ and $\Delta\bar{V}$ do not change much with pressure and can often be considered *constants* for the melting line. When gases are involved that is not really true.

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10.4: The Clausius-Clapeyron Equation

10.4.1: Evaporation

In Section 23.3, the Clapeyron Equation was derived for melting points.

$$\frac{dP}{dT} = \frac{\Delta H_{molar}}{T\Delta V_{molar}}$$

However, our argument is actually quite general and should hold for vapor equilibria as well. The only problem is that the molar volume of gases are by no means so nicely constant as they are for condensed phases. (i. e., for condenses phases, both α and κ are pretty small).

We can write:

$$\frac{dP}{dT} = \frac{\Delta H_{molar}}{T\Delta V_{molar}} = \frac{\Delta H_{molar}}{T}\left[V_{molar}^{gas} - V_{molar}^{liquid}\right]$$

as

$$V_{molar}^{gas} \gg V_{molar}^{liquid}$$

we can approximate

$$V_{molar}^{gas} - V_{molar}^{liquid}$$

by just taking V_{molar}^{gas}. Further more if the vapor is considered an ideal gas, then

$$V_{molar}^{gas} = \frac{RT}{P}$$

We get

$$\frac{1}{P}\cdot\frac{dP}{dT} = \frac{d\ln P}{dT} = \frac{\Delta H_{molar}^{vap}}{RT^2} \tag{10.4.1}$$

Equation 10.4.1 is known as the **Clausius-Clapeyron** equation. We can further work our the integration and find the how the equilibrium vapor pressure changes with temperature:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{molar}^{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Thus if we know the molar enthalpy of vaporization we can predict the vapor lines in the diagram. Of course the approximations made are likely to lead to deviations if the vapor is not ideal or very dense (e.g., approaching the critical point).

10.4.2: The Clapeyron Equation

The Clapeyron attempts to answer the question of what the shape of a two-phase coexistence line is. In the $P-T$ plane, we see the a function $P(T)$, which gives us the dependence of P on T along a coexistence curve.

Consider two phases, denoted α and β, in equilibrium with each other. These could be solid and liquid, liquid and gas, solid and gas, two solid phases, et. Let $\mu_\alpha(P,T)$ and $\mu_\beta(P,T)$ be the chemical potentials of the two phases. We have just seen that

$$\mu_\alpha(P,T) = \mu_\beta(P,T) \tag{10.4.2}$$

Next, suppose that the pressure and temperature are changed by dP and dT. The changes in the chemical potentials of each phase are

$$d\mu_\alpha(P,T) = d\mu_\beta(P,T) \tag{10.4.3}$$

$$\left(\frac{\partial\mu_\alpha}{\partial P}\right)_T dP + \left(\frac{\partial\mu_\alpha}{\partial T}\right)_P dT = \left(\frac{\partial\mu_\beta}{\partial P}\right)_T dP + \left(\frac{\partial\mu_\beta}{\partial T}\right)_P dT \tag{10.4.4}$$

However, since $G(n,P,T) = n\mu(P,T)$, the *molar* free energy $\bar{G}(P,T)$, which is $G(n,P,T)/n$, is also just equal to the chemical potential

$$\bar{G}(P,T) = \frac{G(n,P,T)}{n} = \mu(P,T) \tag{10.4.5}$$

Moreover, the derivatives of $\bar{G}$ are

$$\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}, \qquad \left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S} \tag{10.4.6}$$

Applying these results to the chemical potential condition in Equation 10.4.4, we obtain

$$\left(\frac{\partial \bar{G}_\alpha}{\partial P}\right)_T dP + \left(\frac{\partial \bar{G}_\alpha}{\partial T}\right)_P dT = \left(\frac{\partial \bar{G}_\beta}{\partial P}\right)_T dP + \left(\frac{\partial \bar{G}_\beta}{\partial T}\right)_P dT \tag{10.4.7}$$

$$\bar{V}_\alpha dP - \bar{S}_\alpha dT = \bar{V}_\beta dP - \bar{S}_\beta dT \tag{10.4.8}$$

Dividing through by dT, we obtain

$$\bar{V}_\alpha \frac{\partial P}{\partial T} - \bar{S}_\alpha = \bar{V}_\beta \frac{\partial P}{\partial T} - \bar{S}_\beta \tag{10.4.9}$$

$$(\bar{V}_\alpha - \bar{V}_\beta)\frac{\partial P}{\partial T} = \bar{S}_\alpha - \bar{S}_\beta \tag{10.4.10}$$

$$\frac{dP}{dT} = \frac{\bar{S}_\alpha - \bar{S}_\beta}{\bar{V}_\alpha - \bar{V}_\beta} \tag{10.4.11}$$

The importance of the quantity dP/dT is that is represents the slope of the coexistence curve on the phase diagram between the two phases. Now, in equilibrium $dG = 0$, and since $G = H - TS$, it follows that $dH = T\,dS$ at fixed T. In the narrow temperature range in which the two phases are in equilibrium, we can assume that H is independent of T, hence, we can write $S = H/T$. Consequently, we can write the molar entropy difference as

$$\bar{S}_\alpha - \bar{S}_\beta = \frac{\bar{H}_\alpha - \bar{H}_\beta}{T} \tag{10.4.12}$$

and the pressure derivative dP/dT becomes

$$\frac{dP}{dT} = \frac{\bar{H}_\alpha - \bar{H}_\beta}{T(\bar{V}_\alpha - \bar{V}_\beta)} = \frac{\Delta_{\alpha\beta}\bar{H}}{T\Delta_{\alpha\beta}\bar{V}} \tag{10.4.13}$$

a result known as the **Clapeyron equation**, which tells us that the slope of the coexistence curve is related to the ratio of the molar enthalpy between the phases to the change in the molar volume between the phases. If the phase equilibrium is between the solid and liquid phases, then $\Delta_{\alpha\beta}\bar{H}$ and $\Delta_{\alpha\beta}\bar{V}$ are $\Delta\bar{H}_{\text{fus}}$ and $\Delta\bar{V}_{\text{fus}}$, respectively. If the phase equilibrium is between the liquid and gas phases, then $\Delta_{\alpha\beta}\bar{H}$ and $\Delta_{\alpha\beta}\bar{V}$ are $\Delta\bar{H}_{\text{vap}}$ and $\Delta\bar{V}_{\text{vap}}$, respectively.

For the liquid-gas equilibrium, some interesting approximations can be made in the use of the Clapeyron equation. For this equilibrium, Equation 10.4.13 becomes

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{\text{vap}}}{T(\bar{V}_g - \bar{V}_l)} \tag{10.4.14}$$

In this case, $\bar{V}_g \gg \bar{V}_l$, and we can approximate Equation 10.4.14 as

$$\frac{dP}{dT} \approx \frac{\Delta\bar{H}_{\text{vap}}}{T\bar{V}_g} \tag{10.4.15}$$

Suppose that we can treat the vapor phase as an ideal gas. Certainly, this is not a good approximation so close to the vaporization point, but it leads to an example we can integrate. Since $PV_g = nRT$, $P\bar{V}_g = RT$, Equation 10.4.15 becomes

$$\frac{dP}{dT} = \frac{\Delta \bar{H}_{\text{vap}} P}{RT^2} \tag{10.4.16}$$

$$\frac{1}{P}\frac{dP}{dT} = \frac{\Delta \bar{H}_{\text{vap}}}{RT^2} \tag{10.4.17}$$

$$\frac{d \ln P}{dT} = \frac{\Delta \bar{H}_{\text{vap}}}{RT^2} \tag{10.4.18}$$

which is called the ***Clausius-Clapeyron equation***. We now integrate both sides, which yields

$$\ln P = -\frac{\Delta \bar{H}_{\text{vap}}}{RT} + C$$

where C is a constant of integration. Exponentiating both sides, we find

$$P(T) = C' e^{-\Delta \bar{H}_{\text{vap}}/RT}$$

which actually has the wrong curvature for large T, but since the liquid-vapor coexistence line terminates in a critical point, as long as T is not too large, the approximation leading to the above expression is not that bad.

If we, instead, integrate both sides, the left from P_1 to P_2, and the right from T_1 to T_2, we find

$$\int_{P_1}^{P_2} d \ln P = \int_{T_1}^{T_2} \frac{\Delta \bar{H}_{\text{vap}}}{RT^2} dT \tag{10.4.19}$$

$$\ln \left(\frac{P_2}{P_1} \right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{10.4.20}$$

$$= \frac{\Delta \bar{H}_{\text{vap}}}{R} \left(\frac{T_1 - T_1}{T_1 T_2} \right) \tag{10.4.21}$$

assuming that $\Delta \bar{H}_{\text{vap}}$ is independent of T. Here P_1 is the pressure of the liquid phase, and P_2 is the pressure of the vapor phase. Suppose we know P_2 at a temperature T_2, and we want to know P_3 at another temperature T_3. The above result can be written as

$$\ln \left(\frac{P_3}{P_1} \right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R} \left(\frac{1}{T_3} - \frac{1}{T_1} \right) \tag{10.4.22}$$

Subtracting the two results, we obtain

$$\ln \left(\frac{P_2}{P_3} \right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_3} \right) \tag{10.4.23}$$

so that we can determine the vapor pressure at any temperature if it is known as one temperature.

In order to illustrate the use of this result, consider the following example:

Example 23.4.1

At $1\ \text{bar}$, the boiling point of water is $373\ \text{K}$. At what pressure does water boil at $473\ \text{K}$? Take the heat of vaporization of water to be $40.65\ \text{kJ/mol}$.

Solution

Let $P_1 = 1\ \text{bar}$ and $T_1 = 373\ \text{K}$. Take $T_2 = 473\ \text{K}$, and we need to calculate P_2. Substituting in the numbers, we find

$$\ln P_2(\text{bar}) = -\frac{(40.65\ \text{kJ/mol})(1000\ \text{J/kJ})}{8.3145\ \text{J/mol} \cdot \text{K}} \left(\frac{1}{473\ \text{K}} - \frac{1}{373\ \text{K}} \right) = 2.77 \tag{10.4.24}$$

$$P_2(\text{bar}) = (1\ \text{bar})\, e^{2.77} = 16\ \text{bar} \tag{10.4.25}$$

Learning Objectives

- Apply the Clausius-Clapeyron equation to estimate the vapor pressure at any temperature.
- Estimate the heat of phase transition from the vapor pressures measured at two temperatures.

The *vaporization curves* of most liquids have similar shapes with the vapor pressure steadily increasing as the temperature increases (Figure 10.4.1).

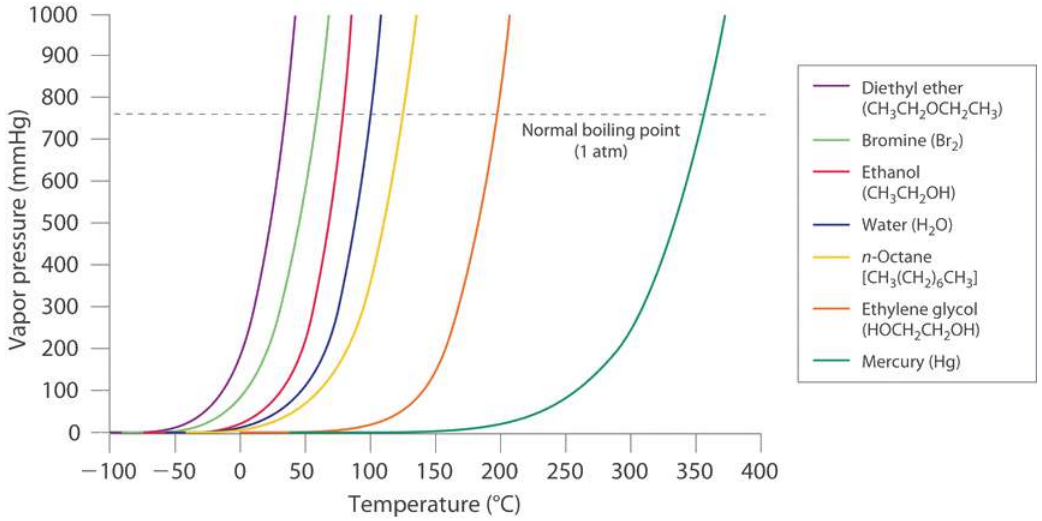


Figure 10.4.1: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC 3.0; Anonymous)

A good approach is to find a mathematical model for the pressure increase as a function of temperature. Experiments showed that the vapor pressure $\boldsymbol{P}$ and temperature $\boldsymbol{T}$ are related,

$$P \propto \exp\left(-\frac{\Delta H_{vap}}{RT}\right) \tag{10.4.26}$$

where $\boldsymbol{\Delta H_{vap}}$ is the Enthalpy (heat) of Vaporization and $\boldsymbol{R}$ is the gas constant (8.3145 J mol^{-1} K^{-1}).

A simple relationship can be found by integrating Equation 10.4.26 between two pressure-temperature endpoints:

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{10.4.27}$$

where $\boldsymbol{P_1}$ and $\boldsymbol{P_2}$ are the vapor pressures at two temperatures $\boldsymbol{T_1}$ and $\boldsymbol{T_2}$. Equation 10.4.27 is known as the **Clausius-Clapeyron Equation** and allows us to estimate the vapor pressure at another temperature, if the vapor pressure is known at some temperature, and if the enthalpy of vaporization is known.

Alternative Formulation

The order of the temperatures in Equation 10.4.27 matters as the Clausius-Clapeyron Equation is sometimes written with a negative sign (and switched order of temperatures):

$$\ln\left(\frac{P_1}{P_2}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{10.4.28}$$

Example 10.4.1: Vapor Pressure of Water

The vapor pressure of water is 1.0 atm at 373 K, and the enthalpy of vaporization is 40.7 kJ mol^{-1}. Estimate the vapor pressure at temperature 363 and 383 K respectively.

Solution

Using the Clausius-Clapeyron equation (Equation 10.4.28), we have:

$$P_{363} = 1.0 \exp\left[-\left(\frac{40,700}{8.3145}\right)\left(\frac{1}{363\ K} - \frac{1}{373\ K}\right)\right]$$
$$= 0.697 \text{ atm}$$

$$P_{383} = 1.0 \exp\left[-\left(\frac{40,700}{8.3145}\right)\left(\frac{1}{383\ K} - \frac{1}{373\ K}\right)\right]$$
$$= 1.409 \text{ atm}$$

Note that the increase in vapor pressure from 363 K to 373 K is 0.303 atm, but the increase from 373 to 383 K is 0.409 atm. The increase in vapor pressure is not a linear process.

Discussion

We can use the Clausius-Clapeyron equation to construct the entire vaporization curve. There is a deviation from experimental value, that is because the enthalpy of vaporization varies slightly with temperature.

The Clausius-Clapeyron equation can be also applied to sublimation; the following example shows its application in estimating the heat of sublimation.

✔ Example 10.4.2: Sublimation of Ice

The vapor pressures of ice at 268 K and 273 K are 2.965 and 4.560 torr respectively. Estimate the heat of sublimation of ice.

Solution

The enthalpy of sublimation is ΔH_{sub}. Use a piece of paper and derive the Clausius-Clapeyron equation so that you can get the form:

$$\Delta H_{sub} = \frac{R \ln\left(\frac{P_{273}}{P_{268}}\right)}{\frac{1}{268\ K} - \frac{1}{273\ K}}$$
$$= \frac{8.3145 \ln\left(\frac{4.560}{2.965}\right)}{\frac{1}{268\ \text{K}} - \frac{1}{273\ \text{K}}}$$
$$= 52,370 \text{ J mol}^{-1}$$

Note that the heat of sublimation is the sum of heat of melting (6,006 J/mol at 0°C and 101 kPa) and the heat of vaporization (45,051 J/mol at 0 °C).

? Exercise 10.4.2

Show that the vapor pressure of ice at 274 K is higher than that of water at the same temperature. Note the curve of vaporization is also called the curve of vaporization.

✔ Example 10.4.3: Vaporization of Ethanol

Calculate ΔH_{vap} for ethanol, given vapor pressure at 40 ^{o}C = 150 torr. The normal boiling point for ethanol is 78 ^{o}C.

Solution

Recognize that we have TWO sets of (P, T) data:

- Set 1: (150 torr at 40+273K)
- Set 2: (760 torr at 78+273K)

We then directly use these data in Equation 10.4.28

$$\ln\left(\frac{150}{760}\right) = \frac{-\Delta H_{vap}}{8.314}\left[\frac{1}{313} - \frac{1}{351}\right]$$

$$\ln 150 - \ln 760 = \frac{-\Delta H_{vap}}{8.314}\left[\frac{1}{313} - \frac{1}{351}\right]$$

$$-1.623 = \frac{-\Delta H_{vap}}{8.314}\left[0.0032 - 0.0028\right]$$

Then solving for ΔH_{vap}

$$\Delta H_{vap} = 3.90 \times 10^4 \text{ J/mol}$$

$$= 39.0 \text{ kJ/mol}$$

Advanced Note

It is important to not use the Clausius-Clapeyron equation for the solid to liquid transition. That requires the use of the more general **Clapeyron equation**

$$\frac{dP}{dT} = \frac{\Delta \bar{H}}{T\Delta \bar{V}}$$

where $\Delta \bar{H}$ and $\Delta \bar{V}$ is the molar change in enthalpy (the enthalpy of fusion in this case) and volume respectively between the two phases in the transition.

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CHAPTER OVERVIEW

11: Solutions Liquid Liquid

11.1: A Mixture is a Combination of Two or More Substances

11.2: The Gibbs-Duhem Equation Relates Chemical Potential and Composition at Equilibrium

11.3: Chemical Potential of Each Component Has the Same Value in Each Phase in Which the Component Appears

11.4: Ideal Solutions obey Raoult's Law

11.5: Most Solutions are Not Ideal

11.6: Vapor Pressures of Volatile Binary Solutions

11.7: Activities of Nonideal Solutions

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11.1: A Mixture is a Combination of Two or More Substances

So far, we have only discussed systems that are comprised of one component. Because a lot of chemistry occurs in mixtures or produces a mixture, chemists need to consider the thermodynamics of mixtures. A mixture can consist of many different components, however, for the sake of simplicity, we will restrict ourselves for now to two-component mixtures. Two-component mixtures can consist of two gases, two liquids, two solids, or even a liquid and a gas.

11.1.1: Partial Quantities and Scaling

Let's consider a two-component system where the volume and number of moles are changing. For example, we could have a system of a certain size of 1 and reduce its size stepwise in successive steps by taking half of it and throwing the other half away. The number of moles of each component, n_1 and n_2, will change as the volume of the system, V, changes:

$$dn_1 = n_1 dV$$

$$dn_2 = n_2 dV$$

The extensive Gibbs free energy will be affected the same way:

$$dG = GdV$$

At constant T and P we can write:

$$dG = \cancel{-SdT} + \cancel{VdP} + \mu_1 dn_1 + \mu_2 dn_2$$

So:

$$dG = \mu_1 dn_1 + \mu_2 dn_2$$

$$GdV = \mu_1 n_1 dV + \mu_2 n_2 dV$$

If we integrate this from the original size, 1, down to 0 (or 0 to 1, it does not matter). We get:

$$\int_0^1 GdV = \int_0^1 \mu_1 n_1 dV + \int_0^1 \mu_2 n_2 dV$$

$$G\int_0^1 dV = \mu_1 n_1 \int_0^1 dV + \mu_2 n_2 \int_0^1 dV$$

$$G = \mu_1 n_1 + \mu_2 n_2$$

By the same argument we have:

$$V = \bar{V}_1 n_1 + \bar{V}_2 n_2$$

where $\bar{V}_i$ is the partial molar volume for component i. These partial molar volumes are generally a function of composition (and P, T) and have been tabulated for a number of liquid systems. They allow us to calculate the real volume of a binary mixture. Volumes are generally speaking ***not strictly additive***. This fact is typically ignored in volumetric analysis and the use of molarities. Fortunately the deviations are often negligible in dilute solutions.

For phase diagrams, molarity (moles per liter) is not a very suitable quantity to use for concentration due to its volume dependence. Usually we work with mole fractions or molalities (moles per kilogram), where there are no volume dependencies.

11.1.2: Gaseous Mixtures

Gases can always mix in any ratio and mixtures typically act close to ideal unless heavily compressed or brought to low temperatures. The only exception is if the gases react (e.g, HCl and NH_3). Gas molecules experience little interaction with each other and, therefore, it does not matter much whether the molecules are different or the same. The total pressure can be computed by adding the partial pressures of the two components (Dalton's Law of Partial Pressures):

$$P_{total} = P_1 + P_2 \tag{11.1.1}$$

11.1.3: Liquid Mixtures

There are binary liquid systems that are fully miscible and are said to act as *ideal solutions*. Liquid molecules typically experience *strong* interactions with their neighbors. For the solution to be ideal, the interactions must remain *equally strong* even when the neighboring substance is different. This means they must be chemically similar. For this reason, liquid binaries are often *not* ideal. The next nearest thing are **regular solutions**. Even these systems can display phase segregation and limited mutual solubilities at low temperatures. Many liquid-liquid binaries diverge from ideality even more than the regular solutions and many of them are hardly miscible at all.

Table 24.1.1: Solutions

Solution/mixture	Interactions	Miscibility
Ideal gas	none	complete
Ideal liquid	strong but similar	complete
Regular liquid	strong, modestly dissimilar	not always complete
Real liquid	often strongly dissimilar	partial or none

11.1.4: Solid Mixtures

Solid binaries tend to be even less miscible than liquid binaries to the point that immiscibility is the rule and miscibility is the exception. Even totally miscible systems like electrum (the alloys of silver and gold) are far from ideal.



Figure 24.1.1: Electrum coin of the Byzantine Emperor Alexius I Comnenus. (CC-BY-SA-3.0; Classical Numismatic Group, Inc. http://www.cngcoins.com)

Another point of practical (kinetic rather than thermodynamic) importance is that even if two compounds are able to form a homogeneous solid solution, it usually takes heating for prolonged periods to get them to mix because solid diffusion is typically very slow. Nevertheless, solid solubility is an important issue for many systems, particularly for metal alloys. Two molecular solid substances that differ vastly in shape, size, polarity and or hydrogen bonding (e.g. organic compounds) typically have *negligible* mutual solid solubility. The latter fact is frequently exploited in organic chemistry to purify compounds through recrystallization.

Note

Solid solutions are relatively infrequent and never ideal.

11.1.5: Ideal liquid/Ideal Gas Phase Diagrams

Let's mix two liquids together. Liquids typically have different boiling points, with one being more volatile than the other. The vapor pressure of a component scales simply with the equilibrium vapor pressure of the pure component. In the gas phase, ***Dalton's law*** is applicable:

$$y_i = \frac{P_i}{P_{total}} \tag{11.1.2}$$

This is a consequence of the fact that ideal gases do not interact. The latter implies that the total pressure is simply the sum of the partial ones:

$$P_{total} = \sum_{i}^{N} P_i$$

If the liquid solution is ideal, then the vapor pressure of both components follow ***Raoult's law***, which states that the equilibrium vapor pressure above the mixture is the equilibrium pressure of the pure component times the mole fraction:

$$P_i = \chi_i P_i^\circ \tag{11.1.3}$$

- P_i is the vapor pressure of component i in the mixture
- P_i° is equilibrium vapor pressure of the pure component i.
- χ_i is the mole fraction of i^{th} component in the liquid phase.

Note that values for pure components are typically indicated by adding an asterisk $^\circ$ superscript.

The idea behind Raoult's law is that if the interactions are similar, it is a matter of random chance which component sits at the interface at any given moment. The equilibrium vapor pressure has to do with the probability that a molecule escapes from the interface into the gas phase and is dependent on both the substances volatility and the number that cover the surface. This leads to Raoult's Law, where we must multiply the vapor pressure of the pure liquid (volatility) by the mole fraction (number on the surface).

Note: Applicability of Raoult's Law

Raoult's law seldom holds completely, which is more applicable if the two components are almost chemically identical like two isomers, e.g., 1-propanol and 2-propanol.

11.1.6: The Pressure Phase Diagram

If we assume that temperature is constant, we can plot the total pressure for both Dalton and Raoult's laws versus composition (of gas: y_1 and liquid: χ_1 on the same axis).

Liquid Phase:

$$\begin{aligned} P_{total} &= P_1 + P_2 \\ &= \chi_1 P_1^\circ + \chi_2 P_2^\circ \\ &= \chi_1 P_1^\circ + (1-\chi_1) P_2^\circ \\ &= P_2^\circ - \chi_1 (P_2^\circ - P_1^\circ) \end{aligned} \tag{11.1.4}$$

Clearly this is a straight line going from P_2° at $x = 0$ to P_1° at $x = 1$.

However the composition of the vapor in equilibrium with a liquid at a given mole fraction χ is *different* than that of the liquid. So y is not χ. If we take Dalton's law (Equation 11.1.2) and substitute Raoult's Law (Equation 11.1.3) in the numerator and the straight line in the denominator we get:

$$y_1 = \frac{\chi_1 P_1^\circ}{P_2^\circ - \chi_1 (P_2^\circ - P_1^\circ)} \tag{11.1.5}$$

Exercise

Suppose $P_1^\circ = 50$ Torr and $P_2^\circ = 25$ Torr. If $\chi_1 = 0.6$ what is the composition of the vapor?

We can rearrange Equations 11.1.4 and 11.1.5 to plot the total pressure as function of y_1:

$$P_{total} = \frac{P_1^\circ P_2^\circ}{P_1^\circ + (P_2^\circ - P_1^\circ) y_1} \tag{11.1.6}$$

This is *not* a straight line.

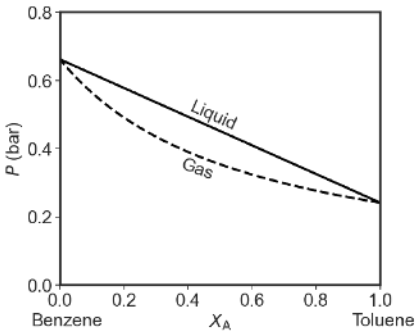


Figure 24.1.1: an ideal-ideal phase diagram for the binary system of toluene (A) and benzene (B). The curves are calculated from Equations 11.1.4 and 11.1.6.

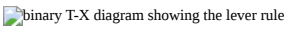
As you can see when we plot both lines we get a diagram with three regions. At high pressures we just have a liquid. At low pressures we just have a gas. In between we have a ***phase gap*** or ***two phase region***. Points inside this region represent states that the system cannot achieve homogeneously. The horizontal ***tie-line*** shows which *two* phases coexists. I used the same 25 and 50 Torr values for the pure equilibrium pressures as in the question above. If you try to make a system with *overall* composition x and impose a pressure that falls in the forbidden zone you get two phases: a gaseous one that is richer in the more volatile component and a liquid one that is poorer in the volatile component than the overall composition would indicate.

11.1.7: The Temperature Phase Diagram

Note that the question: *what phase do we have when?* is really a function of ***both P and T***, so that if we want to represent *all* our knowledge in a diagram we should make it a three dimensional picture. This is not so easy to draw and not easy to comprehend visually either. This is why we usually look at a 2D cross section of the 3D space.

The above diagram is *isothermal*: we vary P, keeping T constant. It is, however, more usual (and easier) to do it the other way around. We keep pressure constant (say 1 bar, that's easy) and start heating things up isobarically.

The boiling points of our mixtures can also be plotted against x (the liquid composition) and y (the gaseous one) on the same horizontal axis. Again because in general y is not equal x we get two different curves. Neither of them are straight lines in this case and we end up with a lens-shaped two phase region:



binary T-X diagram showing the lever rule

What happens to a mixture with a given overall composition x(=x_1) when it is brought to a temperature where it boils can be seen at the intersection of a vertical line (an isopleth) at $x_{overall}$ and a horizontal one (an isotherm) at T_{boil}. If the intersection points in inside the two phase region a vapor phase and a liquid phase result that have a different composition from the overall one. The vapor phase is always richer in the more volatile component (the one with the lowest boiling point, on the left in the diagram). The liquid phase is enriched in the less volatile one.

11.1.7.1: The Lever Rule

How much of each phase is present is represented by the arrows in the diagram. The amount of liquid is proportional to the left arrow, the amount of gas to the right one (i.e. it works crosswise). The composition of the liquid in equilibrium with the vapor is:

$$x_2 = \frac{n_2^{liq}}{n_{1+2}^{liq}}$$

$$x_2^* n_{1+2}^{liq} = n_2^{liq}$$

The composition of the vapor is:

$$y_2 = \frac{n_2^{gas}}{n_{1+2}^{gas}}$$

$$y_2^* n_{1+2}^{gas} = n_2^{gas}$$

The overall composition is:

$$x_{all} = \frac{n_2^{liq+gas}}{n_{1+2}^{liq+gas}}$$

$$x_{all}^* n_{1+2}^{liq+gas} = n_2^{gas} + n_2^{liq}$$

$$x_{all}^* n_{1+2}^{liq+gas} = y_2^* n_{1+2}^{gas} + x_2^* n_{1+2}^{liq}$$

$$x_{all}^* n_{1+2}^{gas} + x_{all}^* n_{1+2}^{liq} = y_2^* n_{1+2}^{gas} + x_2^* n_{1+2}^{liq}$$

Thus:

$$\frac{n_{1+2}^{liq}}{n_{1+2}^{gas}} = \frac{y_2 - x_{all}}{x_{all} - x_2}$$

11.1.7.2: Distillation

The difference in composition between the gas and the liquid can be exploited to separate the two components, at least partially. We could trap the vapor and cool it down to form a liquid with a different composition. We could then boil it again and repeat the process. Each time the vapor will be more enriched in the volatile phase whereas the residual liquid is more enriched in the less volatile one. This process is known as ***distillation***. In practice the process is done one a fractionation column which makes it possible to have a series of vapor-liquid equilibria at once.

A good degree of purity can be reached this way, although 100% purity would take an infinite number of distillation steps.

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11.2: The Gibbs-Duhem Equation Relates Chemical Potential and Composition at Equilibrium

At **equilibrium**, there is no change in chemical potential for the system:

$$\sum_i n_i d\mu_i = 0 \tag{11.2.1}$$

This is the Gibbs-Duhem relationship and it places a compositional constraint upon any changes in the chemical potential in a mixture at constant temperature and pressure for a given composition. This result is easily derived when one considers that μ_i represents the partial molar Gibbs function for component i. And as with other partial molar quantities:

$$G_{\text{tot}} = \sum_i n_i \mu_i$$

Taking the derivative of both sides yields:

$$dG_{\text{tot}} = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i$$

But dG can also be expressed as:

$$dG = Vdp - sdT + \sum_i \mu_i dn_i$$

Setting these two expressions equal to one another:

$$\sum_i n_i d\mu_i + \cancel{\sum_i \mu_i dn_i} = Vdp - sdT + \cancel{\sum_i \mu_i dn_i}$$

And after canceling terms, one gets:

$$\sum_i n_i d\mu_i = Vdp - sdT \tag{11.2.2}$$

For a system at constant temperature and pressure:

$$V\ dp - s\ dT = 0 \tag{11.2.3}$$

Substituting Equation 11.2.3 into 11.2.2 results in the **Gibbs-Duhem equation** (Equation 11.2.1). This expression relates how the chemical potential can change for a given composition while the system maintains equilibrium.

11.2.1: **Gibbs-Duhem for** Binary Systems

For a binary system consisting of components two components, A and B:

$$n_B d\mu_B + n_A d\mu_A = 0$$

Rearranging:

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

Consider a Gibbs free energy that only includes μ_n conjugate variables as we obtained it from our scaling experiment at T and P constant:

$$G = \mu_A n_A + \mu_B n_B$$

Consider a change in G:

$$\begin{aligned} dG &= d(\mu_A n_A) + d(\mu_B n_B) \\ &= n_A d\mu_A + \mu_A dn_A + n_B d\mu_B + \mu_B dn_B \end{aligned}$$

However, if we simply write out a change in G due to the number of moles we have:

$$dG = \mu_A dn_A + \mu_B dn_B$$

Consequently the other terms must add up to zero:

$$0 = n_A d\mu_A + n_B d\mu_B$$

$$d\mu_A = -\frac{n_B}{n_A} d\mu_B$$

$$d\mu_A = -\frac{\chi_B}{\chi_A} d\mu_B$$

In the last step we have simply divided both denominator and numerator by the total number of moles. This expression is the Gibbs-Duhem equation for a 2-component system. It relates the change in one thermodynamic potential ($d\mu_A$) to the other ($d\mu_B$).

> *The Gibbs-Duhem equation relates the change in one thermodynamic potential ($d\mu_A$) to the other ($d\mu_B$).*

11.2.2: Gibbs-Duhem in the Ideal Case

In the ideal case we have:

$$\mu_B = \mu_B^* + RT \ln x_B$$

Gibbs-Duhem gives:

$$d\mu_A = -\frac{\chi_B}{\chi_A} d\mu_B$$

As:

$$d\mu_B = 0 + \frac{RT}{\chi_B}$$

with x_B being the only active variable at constant temperature, we get:

$$d\mu_A = -\frac{\chi_B}{\chi_A} \frac{RT}{\chi_B} = \frac{RT}{\chi_A}$$

If we now wish to find μ_A we need to integrate $d\mu_A$, e.g. form pure 1 to χ_A. This produces:

$$\mu_A = \mu_A^* + RT \ln \chi_A$$

This demonstrates that Raoult's law can only hold over the whole range for one component ***if*** it also holds for the other over the whole range.

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11.3: Chemical Potential of Each Component Has the Same Value in Each Phase in Which the Component Appears

In much the same fashion as the partial molar volume is defined, the **partial molar Gibbs function** is defined for compound i in a mixture:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}} \tag{11.3.1}$$

The partial molar function is of particular importance and is called the **chemical potential**. The chemical potential tells how the Gibbs function will change as the composition of the mixture changes. Since systems tend to seek a minimum aggregate Gibbs function, the chemical potential will point to the direction the system can move in order to reduce the total Gibbs function and reach equilibrium. In general, the total change in the Gibbs function (dG) can be calculated from:

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,n_{j\neq i}} dn_i$$

Or, by substituting the definition for the chemical potential, and evaluating the pressure and temperature derivatives:

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

But as it turns out, the chemical potential can be defined as the partial molar quantity of any of the four major thermodynamic functions U, H, A, or G:

Table **11.3.1**: Chemical potential can be defined as the partial molar derivative any of the four major thermodynamic functions

$dU = TdS - PdV + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}}$
$dH = TdS - VdT + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}}$
$dA = -PdV - TdS + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{j\neq i}}$
$dG = VdP - SdT + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}}$

The last definition, in which the chemical potential is defined as the partial molar Gibbs function, is the most commonly used, and perhaps the most useful (Equation 11.3.1). As the partial most Gibbs function, it is easy to show that:

$$d\mu = VdP - SdT$$

where V is the molar volume, and S is the molar entropy. Using this expression, it is easy to show that:

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V$$

and so at constant temperature:

$$\int_{\mu^o}^{\mu} d\mu = \int_{P^o}^{P} V\, dP \tag{11.3.2}$$

So that for a substance for which the molar volume is fairly independent of pressure at constant temperature (i. e., κ_T is very small), therefore Equation 11.3.2 becomes:

$$\int_{\mu^o}^{\mu} d\mu = V \int_{P^o}^{P} dP$$

$$\mu - \mu^o = V(P - P^o)$$

or:

$$\mu = \mu^o + V(P - P^o)$$

Where P^o is the standard state pressure (1 bar) and μ^o is the chemical potential at the standard pressure. If the substance is highly compressible (such as a gas) the pressure dependence of the molar volume is needed to complete the integral. If the substance is an ideal gas:

$$V = \frac{RT}{P}$$

So at constant temperature, Equation 11.3.2 then becomes:

$$\int_{\mu^o}^{\mu} d\mu = RTint_{P^o}^{P} \frac{dP}{P} \tag{11.3.3}$$

or:

$$\mu = \mu^o + RT \ln\left(\frac{P}{P^o}\right)$$

A lot of chemistry takes place in solution and therefore this topic is of prime interest for chemistry.

11.3.1: Thermodynamic potentials of solutions

The Gibbs free energy of an ideal gas depends logarithmically on pressure:

$$G = G^o + RT \ln \frac{P}{P^o}$$

$P^{\ominus}$ is *is often dropped out of the formula.* and we write:

$$G = G^o + RT \ln P$$

> Notice however that although P and P/P^o have the same numerical value, the dimensions are different. P usually has dimensions of bar, but P/P^o is *dimensionless*.

If we have a gas mixture we can hold the same logarithmic argument for each partial pressure as the gases do not notice each other. We do need to take into account the number of moles of each and work with (partial) molar values, i.e. the thermodynamic potential:

$$\mu_j = \mu_j^o + RT \ln \frac{P_j}{P^o} \tag{11.3.4}$$

If we are dealing with an equilibrium over an ideal liquid solution the situation in the gas phase gives us a probe for the situation in the liquid. The equilibrium must hold for each of *all* components j (say two in binary mixture). That means that for each of them the thermodynamic potential in the liquid and in the gas must be equal:

$$\mu_j^{sln} = \mu_j^{gas}$$

for all j. Consider what happens to a pure component, e.g. $j = 1$ in equilibrium with its vapor. We can write:

$$\mu_1^{pure\ liq} = \mu_1^{pure\ vapor} = \mu_1^o + RT \ln \frac{P_1^*}{P^o}$$

The asterisk in P_1^* denotes the equilibrium vapor pressure of pure component 1 and we will use that to indicate the thermodynamic potential of pure compounds too:

$$\mu_1^{*liq} = \mu_1^o + RT \ln \frac{P_1^*}{P^o} \tag{11.3.5}$$

Combining Equations 11.3.5 and 11.3.4 we find a relationship between the solution and the pure liquid:

$$\mu_j^{sln} = \mu_j^* + RT \ln \frac{P_j}{P_j^*}$$

Notice that the *gas* and its pressure is used to link the mixture and the pure compound.

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11.4: Ideal Solutions obey Raoult's Law

Liquids tend to be volatile, and as such will enter the vapor phase when the temperature is increased to a high enough value, provided they do not decompose first. A volatile liquid is one that has an appreciable vapor pressure at the specified temperature. An ideal mixture containing at least one volatile liquid can be described using **Raoult's Law:**

$$P_j = x_j P_j^*$$

Raoult's law can be used to predict the total vapor pressure above a mixture of two volatile liquids. As it turns out, the composition of the vapor will be different than that of the two liquids, with the more volatile compound having a larger mole fraction in the vapor phase than in the liquid phase. This is summarized in the following diagram for an ideal mixture of two compounds, water and ethanol at 75 °C. At this temperature, water a pure vapor pressure of 384 Torr and ethanol has a pure vapor pressure of 945 Torr. In Figure 24.4.1, the composition of the liquid phase is represented by the solid line and the composition of the vapor phase is represented by the dashed line.

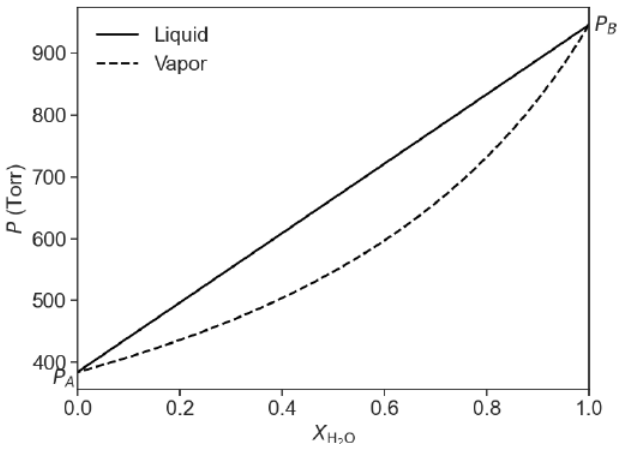


Figure 24.4.1: The composition of the liquid phase (solid line) and the vapor phase (dashed lined) as a function of mole fraction according to Raoult's law. The solution is a mixture of water and ethanol. P_A is the vapor pressure of pure water and P_B is the vapor pressure of pure ethanol at 75 °C

Often, it is desirable to depict the phase diagram at a single pressure so that temperature and composition are the variables included in the graphical representation. In such a diagram, the vapor, which exists at higher temperatures) is indicated at the top of the diagram, while the liquid is at the bottom. A typical temperature vs. composition diagram is depicted in Figure 24.4.2 for an ideal mixture of two volatile liquids.

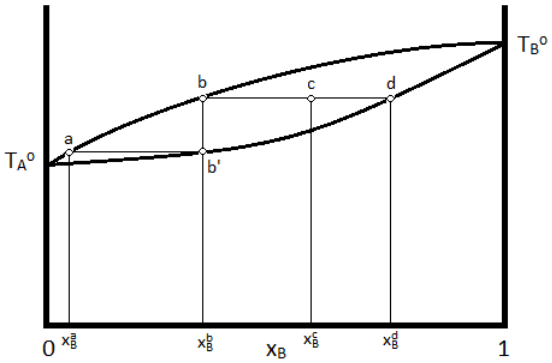


Figure 24.4.2: A typical temperature vs. composition diagram.

https://chem.libretexts.org/@go/page/426477

In this diagram, T_A and T_B represent the boiling points of pure compounds A and B. If a system having the composition indicated by χ_B^c has its temperature increased to that indicated by point c, The system will consist of two phases, a liquid phase, with a composition indicated by χ_B^d and a vapor phase indicated with a composition indicated by χ_B^b. The relative amounts of material in each phase can be described by the lever rule, as described previously.

Further, if the vapor with composition χ_B^b is condensed (the temperature is lowered to that indicated by point b') and re-vaporized, the new vapor will have the composition consistent with χ_B^a. This demonstrates how the more volatile liquid (the one with the lower boiling temperature, which is A in the case of the above diagram) can be purified from the mixture by collecting and re-evaporating fractions of the vapor. If the liquid was the desired product, one would collect fractions of the residual liquid to achieve the desired result. This process is known as distillation.

11.4.1: The Gibbs energy of mixing is always negative

When we add n_A moles of component A and n_B moles of component B to form an ideal liquid solution, this is generally a spontaneous process. Let us consider the Gibbs free energy change of that process:

$$\Delta_{mix}G = n_1\mu_1^{sln} + n_2\mu_2^{sln} - (n_1\mu_1^* + n_2\mu_2^*)$$

Using:

$$\mu_i^{sln} \equiv \mu_i^* + nRTx_i \ln x_i$$

his expression simplifies to:

$$\Delta_{mix}G = nRTx_A \ln x_A + nRTx_B \ln x_B$$

where n is the total moles. Mole fraction, x_i, is always less than one, so the Gibbs energy of mixing is always negative; mixing is always spontaneous. We can generalize this to mixtures with more than two components:

$$\Delta_{mix}G = nRT\sum_i x_i \ln x_i$$

This expression looks suspiciously familiar. Apart from a factor of $-T$, it is just like the **entropy of mixing**:

$$\Delta_{mix}S = -nR\sum_i x_i \ln x_i$$

Recalling the relationship between Gibbs energy and entropy:

$$\Delta_{mix}G = \Delta_{mix}H - T\Delta_{mix}S$$

This leaves no room at all for an enthalpy effect:

$$\Delta_{mix}H = 0$$

Even though there are strong interactions between neighboring particles in liquids, there is no enthalpy change. This implies that it does not matter what the neighboring molecules are. If we represent the average interaction energy between molecule i and j by U_{ij}, we are assuming that U_{ij} is always the same. In practice, this is *seldom* the case. It usually does matter and then the enthalpy term is not zero. As this affects the thermodynamics of the liquid solution, it should also affect the vapor pressures that are in equilibrium with it.

11.4.2: In the ideal case, volumes are additive

From the change of G in its natural variables, we know that:

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

This means that if we take

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V_{mix}$$

In the ideal case we get:

$$\left(\frac{\partial \Delta G^{ideal}}{\partial P}\right)_T = \Delta V_{mix}^{ideal}$$

$$\left(\frac{\partial RT(n_1 \ln x_1 + n_2 \ln x_2)}{\partial P}\right)_T = \Delta V_{mix}^{ideal} = 0$$

In the ideal case, volumes are *additive* and we need not worry about how the partial molar volumes change with composition.

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11.5: Most Solutions are Not Ideal

If we plot the partial pressure of one component, P_1, above a mixture with a mole fraction x_1, we should get a straight line with a slope of P_1^* (Raoult's law). Above non-ideal solutions the graph will no longer be a straight line but a curve. However towards $x_1 = 1$ the curve typically approaches the Raoult line. On the other extreme, there often is a more or less linear region as well, ***but with a different slope*** (Figure 24.5.1). This means that we can identify two *limiting* laws:

- For $x \to 0$: **Henry's law**:

$$P_1 = K_H x_1$$

- For $x \to 1$: **Raoult's law**:

$$P_1 = P_1^* x_1$$

This implies that the straight line that indicates the Henry expression will intersect the y-axis at $x = 1$ (pure compound) at a ***different*** point than P^*. For $x \to 0$ (low concentrations) we can speak of component 1 being the *solute* (the minority component). At the other end $x \to 1$ it plays the role of the *solvent* (majority component).

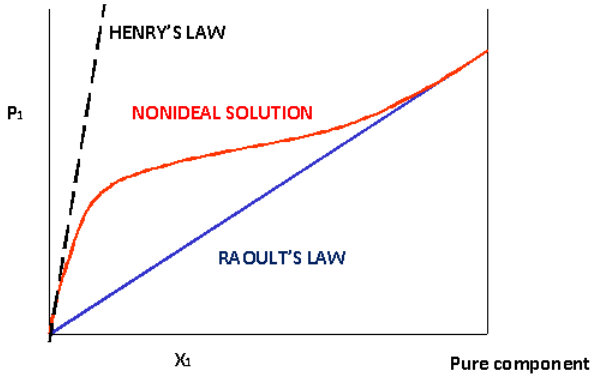


Figure 24.5.1 : Vapor pressure above an ideal and a non-ideal solution

> Another thing to note is that P^* is a property of *one pure component*, the value of K_H by contrast is a property of the *combination of two components*, so it needs to be measured for each solute-solvent combination.

As you can see we have a description for both the high and the low end, but not in the middle. In general, the more modest the deviations from ideality the larger the range of validity of the two limiting laws. The way to determine K_H would be to actually determine vapor pressures. How about the other component? Do we need to measure them too? Fortunately we can use thermodynamics to answer this question with no. There is a handy expression that saves us the trouble.

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11.6: Vapor Pressures of Volatile Binary Solutions

The behaviors of ideal solutions of volatile compounds follow Raoult's Law. Henry's Law can be used to describe the deviations from ideality. Henry's law states:

$$P_B = k_H P_B^o$$

For which the Henry's Law constant (k_H) is determined for the specific compound. Henry's Law is often used to describe the solubilities of gases in liquids. The relationship to Raoult's Law is summarized in Figure **11.6.1**.

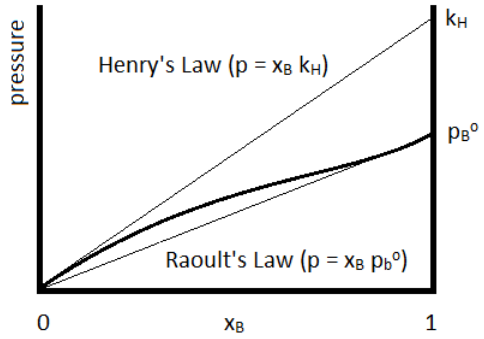


Figure **11.6.1**: The relationship between Raoult's Law and Henry's Law for a binary mixture.

Henry's Law is depicted by the upper straight line and Raoult's Law by the lower.

Example 11.6.1: Solubility of Carbon Dioxide in Water

The solubility of $CO_2(g)$ in water at 25 °C is 3.32 x 10^{-2} M with a partial pressure of CO_2 over the solution of 1 bar. Assuming the density of a saturated solution to be 1 kg/L, calculate the Henry's Law constant for CO_2.

Solution:

In one L of solution, there is 1000 g of water (assuming the mass of CO_2 dissolved is negligible.)

$$(1000\,g)\left(\frac{1\,mol}{18.02\,g}\right) = 55\,mol\,H_2O$$

The solubility of CO_2 can be used to find the number of moles of CO_2 dissolved in 1 L of solution also:

$$\frac{3.32\times10^{-2}mol}{L}\cdot 1\,L = 3.32\times10^{-2}mol\,CO_2$$

and so the mol fraction of CO_2 is

$$\chi_b = \frac{3.32\times10^{-2}mol}{55.5\,mol} = 5.98\times10^{-4}$$

And so

$$10^5\,Pa = 5.98\times10^{-4}k_H$$

or

$$k_H = 1.67\times10^9\,Pa$$

11.6.1: Azeotropes

An azeotrope is defined as the common composition of vapor and liquid when they have the same composition.

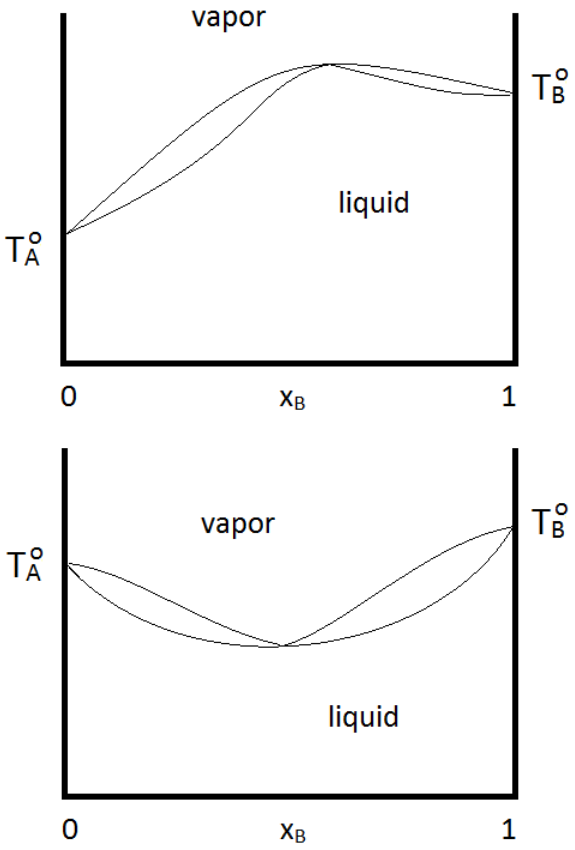


Figure **11.6.2**: Phase diagrams for (left) a maximum boiling point azeotrope and (right) Ta maximum boiling point azeotrope.

Azeotropes can be either maximum boiling or minimum boiling, as show in Figure **11.6.2;**. Regardless, distillation cannot purify past the azeotrope point, since the vapor and the liquid phases have the same composition. If a system forms a minimum boiling azeotrope and has a range of compositions and temperatures at which two liquid phases exist, the phase diagram might look like Figure **11.6.2;**:

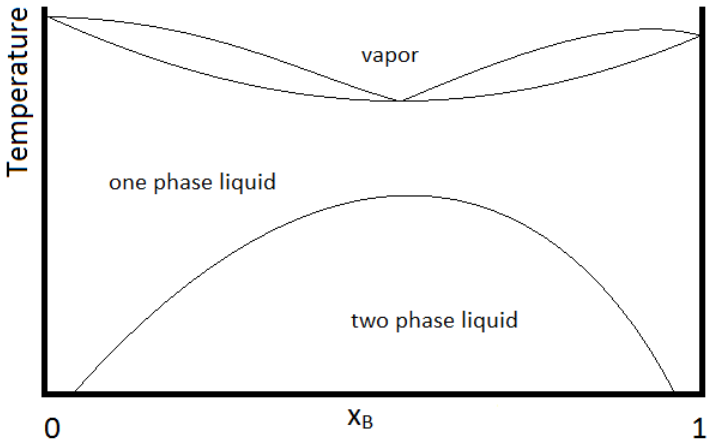
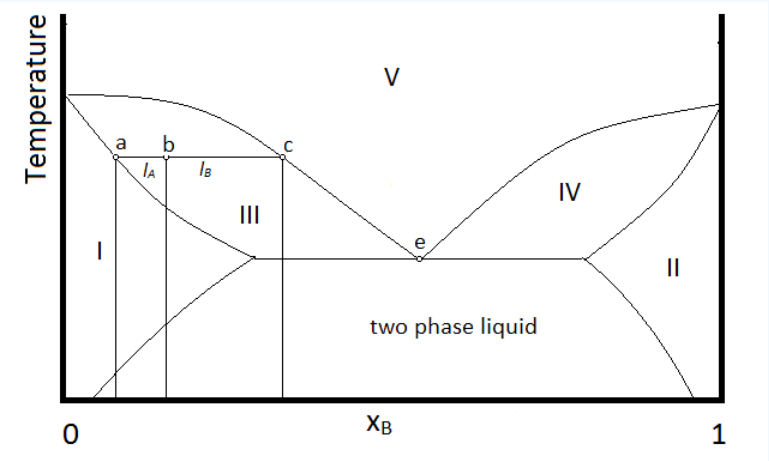


Figure **11.6.3**: *Phase diagram for a binary solution with the boiling point of a minimum boiling azeotrope that is higher that when components are miscible (single phase).*

Another possibility that is common is for two substances to form a two-phase liquid, form a minimum boiling azeotrope, but for the azeotrope to boil at a temperature below which the two liquid phases become miscible. In this case, the phase diagram will look like Figure **11.6.3**.

Example 11.6.1:

In the diagram, make up of a system in each region is summarized below the diagram. The point e indicates the azeotrope composition and boiling temperature.



I. Single phase liquid (mostly compound A)
II. Single phase liquid (mostly compound B)
III. Single phase liquid (mostly A) and vapor
IV. Single phase liquid (mostly B) and vapor
V. Vapor (miscible at all mole fractions since it is a gas)

Solution

Within each two-phase region (III, IV, and the two-phase liquid region, the lever rule will apply to describe the composition of each phase present. So, for example, the system with the composition and temperature represented by point b (a single-phase liquid which is mostly compound A, designated by the composition at point a, and vapor with a composition designated by that at point c), will be described by the lever rule using the lengths of tie lines l_A and l_B.

11.6.1.1: Gibbs-Duhem and Henry's law

What happens when Raoult does *not* hold over the whole range? Recall that in a gas:

$$\mu_j = \mu_j^o + RT \ln \frac{P_j}{P^o} \tag{11.6.1}$$

or

$$\mu_j = \mu_j^o + RT \ln P_j$$

after dropping $P^o = 1\ bar$ out of the notation. Note that numerically this does not matter, since P_j is now *assumed* to be dimensionless.

Let's consider $d\mu_1$ at constant temperature:

$$d\mu_1 = RT \left(\frac{\partial \ln P_1}{\partial x_1} \right) dx_1$$

likewise:

$$d\mu_2 = RT \left(\frac{\partial \ln P_2}{\partial x_2} \right) dx_2$$

If we substitute into the Gibbs-Duhem expression we get:

$$x_1\left(\frac{\partial \ln P_1}{\partial x_1}\right)dx_1 + x_2\left(\frac{\partial \ln P_2}{\partial x_2}\right)dx_2 = 0$$

Because $dx_1 = -dx_2$:

$$x_1\left(\frac{\partial \ln P_1}{\partial x_1}\right) = x_2\left(\frac{\partial \ln P_2}{\partial x_2}\right)$$

(This is an alternative way of writing Gibbs-Duhem).

If in the limit for $x_1 \to 1$ Raoult Law holds then

$$P_1 \to x_1 P_1^*$$

Thus:

$$\frac{\partial \ln P_1}{\partial x_1} = \frac{1}{x_1}$$

and

$$\frac{x_1}{x_1} = x_2\frac{\partial \ln P_2}{\partial x_2}$$

$$1 = x_2\frac{\partial \ln P_2}{\partial x_2}$$

$$\frac{1}{x_2} = \frac{\partial \ln P_2}{\partial x_2} \tag{11.6.2}$$

We can integrate Equation 11.6.2 to form a logarithmic impression, but it will have an integration constant:

$$\ln P_2 = \ln x_2 + constant$$

This constant of integration can be folded into the logarithm as a multiplicative constant, K

$$\ln P_2 = \ln (K x_2)$$

So for $x_1 \to 1$ (i.e., $x_2 \to 0$), we get that

$$P_2 = K x_2$$

where K is *some* constant, but not necessarily P^*. What this shows is that when one component follows Raoult the other *must* follow Henry and vice versa. (Note that the ideal case is a subset of this case, in that the value of K then becomes P^* and the linearity must hold over the whole range.)

11.6.2: Margules Functions

Of course a big drawback of the Henry law is that it only describes what happens at the two extremes of the phase diagram and not in the middle. In cases of moderate non-ideality, it is possible to describe the whole range (at least in good approximation) using a **Margules function**:

$$P_1 = (x_1 P_1^*)\, f_{Mar}$$

The function f_{Mar} has the shape:

$$f_{Mar} = \exp\left[\alpha x_2^2 + \beta x_2^3 + \delta x_2^3 + ...\right]$$

Notice that the Margules function involves the mole fraction of the *opposite* component. It is an exponential with a series expansion. with the constant and linear term missing. As you can see the function has a number of parameters α, β, δ etc. that need to be determined by experiment. In general, the more the system diverges from ideality, the more parameters you need. Using Gibbs-Duhem is is possible to translate the expression for P_1 into the corresponding one for P_2.

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11.7: Activities of Nonideal Solutions

The bulk of the discussion in this chapter dealt with ideal solutions. However, real solutions will deviate from this kind of behavior. So much as in the case of gases, where fugacity was introduced to allow us to use the ideal models, **activity** is used to allow for the deviation of real solutes from limiting ideal behavior. The activity of a solute is related to its concentration by

$$a_B = \gamma \frac{m_B}{m^o}$$

where γ is the **activity coefficient**, m_B is the molaliy of the solute, and m^o is unit molality. The activity coefficient is unitless in this definition, and so the activity itself is also unitless. Furthermore, the activity coefficient approaches unity as the molality of the solute approaches zero, insuring that dilute solutions behave ideally. The use of activity to describe the solute allows us to use the simple model for chemical potential by inserting the activity of a solute in place of its mole fraction:

$$\mu_B = \mu_B^o + RT \ln a_B$$

The problem that then remains is the measurement of the activity coefficients themselves, which may depend on temperature, pressure, and even concentration.

11.7.1: Activity Coefficients for Ionic Solutes

For an ionic substance that dissociates upon dissolving

$$MX(s) \rightarrow M^+(aq) + X^-(aq)$$

the chemical potential of the cation can be denoted μ_+ and that of the anion as μ_-. For a solution, the total molar Gibbs function of the solutes is given by

$$G = \mu_+ + \mu_-$$

where

$$\mu = \mu^* + RT \ln a$$

where \(\mu^*\) denotes the chemical potential of an ideal solution, and a is the activity of the solute. Substituting his into the above relationship yields

$$G = \mu_+^* + RT \ln a_+ + \mu_-^* + RT \ln a_-$$

Using a molal definition for the activity coefficient

$$a_i = \gamma_i m_i$$

The expression for the total molar Gibbs function of the solutes becomes

$$G = \mu_+^* + RT \ln \gamma_+ m_+ + \mu_-^* + RT \ln \gamma_- m_-$$

This expression can be rearranged to yield

$$G = \mu_+^* + \mu_-^* + RT \ln m_+ m_- + RT \ln \gamma_+ \gamma_-$$

where all of the deviation from ideal behavior comes from the last term. Unfortunately, it impossible to experimentally deconvolute the term into the specific contributions of the two ions. So instead, we use a geometric average to define the **mean activity coefficient**, $\gamma_\pm$.

$$\gamma_\pm = \sqrt{\gamma_+ \gamma_-}$$

For a substance that dissociates according to the general process

$$M_x X_y(s) \rightarrow xM^{y+}(aq) + yX^{x-}(aq)$$

the expression for the mean activity coefficient is given by

$$\gamma_\pm = (\gamma_+^x \gamma_-^y)^{1/x+y}$$

11.7.1.1: Debeye-Hückel Law

In 1923, Debeye and Hückel (Debye & Hückel, 1923) suggested a means of calculating the mean activity coefficients from experimental data. Briefly, they suggest that

$$\log_{10}\gamma_{\pm} = \frac{1.824 \times 10^6}{(\epsilon T)^{3/2}}|z_+ + z_-|\sqrt{I}$$

where ϵ is the dielectric constant of the solvent, T is the temperature in K, z_+ and z_- are the charges on the ions, and I is the **ionic strength** of the solution. I is given by

$$I = \frac{1}{2}\frac{m_+ z_+^2 + m_- z_-^2}{m^o}$$

For a solution in water at 25 ^oC,

As seen before activities are a way to account for deviation from ideal behavior while still keeping the formulism for the ideal case intact. For example in a ideal solution we have:

$$\mu^{sln} = \mu^* + RT\ln x_i$$

is replaced by

$$\mu^{sln} = \mu^* + RT\ln a_i$$

The relationship between a_i and x_i is often written using an activity coefficient γ:

$$a_i = \gamma_i x_i$$

11.7.2: Raoult versus Henry

Implicitly we have made use of Raoult's law here because we originally used

$$x_i = \frac{P_i}{P_i^*}$$

In the case of a solvent this makes sense because Raoult's law is still valid in the limiting case, but for the solute it would make more sense to use Henry's law as a basis for the definition of activity:

$$a_{solute,H} \equiv \frac{P_{solute}}{K_{x,H}}$$

This does mean that the μ^* now becomes a μ^{*Henry} because the extrapolation of the Henry law all the way to the other side of the diagram where $x_{solute} = 1$ points to a point that is not the equilibrium vapor pressure of this component. In fact it represents a virtual state of the system that cannot be realized. This however does not affect the usefulness of the convention.

11.7.3: Various concentration units

The subscript X was added to the K value because we are still using mole fractions. However Henry's law is often used with other concentration measures. The most important are:

- molarity
- molality
- mole fraction

Both the numerical values and the dimensions of K will differ depending on which concentration measure is used. In addition the pressure units can differ. For example for oxygen in water we have:

$K_{x,H}$= 4.259 10^4 atm

$K_{cp,H}$= 1.3 10^{-3} mol/lit.atm

$K_{pc,H}$= 769.23 lit.atm/mol

As you can see $K_{cp,H}$ is simply $1/K_{pc,H}$, both conventions are used..

Note that in this case a choice based on Raoult is really not feasible. At room temperature we are far above the critical point of oxygen which make the equilibrium vapor pressure a non-existent entity. Returning to activities we could use each of the versions of K as a basis for the activity definition. This means that when using activities it must be specified what scale we are using. Activities and Henry coefficients of dissolved gases in water (both fresh and salt) are quite important in geochemistry, environmental chemistry etc.

11.7.4: Non-volatile solutes

A special case arises if the vapor pressure of a solute is negligible. For example if we dissolve sucrose in water. In that case we can still use the Henry based definition

$$a_{solute,H} \equiv \frac{P_{solute}}{K_{x,H}}$$

Even though both K and P will be exceedingly small their ratio is still finite. However how do we determine either?

The answer lies in the solvent. Even if the vapor pressure of sucrose is immeasurably small, the water vapor pressure above the solution can be measured. The Gibbs-Duhem equation can then be used to translate one into the other. We can use Raoult Law to define the activity of the solvent:

$$a_1 = \frac{P_1}{P_1^*}$$

We can measure the pressures as a function of the solute concentrations. At low concentrations

$$\ln a_1 \ln x - 1 \approx -x - 2$$

At higher concentrations we will get deviations, we can write:

$$\ln \frac{P_1}{P_1^*} = \ln a_1 \approx -x_2 \varphi$$

The 'fudge factor' φ is known as the *osmotic coefficient* and can thus be determined as a function of the solute concentration from the pressure data. What we are really interested in is a_2, not a_1:

$$a_2 = \gamma_2 x_2$$

Using Gibbs-Duhem we can convert φ into γ_2. Usually this is done in terms of molalities rather than mole fractions and it leads to this integral:

$$\ln \gamma_{2,m} = \varphi - 1 + \int_{m'=0}^{m} \frac{\varphi - 1}{m'} dm'$$

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CHAPTER OVERVIEW

12: Chemical Equilibrium

12.1: Reaction Quotient and Equilibrium Constant

12.2: Equilibrium Results when Gibbs Energy is Minimized

12.3: The Equilibrium Constant

12.4: An Equilibrium Constant is a Function of Temperature Only

12.5: Reaction Quotient and Equilibrium Constant Ratio Determines Reaction Direction

12.6: The Sign of ΔG and not ΔG° Determines the Direction of Reaction Spontaneity

12.7: The van 't Hoff Equation

12.8: Equilibrium Constants in Terms of Partition Functions

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12.1: Reaction Quotient and Equilibrium Constant

Let's consider a prototypical reaction at constant T, P:

$$aA + bB \rightarrow cC + dD \tag{12.1.1}$$

The Gibbs free energy of the reaction is defined as:

$$\Delta_{rxn}G = G_{products} - G_{reactants} = G^C + G^D - G^A - G^B, \tag{12.1.2}$$

and replacing the absolute Gibbs free energies with the chemical potentials μ_i, we obtain:

$$\Delta_{rxn}G = c\mu_C + d\mu_D - a\mu_A - b\mu_B. \tag{12.1.3}$$

Assuming the reaction is happening in the gas phase, we can then use Equation 9.4.6 to replace the chemical potentials with their value in the reaction mixture, as:

$$\begin{aligned}\Delta_{rxn}G &= c(\mu_C^{\ominus} + RT\ln P_C) + d(\mu_D^{\ominus} + RT\ln P_D) - a(\mu_A^{\ominus} + RT\ln P_A) - b(\mu_B^{\ominus} + RT\ln P_B) \\ &= \underbrace{c\mu_C^{\ominus} + d\mu_D^{\ominus} - a\mu_A^{\ominus} - b\mu_B^{\ominus}}_{\Delta_{rxn}G^{\ominus}} + RT\ln\frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}.\end{aligned} \tag{12.1.4}$$

We can define a new quantity called the *reaction quotient* as a function of the partial pressures of each substance:[1])

$$Q_P = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}, \tag{12.1.5}$$

and we can then simply rewrite Equation ??? using Equation 12.1.5 as:

$$\Delta_{rxn}G = \Delta_{rxn}G^{\ominus} + RT\ln Q_P. \tag{12.1.6}$$

This equation tells us that the sign of $\Delta_{rxn}G$ is influenced by the reaction quotient Q_P. For a spontaneous reaction at the beginning, the partial pressures of the reactants are much higher than the partial pressures of the products, therefore $Q_P \ll 1$ and $\Delta_{rxn}G < 0$, as we expect. As the reaction proceeds, the partial pressures of the products will increase, while the partial pressures of the reactants will decrease. Consequently, both Q_P and $\Delta_{rxn}G$ will increase. The reaction will completely stop when $\Delta_{rxn}G = 0$, which is the chemical equilibrium point. At the reaction equilibrium:

$$\Delta_{rxn}G = 0 = \Delta_{rxn}G^{\ominus} + RT\ln K_P, \tag{12.1.7}$$

where we have defined a new quantity called **equilibrium constant**, as the value the reaction quotient assumes when the reaction reaches equilibrium, and we have denoted it with the symbol K_P.[2] From Equation 12.1.7 we can derive the following fundamental equation on the standard Gibbs free energy of reaction:

$$\Delta_{rxn}G^{\ominus} = -RT\ln K_P. \tag{12.1.8}$$

To extend the concept of K_P beyond the four species in the prototypical reaction (10.1), we can use the product of a series symbol ($\prod_i$), and write:

$$K_P = \prod_i P_{i,eq}^{\nu_i}, \tag{12.1.9}$$

where $P_{i,eq}$ are the partial pressure of each species at equilibrium. Eq. (10.1.9) is in principle valid for ideal gases only. However, reaction involving ideal gases are pretty rare. As such, we can further extend the concept of equilibrium constant and write:

$$K_{eq} = \prod_i a_{i,eq}^{\nu_i}, \tag{12.1.10}$$

where we have replaced the partial pressure at equilibrium, $P_{i,eq}$, with a new concept introduced initially by Gilbert Newton Lewis (1875–1946),[3] that he termed **activity**, and represented by the letter a. For ideal gases, it is clear that $a_i = P_i/P^{\ominus}$. For non-ideal gases, the activity is equal to the fugacity $a_i = f_i/P^{\ominus}$, a concept that we will investigate in the next chapter. For pure liquids and solids, the activity is simply $a_i = 1$. For diluted solutions, the activity is equal to a measured concentration (such as, for example, the mole fraction x_i in the liquid phase, and y_i in the gas phase, or the molar concentration $[i]/[i]^{\ominus}$ with $[i]^{\ominus} = 1\ [mol/L]$). Finally

for concentrated solutions, the activity is related to the measured concentration via an activity coefficient. We will return to the concept of activity in chapter 14, when we will specifically deal with solutions. For now, it is interesting to use the activity to write the definition of the following two constants:

$$K_y = \prod_i (y_{i,\text{eq}})^{\nu_i} \qquad K_C = \left(\prod_i [i]_{\text{eq}} / [i]^{\ominus} \right)^{\nu_i}, \tag{12.1.11}$$

which can then be related with K_P for a mixture of ideal gases using:

$$P_i = y_i P \qquad P_i = \frac{n_i}{V} RT = [i]RT, \tag{12.1.12}$$

which then results in:

$$K_P = K_y \cdot \left(\frac{P}{P^{\ominus}} \right)^{\Delta\nu} \qquad K_P = K_C \left(\frac{[i]^{\ominus} RT}{P^{\ominus}} \right)^{\Delta\nu}, \tag{12.1.13}$$

with $\Delta\nu = \sum_i \nu_i$.

Using the general equilibrium constant, K_{eq}, we can also rewrite the fundamental equation on $\Delta_{\text{rxn}} G^{\ominus}$ that we derived in Equation 12.1.8 to be applicable at most conditions, as:

$$\Delta_{\text{rxn}} G^{\ominus} = -RT \ln K_{\text{eq}}, \tag{12.1.14}$$

and since $\Delta_{\text{rxn}} G^{\ominus}$ depends on T, P and $\{n_i\}$, it is useful to explore how K_{eq} depends on those variables as well.

---

1. Notice that since we used Equation 9.4.5 to derive the reaction quotient, the partial pressures inside it are always dimensionless since they are divided by $P^{\ominus}$.
2. The subscript P refers to the fact that the equilibrium constant is measured in terms of partial pressures.
3. Gilber Lewis is the same scientist that invented the concept of Lewis Structures.

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12.2: Equilibrium Results when Gibbs Energy is Minimized

Many important chemical reactions -if not *most*- are performed in *solution* rather than between solids or gases. Solid state reactions are often very slow and not all chemical species can be put in the vapor phase because they decompose before evaporating.

Often we are not concerned with the temporal aspects of a reaction. That can be technologically very important but it is the domain of *kinetics* - a different branch of Physical Chemistry - rather than classical thermodynamics.. The latter is more concerned with the endpoint. This is the thermodynamically speaking the (stable) equilibrium, but chemically it can either represent a *completed* reaction or a *chemical equilibrium*.

Unfortunately, of the three main aggregation states: gas – liquid – solid, the structure of liquids is least understood and one of the most complex liquids is also one of the most extensively used ones: water. It is vital to many branches of chemistry varying from geochemistry to environmental chemistry to biochemistry. We shall make just a small inroad into its complexity.

12.2.1: Extent of reaction

To describe the progress of a reaction we define the **extent of reaction**. It is usually denoted by the Greek letter ξ.

Consider a generic reaction:

$$v_A A + v_B B \rightleftharpoons v_Y Y + v_Z Z$$

Using stoichiometry we can define the extent by considering how the number of moles (or molar amounts) of each species changes during the reaction:

reactants

- $n_A = n_{A,0} - v_A \xi$
- $n_B = n_{B,0} - v_B \xi$

products

- $n_Y = n_{Y,0} + v_Y \xi$
- $n_Z = n_{Z,0} + v_Z \xi$

The dimension of ξ is [mol] because the stoichiometric coefficients v_i are dimensionless integers. If the reaction goes to completion for one of the reactants -the *limiting reactant*- $n_{A \text{ or } B}$=n_{limiting} will go to zero. If we start with $n_{limiting} = v_{limiting}$ moles, the value of ξ starts at 0 (no products) and goes to 1 at completion (limiting reactant depleted). When approaching an equilibrium ξ will not go beyond ξ_{eq}.

12.2.2: Measuring ξ

The extent of reaction is what is the central subject of reaction kinetics. Its value is typically measured as a function of time indirectly by measuring a quantity q that is *linearly dependent* on ξ(t):

$$q(\xi) = a\xi + b$$

Consider the situation at the extremes $\xi = 0$ and $\xi = 1$:

$$q_0 = a.0 + b = b$$

$$q_1 = a.1 + b = a + b$$

$$q_1 - q_0 = a$$

Thus, ξ can be found from

$$\frac{q(t) - q0}{q_1 - q_0} = \frac{q(t) - b}{a}$$

The nature of q can vary widely from UV/Vis absorption, conductivity, gravimetric to caloric data.

In practice, q_0 at $\xi = 0$ is often hard to observe because it takes time to mix the reactants, particularly in solutions, and q_1 at ξ=1 may never be reached if the reaction goes to equilibrium. Nevertheless the values of a and b can often be found from the available data by fitting techniques.

In (equilibrium, static) thermodynamics we are only concerned with the endpoint:

- $\xi = 1$: the reaction runs to completion
- $\xi = \xi_{eq}$: the react ion goes to a state of chemical equilibrium

12.2.3: Thermodynamic Potentials

As we have seen we can write any change in the Gibbs free energy due to changes in the molar amounts of the species involved in the reaction (at T, P constant) as:

$$dG = \sum \frac{\partial G}{\partial n_i} dn_i = \sum \mu_i dn_i$$

where μ is the *thermodynamic potential*, often called *chemical potential* when dealing with reactions. From the definition of ξ we can see by differentiation that

- $dn_A = -v_A d\xi$
- $dn_B = -v_A d\xi$
- $dn_Y = v_Y d\xi$
- $dn_Z = v_Z d\xi$

This allows us to *unify the changes* in the molar amount of all the species into *one single variable* $d\xi$. We get:

$$dG = \left[\sum -v_{i,reactants}\mu_{i,reactants} + \sum +v_{i,products}\mu_{j,products}\right] d\xi$$

or

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = -\sum v_{i,r}\mu_{i,r} + \sum v_{i,p}\mu_{j,p}$$

This quantity is also written as:

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta_r G$$

This quantity gives the change in Gibbs free energy for the reaction (as written!!) for $\Delta\xi$=1 mole. (Units are [J/mol] therefore). This is the change in Gibbs energy (the slope of G vs ξ) when the extent of reaction changes by one mole with a fixed composition. Equilibrium results when Gibbs energy is at a minimum with respect to the extent of reaction.

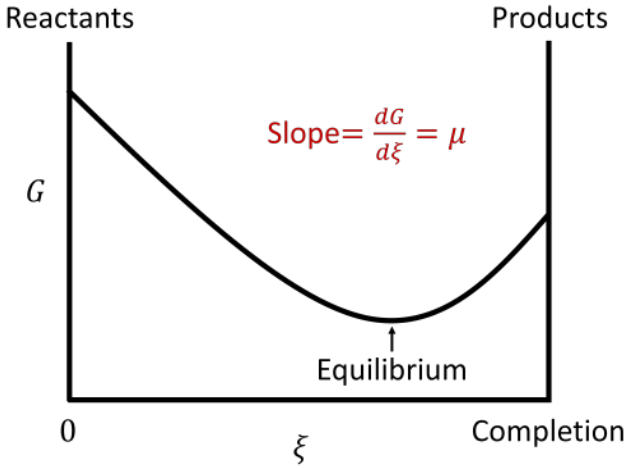


Figure 1. Gibbs energy plotted as a function of the extent of reaction. Equilibrium results when the Gibbs energy is minimized.

12.2.4: Gas Reactions

Let us assume that our reaction is entirely between gas species and that the gas is sufficiently dilute that we can use the ideal gas law. Then we can write for each species:

$$\mu_i = \mu_i^o + RT \ln \frac{P_i}{P_i^o}$$

We can then split up the $\Delta_r G$ expression in two parts:

$$\Delta_r G = \Delta_r G^o + RT \ln Q$$

The standard potentials:

$$\Delta_r G^o = -\sum v_{i,r}\, \mu_{i,r}^o + \sum v_{i,p} \mu_{j,p}^o$$

and the logarithmic terms:

$$RT \ln Q = -v_A RT \ln \left(\frac{P_A}{P_A^o} \right) - v_B RT \ln \left(\frac{P_B}{P_B^o} \right) + v_Y RT \ln \left(\frac{P_Y}{P_Y^o} \right) + v_Z RT \ln \left(\frac{P_Z}{P_Z^o} \right)$$

We can combine all the logarithmic terms into Q, called the ***reaction quotient***. The stoichiometric coefficients become exponents and the reactants' factors will be 'upside down' compared to the products, because of the properties of logarithms:

$$a \ln x = \ln x^a$$

$$-a \ln x = \ln \left(\frac{1}{x^a} \right)$$

We have kept the standard pressures P_i^o in the expression, but often they are omitted. They are usually all 1 bar, but in principle we could choose 1 bar for A 1 Torr for B an 1 psi for the products. It creates a valid (though ridiculous) definition of what $^\ominus$ stands for. (Of course the value of $\Delta_r G^o$ does *depend* on that choice!).

We could write

$$RT \ln Q = RT \ln \frac{Q_P}{Q^o}$$

Q^o is typically unity in magnitude but it *cancels the dimensions* of Q_P. That means that Q and Q_P are equal in magnitude and we can get Q from Q_P by simply dropping the dimensions. Q is dimensionless but Q_P usually is not. Often this fine distinction is simply not made and Q^o is *omitted*, we get:

$$\Delta_r G = \Delta_r G^o + RT \ln \frac{P_Y^{v_Y} P_Z^{v_Z}}{P_A^{v_A} P_B^{v_B}}$$

Notice the difference between $\Delta_r G$ which denotes the conditions (e.g. pressures) of *your reaction* and $\Delta_r G^o$ denotes standard conditions.

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12.3: The Equilibrium Constant

The equilibrium constant, K, expresses the relationship between products and reactants of a reaction at equilibrium with respect to a specific unit.This article explains how to write equilibrium constant expressions, and introduces the calculations involved with both the concentration and the partial pressure equilibrium constant.

Homogeneous Reactions

A homogeneous reaction is one where the states of matter of the products and reactions are all the same (the word "homo" means "same"). In most cases, the solvent determines the state of matter for the overall reaction. For example, the synthesis of methanol from a carbon monoxide-hydrogen mixture is a *gaseous* **homogeneous** mixture, which contains two or more substances:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \tag{12.3.1}$$

At equilibrium, the rate of the forward and reverse reaction are equal, which is demonstrated by the arrows. The equilibrium constant, however, gives the ratio of the units (pressure or concentration) of the products to the reactants when the reaction is at equilibrium.

The synthesis of ammonia is another example of a *gaseous* **homogeneous** mixture:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \tag{12.3.2}$$

Heterogeneous Reactions

A heterogeneous reaction is one in which one or more states within the reaction differ (the Greek word "heteros" means "different"). For example, the formation of an aqueous solution of lead(II) iodide creates a **heterogeneous** mixture dealing with particles in both the *solid* and *aqueous* states:

$$PbI_{2(s)} \rightleftharpoons Pb^{+2}_{(aq)} + 2I^{-}_{(aq)} \tag{12.3.3}$$

The decomposition of sodium hydrogen carbonate (baking soda) at high elevations is another example of a **heterogeneous** mixture, this reaction deals with molecules in both the *solid* and *gaseous* states:

$$2NaHCO_{3(s)} \rightleftharpoons Na_2CO_{3(s)} + H_2O_{(g)} + CO_{2(g)} \tag{12.3.4}$$

$$C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)} \tag{12.3.5}$$

This difference between homogeneous and heterogeneous reactions is emphasized so that students remember that solids, pure liquids, and solvents are treated differently than gases and solutes when approximating the activities of the substances in equilibrium constant expressions.

Writing Equilibrium Constant Expressions

The numerical value of an equilibrium constant is obtained by letting a single reaction proceed to equilibrium and then measuring the concentrations of each substance involved in that reaction. The ratio of the product concentrations to reactant concentrations is calculated. Because the concentrations are measured at equilibrium, the equilibrium constant remains the same for a given reaction independent of initial concentrations. This knowledge allowed scientists to derive a model expression that can serve as a "template" for any reaction. This basic "template" form of an equilibrium constant expression is examined here.

Equilibrium Constant of Activities

The thermodynamically correct equilibrium constant expression relates the activities of **all** of the species present in the reaction. Although the concept of activity is too advanced for a typical General Chemistry course, it is essential that the explanation of the derivation of the equilibrium constant expression starts with activities so that no misconceptions occur. For the hypothetical reaction:

$$bB + cC \rightleftharpoons dD + eE \tag{12.3.6}$$

the equilibrium constant expression is written as

$$K = \frac{a_D^d \cdot a_E^e}{a_B^b \cdot a_C^c} \tag{12.3.7}$$

*The lower case letters in the balanced equation represent the number of moles of each substance, the upper case letters represent the substance itself.

- If $K > 1$ then equilibrium favors products
- If $K < 1$ then equilibrium favors the reactants

Equilibrium Constant of Concentration

To avoid the use of activities, and to simplify experimental measurements, the equilibrium constant of concentration approximates the activities of solutes and gases in dilute solutions with their respective molarities. However, the activities of solids, pure liquids, and solvents are **not** approximated with their molarities. Instead these activities are defined to have a value equal to 1 (one).The equilibrium constant expression is written as K_c, as in the expression for the reaction:

$$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)} \tag{12.3.8}$$

$$K_c = \frac{a_{H_3O^+} \cdot a_{F^-}}{a_{HF} \cdot a_{H_2O}} \approx \frac{[H_3O^+][F^-]}{[HF](1)} = \frac{[H_3O^+][F^-]}{[HF]} \tag{12.3.9}$$

Here, the letters inside the brackets represent the concentration (in molarity) of each substance. Notice the mathematical product of the chemical products raised to the powers of their respective coefficients is the numerator of the ratio and the mathematical product of the reactants raised to the powers of their respective coefficients is the denominator. This is the case for every equilibrium constant. A ratio of molarities of products over reactants is usually used when most of the species involved are dissolved in water. A ratio of concentrations can also be used for reactions involving gases if the volume of the container is known.

.

Equilibrium Constant of Pressure

Gaseous reaction equilibria are often expressed in terms of partial pressures. The equilibrium constant of pressure gives the ratio of pressure of products over reactants for a reaction that is at equilibrium (again, the pressures of all species are raised to the powers of their respective coefficients). The equilibrium constant is written as K_p, as shown for the reaction:

$$aA_{(g)} + bB_{(g)} \rightleftharpoons gG_{(g)} + hH_{(g)} \tag{12.3.10}$$

$$K_p = \frac{p_G^g p_H^h}{p_A^a p_B^b} \tag{12.3.11}$$

- Where p can have units of pressure (e.g., atm or bar).

Conversion of K_c to K_p

To convert K_c to K_p, the following equation is used:

$$K_p = K_c(RT)^{\Delta n_{gas}} \tag{12.3.12}$$

where:

- R=0.0820575 L atm mol^{-1} K^{-1} or 8.31447 J mol^{-1} K^{-1}
- T= Temperature in Kelvin
- Δn_{gas}= Moles of gas (product) - Moles of Gas (Reactant)

Reaction Quotient

Another quantity of interest is the reaction quotient, Q, which is the numerical value of the ratio of products to reactants at any point in the reaction. The reaction quotient is calculated the same way as is K, but is not necessarily equal to K. It is used to determine which way the reaction will proceed at any given point in time.

$$Q = \frac{[G]^g[H]^h}{[A]^a[B]^b} \tag{12.3.13}$$

- If $Q > K$, then the reactions shifts to the left to reach equilibrium
- If $Q < K$, then the reactions shifts to the right to reach equilibrium
- If $Q = K$ then the reaction is at equilibrium

The same process is employed whether calculating Q_c or Q_p.

Heterogeneous Mixture

The most important consideration for a heterogeneous mixture is that **solids and pure liquids and solvents have an activity that has a fixed value of 1**. From a mathematical perspective, with the activities of solids and liquids and solvents equal one, these substances do not affect the overall K or Q value. This convention is extremely important to remember, especially in dealing with heterogeneous solutions.

Example 12.3.1

In a hypothetical reaction:

$$aA_{(s)} + bB_{(l)} \rightleftharpoons gG_{(aq)} + hH_{(aq)} \tag{12.3.14}$$

The equilibrium constant expression is written as follows:

$$K_c = \frac{[G]^g[H]^h}{1 \times 1} = [G]^g[H]^h \tag{12.3.15}$$

In this case, since solids and liquids have a fixed value of 1, the numerical value of the expression is independent of the amounts of A and B. If the product of the reaction is a solvent, the numerator equals one, which is illustrated in the following reaction:

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \tag{12.3.16}$$

The equilibrium constant expression would be:

$$K_c = \frac{1}{[H^+][OH^-]} \tag{12.3.17}$$

which is the reciprocal of the autoionization constant of water (K_w)

$$K_c = \frac{1}{K_w} = 1 \times 10^{14} \tag{12.3.18}$$

Manipulation of Constants

The equilibrium constant expression must be manipulated if a reaction is reversed or split into elementary steps. When the reaction is reversed, the equilibrium constant expression is inverted. The new expression would be written as:

$$K' = \frac{1}{\frac{[G]^g[H]^h}{[A]^a[B]^b}} = \frac{[A]^a[B]^b}{[G]^g[H]^h} \tag{12.3.19}$$

When there are multiple steps in the reaction, each with its own K (in a scenario similar to Hess's law problems), then the successive K values for each step are *multiplied* together to calculate the overall K.

Activities

Because the concentration of reactants and products are not dimensionless (i.e. they have units) in a reaction, the actual quantities used in an equilibrium constant expression are *activities*. *Activity* is expressed by the dimensionless ratio $\frac{[X]}{c^\circ}$ where $[X]$ signifies the molarity of the molecule and c is the chosen reference state:

$$a_b = \frac{[B]}{c^\circ} \tag{12.3.20}$$

For gases that do not follow the ideal gas laws, using activities will accurately determine the equilibrium constant that changes when concentration or pressure varies. Thus, the units are canceled and K becomes unitless.

Practice Problems

1. Write the equilibrium constant expression for each reaction.
   a. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
   b. $N_2O_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons 2NO_{(g)}$
   c. $Cu_{(s)} + 2Ag^{+}_{(aq)} \rightleftharpoons Cu^{+2}_{(aq)} + 2Ag_{(s)}$
   d. $CaCO_{3(g)} \rightleftharpoons CaCO_{(s)} + CO_{2(g)}$
   e. $2NaHCO_{3(s)} \rightleftharpoons Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$
2. What is the K_c of the following reaction?

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \tag{12.3.21}$$

   with concentration $SO_{2(g)} = 0.2MO_{2(g)} = 0.5MSO_{3(g)} = 0.7\ M$ Also, What is the K_p of this reaction? At room temperature?
3. For the same reaction, the differing concentrations:

$$SO_{2(g)} = 0.1\ MO_{2(g)} = 0.3\ M\ SO_{3(g)} = 0.5\ M \tag{12.3.22}$$

   Would this go towards to product or reactant?
4. Write the Partial Pressure Equilibrium:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \tag{12.3.23}$$

5. Write the chemicl reaction for the following equilibrium constant:

$$K_p = \frac{P^2_{HI}}{P_{H_2} \times P_{I_2}} \tag{12.3.24}$$

References

1. Petrucci, Ralph H. General Chemistry: Principles and Modern Applications 9th Ed. New Jersey: Pearson Education Inc. 2007.

Outside Links

- For more information on equilibrium constant expressions please visit the Wikipedia site: http://en.Wikipedia.org/wiki/Equilibrium_constant
- The image below can be found here: image.tutorvista.com/content/chemical-equilibrium/reaction-rate-time-graph.gif

Answers to Practice Problems

1. $K_c = \frac{[SO_3]^2}{[O_2][SO_2]^2}$
2. $Kc = \frac{[NO]^2}{[O_2]^{0.5}[N_2O]}$
3. $Kc = \frac{[Cu^{+2}]}{[Ag^{+}]^2}$
4. $Kc = \frac{[CO_2]}{[CaCO_3]}$
5. $K_c = [H_2O][CO_2]$

What is K_c for the Reaction

1) Kc: 24.5

Kp: 1.002 Atm

2) Q_c= 83.33 > K_c therefore the reaction shifts to the left

1. $K_p = \frac{P_{CO_2}}{P_{O_2}}$
2. $H_2(g) + I_2(g) \rightarrow 2HI(g)$

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12.4: An Equilibrium Constant is a Function of Temperature Only

Consider a generic reaction:

$$v_A A + v_B B \rightleftharpoons v_Y Y + v_Z Z$$

When the reaction reaches equilibrium, the Gibbs energy of reaction, $\Delta_r G$, goes to zero. In this case, the reaction quotient, Q, is usually rewritten as the **equilibrium constant**, K, and we get:

$$\Delta_r G = \Delta_r G^o + RT \ln K = 0$$

$$\Delta_r G^o = -RT \ln K$$

where

$$K = \frac{P_{eq,Y}^{vY} P_{eq,Z}^{vZ}}{P_{eq,A}^{vA} P_{eq,B}^{vB}}$$

> **Note**
>
> As you see $\Delta_r G^o$ is ***not*** zero, because the standard state does ***not*** represent an equilibrium state (typically).

We can calculate the temperature dependence of K. Rather than look at:

$$\left(\frac{\partial K}{\partial T}\right)_P$$

We will look at:

$$\left(\frac{\partial \ln K}{\partial T}\right)_P$$

Starting with Gibbs energy:

$$\Delta_r G^\circ = -RT \ln K$$

$$\therefore \ln K = -\frac{\Delta r G^\circ}{RT}$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = -\frac{1}{R}\left[\frac{\partial (\Delta_r G^\circ / T)}{\partial T}\right]_P$$

We need to take the Gibbs-Helmholtz equation:

$$\Delta \bar{H} = -T^2 \left[\frac{\partial (\Delta \bar{G}/T)}{\partial T}\right]_P$$

We can also write it as:

$$\left[\frac{\partial \left(\Delta \bar{G}/T\right)}{\partial T}\right]_P = -\frac{\Delta \bar{H}}{T^2}$$

Plugging the Gibbs-Helmholtz equation into our earlier equation, we obtain the Van't Hoff equation:

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta_r H^\circ}{RT^2}$$

The temperature dependence of the equilibrium constant depends on enthalpy of reaction. Rearranging:

$$d(\ln K) = \frac{\Delta_r H^\circ (T)}{RT^2} dT$$

This is the Van't Hoff equation. We can use it to find K at other temperatures. Assuming enthalpy is independent of temperature, the integrated form becomes:

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

12.4.1: Le Chatelier's Principle

In the ideal gas reaction case, K **only** depends on temperature, T, (just like U) not on the total pressure, P. This leads to the well-known principle of Le Chatelier. Consider a gas reaction like:

\[A \rightleftharpoons B + C \nonumber \nonumber \]

e.g.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

In pressures, the equilibrium constant becomes:

$$K = \frac{P_B P_C}{P_A}$$

If initially n_A =1 we have at an extent ξ:

n_A = 1- ξ

n_B= ξ

n_C= ξ

n_{Total} = 1+ ξ

The partial pressures are given by Dalton's law:

P_A= [1- ξ /1+ ξ] P

P_B [ξ / 1+ ξ] P

P_C [ξ /1+ ξ] P

The equilibrium constant becomes:

$$K = P\frac{\xi_{eq}^2}{1-\xi_{eq}^2}$$

Even though the total pressure, P, does occur in this equation, K is *not* dependent on P. If the total pressure is changed (e.g. by compression of the gas) the value of ξ_{eq} will change (the equilibrium shifts) in response. It will go to the side with the fewer molecules. This fact is known as le Chatelier's principle

If the system is not ideal we will also get a Chatelier shift, but the value of K may change a little because the value of the activity coefficients (or fugacity) is a little dependent on the pressure too. In solution the same thing holds. In ideal solutions K is only T dependent, but as we saw these systems are rare. Particularly in ionic solutions equilibrium constants will be effected by other things than just temperature, e.g. changes in the ionic strength and we need to find the activity coefficients to make any predictions.

Example

Consider the reaction of ammonia decomposition:

$$2NH_3\,(g) \leftrightharpoons N_2\,(g) + 3H_2\,(g)$$

$$\Delta_f H^\circ(NH_3, g) = -45.90\ \text{kJ/mol}$$

The reaction is initially at equilibrium. For each of the stresses, use your General Chemistry knowledge to decide if equilibrium will be unaffected, or if it will shift towards reactants or products.

Process	Shifts towards
Isothermal removal of H_2 gas	
Isothermal addition of N_2 gas	
Isothermal decrease of container volume	
Isothermal and isochoric addition of argon gas	
Isobaric increase of temperature	

Write the equilibrium constant expression for the above chemical reaction in terms of gas-phase mole fractions.

12.4.2: Concentration

The gas law contains a hidden definition of concentration:

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right) RT$$

$$P = cRT$$

$$c = \frac{P}{RT} \tag{12.4.1}$$

Here c stands for the molar amount per unit volume or ***molarity***. For gaseous mixtures we do not use this fact much, but it provides the link to the more important liquid solution as a reaction medium. We can rewrite the equilibrium constant as

$$K = \frac{c_{eq,Y}^{v_Y} c_{eq,Z}^{v_Z}}{c_{eq,A}^{v_A} c_{eq,B}^{v_B}} \tag{12.4.2}$$

However, c (Equation 12.4.1) is substituted into K (Equation 12.4.2), then not all the factors of RT cancel. The missing term g. ln[RT] depends on the stoichiometric coefficients:

$$g = v_Y + v_Z - v_A - v_B$$

The term is generally *incorporated* in $\Delta_r G^\circ$ so that the latter now refers to a new standard state of 1 mole per liter of each species rather than 1 bar of each (or so).

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12.5: Reaction Quotient and Equilibrium Constant Ratio Determines Reaction Direction

The Gibbs free energy function was constructed to be able to predict which changes could occur spontaneously. If we start with a set of initial concentrations we can write them in a reaction quotient

$$\Delta_r G = \Delta_r G^o + RT \ln Q$$

if we subtract the equilibrium version of this expression:

$$0 = \Delta_r G^o + RT \ln K$$

we get

$$\Delta_r G = RT \ln \left(\frac{Q}{K} \right)$$

That gives us the sign of $\Delta_r G$. If this is negative the reaction will spontaneously proceed from left to right as written, if positive it will run in reverse. In both case the value of Q will change until $Q = K$ and equilibrium has been reached.

The main difference between K and Q is that K describes a reaction that is at equilibrium, whereas Q describes a reaction that is not at equilibrium. To determine Q, the concentrations of the reactants and products must be known. For a given general chemical equation:

$$aA + bB \rightleftharpoons cC + dD \tag{12.5.1}$$

the Q equation is written by multiplying the activities for the species of the products and dividing by the activities of the reactants. If any component in the reaction has a coefficient, indicated above with lower case letters, the concentration is raised to the power of the coefficient. Q for the above equation is therefore:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{12.5.2}$$

Note

A comparison of Q with K indicates which way the reaction shifts and which side of the reaction is favored:

- If $Q > K$, then the reaction favors the reactants. This means that in the Q equation, the ratio of the numerator (the concentration or pressure of the products) to the denominator (the concentration or pressure of the reactants) is larger than that for K, indicating that more products are present than there would be at equilibrium. Because reactions always tend toward equilibrium (Le Châtelier's Principle), the reaction produces more reactants from the excess products, therefore causing the system to shift to the **LEFT.** This allows the system to reach equilibrium.
- If $Q < K$, then the reaction favors the products. The ratio of products to reactants is less than that for the system at equilibrium—the concentration or the pressure of the reactants is greater than the concentration or pressure of the products. Because the reaction tends toward reach equilibrium, the system shifts to the **RIGHT** to make more products.
- If $Q = K$, then the reaction is already at equilibrium. There is no tendency to form more reactants or more products at this point. No side is favored and no shift occurs.

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12.6: The Sign of ΔG and not ΔG° Determines the Direction of Reaction Spontaneity

It is important to distinguish between the Gibbs energy of reaction, $\Delta_r G$ and the standard state Gibbs energy of reaction, $\Delta_r G°$. The ° refers to standard state conditions. That is, each reactant and product has a partial pressure of 1 bar if a gas, a concentration of 1 M if a solution, and they are all unmixed from each other. Such idealized conditions, while convenient for serving as a reference state, do not actually represent real reaction conditions. Consider the reaction of nitrogen with hydrogen to form ammonia:

$$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \rightarrow 2\mathrm{NH_3}\,(g)$$

$$\Delta_r G° = -32.9\ \frac{\mathrm{kJ}}{\mathrm{mol\ K}}$$

If the reaction was run under standard state conditions (1 bar partial pressure of each gas), the reaction would shift towards the products since $\Delta_r G° < 0$. That is, the partial pressures of N_2 and O_2 will decrease and the partial pressure of NH_3 will increase until equilibrium is reached. The Gibbs energy of reaction is dependent on the composition:

$$\Delta_r G = \Delta_r G° + RT \ln Q = \Delta_r G° + RT \ln \left(\frac{P_{\mathrm{NH_3}}^2}{P_{\mathrm{N_2}} P_{\mathrm{H_2}}^3} \right)$$

At equilibrium, the minimum Gibbs energy of reaction will be reached:

$$\Delta_r G = 0\ \frac{\mathrm{kJ}}{\mathrm{mol\ K}}$$

And the reaction quotient will equal the equilibrium constant:

$$Q = K$$

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12.7: The van 't Hoff Equation

We can use Gibbs-Helmholtz to get the temperature dependence of K

$$\left(\frac{\partial[\Delta G^o/T]}{\partial T}\right)_P = \frac{-\Delta H^o}{T^2}$$

At equilibrium, we can equate ΔG^o to $-RT\ln K$ so we get:

$$\left(\frac{\partial[\ln K]}{\partial T}\right)_P = \frac{\Delta H^o}{RT^2}$$

We see that whether K increases or decreases with temperature is linked to whether the reaction enthalpy is positive or negative. If temperature is changed little enough that ΔH^o can be considered constant, we can translate a K value at one temperature into another by integrating the above expression, we get a similar derivation as with melting point depression:

$$\ln\frac{K(T_2)}{K(T_1)} = \frac{-\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

If more precision is required we could correct for the temperature changes of ΔH^o by using heat capacity data.

> *How K increases or decreases with temperature is linked to whether the reaction enthalpy is positive or negative.*

The expression for K is a rather sensitive function of temperature given its exponential dependence on the difference of stoichiometric coefficients One way to see the sensitive temperature dependence of equilibrium constants is to recall that

$$K = e^{-\Delta_r G^o/RT} \tag{12.7.1}$$

However, since under constant pressure and temperature

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Equation 12.7.1 becomes

$$K = e^{-\Delta H^o/RT} e^{\Delta S^o/R} \tag{12.7.2}$$

Taking the natural log of both sides, we obtain a linear relation between $\ln K$and the standard enthalpies and entropies:

$$\ln K = -\frac{\Delta H^o}{R}\frac{1}{T} + \frac{\Delta S^o}{R} \tag{12.7.3}$$

which is known as the van 't Hoff equation. It shows that a plot of $\ln K$ vs. $1/T$ should be a line with slope $-\Delta_r H^o/R$ and intercept $\Delta_r S^o/R$.

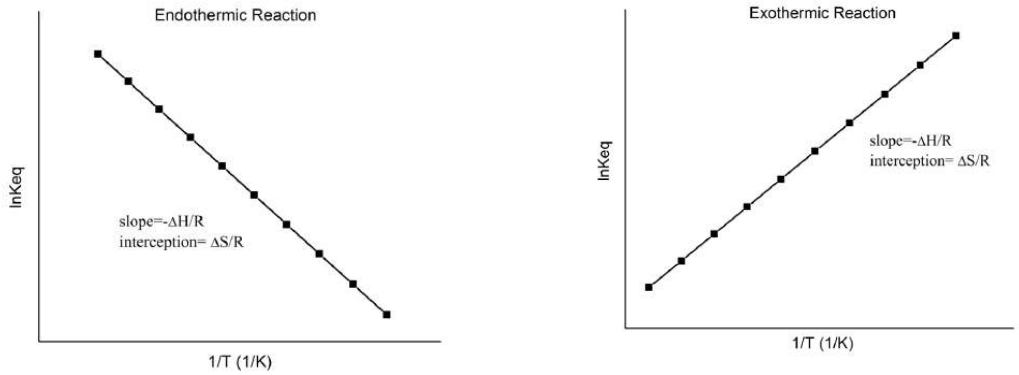


Figure 26.7.1 : Endothermic Reaction (left) and Exothermic Reaction van 't Hoff Plots (right). Figures used with permission of Wikipedia

Hence, these quantities can be determined from the $\ln K$ vs. $1/T$ data without doing calorimetry. Of course, the main assumption here is that $\Delta_r H^o$ and $\Delta_r S^o$ are only very weakly dependent on T, which is usually valid.

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12.8: Equilibrium Constants in Terms of Partition Functions

Consider the general gas phase chemical reaction represented by

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D \tag{12.8.1}$$

where A, B, C and D are the reactants and products of the reaction, and ν_A is the stoichiometric coefficient of chemical A, ν_B is the stoichiometric coefficient of chemical B, and so on. Each of the gases involved in the reaction will eventually reach an equilibrium concentration when the forward and reverse reaction rates become equal. The distribution of reactants to products at the equilibrium point is represented by the equilibrium constant (K_c):

$$K_c = \frac{[C]^{\nu_C}[D]^{\nu_D}}{[A]^{\nu_A}[B]^{\nu_B}}$$

If the system is not at equilibrium, a shift in the number of reactants and products will occur to lower the overall energy of the system. The difference in the energy of the system at this non-equilibrated point and the energy of the system at equilibrium for any particular species is termed chemical potential. When both temperature and volume are constant for both points aforementioned, the chemical potential μ of species i is expressed by the equation

$$\mu_i = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq 1}} \tag{12.8.2}$$

where A is the Helmholtz energy, and N_i is the number of molecules of species i. The Helmholtz energy can be determined as a function of the total partition function, Q:

$$A = -k_B T \ln Q$$

where k_B is the Boltzmann constant and T is the temperature of the system. The total partition function is given by

$$Q = \frac{q_i(V,T)^{Ni}}{N_i!}$$

where q_i is the molecular partition function of chemical species i. Substituting the molecular partition function into the equation for Helmholtz energy yields:

$$A = -k_B T \ln\left(\frac{q_i(V,T)^{N_i}}{N_i!}\right)$$

and then further substituting this equation into the definition of chemical potential (Equation 12.8.2) yields:

$$\mu_i = \left(\frac{\partial -k_B T \ln\left(\frac{q_i(V,T)^{Ni}}{N_i!}\right)}{\partial N_i}\right)_{T,V,N_{j\neq 1}}$$

rearranging this equation the following derivative can be set-up:

$$\mu_i = -k_B T\left[\left(\frac{\partial N_i \ln(q_i(V,T))}{\partial N_i}\right) - \left(\frac{\partial \ln(N_i!)}{\partial N_i}\right)\right]_{T,V,N_{j\neq 1}}$$

From this point Sterling's approximation

$$\ln N! = N \ln N - N$$

can be substituted into the derivative to yield:

$$\mu_i = -k_B T\left[\left(\frac{\partial N_i \ln(q_i(V,T))}{\partial N_i}\right) - \left(\frac{\partial (N_i \ln N_i - N_i)}{\partial N_i}\right)\right]_{T,V,N_{j\neq 1}}$$

From here the derivative can be rearranged and solved:

$$\mu_i = -k_B T \left[\ln(q_i(V,T)) \frac{\partial N_i}{\partial N_i} + N_i \frac{\partial \ln(q_i(V,T))}{\partial N_i} - \ln(N_i) \frac{\partial N_i}{\partial N_i} - N_i \frac{\partial \ln(N_i)}{\partial N_i} + \frac{\partial N_i}{\partial N_i} \right]_{T,V,N_{j \neq 1}}$$

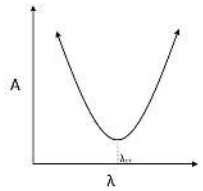
$$= -k_B T \left(\ln(q_i(V,T)) + 0 - \ln(N_i) - N_i \frac{1}{N_i} + 1 \right)$$

$$= -k_B T (\ln(q_i(V,T)) - \ln(N_i))$$

$$= -k_B T \ln\left(\frac{q_i(V,T)}{N_i} \right) \tag{12.8.3}$$

A variable, λ, is then defined such that $dN_j = \nu_j d\lambda$, where j = A, B, C or D and ν_j is taken to be positive for products and negative for reactants. A change in λ therefore corresponds to a change in the concentrations of the reactants and products. Thus, at equilibrium,

$$\left(\frac{\partial A}{\partial \lambda} \right)_{T,V} = 0$$



Helmholtz Energy with respect to Equilibrium Shifts

From Classical thermodynamics, the total differential of A is:

$$dA = -SdT - pdV + \sum_j \mu_j dN_j$$

For a reaction at a fixed volume and temperature (such as in the canonical ensemble), dT and dV equal 0. Therefore,

$$dA = \sum_j \mu_j dN_j$$

$$= \sum_j \mu_j \nu_j d\lambda$$

$$= d\lambda \sum_j \mu_j \nu_j$$

with

$$\sum_j \mu_j \nu_j = 0$$

Substituting the expanded form of chemical potential (Equation 12.8.3):

$$-k_B T \sum_j \ln\left(\frac{q_i}{N_i} \right) \nu_j = 0$$

$$\sum_j \ln\left(\frac{q_i}{N_i} \right) \nu_j = 0$$

$$\sum_j \nu_j [\ln(q_j) - \ln(N_j)] = 0$$

For the reaction in Equation 12.8.1:

$$[\nu_C \ln(q_C) - \nu_C \ln(N_C)] + [\nu_D \ln(q_D) - \nu_D \ln(N_D)]$$
$$- [\nu_A \ln(q_A) - \nu_A \ln(N_A)] - [\nu_B \ln(q_B) - \nu_B \ln(N_B)] = 0$$

This equation simplifies to

$$\frac{(q_C)^{\nu_C}(q_D)^{\nu_D}}{(q_A)^{\nu_A}(q_B)^{\nu_B}} = \frac{(N_C)^{\nu_C}(N_D)^{\nu_D}}{(N_A)^{\nu_A}(N_B)^{\nu_B}}$$

By dividing all terms by volume, and noting the relationship $\frac{N_A}{V} = \frac{\#molecules}{volume} = \rho_A = [A]$ where ρ is referred to a number density, the following equation is obtained:

$$K_c = \frac{\rho_C^{\nu_C}\rho_D^{\nu_D}}{\rho_A^{\nu_A}\rho_B^{\nu_B}} = \frac{(q_C/V)^{\nu_C}(q_D/V)^{\nu_D}}{(q_A/V)^{\nu_A}(q_B/V)^{\nu_B}} \tag{12.8.4}$$

Hence, knowledge of the molecular partition function for all species in the reaction will ensure the calculation of the equilibrium constant.

Example 12.8.1: Reacting Diatomic Molecules

Calculate the equilibrium constant (K_c) for the reaction of $\mathbf{H_2\,(g)}$ and $\mathbf{Cl_2\,(g)}$ at 650 K.

$$\mathrm{H_2\,(g) + Cl_2\,(g) \rightleftharpoons 2\,HCl\,(g)}$$

Solution

We will use Equation 12.8.4 that uses Molecular Partition Functions to evaluate K_c.

$$K_c(T) = \frac{\left(\frac{q_{\mathrm{HCl}}}{V}\right)^2}{\left(\frac{q_{\mathrm{H_2}}}{V}\right)\left(\frac{q_{\mathrm{Cl_2}}}{V}\right)} \tag{12.8.5}$$

This equation is expanded into the rotational, vibrational, translational and electronic molecular partition functions of each species.

$$K_c(T) = \frac{\left(\frac{q_{\mathrm{trans\ HCl}}q_{rot\mathrm{HCl}}q_{vib\mathrm{HCl}}q_{elec\mathrm{HCl}}}{V}\right)^2}{\left(\frac{q_{\mathrm{trans H_2}}q_{\mathrm{rot\ H_2}}q_{vib\mathrm{H_2}}q_{elec\mathrm{H_2}}}{V}\right)\left(\frac{q_{\mathrm{trans Cl_2}}q_{\mathrm{rot\ Cl_2}}q_{vib\mathrm{Cl_2}}q_{elec\mathrm{Cl_2}}}{V}\right)}$$

A simple problem solving strategy for finding equilibrium constants via statistical mechanics is to separate the equation into the molecular partition functions of each of the reactant and product species, solve for each one, and recombine them to arrive at a final answer (e.g., for **HCl**.

$$\frac{q_{\mathrm{HCl}}}{V} = \underbrace{\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}}_{\text{translation}} \times \underbrace{\frac{2k_BT\mu r_e^2}{\sigma\hbar^2}}_{\text{rotation}} \times \underbrace{\frac{1}{1-\exp\left(\frac{-h\nu}{k_BT}\right)}}_{\text{vibration}} \times \underbrace{g_1\exp\left(\frac{D_0}{k_BT}\right)}_{\text{electronic}}$$

To simplify the calculations of molecular partition functions, the characteristic temperature of rotation (Θ_r) and vibration (Θ_ν) are used.

$$\frac{q_{\mathrm{HCl}}}{V} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \times \frac{T}{\sigma\Theta_r} \times \frac{1}{1-\exp\left(\frac{-\Theta_\nu}{T}\right)} \times g_1 \exp\left(\frac{D_0}{RT}\right) \tag{12.8.6}$$

These values are constants that incorporate the physical constants found in the rotational and vibrational partition functions of the molecules. Tabulated values of Θ_r and Θ_ν for select molecules can be found here.

Species	Θ_ν (K)	Θ_r (K)	D_0 (kJ mol^{-1})
$\mathbf{Cl_2\,(g)}$	6125	0.351	239.0
$\mathbf{H_2\,(g)}$	808	87.6	431.9
$\mathbf{HCl\,(g)}$	4303	15.2	427.7

We need to evaluate Equation 12.8.6 for each species then then evaluate Equation 12.8.5 directly.

For $\mathbf{HCl}$:

$$\frac{q_{HCl}}{V} = \left(\frac{2\pi\left(2.1957\times10^{-24}\ \text{kg}\right)\left(1.38065\times10^{-23}\text{JK}^{-1}\right)(650K)}{\left(6.62607\times10^{-34}\text{Js}\right)^2}\right)^{3/2} \times \frac{650\ \text{K}}{(1)(15.2\ \text{K})} \times \frac{1}{1-\exp\left(\frac{-4303\ \text{K}}{650\ \text{K}}\right)} \times (1)\exp\left(\frac{427,700\text{Jmol}^{-1}}{(8.3145\,\text{J K mol}^{-1})\,(650\ \text{K})}\right)$$

$$\frac{q_{HCl}}{V} = \left(1.4975\times10^{35}\ \text{m}^{-3}\right)(42.76)(1.0013)\left(2.3419\times10^{34}\right)$$

For $\mathbf{H_2}$:

$$\frac{q_{H_2}}{V} = \left(\frac{2\pi\left(1.2140\times10^{-25}\ \text{kg}\right)\left(1.38065\times10^{-23}\text{JK}^{-1}\right)(650\ \text{K})}{\left(6.62607\times10^{-34}\text{Js}\right)^2}\right)^{3/2} \times \frac{650\ \text{K}}{(2)(87.6\ \text{K})} \times \frac{1}{1-\exp\left(\frac{-808\ \text{K}}{650\ \text{K}}\right)} \times (1)\exp\left(\frac{431,900\text{Jmol}^{-1}}{(8.3145\ \text{J Kmol}^{-1})\,(650\ \text{K})}\right)$$

$$\frac{q_{H_2}}{V} = \left(1.9468\times10^{33}\ \text{m}^{-3}\right)(3.71)(1.41)\left(5.0942\times10^{34}\right)$$

For $\mathbf{Cl_2}$:

$$\frac{q_{Cl_2}}{V} = \left(\frac{2\pi\left(4.2700\times10^{-24}\ \text{kg}\right)\left(1.38065\times10^{-23}\text{JK}^{-1}\right)(650K)}{\left(6.62607\times10^{-34}\text{Js}^2\right.}\right)^{3/2} \times \frac{650\ \text{K}}{(2)(0.351\ \text{K})} \times \frac{1}{1-\exp\left(\frac{-6125\ \text{K}}{650\ \text{K}}\right)} \times (1)\exp\left(\frac{239,000\text{Jmol}^{-1}}{(8.3145\ \text{J K mol}^{-1})\,(650\ \text{K})}\right)$$

$$\frac{q_{Cl_2}}{V} = \left(5.4839\times10^{35}\ \text{m}^{-3}\right)(925.9)(1.00)\left(1.606\times10^{19}\right)$$

Combining the terms from each species, the following expression is obtained:

$$\begin{aligned} K_c &= \frac{\left(1.9468\times10^{33}\ \text{m}^{-3}\right)^2}{\left(1.9468\times10^{33}\ \text{m}^{-3}\right)\left(5.4839\times10^{35}\ \text{m}^{-3}\right)} \times \frac{(42.76)^2}{(3.71)(925.9)} \times \frac{(1.0013)^2}{(1.41)(1.00)} \times \frac{\left(2.3419\times10^{34}\right)^2}{\left(1.606\times10^{19}\right)\left(5.0942\times10^{34}\right)} \\ &= (0.003550)(0.1333)(0.711)\left(6.7037\times10^{14}\right) \\ &= \left(2.26\times10^{11}\right) \end{aligned}$$

At 650 K, the reaction between $\mathbf{H_2\,(g)}$ and $\mathbf{Cl_2\,(g)}$ proceeds spontaneously towards the products. From a statistical mechanics point of view, the product $\mathbf{HCl\,(g)}$ molecule has more states accessible to it than the reactant species. The spontaneity of this reaction is largely due to the electronic partition function: two very strong H—Cl bonds are formed at the expense of a very strong H—H bond and a relatively weak Cl—Cl bond.

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CHAPTER OVERVIEW

13: The Kinetic Theory of Gases

13.1: The Average Translational Kinetic Energy of a Gas

13.2: The Distribution of Molecular Speeds is Given by the Maxwell-Boltzmann Distribution

13.3: Mean Free Path

13.4: Rates of Gas-Phase Chemical Reactions

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13.1: The Average Translational Kinetic Energy of a Gas

The laws that describe the behavior of gases were well established long before anyone had developed a coherent model of the properties of gases. In this section, we introduce a theory that describes why gases behave the way they do. The theory we introduce can also be used to derive laws such as the ideal gas law from fundamental principles and the properties of individual particles.

One key property of the individual particles is their velocity. However, in a sample of many gas particles, the particles will likely have various velocities. Rather than list the velocity of each individual gas molecule, we can combine these individual velocities in several ways to obtain "collective" velocities that describe the sample as a whole.

Table 27.1.1: Kinetic Properties of a Thermalized Ensemble (i.e., follows Maxwell-Boltzmann Distribution)

Property	Speed	Kinetic Energy
Most probable	$\sqrt{\frac{2k_bT}{m}}$	k_BT
Average	$\sqrt{\frac{8k_bT}{\pi m}}$	$\frac{4k_BT}{\pi}$
Root-mean-square	$\sqrt{\frac{3k_bT}{m}}$	$\frac{3}{2}k_BT$

In the following example, these three collective velocities are defined and calculated for a sample of gas consisting of only eight molecules.

Example 27.1.1 : A Gas Sample with Few Molecules

The speeds of eight molecules were found to be 1.0, 4.0, 4.0, 6.0, 6.0, 6.0, 8.0, and 10.0 m/s. Calculate their average speed (v_{avg}) root mean square speed (v_{rms}), and most probable speed (v_{mp}).

Solution

Start with definitions:

- **average speed** (v_{avg}) = the sum of all the speeds divided by the number of molecules
- **root-mean square speed** (v_{rms}) = the square root of the sum of the squared speeds divided by the number of molecules
- **most probable speed** (v_{mp}) = the speed at which the greatest number of molecules is moving

The average speed:

$$v_{\text{avg}} = \frac{(1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0)\ \text{m/s}}{8}$$
$$= 5.6\ m/s$$

The root-mean square speed:

$$v_{\text{rms}} = \sqrt{\frac{(1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2)\ \text{m}^2/\text{s}^2}{8}}$$
$$= 6.2\ m/s$$

The most probable speed:

Of the eight molecules, three have speeds of 6.0 m/s, two have speeds of 4.0 m/s, and the other three molecules have different speeds. Hence

$$v_{\text{mp}} = 6.0\,m/s.$$

Using expressions for v_{mp}, v_{ave}, or v_{rms}, it is fairly simple to derive expressions for kinetic energy from the expression

$$E_{kin} = \frac{1}{2}mv^2$$

It is important to remember that there will be a full distribution of molecular speeds in a thermalized sample of gas. Some molecules will be traveling faster and some more slowly. It is also important to recognize that the most probable, average, and RMS kinetic energy terms that can be derived from the kinetic molecular theory do not depend on the mass of the molecules (Table 27.1.1). As such, it can be concluded that the average kinetic energy of the molecules in a thermalized sample of gas depends only on the temperature. However, the average speed depends on the molecular mass. So, for a given temperature, light molecules will travel faster on average than heavier molecules.

The calculations carried out in Example 27.1.1 become cumbersome as the number of molecules in the sample of gas increases. Thus, a more efficient way to determine the various collective velocities for a gas sample containing a large number of molecules is required.

13.1.1: A Molecular Description of Pressure and Molecular Speed

The kinetic molecular theory of gases explains the laws that describe the behavior of gases. Developed during the mid-19th century by several physicists, including the Austrian Ludwig Boltzmann (1844–1906), the German Rudolf Clausius (1822–1888), and the Scotsman James Clerk Maxwell (1831–1879), this theory is based on the properties of individual particles as defined for an ideal gas and the fundamental concepts of physics. Thus the kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following five postulates:

1. A gas is composed of a large number of particles called molecules (whether monatomic or polyatomic) that are in constant random motion.
2. Because the distance between gas molecules is much greater than the size of the molecules, the volume of the molecules is negligible.
3. Intermolecular interactions, whether repulsive or attractive, are so weak that they are also negligible.
4. Gas molecules collide with one another and with the walls of the container, but these collisions are perfectly elastic; that is, they do not change the average kinetic energy of the molecules.
5. The average kinetic energy of the molecules of any gas depends on only the temperature, and at a given temperature, all gaseous molecules have exactly the same average kinetic energy.

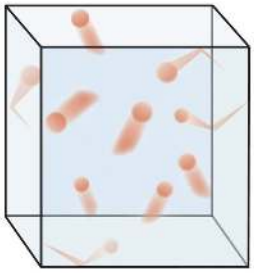


Figure 27.1.1 : Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.

Although the molecules of real gases have nonzero volumes and exert both attractive and repulsive forces on one another, for the moment we will focus on how the kinetic molecular theory of gases relates to the properties of gases we have been discussing. In Topic 1C, we explain how this theory must be modified to account for the behavior of real gases.

Postulates 1 and 4 state that gas molecules are in constant motion and collide frequently with the walls of their containers. The collision of molecules with their container walls results in a **momentum transfer** (impulse) from molecules to the walls (Figure 27.1.2).

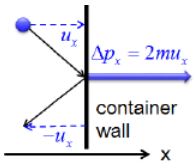


Figure 27.1.2 : Note: In this figure, the symbol u is used to represent velocity. In the rest of this text, velocity will be represented with the symbol v. Momentum transfer (Impulse) from a molecule to the container wall as it bounces off the wall. Momentum transfer ($\Delta\rho_x$) for an elastic collision is equal to mΔv_x, where m is the mass of the molecule and Δv_x is the change in the x component of the molecular velocity ($v_{x_{final}} - v_{x_{initial}}$).The wall is perpendicular to x axis. Since the collisions are elastic, the molecule bounces back with the same velocity in the opposite direction, and Δv_x equals $2v_x$.

The **momentum transfer** to the wall perpendicular to x axis as a molecule with an initial velocity v_x in the x direction hits is expressed as:

$$\text{momentum transfer}_x = \Delta\rho_x = m\Delta v_x = 2mv_x \tag{13.1.1}$$

The **collision frequency**, a number of collisions of the molecules to the wall per unit area and per second, increases with the molecular speed and the number of molecules per unit volume.

$$f \propto (v_x) \times \left(\frac{N}{V}\right) \tag{13.1.2}$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mv_x) \times (v_x) \times \left(\frac{N}{V}\right) \propto \left(\frac{N}{V}\right) mv_x^2 \tag{13.1.3}$$

At any instant, however, the molecules in a gas sample are traveling at different speed. Therefore, we must replace v_x^2 in the expression above with the average value of v_x^2, which is denoted by $\bar{v_x^2}$. The overbar designates the average value over all molecules.

The exact expression for pressure is given as :

$$P = \frac{N}{V} m\bar{v_x^2} \tag{13.1.4}$$

Finally, we must consider that there is nothing special about x direction. We should expect that $\bar{v_x^2} = \bar{v_y^2} = \bar{v_z^2} = \frac{1}{3}\bar{v^2}$. Here the quantity $\bar{v^2}$ is called the **mean-square speed** defined as the average value of square-speed (v^2) over all molecules. Since $v^2 = v_x^2 + v_y^2 + v_z^2$ for each molecule, $\bar{v^2} = \bar{v_x^2} + \bar{v_y^2} + \bar{v_z^2}$. By substituting $\frac{1}{3}\bar{v^2}$ for $\bar{v_x^2}$ in the expression above, we can get the final expression for the pressure:

$$P = \frac{1}{3}\frac{N}{V} m\bar{v^2} \tag{13.1.5}$$

Because volumes and intermolecular interactions are negligible, postulates 2 and 3 state that all gaseous particles behave identically, regardless of the chemical nature of their component molecules. This is the essence of the ideal gas law, which treats all gases as collections of particles that are identical in all respects except mass. Postulate 2 also explains why it is relatively easy to compress a gas; you simply decrease the distance between the gas molecules.

Postulate 5 provides a molecular explanation for the temperature of a gas. Postulate 5 refers to the *average translational* kinetic energy of the molecules of a gas,

$$\epsilon = m\bar{v^2}/2 \tag{13.1.6}$$

By rearranging equation 13.1.5 and substituting in equation 13.1.6, we obtain

$$PV = \frac{1}{3}Nm\bar{v^2} = \frac{2}{3}N\epsilon \tag{13.1.7}$$

The 2/3 factor in the proportionality reflects the fact that velocity components in each of the three directions contributes ½ *kT* to the kinetic energy of the particle. The average translational kinetic energy is directly proportional to temperature:

$$\epsilon = \frac{3}{2}kT \tag{13.1.8}$$

in which the proportionality constant k is known as the *Boltzmann constant*. Substituting Equation 13.1.8 into Equation 13.1.7 yields

$$PV = \left(\frac{2}{3}N\right)\left(\frac{3}{2}kT\right) = NkT \tag{13.1.9}$$

The Boltzmann constant k is just the gas constant per molecule, so if N is chosen as Avogadro's number, N_A, then N_Ak is R, the gas constant per mole. Thus, for *n* moles of particles, the Equation 13.1.9 becomes

$$PV = nRT \tag{13.1.10}$$

which is the ideal gas law.

As noted in Example 27.1.1 , the root-mean square speed (v_{rms}) is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{rms} = \sqrt{\bar{v^2}} = \sqrt{\frac{v_1^2 + v_2^2 + \cdots v_N^2}{N}} \tag{13.1.11}$$

where N is the number of particles and v_i is the speed of particle i.

The v_{rms} for a sample containing a large number of molecules can be obtained by combining equations 13.1.7 and 13.1.8 in a slightly different fashion than that used to obtain equation 13.1.10:

$$PV = \frac{1}{3}Nm\bar{v^2} = \frac{2}{3}N\epsilon \tag{27.1.10}$$

$$\epsilon = \frac{3}{2}kT \tag{27.1.11}$$

$$\frac{1}{3}Nm\bar{v^2} = \left(\frac{2}{3}\right)\left(\frac{3}{2}\right)NkT \tag{13.1.12}$$

$$\frac{1}{3}Nm\bar{v^2} = NkT \tag{13.1.13}$$

$$Nm\bar{v^2} = 3NkT \tag{13.1.14}$$

If N is chosen to be Avogadro's number, N_A, then $N_Am = M$, the molar mass, and $N_Ak = R$, the gas constant per mole,

$$\bar{v^2} = \frac{3RT}{M} \tag{13.1.15}$$

$$v_{rms} = \sqrt{\bar{v^2}} = \sqrt{\frac{3RT}{M}} \tag{13.1.16}$$

In Equation 13.1.16, v_{rms} has units of meters per second; consequently, the units of molar mass M are kilograms per mole, temperature T is expressed in kelvins, and the ideal gas constant R has the value 8.3145 J/(K•mol). Equation 13.1.16 shows that v_{rms} of a gas is proportional to the square root of its Kelvin temperature and inversely proportional to the square root of its molar mass. The root mean-square speed of a gas increase with increasing temperature. At a given temperature, heavier gas molecules have slower speeds than do lighter ones.

✔ Example 27.1.2 :

What is the root mean-square speed for O_2 molecules at 25ºC?

Given: Temperature in ºC, type of molecules, ideal gas gas constant

Asked for: v_{rms}, the root mean-square speed

Strategy:

Convert temperature to kelvins:

$$\text{T (in kelvin)} = (25^{\circ}\text{C} + 273^{\circ}\text{C})\frac{1\text{ K}}{1\ ^{\circ}\text{C}} = 298\text{ K}$$

Convert molar mass of O_2 molecules to kg per mole:

$$\text{M (in } \frac{\text{kg}}{\text{mole}}) = 32.00\frac{\text{g}}{\text{mole}}\text{x}\frac{1\text{ kg}}{1000\text{ g}} = 0.03200\frac{\text{kg}}{\text{mole}}$$

Use equation 13.1.16 to calculate the rms speed.

Solution

$$v_{\text{rms}_{O_2}} = \sqrt{\frac{3(8.3145\frac{\text{J}}{\text{K}\cdot\text{mole}})(298.15\text{ K})}{0.03200\frac{\text{kg}}{\text{mole}}}} = 482\frac{m}{s}$$

? Exercise 27.1.2

What is the root mean-square speed for Cl_2 molecules at 25°C?

$v_{\text{rms}_{Cl_2}} = 324\frac{m}{s}$

13.1.2: Many molecules, many velocities

At temperatures above absolute zero, all molecules are in motion. In the case of a gas, this motion consists of straight-line jumps whose lengths are quite great compared to the dimensions of the molecule. Although we can never predict the velocity of a particular *individual* molecule, the fact that we are usually dealing with a huge number of them allows us to know what fraction of the molecules have kinetic energies (and hence velocities) that lie within any given range.

The trajectory of an individual gas molecule consists of a series of straight-line paths interrupted by collisions. What happens when two molecules collide depends on their relative kinetic energies; in general, a faster or heavier molecule will impart some of its kinetic energy to a slower or lighter one. Two molecules having identical masses and moving in opposite directions at the same speed will momentarily remain motionless after their collision.

If we could measure the instantaneous velocities of all the molecules in a sample of a gas at some fixed temperature, we would obtain a wide range of values. A few would be zero, and a few would be very high velocities, but the majority would fall into a more or less well-defined range. We might be tempted to define an average velocity for a collection of molecules, but here we would need to be careful: molecules moving in opposite directions have velocities of opposite signs. Because the molecules are in a gas are in random thermal motion, there will be just about as many molecules moving in one direction as in the opposite direction, so the velocity vectors of opposite signs would all cancel and the average velocity would come out to zero. Since this answer is not very useful, we need to do our averaging in a slightly different way.

The proper treatment is to average the *squares* of the velocities, and then take the square root of this value to obtain the root-mean-square velocity (v_{rms}), which is what we developed above. This velocity describes the gas sample as a whole, but it does not tell us about the range of velocities possible, nor does it tell us the distribution of velocities. To obtain a more complete description of how many gas molecules are likely to be traveling at a given velocity range we need to make use of the Maxwell-Boltzmann distribution law.

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13.2: The Distribution of Molecular Speeds is Given by the Maxwell-Boltzmann Distribution

13.2.1: The Boltzmann Distribution

If we were to plot the number of molecules whose velocities fall within a series of narrow ranges, we would obtain a slightly asymmetric curve known as a *velocity distribution*. The peak of this curve would correspond to the *most probable* velocity. This velocity distribution curve is known as the *Maxwell-Boltzmann distribution*, but is frequently referred to only by Boltzmann's name. The **Maxwell-Boltzmann distribution law** was first worked out around 1860 by the great Scottish physicist, **James Clerk Maxwell** (1831-1879), who is better known for discovering the laws of electromagnetic radiation. Later, the Austrian physicist **Ludwig Boltzmann** (1844-1906) put the relation on a sounder theoretical basis and simplified the mathematics somewhat. Boltzmann pioneered the application of statistics to the physics and thermodynamics of matter and was an ardent supporter of the atomic theory of matter at a time when it was still not accepted by many of his contemporaries.

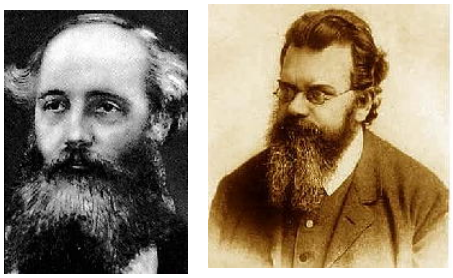


Figure 27.3.1 : Maxwell (left) and Boltzmann (right) are responsible for describing the velocity distribution of gas molecules

In section 27.2 we saw that the distribution function for molecular speeds in the x direction is given by:

$$f(v_x) = \underbrace{\sqrt{\frac{m}{2\pi k_B T}}}_{\text{normalization term}} \underbrace{\exp\left(\frac{-mv_x^2}{2k_B T}\right)}_{\text{exponential term}}$$

However, real gas samples have molecules not only with a distribution of molecular speeds and but also a random distribution of directions. Using normal vector magnitude properties (or simply using the Pythagorean Theorem), it can be seen that

$$\langle v \rangle^2 = \langle v_x \rangle^2 + \langle v_y \rangle^2 + \langle v_z \rangle^2$$

Since the direction of travel is random, the velocity can have any component in x, y, or z directions with equal probability. As such, the average value of the x, y, or z components of velocity should be the same. And so

$$\langle v \rangle^2 = 3\langle v_x \rangle^2$$

Substituting this into the expression for pressure yields

$$p = \frac{N_{tot} m}{3V} \langle v \rangle^2$$

All that remains is to determine the form of the distribution of velocity magnitudes the gas molecules can take. In his 1860 paper (Illustrations of the dynamical theory of gases. Part 1. On the motions and collisions of perfectly elastic spheres, 1860), Maxwell proposed a form for this distribution of speeds which proved to be consistent with observed properties of gases (such as their viscosities). He derived this expression based on a transformation of coordinate system from Cartesian coordinates (x, y, z) to spherical polar coordinates (v, θ, ϕ). In this new coordinate system, v represents the magnitude of the velocity (or the speed) and all of the directional data is carried in the angles θ and ϕ. The infinitesimal volume unit becomes

$$dx\, dy\, dz = v^2 \sin(\theta)\, dv\, d\theta\, d\phi$$

Applying this transformation of coordinates **Maxwell's distribution** took the following form

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right) \tag{13.2.1}$$

The Distribution of Speed over all Directions

The Distribution of Kinetic Energy in Three Dimensions

As noted above, the distribution function of molecular energies for one dimension is

$$f(v_x) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(\frac{-mv_x^2}{2k_B T}\right)$$

To obtain a three-dimensional probability distribution, you multiply the distribution function for each of the three dimensions so that

$$f(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right)$$

given

$$\langle v \rangle^2 = \langle v_x \rangle^2 + \langle v_y \rangle^2 + \langle v_z \rangle^2$$

The Conversion of Energy Distribution to Speed Distribution

To convert the three-dimensional energy distribution to a speed distribution over all space, the energy distribution must be summed over all directions. This sum is usually described by imagining a "velocity space" in spherical polar coordinates. As noted above, in this new coordinate system, v represents the magnitude of the velocity (or the speed) and all of the directional data is carried in the angles θ and ϕ. The infinitesimal volume unit becomes

$$dx\, dy\, dz = v^2 \sin(\theta)\, dv\, d\theta\, d\phi$$

You integrate over θ and ϕ to sum over all space, thus

$$f(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right) \underbrace{\int_0^{\pi} \int_0^{2\pi} v^2 \sin\theta d\phi d\theta}_{=4\pi v^2}$$

This equation is rearranged to give

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right)$$

This function can be thought of as having three basic parts to it: **a normalization constant** (N), a velocity dependence (v^2), and an exponential term that contains the kinetic energy ($\frac{1}{2}mv^2$).

Because the function represents the fraction of molecules with the speed v, the sum of the fractions for all possible velocities must be unity. This sum can be calculated as an integral. The normalization constant ensures that

$$\int_0^{\infty} f(v) dv = 1$$

Thus the normalization constant is

$$N = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3}$$

13.2.2: Velocity distributions depend on temperature and mass

Higher temperatures allow a larger fraction of molecules to acquire greater amounts of kinetic energy, causing the Boltzmann plots to spread out. Figure 27.3.2 shows how the Maxwell-Boltzmann distribution is affected by temperature. At lower temperatures, the molecules have less energy. Therefore, the speeds of the molecules are lower and the distribution has a smaller range. As the temperature of the molecules increases, the distribution flattens out. Because the molecules have greater energy at higher temperature, the molecules are moving faster.

Notice how the left ends of the plots are anchored at zero velocity (there will always be a few molecules that happen to be at rest.) As a consequence, the curves flatten out as the higher temperatures make additional higher-velocity states of motion more accessible. The area under each plot is the same for a constant number of molecules.

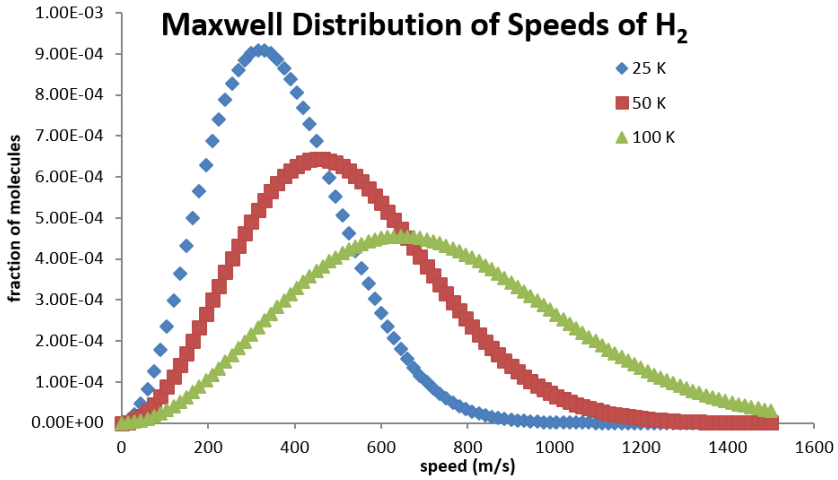


Figure 27.3.2: Maxwell Distribution of speeds for hydrogen molecules at differing temperatures.

Calculating the Average Speed

Using the Maxwell distribution as a distribution of probabilities, the average molecular speed in a sample of gas molecules can be determined.

$$\begin{aligned}\langle v\rangle &= \int_{-\infty}^{\infty} v\, f(v) dv \\ &= \int_{-\infty}^{\infty} v\, 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} v^2 \exp\left(\frac{-mv^2}{2k_B T}\right)\, dv \\ &= 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \int_{-\infty}^{\infty} v^3 \exp\left(\frac{-mv^2}{2k_B T}\right)\, dv\end{aligned}$$

The following can be found in a table of integrals:

$$\int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}}$$

So

$$\langle v\rangle = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \left[\frac{1}{2\left(\frac{m}{2k_B T}\right)^2}\right]$$

Which simplifies to

$$\langle v\rangle = \left(\frac{8k_B T}{\pi m}\right)^{1/2}$$

Note: the value of $\langle v\rangle$ is twice that of $\langle v_x\rangle$ which was derived in an earlier example!

$$\langle v\rangle = 2\langle v_x\rangle$$

Example 27.3.1 :

What is the average value of the squared speed according to the Maxwell distribution law?

Solution:

$$\begin{aligned}\langle v^2\rangle &= \int_{-\infty}^{\infty} v^2\, f(v) dv \\ &= \int_{-\infty}^{\infty} v^2\, 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3}\, v^2 \exp\left(\frac{-mv^2}{2k_B T}\right)\, dv \\ &= 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \int_{-\infty}^{\infty} v^4 \exp\left(\frac{-mv^2}{2k_B T}\right)\, dv\end{aligned}$$

A table of integrals indicates that

$$\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \ldots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$$

Substitution (noting that $n = 2$) yields

$$\langle v^2\rangle = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \left[\frac{1 \cdot 3}{2^3 \left(\frac{m}{2k_B T}\right)^2} \sqrt{\frac{\pi}{\left(\frac{m}{2k_B T}\right)}}\right]$$

which simplifies to

$$\langle v^2\rangle = \frac{3k_B T}{m}$$

Note: The square root of this average squared speed is called the **root mean square** (RMS) speed, and has the value

$$v_{rms} = \sqrt{\langle v^2\rangle} = \left(\frac{3k_B T}{m}\right)^{1/2}$$

All molecules have the same kinetic energy ($\frac{1}{2}mv^2$) at the same temperature, so the fraction of molecules with higher velocities will increase as m, and thus the molecular weight, decreases. Figure 27.3.3 shows the dependence of the Maxwell-Boltzmann distribution on molecule mass. On average, heavier molecules move more slowly than lighter molecules. Therefore, heavier molecules will have a smaller speed distribution, while lighter molecules will have a speed distribution that is more spread out.

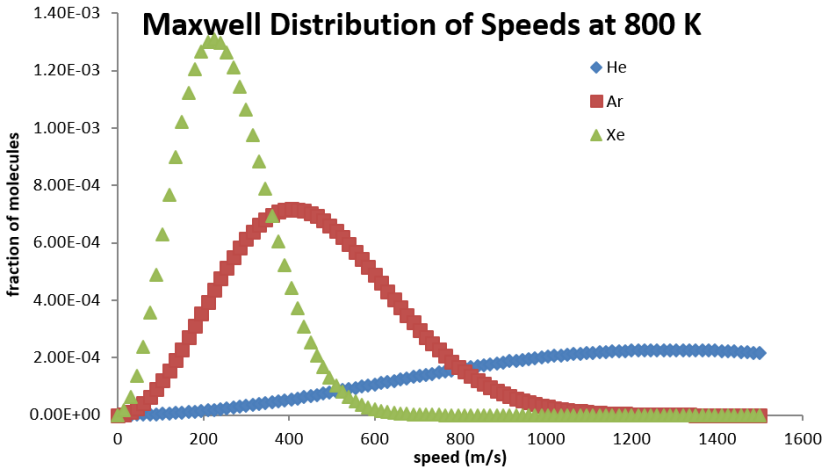


Figure 27.3.3: Maxwell Distribution of speeds at 800 K for different gasses of differing molecular masses.

13.2.3: Related Speed Expressions

Usually, we are more interested in the speeds of molecules rather than their component velocities. The Maxwell–Boltzmann distribution for the speed follows immediately from the distribution of the velocity vector, above. Note that the speed of an individual gas particle is:

$$v = \sqrt{v_x^2 + v_y^2 = v_z^2}$$

Three speed expressions can be derived from the Maxwell-Boltzmann distribution:

- the most probable speed,
- the average speed, and
- the root-mean-square speed.

The **most probable speed** is the maximum value on the distribution plot (Figure 27.3.4). This is established by finding the velocity when the derivative of Equation 13.2.1 is zero

$$\frac{df(v)}{dv} = 0$$

which is

$$v_{mp} = \sqrt{\frac{2RT}{M}} \tag{13.2.2}$$

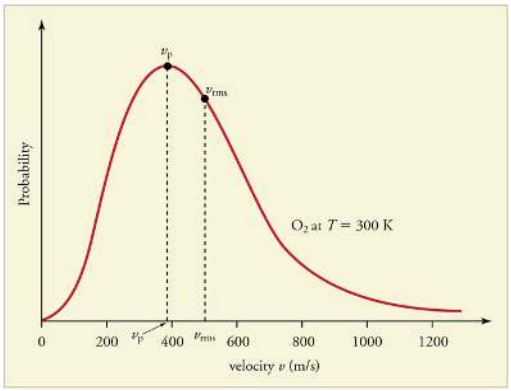


Figure 27.3.4 : The Maxwell-Boltzmann distribution is shifted to higher speeds and is broadened at higher temperatures. from OpenStax. The speed at the top of the curve is called the most probable speed because the largest number of molecules have that speed.

The **average speed** is the sum of the speeds of all the molecules divided by the number of molecules.

$$v_{avg} = \bar{v} = \int_0^\infty vf(v)dv = \sqrt{\frac{8RT}{\pi M}}$$

The **root-mean-square speed** is square root of the average speed-squared.

$$v_{rms} = \bar{v^2} = \sqrt{\frac{3RT}{M}}$$

where

- R is the gas constant,
- T is the absolute temperature and
- M is the molar mass of the gas.

It *always* follows that for gases that follow the Maxwell-Boltzmann distribution:

$$v_{mp} < v_{avg} < v_{rms}$$

13.2.4: Problems

1. Using the Maxwell-Boltzman function, calculate the fraction of argon gas molecules with a speed of 305 m/s at 500 K.
2. If the system in problem 1 has 0.46 moles of argon gas, how many molecules have the speed of 305 m/s?
3. Calculate the values of C_{mp}, C_{avg}, and C_{rms} for xenon gas at 298 K.
4. From the values calculated above, label the Boltzmann distribution plot with the approximate locations of (C_{mp}\), C_{avg}, and C_{rms}.

5. What will have a larger speed distribution, helium at 500 K or argon at 300 K? Helium at 300 K or argon at 500 K? Argon at 400 K or argon at 1000 K?

13.2.4.1: Answers

1. 0.00141
2. 3.92×10^{20} argon molecules
3. c_{mp} = 194.27 m/s, c_{avg} = 219.21 m/s, c_{rms} = 237.93 m/s
4. As stated above, C_{mp} is the most probable speed, thus it will be at the top of the distribution curve. To the right of the most probable speed will be the average speed, followed by the root-mean-square speed.
5. Hint: Use the related speed expressions to determine the distribution of the gas molecules: helium at 500 K. helium at at 300 K. argon at 1000 K.

13.2.5: Sources

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13.3: Mean Free Path

13.3.1: Collision energy

Consider two particles A and B in a system. The kinetic energy of these two particles is

$$K_{AB} = \frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B} \tag{13.3.1}$$

We can describe kinetic energy in terms of center-of-mass ($\mathbf{P}$) and relative momentum ($\mathbf{p}$), which are given by

$$\mathbf{P} = \mathbf{p}_A + \mathbf{p}_B$$

and

$$\begin{aligned} \mathbf{p} &= \text{relative velocity} \times \mu \\ &= (\mathbf{v}_A - \mathbf{v}_B) \times \left(\frac{m_A m_B}{m_A + m_B}\right) \\ &= \frac{m_B \mathbf{p}_A - m_A \mathbf{p}_B}{M} \end{aligned}$$

where

$$M = m_A + m_B$$

is the total mass of the two particles, and

$$\mu = \frac{m_A m_B}{M}$$

is the **reduced mass** of the two particles.

Substituting these terms into equation 13.3.1, we find

$$K_{AB} = \frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B} = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu}$$

Note that the kinetic energy separates into a sum of a center-of-mass term and a relative momentum term.

Now the relative position of the two particles is $\mathbf{r} = \mathbf{r}_A - \mathbf{r}_B$ so that the relative velocity is $\dot{\mathbf{r}} = \dot{\mathbf{r}}_A - \dot{\mathbf{r}}_B$ or $\mathbf{v} = \mathbf{v}_A - \mathbf{v}_B$. Thus, if the two particles are approaching each other such that $\mathbf{v}_A = -\mathbf{v}_B$, then $\mathbf{v} = 2\mathbf{v}_A$. However, by equipartitioning the relative kinetic energy, which is mass independent, we get

$$\left\langle \frac{\mathbf{p}^2}{2\mu} \right\rangle = \frac{3}{2} k_B T$$

which is called the *collision energy*

13.3.2: Collision cross-section

Consider two molecules in a system. The probability that they will collide increases with the effective “size” of each particle. However, the size measure that is relevant is the apparent cross-section area of each particle. For simplicity, suppose the particles are spherical, which is not a bad approximation for small molecules. If we are looking at a sphere, what we perceive as the size of the sphere is the cross section area of a great circle. Recall that each spherical particle has an associated “collision sphere” that just encloses two particles at closest contact, i.e., at the moment of a collision, and that this sphere is a radius d, where d is the diameter of each spherical particle. The cross-section of this collision sphere represents an effective cross section for each particle inside which a collision is imminent. The cross-section of the collision sphere is the area of a great circle, which is πd^2. We denote this apparent cross section area σ. Thus, for spherical particles A and B with diameters d_A and d_B, the individual cross sections are

$$\sigma_A = \pi d_A^2, \quad \sigma_B = \pi d_B^2$$

The *collision cross section*, σ_{AB} is determined by an effective diameter d_{AB} characteristic of both particles. The collision probability increases of both particles have large diameters and decreases if one of them has a smaller diameter than the other. Hence, a simple

measure sensitive to this is the arithmetic average

$$d_{AB} = \frac{1}{2}(d_A + d_B)$$

and the resulting collision cross section becomes

$$\begin{aligned}\sigma_{AB} &= \pi d_{AB}^2 \\ &= \pi\left(\frac{d_A+d_B}{2}\right)^2 \\ &= \frac{\pi}{4}(d_A^2 + 2d_A d_B + d_B^2) \\ &= \frac{1}{4}(\sigma_A + 2\sqrt{\sigma_A\sigma_B} + \sigma_B) \\ &= \frac{1}{2}\left[\left(\frac{\sigma_A+\sigma_B}{2}\right) + \sqrt{\sigma_A\sigma_B}\right]\end{aligned}$$

which, interestingly, is an average of the two types of averages of the two individual cross sections, the arithmetic and geometric averages!

13.3.3: Average collision Frequency

Consider a system of particles with individual cross sections σ. A particle of cross section σ that moves a distance l in a time Δt will sweep out a cylindrical volume (ignoring the spherical caps) of volume σl (Figure 27.6.1). If the system has a number density ρ, then the number of collisions that will occur is

$$N_{\text{coll}} = \rho\sigma l$$

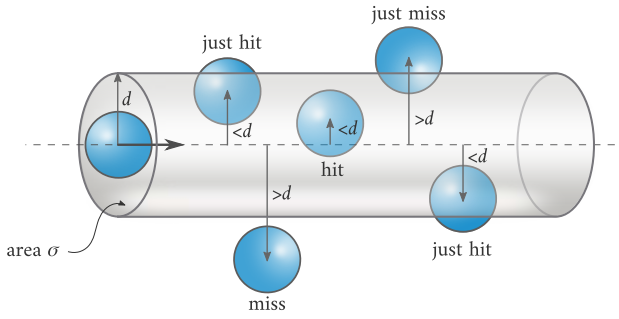


Figure 27.6.1 : Collision cylinder. Any particle that partially overlaps with this volume will experience a collision with a test particle tracing out this volume. (CC BY-NC; Ümit Kaya)

We define the collision frequency for a single molecule, z_A, also known as the average collision rate as $N_{\text{coll}}/\Delta t$, i.e.,

$$z_A = \frac{N_{\text{coll}}}{\Delta t} = \frac{\rho\sigma l}{\Delta t} = \rho\sigma\langle v\rangle \tag{13.3.2}$$

where $\langle v\rangle$ is the average speed of a particle

$$\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m_A}}$$

Equation 13.3.2 is not quite correct because it is based on the assumption that only the molecule of interest is moving. If we take into account the fact that all of the particles are moving relative to one another, and assume that all of the particles are of the same type (say, type A), then performing the average over a Maxwell-Boltzmann speed distribution gives

$$\langle v_r\rangle = \sqrt{\frac{8k_BT}{\pi\mu}}$$

where $\mu = m_A/2$ is the reduced mass.

Thus,

$$\langle v_r \rangle = \sqrt{2}\langle v \rangle$$

and

$$z_A = \sqrt{2}\rho\sigma\langle v \rangle \ = \rho\sigma\langle v_r \rangle$$

The reciprocal of z_A is a measure of the average time between collisions for a single molecule.

13.3.4: Mean Free Path

The mean free path is the distance a particle will travel, on average, before experiencing a collision event. This is defined as the product of the average speed of a particle and the time between collisions. The former is $\langle v \rangle$, while the latter is $1/z_A$. Hence, we have

$$\lambda = \frac{\langle v \rangle}{\sqrt{2}\rho\sigma\langle v \rangle} = \frac{1}{\sqrt{2}\rho\sigma}$$

The mean free path can also be described using terms from the ideal gas law, because $\rho = \frac{P \cdot N_A}{R \cdot T}$:

$$\lambda = \frac{R \cdot T}{\sqrt{2} \cdot N_A \cdot \sigma \cdot P}$$

13.3.5: Random Walks

In any system, a particle undergoing frequent collisions will have the direction of its motion changed with each collision and will trace out a path that appears to be random. In fact, if we treat the process as statistical, then, we are, in fact, treating each collision event as a random event, and the particle will change its direction at random times in random ways! Such a path might appear as shown in Figure **13.3.2**. Such a path is often referred to as a *random walk path*.

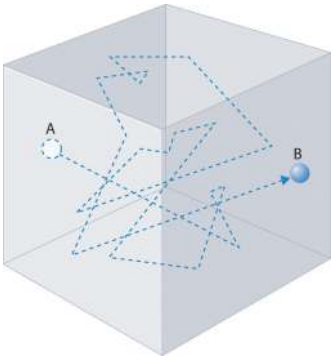


Figure **13.3.2**: Random walk path. The Path of a Single Particle in a Gas Sample. The frequent changes in direction are the result of collisions with other gas molecules and with the walls of the container.

In order to analyze such paths, let us consider a random walk in one dimension. We'll assume that the particle move a mean-free path length λ between collisions and that each collision changes the direction of the particles motion, which in one dimension, means that the particle moves either to the right or to the left after each event. This can be mapped onto a metaphoric "coin toss" that can come up heads "H" or tails "T", with "H" causing motion to the right, and "T" causing motion to the left. Let there be N such coin tosses, let i be the number of times "H" comes up and j denote the number of times "T" comes up. Thus, the progress of the particle, which we define as net motion to the right, is given by $(i-j)\lambda$. Letting $k = i - j$, this is just $k\lambda$. Thus, we need to know what the probability is for obtaining a particular value of k in a very large number N of coin tosses. Denote this $P(k)$.

In N coin tosses, the total number of possible sequences of "H" and "T" is 2^N. However, the number of ways we can obtain i heads and \)j\) tails, with $i + j = N$ is a binomial coefficient $N!/i!j!$. Now

$$j = N - i = N - (j + k) = N - j - k$$

so that $j = (N - k)/2$. Similarly,

$$i = N - j = N - (i - k) = N - i + k$$

so that $i = (N + k)/2$. Thus, the probability $P(k)$ is

$$P(k) = \frac{N!}{2^N i! j!} = \frac{1}{2^N} \frac{N!}{\left(\frac{N+k}{2}\right)! \left(\frac{N-k}{2}\right)!}$$

We now take the logarithm of both sides:

$$\ln P(k) = \ln N! - \ln 2^N - \ln \left(\frac{N+k}{2}\right)! - \ln \left(\frac{N-k}{2}\right)!$$

and use Stirling's approximation:

$$\ln N! \approx N \ln N - N$$

and write $\ln P(k)$ as

$$\begin{aligned}
\ln P(k) &\approx N \ln N - N - N \ln 2 - \frac{1}{2}(N+k) \ln \frac{1}{2}(N+k) + \frac{1}{2}(N+k) \\
&\quad - \frac{1}{2}(N-k) \ln \frac{1}{2}(N-k) + \frac{1}{2}(N-k) \\
&= N \ln N - N \ln 2 + \frac{1}{2}(N+k) \ln \frac{1}{2} - \frac{1}{2}(N+k) \ln (N+k) \\
&\quad - \frac{1}{2}(N-k) \ln \frac{1}{2} - \frac{1}{2}(N-k) \ln (N-k) \\
&= N \ln N - N \ln 2 + \frac{1}{2}(N+k) \ln 2 - \frac{1}{2}(N+k) \ln (N+k) + \frac{1}{2}(N-k) \ln 2 \\
&\quad - \frac{1}{2}(N-k) \ln (N-k) \\
&= N \ln N - \frac{1}{2} \left[(N+k) \ln (N+k) + (N-k) \ln (N-k)\right]
\end{aligned}$$

Now, write

$$\ln (N+k) = \ln N \left(1 + \frac{k}{N}\right) = \ln N + \ln \left(1 + \frac{k}{N}\right)$$

and

$$\ln (N-k) = \ln N \left(1 - \frac{k}{N}\right) = \ln N + \ln \left(1 - \frac{k}{N}\right)$$

We now use the expansions

$$\begin{aligned}
\ln \left(1 + \frac{k}{N}\right) &= \left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2 + \cdots \\
\ln \left(1 - \frac{k}{N}\right) &= -\left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2 + \cdots
\end{aligned}$$

If we stop at the second-order term, then

$$\begin{aligned}
\ln P(k) &= N \ln N - \frac{1}{2}(N+k) \left[\ln N + \left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2\right] \\
&\quad - \frac{1}{2}(N-k) \left[\ln N - \left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2\right] \\
&= -\frac{1}{2}(N+k) \left[\left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2\right] + \frac{1}{2}(N-k) \left[\left(\frac{k}{N}\right) + \frac{1}{2}\left(\frac{k}{N}\right)^2\right] \\
&= \frac{1}{2} N \left(\frac{k}{N}\right)^2 - k \left(\frac{k}{N}\right) \\
&= \frac{k^2}{2N} - \frac{k^2}{N} = -\frac{k^2}{2N}
\end{aligned}$$

so that

$$P(k) = e^{-k^2/2N}$$

Now, if we let $x = k\lambda$ and $L = \sqrt{N}\lambda$, and if we let x be a continuous random variable, then the corresponding probability distribution $P(x)$ becomes

$$P(x) = \frac{1}{L\sqrt{2\pi}}\, e^{-x^2/2L^2} = \frac{1}{\sqrt{2\pi N\lambda^2}}\, e^{-x^2/2N\lambda^2} \tag{13.3.3}$$

which is a simple Gaussian distribution. Now, N is the number of collisions, which is given by $z_A t$, so we can write the probability distribution for the particle to diffuse a distance x in time t as

$$P(x,t) = \frac{1}{\sqrt{2\pi z_A t\lambda^2}}\, e^{-x^2/2z_A t\lambda^2}$$

Define $D = z_A\lambda^2/2$ as the *diffusion constant*, which has units of (length)^2/time. The distribution then becomes

$$P(x,t) = \frac{1}{\sqrt{4\pi Dt}}\, e^{-x^2/4Dt}$$

Note that this distribution satisfies the following equation:

$$\frac{\partial}{\partial t}P(x,t) = D\frac{\partial^2}{\partial x^2}P(x,t)$$

which is called the diffusion equation. The diffusion equation is, in fact, more general than the Gaussian distribution in Equation 13.3.3. It is capable of predicting the distribution in any one-dimensional geometry subject to any initial distribution $P(x,0)$ and any imposed boundary conditions.

In three dimensions, we consider the three spatial directions to be independent, hence, the probability distribution for a particle to diffuse to a location $\mathbf{r} = (x,y,z)$ is just a product of the three one-dimensional distributions:

$$\mathcal{P}(\mathbf{r}) = P(x)\,P(y)\,P(z) = \frac{1}{(4\pi Dt)^{3/2}}\, e^{-(x^2+y^2+z^2)/4Dt}$$

and if we are only interested in diffusion over a distance r, we can introduce spherical coordinates, integrate over the angles, and we find that

$$P(r,t) = \frac{4\pi}{(4\pi Dt)^{3/2}}\, e^{-r^2/4Dt}$$

13.3.6: Total collision frequency per unit volume

In equation 27.6.18, z_A represents the collision frequency for one specific molecule in a gas sample. If we wish to calculate the total collision frequency per unit volume, the number density of the molecules, ρ, must be taken into account. The total collision frequency in a sample that contains only A molecules, Z_{AA}, is

$$Z_{AA} = \frac{1}{2}\rho z_A = \frac{1}{2}\sigma\langle v_r\rangle\rho^2 = \frac{\sigma\langle v\rangle\rho^2}{\sqrt{2}}$$

The factor of $\frac{1}{2}$ must be included to avoid double counting collisions between similar molecules. (This is identical reasoning to the fact that there is only one way to roll double 3 with two dice.)

If you have a gas sample that contains A molecules and B molecules, then

$$Z_{AB} = \sigma_{AB}\langle v_r\rangle\rho_A\rho_B \tag{13.3.4}$$

where

$$\sigma_{AB} = \pi\left(\frac{d_A+d_B}{2}\right)^2 \text{ and } \langle v_r\rangle = \sqrt{\frac{8k_BT}{\pi\mu}}$$

Example 13.3.1

Calculate the frequency of hydrogen-hydrogen collisions in a 1.00 cubic centimeter container at 1.00 bar and 298 K.

Solution

The collisional frquency requires knowledge of (1) the number denisty, the average speed (Equation 13.3.4).

The value of σ_{H_2} is 2.30 x 10^{-19} m^2.

The number density:

$$\rho = \left(\frac{N_A P_{H_2}}{RT}\right) = \left(\frac{(6.022x10^{23} mole^{-1})(1.00\ \text{bar})}{(0.08314 L \cdot bar \cdot mol^{-1} \cdot K^{-1})(298 K)}\right)$$
$$= 2.43 \times 10^{22} L^{-1} = 2.43 \times 10^{25} m^{-3}$$

The average speed:

$$\langle \text{v} \rangle = \sqrt{\frac{8\text{R T}}{\pi \text{M}}} = \sqrt{\left(\frac{8(8.314 J \cdot K^{-1})(298 K)}{\pi(0.002016 kg)}\right)} = 1770 \frac{m}{s}$$

These are substituted into Equation 13.3.4 to get the collisional frequency

$$Z_{H_2,H_2} = \frac{(2.30x10^{-19} m^2)(1770 \frac{m}{s})(2.43x10^{25} m^{-3})^2}{\sqrt{2}}$$
$$= 1.7x10^{35} s^{-1} m^{-3}$$
$$= 1.7 \times 10^{29} s^{-1} cm^{-3}$$

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13.4: Rates of Gas-Phase Chemical Reactions

Now that we have a description of how often gas molecules will collide with one another, we can make an initial attempt to describe how the collision of gas molecules can lead to reactions between the molecules. This topic will be covered in much more detail in Chapter 30.

13.4.1: Collision Frequency, Collision Energy, and Effective Collisions

In example 27.6.1, we calculated that the number of collision between H_2 molecules at one bar and 25ºC is around 10^8 $\frac{\text{moles}}{\text{dm}\cdot\text{s}}$. Consider the elementary reaction

$$\text{A} + \text{B} \longrightarrow \text{C}$$

If all of the collisions between A and B resulted in a reaction, then the rate of the reaction would be about 10^8 $\frac{\text{moles}}{\text{dm}\cdot\text{s}}$. We know from experiment that most chemical reactions do not occur this quickly. It must be true, then, that not all collisions result in a reaction. It is intuitive that molecules traveling at faster speeds should be more likely to react because they have sufficient energy to overcome electronic repulsions, and to break existing bonds.

One way to approach this estimate is to use a modified version of the equation for the collision frequency with a wall. The reason for starting with this equation is that it is reasonable to assume that the faster a molecule is traveling, the more likely it is to hit the wall. If this is so, then the faster a molecule is traveling, the more likely it is to collide with other molecules so as to react.

Recall equation 26.4.1

$$z_w = \frac{1}{4}\frac{N}{V}\langle v \rangle$$

which can be rewritten for the molecular level by substituting ρ for $\frac{N}{V}$

$$z_w = \frac{1}{4}\rho\langle v \rangle$$

This equation was obtained by carrying out the integration

$$z_w = \frac{\rho}{4\pi}\int_0^\infty vF(v)dv \int_0^{\pi/2} \cos\theta \sin\theta d\theta \int_0^{2\pi} d\phi \tag{13.4.1}$$

which takes into account the fact that molecules will only hit the wall from one direction.

Recall from equation 27.3.1, the Maxwell-Boltzmann distribution of speeds

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right)$$

that $f(v)$ has a factor of v^2. Thus, equation 13.4.1 has a factor of v^3, meaning that the molecules colliding with the wall are traveling faster than the molecule in the bulk of the sample. The assumption is that the faster molecules are more likely to hit the wall in a given amount of time.

We must modify equation 13.4.1 to take into account the collision of molecules with each other, rather than with the wall. This is done by replacing the mass of a single molecule m with the reduced mass of the two colliding molecules μ. The resulting speed is the relative average speed v_r. The result of these assumptions is that the collision frequency of molecules A and B per unit volume in which the molecules collide with a relative speed between v_r and $v_r + dv_r$ is

$$dZ_{AB} = Av_r^3 e^{-\mu v_r^2/2k_B T} dv_r \tag{13.4.2}$$

where A is a proportionality constant.

If we require the integral of this equation over all relative speeds to be equal to Z_{AB}, then

$$Z_{AB} = \sigma_{AB}\rho_A\rho_B \left(\frac{8k_B T}{\pi\mu}\right)^{1/2} = A\int_0^\infty v_r^3 e^{-\mu v_r^2/2k_B T} dv_r$$

$$Z_{AB} = \sigma_{AB}\rho_A\rho_B\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} = 2A\left(\frac{k_BT}{\mu}\right)^2$$

Rearranging to solve for A gives

$$A = \sigma_{AB}\rho_A\rho_B\left(\frac{\mu}{k_BT}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} \tag{13.4.3}$$

Substituting equation 13.4.3 into equation 13.4.2 gives

$$dZ_{AB} = \sigma_{AB}\rho_A\rho_B\left(\frac{\mu}{k_BT}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} v_r^3 e^{-\mu v_r^2/2k_BT}dv_r$$

With this equation, we can describe the collision frequency per unit volume between A molecules and B molecules with relative speeds in the range of v_r and $v_r + dv_r$. In this equation, the portion

$$\left(\frac{\mu}{k_BT}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} v_r^3 e^{-\mu v_r^2/2k_BT}dv_r$$

which is $v_r f(v_r)dv_r$, is the probability that the relative speed of the molecules will fall between v_r and $v_r + dv_r$.

Contributors and Attributions

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- Tom Neils, Grand Rapids Community College

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CHAPTER OVERVIEW

14: Chemical Kinetics I - Rate Laws

14.1: The Time Dependence of a Chemical Reaction is Described by a Rate Law

14.2: First-Order Reactions Show an Exponential Decay of Reactant Concentration with Time

14.3: Different Rate Laws Predict Different Kinetics

14.4: Arrhenius Equation

14.5: Eyring equation

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14.1: The Time Dependence of a Chemical Reaction is Described by a Rate Law

14.1.1: The Reaction Rate

The rate of a chemical reaction (or the **reaction rate**) can be defined by the time needed for a change in concentration to occur. But there is a problem in that this allows for the definition to be made based on concentration changes for either the reactants or the products. Plus, due to stoichiometric concerns, the rates at which the concentrations are generally different! Toward this end, the following convention is used.

For a general reaction

$$aA + bB \rightarrow cC + dD$$

the reaction rate can be defined by any of the ratios

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{dt} = -\frac{1}{b}\frac{\Delta[B]}{dt} = +\frac{1}{c}\frac{\Delta[C]}{dt} = +\frac{1}{d}\frac{\Delta[D]}{dt}$$

Or for infinitesimal time intervals

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[C]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

Example 14.1.1:

Under a certain set of conditions, the rate of the reaction

$$\mathrm{N_2 + 3\,H_2 \rightarrow 2\,NH_3}$$

the reaction rate is $6.0 \times 10^{-4}\ M/s$. Calculate the time-rate of change for the concentrations of N_2, H_2, and NH_3.

Solution:

Due to the stoichiometry of the reaction,

$$\text{rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

so

$$\frac{d[N_2]}{dt} = -6.0 \times 10^{-4}\ M/s$$
$$\frac{d[H_2]}{dt} = -2.0 \times 10^{-4}\ M/s$$
$$\frac{d[NH_3]}{dt} = 3.0 \times 10^{-4}\ M/s$$

Note: The time derivatives for the reactants are negative because the reactant concentrations are decreasing, and those of products are positive since the concentrations of products increase as the reaction progresses.

14.1.2: The Rate Law

As shown above, the rate of the reaction can be followed experimentally by measuring the rate of the loss of a reactant or the rate of the production of a product. The rate of the reaction is often related to the concentration of some or all of the chemical species present at a given time. An equation called the *rate law* is used to show this relationship. The rate law **cannot** be predicted by looking at the balanced chemical reaction but must be determined by experiment. For example, the rate law for the reaction

$$\mathrm{Cl_2\,(g) + CO\,(g) \longrightarrow Cl_2CO\,(g)}$$

was experimentally determined to be

$$\text{rate} = k[Cl_2]^{3/2}[CO]$$

In this equation, k is the rate constant, and $[Cl_2]$ and $[CO]$ are the molar concentrations of Cl_2 and of CO. Each exponent is called the *order* of the given species. Thus, the rate law is second order in Cl_2 and first order in CO. The sum of the individual reactant orders is called the **reaction order**. This reaction has a reaction order of two and a half.

In the next section, we will discuss methods to experimentally determine the rate law.

14.1.3: Contributors and Attributions

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14.2: First-Order Reactions Show an Exponential Decay of Reactant Concentration with Time

A first order rate law would take the form

$$\frac{d[A]}{dt} = k[A]$$

Again, separating the variables by placing all of the concentration terms on the left and all of the time terms on the right yields

$$\frac{d[A]}{[A]} = -k\,dt$$

This expression is also easily integrated as before

$$\int_{[A]=0}^{[A]} \frac{d[A]}{[A]} = -k \int_{t=0}^{t=t} dt$$

Noting that

$$\frac{dx}{x} = d(\ln x)$$

The form of the integrated rate law becomes

$$\ln[A] - \ln[A]_o = kt$$

or

$$\ln[A] = \ln[A]_o - kt \tag{14.2.1}$$

This form implies that a plot of the natural logarithm of the concentration is a linear function of the time. And so a plot of ln[A] as a function of time should produce a linear plot, the slope of which is -k, and the intercept of which is $\ln[A]_0$.

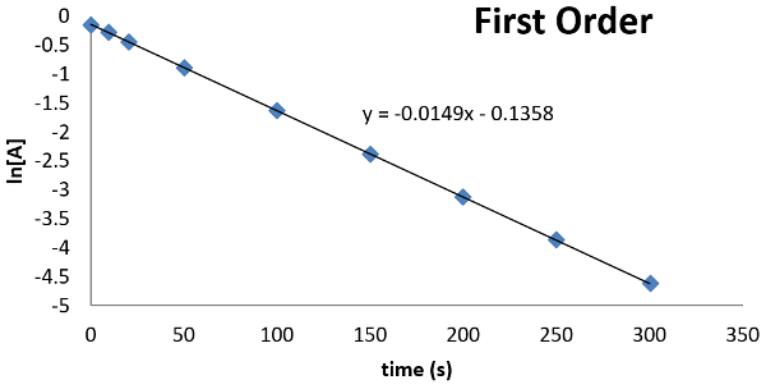
Example 14.2.1:

Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with first order kinetics. Also, if the data are first order, determine the value of the rate constant for the reaction.

Time (s)	0	10	20	50	100	150	200	250	300
[A] (M)	0.873	0.752	0.648	0.414	0.196	0.093	0.044	0.021	0.010

Solution

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.0149 s^{-1}. The concentration at time $t = 0$ can also be inferred from the intercept.

It should also be noted that the integrated rate law (Equation 14.2.1) can be expressed in exponential form:

$$[A] = [A]_o e^{-kt}$$

Because of this functional form, 1st order kinetics are sometimes referred to as exponential decay kinetics. Many processes, including radioactive decay of nuclides follow this type of rate law.

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14.3: Different Rate Laws Predict Different Kinetics

Difference rate laws predict different kinetics

14.3.1: Zero-order Kinetics

If the reaction follows a zeroth order rate law, it can be expressed in terms of the time-rate of change of [A] (which will be negative since A is a reactant):

$$-\frac{d[A]}{dt} = k$$

In this case, it is straightforward to separate the variables. Placing time variables on the right and [A] on the left

$$d[A] = -k\,dt$$

In this form, it is easy to integrate. If the concentration of A is $[A]_0$ at time t = 0, and the concentration of A is [A] at some arbitrary time later, the form of the integral is

$$\int_{[A]_o}^{[A]} d[A] = -k\int_{t_o}^{t} dt$$

which yields

$$[A] - [A]_o = -kt$$

or

$$[A] = [A]_o - kt$$

This suggests that a plot of concentration as a function of time will produce a straight line, the slope of which is –k, and the intercept of which is $[A]_0$. If such a plot is linear, then the data are consistent with 0^{th} order kinetics. If they are not, other possibilities must be considered.

14.3.2: Second Order Kinetics

If the reaction follows a second order rate law, the some methodology can be employed. The rate can be written as

$$-\frac{d[A]}{dt} = k[A]^2 \tag{14.3.1}$$

The separation of concentration and time terms (this time keeping the negative sign on the left for convenience) yields

$$-\frac{d[A]}{[A]^2} = k\,dt$$

The integration then becomes

$$-\int_{[A]_o}^{[A]} \frac{d[A]}{[A]^2} = \int_{t=0}^{t} k\,dt \tag{14.3.2}$$

And noting that

$$-\frac{dx}{x^2} = d\left(\frac{1}{x}\right)$$

the result of integration Equation 14.3.2 is

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt$$

or

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt$$

And so a plot of $1/[A]$ as a function of time should produce a linear plot, the slope of which is k, and the intercept of which is $1/[A]_0$.

Other 2nd order rate laws are a little bit trickier to integrate, as the integration depends on the actual stoichiometry of the reaction being investigated. For example, for a reaction of the type

$$A + B \rightarrow P$$

That has rate laws given by

$$-\frac{d[A]}{dt} = k[A][B]$$

and

$$-\frac{d[B]}{dt} = k[A][B]$$

the integration will depend on the decrease of [A] and [B] (which will be related by the stoichiometry) which can be expressed in terms the concentration of the product [P].

$$[A] = [A]_o - [P] \tag{14.3.3}$$

and

$$[B] = [B]_o - [P] \tag{14.3.4}$$

The concentration dependence on A and B can then be eliminated if the rate law is expressed in terms of the production of the product.

$$\frac{d[P]}{dt} = k[A][B] \tag{14.3.5}$$

Substituting the relationships for $[A]$ and $[B]$ (Equations 14.3.3 and 14.3.4) into the rate law expression (Equation 14.3.5) yields

$$\frac{d[P]}{dt} = k([A]_o - [P])([B] = [B]_o - [P]) \tag{14.3.6}$$

Separation of concentration and time variables results in

$$\frac{d[P]}{([A]_o - [P])([B] = [B]_o - [P])} = k\,dt$$

Noting that at time $t = 0$, $[P] = 0$, the integrated form of the rate law can be generated by solving the integral

$$\int_{[A]_o}^{[A]} \frac{d[P]}{([A]_o - [P])([B]_o - [P])} = \int_{t=0}^{t} k\,dt$$

Consulting a table of integrals reveals that for $a \neq b$[1],

$$\int \frac{dx}{(a-x)(b-x)} = \frac{1}{b-a}\ln\left(\frac{b-x}{a-x}\right)$$

Applying the definite integral (as long as $[A]_0 \neq [B]_0$) results in

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0 - [P]}{[A]_0 - [P]}\right)\Bigg|_0^{[A]} = k\,t\Big|_0^t$$

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0 - [P]}{[A]_0 - [P]}\right) - \frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0}{[A]_0}\right) = k\,t \tag{14.3.7}$$

Substituting Equations 14.3.3 and 14.3.4 into Equation 14.3.7 and simplifying (combining the natural logarithm terms) yields

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B][A]_o}{[A][B]_o}\right) = kt$$

For this rate law, a plot of $\ln([B]/[A])$ as a function of time will produce a straight line, the slope of which is

$$m = ([B]_0 - [A]_0)k.$$

In the limit at $[A]_0 = [B]_0$, then $[A] = [B]$ at all times, due to the stoichiometry of the reaction. As such, the rate law becomes

$$\text{rate} = k[A]^2$$

and integrate direct like in Equation 14.3.1 and the integrated rate law is (as before)

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt$$

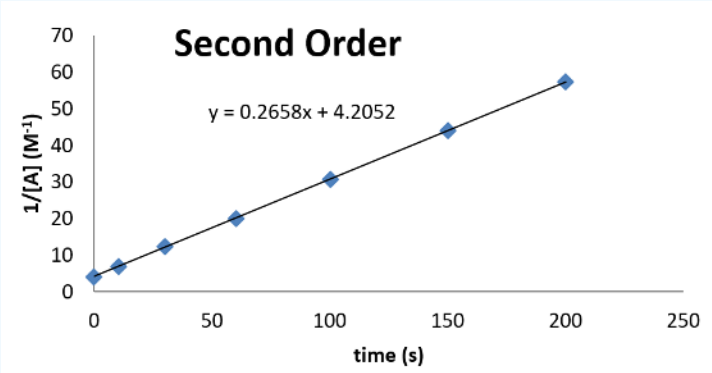
Example 14.3.2: Confirming Second Order Kinetics

Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with second order kinetics. Also, if the data are second order, determine the value of the rate constant for the reaction.

time (s)	0	10	30	60	100	150	200
[A] (M)	0.238	0.161	0.098	0.062	0.041	0.029	0.023

Solution

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.2658 M^{-1} s^{-1}. The concentration at time $t = 0$ can also be inferred from the intercept.

---

[1] This integral form can be generated by using the method of partial fractions. See (House, 2007) for a full derivation.

Example 14.3.3

Dinitrogen pentoxide (N_2O_5) decomposes to NO_2 and O_2 at relatively low temperatures in the following reaction:

$$2N_2O_5\,(soln) \rightarrow 4NO_2\,(soln) + O_2\,(g)$$

This reaction is carried out in a CCl_4 solution at 45°C. The concentrations of N_2O_5 as a function of time are listed in the following table, together with the natural logarithms and reciprocal N_2O_5 concentrations. Plot a graph of the concentration versus *t*, ln concentration versus *t*, and 1/concentration versus *t* and then determine the rate law and calculate the rate constant.

Time (s)	$[N_2O_5]$ (M)	$\ln[N_2O_5]$	$1/[N_2O_5]$ (M^{-1})
0	0.0365	−3.310	27.4
600	0.0274	−3.597	36.5
1200	0.0206	−3.882	48.5
1800	0.0157	−4.154	63.7
2400	0.0117	−4.448	85.5
3000	0.00860	−4.756	116
3600	0.00640	−5.051	156

Given: balanced chemical equation, reaction times, and concentrations

Asked for: graph of data, rate law, and rate constant

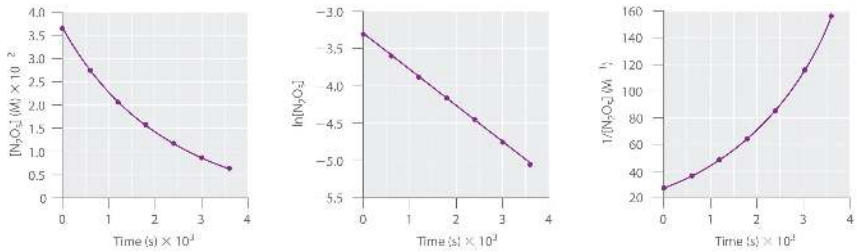
Strategy:

A Use the data in the table to separately plot concentration, the natural logarithm of the concentration, and the reciprocal of the concentration (the vertical axis) versus time (the horizontal axis). Compare the graphs with those in Figure 13.4.2 to determine the reaction order.

B Write the rate law for the reaction. Using the appropriate data from the table and the linear graph corresponding to the rate law for the reaction, calculate the slope of the plotted line to obtain the rate constant for the reaction.

Solution:

A Here are plots of $[N_2O_5]$ versus t, $\ln[N_2O_5]$ versus t, and $1/[N_2O_5]$ versus t:



The plot of $\ln[N_2O_5]$ versus t gives a straight line, whereas the plots of $[N_2O_5]$ versus t and $1/[N_2O_5]$ versus t do not. This means that the decomposition of N_2O_5 is first order in $[N_2O_5]$.

B The rate law for the reaction is therefore

$$rate = k\,[N_2O_5]$$

Calculating the rate constant is straightforward because we know that the slope of the plot of ln[A] versus t for a first-order reaction is $-k$. We can calculate the slope using any two points that lie on the line in the plot of $\ln[N_2O_5]$ versus t. Using the points for t = 0 and 3000 s,

$$slope = \frac{ln\,[N_2O_5]_{3000} - ln\,[N_2O_5]_0}{3000\ s - 0\ s} = \frac{[-4.756] - [-3.310]}{3000\ s} = 4.820 \times 10^{-4}\ s^{-1}$$

Thus $k = 4.820 \times 10^{-4}\ s^{-1}$.

14.3.3: Contributors

- Anonymous

Modified by Joshua Halpern (Howard University), Scott Sinex, and Scott Johnson (PGCC)

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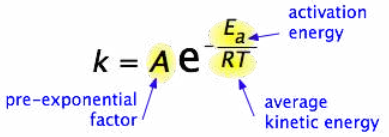
14.4: Arrhenius Equation

It is common knowledge that chemical reactions occur more rapidly at higher temperatures. Milk turns sour much more rapidly if stored at room temperature rather than in a refrigerator; butter goes rancid more quickly in the summer than in the winter; and eggs hard-boil more quickly at sea level than in the mountains. For the same reason, cold-blooded animals such as reptiles and insects tend to be more lethargic on cold days.

The reason for this is not hard to understand. Thermal energy relates direction to motion at the molecular level. As the temperature rises, molecules move faster and collide more vigorously, greatly increasing the likelihood of bond cleavages and rearrangements. Whether it is through the collision theory, transition state theory, or just common sense, chemical reactions are typically expected to proceed faster at higher temperatures and slower at lower temperatures.



By 1890 it was common knowledge that higher temperatures speed up reactions, often doubling the rate for a 10-degree rise, but the reasons for this were not clear. Finally, in 1899, the Swedish chemist Svante Arrhenius (1859-1927) combined the concepts of activation energy and the Boltzmann distribution law into one of the most important relationships in physical chemistry:



Take a moment to focus on the meaning of this equation, neglecting the *A* factor for the time being. First, note that this is another form of the exponential decay law discussed in the previous section of this series. What is "decaying" here is not the concentration of a reactant as a function of time, but the magnitude of the rate constant as a function of the exponent $-E_a/RT$. And what is the significance of this quantity? Recalling that *RT* is the *average kinetic energy*, it becomes apparent that the exponent is just the ratio of the activation energy E_a to the average kinetic energy. The larger this ratio, the smaller the rate (hence the negative sign). This means that high temperature and low activation energy favor larger rate constants, and thus speed up the reaction. Because these terms occur in an exponent, their effects on the rate are quite substantial.

The two plots below show the effects of the activation energy (denoted here by $E^{\ddagger}$) on the rate constant. Even a modest activation energy of 50 kJ/mol reduces the rate by a factor of 10^8.

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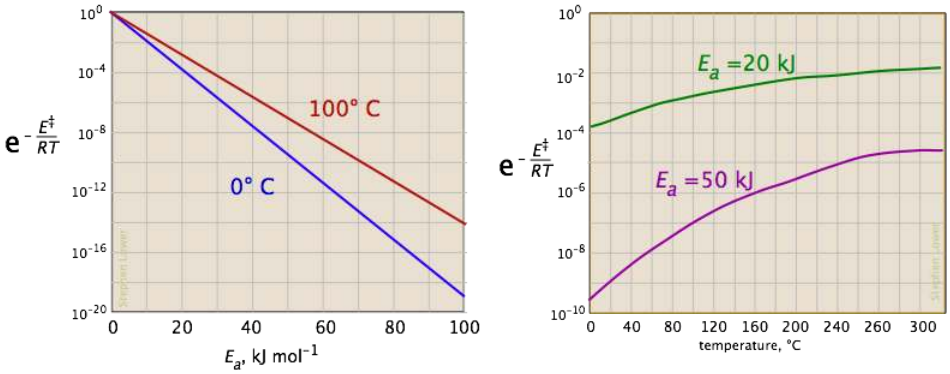


Figure **14.4.1**: Arrhenius plots. The logarithmic scale in the right-hand plot leads to nice straight lines.

Looking at the role of temperature, a similar effect is observed. (If the *x*-axis were in "kilodegrees" the slopes would be more comparable in magnitude with those of the kilojoule plot at the above right.)

Determining the Activation Energy

The Arrhenius equation,

$$k = Ae^{-E_a/RT} \tag{14.4.1}$$

can be written in a non-exponential form that is often more convenient to use and to interpret graphically. Taking the logarithms of both sides and separating the exponential and pre-exponential terms yields

$$\ln k = \ln\left(Ae^{-E_a/RT}\right) \tag{14.4.2}$$

$$= \ln A + \ln\left(e^{-E_a/RT}\right) \tag{14.4.3}$$

$$= \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \tag{14.4.4}$$

Equation 14.4.4 is in the form of $y = mx + b$ - the equation of a straight line.

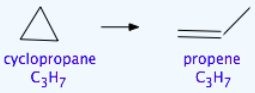
$$\ln k = \ln A - \frac{E_a}{RT}$$

where temperature is the independent variable and the rate constant is the dependent variable. So if one were given a data set of various values of k, the rate constant of a certain chemical reaction at varying temperature T, one could graph $\ln(k)$ versus $1/T$. From the graph, one can then determine the slope of the line and realize that this value is equal to $-E_a/R$. One can then solve for the activation energy by multiplying through by -R, where R is the gas constant.

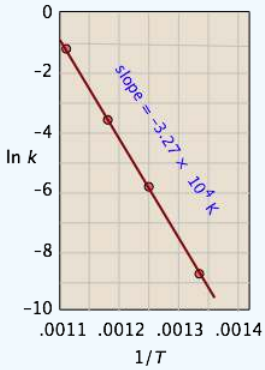
This affords a simple way of determining the activation energy from values of *k* observed at different temperatures, by plotting $\ln k$ as a function of $1/T$.

Example 14.4.1: Isomerization of Cyclopropane

For the isomerization of cyclopropane to propene,



the following data were obtained (calculated values shaded in pink):



T, °C	477	523	577	623
$1/T$, $K^{-1} \times 10^3$	1.33	1.25	1.18	1.11
k, s^{-1}	0.00018	0.0027	0.030	0.26
ln k	–8.62	–5.92	–3.51	–1.35

From the calculated slope, we have

$$-\left(\frac{E_a}{R}\right) = -3.27 \times 10^4 K$$
$$E_a = -(8.314\, J\, mol^{-1} K^{-1})(-3.27 \times 10^4\, K)$$
$$= 273\, kJ\, mol^{-1}$$

Comment: This activation energy is high, which is not surprising because a carbon-carbon bond must be broken in order to open the cyclopropane ring. (C–C bond energies are typically around 350 kJ/mol.) This is why the reaction must be carried out at high temperature.

Calculating E_a without a plot

Because the ln k-vs.-$1/T$ plot yields a straight line, it is often convenient to estimate the activation energy from experiments at only two temperatures. To see how this is done, consider that

$$\ln k_2 - \ln k_1 = \left(\ln A - \frac{E_a}{RT_2}\right) - \left(\ln A - \frac{E_a}{RT_1}\right)$$
$$= \boxed{\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

The ln-A term is eliminated by subtracting the expressions for the two ln-k terms.) Solving the expression on the right for the activation energy yields

$$E_a = \frac{R \ln \dfrac{k_2}{k_1}}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}$$

Example 14.4.2

A widely used rule-of-thumb for the temperature dependence of a reaction rate is that a **ten degree** rise in the temperature approximately doubles the rate. This is not generally true, especially when a strong covalent bond must be broken. For a reaction that does show this behavior, what would the activation energy be?

Solution

Center the ten degree interval at 300 K. Substituting into the above expression yields

$$E_a = \frac{(8.314)(\ln 2/1)}{\frac{1}{295} - \frac{1}{305}}$$
$$= \frac{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(0.693)}{0.00339\,\text{K}^{-1} - 0.00328\,\text{K}^{-1}}$$
$$= \frac{5.76\,J\,mol^{-1}K^{-1}}{(0.00011\,K^{-1}}$$
$$= 52,400\,J\,mol^{-1} = 52.4\,kJ\,mol^{-1}$$

Example 14.4.3

It takes about 3.0 minutes to cook a hard-boiled egg in Los Angeles, but at the higher altitude of Denver, where water boils at 92°C, the cooking time is 4.5 minutes. Use this information to estimate the activation energy for the coagulation of egg albumin protein.

Solution

The ratio of the rate constants at the elevations of Los Angeles and Denver is 4.5/3.0 = 1.5, and the respective temperatures are **373 K** and **365 K**. With the subscripts 2 and 1 referring to Los Angeles and Denver respectively:

$$E_a = \frac{(8.314)(\ln 1.5)}{\frac{1}{365\ \text{K}} - \frac{1}{373\ \text{K}}}$$
$$= \frac{(8.314)(0.405)}{0.00274\ \text{K}^{-1} - 0.00268\ \text{K}^{-1}}$$
$$= \frac{(3.37\ \text{J mol}^{-1}\text{K}^{-1})}{5.87 \times 10^{-5}\ \text{K}^{-1}}$$
$$= 57,400\ \text{J mol}^{-1}$$
$$= 57.4\ \text{kJ mol}^{-1}$$

Comment: This low value seems reasonable because thermal denaturation of proteins primarily involves the disruption of relatively weak hydrogen bonds; no covalent bonds are broken (although disulfide bonds can interfere with this interpretation).

The Pre-exponential Factor

Up to this point, the pre-exponential term, A in the Arrhenius equation (Equation 14.4.1), has been ignored because it is not directly involved in relating temperature and activation energy, which is the main practical use of the equation.

$$k = Ae^{-E_a/RT}$$

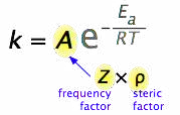
However, because A multiplies the exponential term, its value clearly contributes to the value of the rate constant and thus of the rate. Recall that the exponential part of the Arrhenius equation expresses the fraction of reactant molecules that possess enough kinetic energy to react, as governed by the Maxwell-Boltzmann law. This fraction can run from zero to nearly unity, depending on the magnitudes of E_a and of the temperature.

If this fraction were 0, the Arrhenius law would reduce to

$$k = A$$

In other words, A is the fraction of molecules that would react if either the activation energy were zero, or if the kinetic energy of all molecules exceeded E_a — admittedly, an uncommon scenario (although barrierless reactions have been characterized).

What would limit the rate constant if there were no activation energy requirements? The most obvious factor would be the rate at which reactant molecules come into contact. This can be calculated from kinetic molecular theory and is known as the **frequency-** or **collision factor**, Z.



In some reactions, the relative orientation of the molecules at the point of collision is important, so a geometrical or **steric factor** (commonly denoted by ρ) can be defined. In general, we can express A as the product of these two factors:

$$A = Z\rho$$

Values of ρ are generally very difficult to assess; they are sometime estimated by comparing the observed rate constant with the one in which A is assumed to be the same as Z.

Implications

The exponential term in the Arrhenius equation implies that the rate constant of a reaction increases exponentially when the activation energy decreases. Because the rate of a reaction is directly proportional to the rate constant of a reaction, the rate increases exponentially as well. Because a reaction with a small activation energy does not require much energy to reach the transition state, it should proceed faster than a reaction with a larger activation energy.

In addition, the Arrhenius equation implies that the rate of an uncatalyzed reaction is more affected by temperature than the rate of a catalyzed reaction. This is because the activation energy of an uncatalyzed reaction is greater than the activation energy of the corresponding catalyzed reaction. Since the exponential term includes the activation energy as the numerator and the temperature as the denominator, a smaller activation energy will have less of an impact on the rate constant compared to a larger activation energy. Hence, the rate of an uncatalyzed reaction is more affected by temperature changes than a catalyzed reaction.

The Math in Eliminating the Constant A

To eliminate the constant A, there must be two known temperatures and/or rate constants. With this knowledge, the following equations can be written:

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \tag{14.4.5}$$

at T_1 and

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \tag{14.4.6}$$

at T_2. By rewriting Equation 14.4.6:

$$\ln A = \ln k_2 + \frac{E_a}{RT_2} \tag{14.4.7}$$

and substitute for $\ln A$ into Equation 14.4.5:

$$\ln k_1 = \ln k_2 + \frac{E_a}{RT_2} - \frac{E_a}{RT_1} \tag{14.4.8}$$

This simplifies to:

$$\ln k_1 - \ln k_2 = -\frac{E_a}{RT_1} + \frac{E_a}{RT_2}$$

$$\ln \frac{k_1}{k_2} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Summary

After observing that many chemical reaction rates depended on the temperature, Arrhenius developed this equation to characterize the temperature-dependent reactions:

$$k = Ae^{\frac{-E_a}{RT}}$$

or

$$\ln k = \ln A - \frac{E_a}{RT}$$

with the following terms:

k: Chemical reaction rate constant

- In unit of s^{-1}(for 1st order rate constant) or $M^{-1}s^{-1}$(for 2nd order rate constant)

A: The pre-exponential factor or frequency factor

- Specifically relates to molecular collision
- Deals with the frequency of molecules that collide in the correct orientation and with enough energy to initiate a reaction.
- *It is a factor that is determined experimentally, as it varies with different reactions.*
- In unit of L $mol^{-1}s^{-1}$ or $M^{-1}s^{-1}$(for 2nd order rate constant) and s^{-1}(for 1st order rate constant)
- Because frequency factor A is related to molecular collision, it is temperature dependent
- Hard to extrapolate pre-exponential factor because lnk is only linear over a narrow range of temperature

E_a: The activation energy is the threshold energy that the reactant(s) must acquire before reaching the transition state.

- Once in the transition state, the reaction can go in the forward direction towards product(s), or in the opposite direction towards reactant(s).
- A reaction with a large activation energy requires much more energy to reach the transition state.
- Likewise, a reaction with a small activation energy doesn't require as much energy to reach the transition state.
- In units of J/mol.
- $-E_a/RT$ resembles the Boltzmann distribution law.

R: The gas constant.

- Its value is 8.314 J/mol K.

T: The absolute temperature at which the reaction takes place.

- In units of Kelvin (K).

Problems

1. Find the activation energy (in kJ/mol) of the reaction if the rate constant at 600K is 3.4 $M^{-1}s^{-1}$ and 31.0 at 750K.
2. Find the rate constant if the temperature is 289K, Activation Energy is 200kJ/mol and pre-exponential factor is 9 $M^{-1}s^{-1}$
3. Find the new rate constant at 310K if the rate constant is 7 $M^{-1}s^{-1}$ at 370K, Activation Energy is 900kJ/mol
4. Calculate the activation energy if the pre-exponential factor is 15 $M^{-1}s^{-1,}$ rate constant is 12$M^{-1}s^{-1}$and it is at 22K
5. Find the new temperature if the rate constant at that temperature is 15$M^{-1}s^{-1}$ while at temperature 389K the rate constant is 7$M^{-1}s^{1,}$ the Activation Energy is 600kJ/mol

Solutions

1. E_a is the factor the question asks to be solved. Therefore it is much simpler to use

$$\ln k = -\frac{E_a}{RT} + \ln A$$

To find E_a, subtract ln A from both sides and multiply by -RT.

This will give us:

$$E_a = \ln A - \ln k)RT$$

2. Substitute the numbers into the equation:

$$lnk = \frac{-(200\times1000\ \text{J})}{(8.314\ \text{J mol}^{-1}\text{K}^{-1})(289\ \text{K})} + \ln 9$$

$k = 6.37X10^{-36}\ M^{-1}s^{-1}$

3. Use the equation $ln(k_1/k_2)=-Ea/R(1/T_1-1/T_2)$

$\ln(7/k_2)$=-[(900 X 1000)/8.314](1/370-1/310)

$k_2=1.788X10^{-24}\ M^{-1}s^{-1}$

4. Use the equation $k = Ae^{-Ea/RT}$

$12 = 15e^{-Ea/(8.314)(22)}$

$Ea = 40.82J/mol$

5. Use the equatioin $ln(k_1/k_2)=-Ea/R(1/T_1-1/T_2)$

$\ln(15/7)$=-[(600 X 1000)/8.314](1/T_1 - 1/389)

$T_1 = 390.6K$

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Contributors and Attributions

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14.5: Eyring equation

The Eyring Equation, developed by Henry Eyring in 1935, is based on transition state theory and is used to describe the relationship between reaction rate and temperature. It is similar to the Arrhenius Equation, which also describes the temperature dependence of reaction rates. However, whereas Arrhenius Equation can be applied only to gas-phase kinetics, the Eyring Equation is useful in the study of gas, condensed, and mixed-phase reactions that have no relevance to the collision model.

Introduction

The Eyring Equation gives a more accurate calculation of rate constants and provides insight into how a reaction progresses at the molecular level. The Equation is given below:

$$k = \frac{k_B T}{h} e^{-\left(\frac{\Delta H^{\ddagger}}{RT}\right)} e^{\left(\frac{\Delta S^{\ddagger}}{R}\right)} \tag{14.5.1}$$

Consider a bimolecular reaction:

$$A + B \rightarrow C \tag{14.5.2}$$

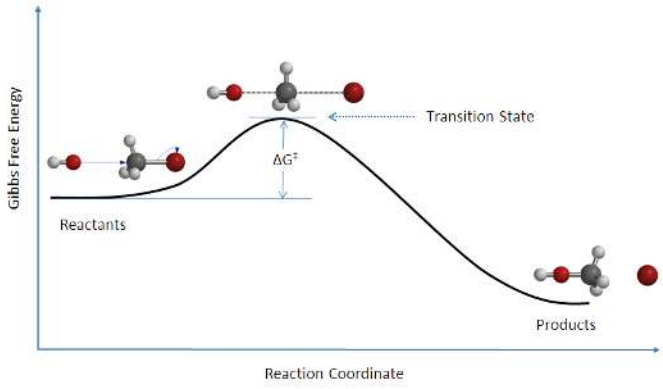
$$K = \frac{[C]}{[A][B]} \tag{14.5.3}$$

where K is the equilibrium constant. In the transition state model, the activated complex AB is formed:

$$A + B \rightleftharpoons AB^{\ddagger} \rightarrow C \tag{14.5.4}$$

$$K^{\ddagger} = \frac{[AB]^{\ddagger}}{[A][B]} \tag{14.5.5}$$

There is an energy barrier, called activation energy, in the reaction pathway. A certain amount of energy is required for the reaction to occur. The transition state, $AB^{\ddagger}$, is formed at maximum energy. This high-energy complex represents an unstable intermediate. Once the energy barrier is overcome, the reaction is able to proceed and product formation occurs.



Reaction: $HO^- + CH_3Br \rightarrow [HO{-}{-}{-}CH_3{-}{-}{-}Br]^{\ddagger} \rightarrow CH_3OH + Br^-$

Figure **14.5.1:** Reaction coordinate diagram for the bimolecular nucleophilic substitution (S_N2) reaction between bromomethane and the hydroxide anion. form Wikipedia.

The rate of a reaction is equal to the number of activated complexes decomposing to form products. Hence, it is the concentration of the high-energy complex multiplied by the frequency of it surmounting the barrier.

$$rate = v[AB^{\ddagger}] \tag{14.5.6}$$

$$= v[A][B]K^{\ddagger} \tag{14.5.7}$$

The rate can be rewritten:

$$rate = k[A][B] \tag{14.5.8}$$

Combining Equations 14.5.8 and 14.5.7 gives:

$$k[A][B] = v[A][B]K^{\ddagger} \tag{14.5.9}$$
$$k = vK^{\ddagger} \tag{14.5.10}$$

where

- v is the frequency of vibration,
- k is the rate constant and
- $K^{\ddagger}$ is the thermodynamic equilibrium constant.

The frequency of vibration is given by:

$$v = \frac{k_B T}{h} \tag{14.5.11}$$

where

- k_B is the Boltzmann's constant (1.381 x 10^{-23} J/K),
- T is the absolute temperature in Kelvin (K) and
- h is Planck's constant (6.626 x 10^{-34} Js).

Substituting Equation 14.5.11 into Equation 14.5.10 :

$$k = \frac{k_B T}{h} K^{\ddagger} \tag{14.5.12}$$

Equation ref is often tagged with another term (M^{1-m}) that makes the units equal with M is the molarity and m is the molecularly of the reaction.

$$k = \frac{k_B T}{h} K^{\ddagger} (M^{1-m}) \tag{14.5.13}$$

The following thermodynamic equations further describe the equilibrium constant:

$$\Delta G^{\ddagger} = -RT \ln K^{\ddagger} \tag{14.5.14}$$
$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{14.5.15}$$

where $\Delta G^{\ddagger}$ is the Gibbs energy of activation, $\Delta H^{\ddagger}$ is the **enthalpy of activation** and $\Delta S^{\ddagger}$ is the **entropy of activation**. Combining Equations 14.5.10 and 14.5.11 to solve for $\ln K^{\ddagger}$ gives:

$$\ln K^{\ddagger} = -\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} \tag{14.5.16}$$

The Eyring Equation is finally given by substituting Equation 14.5.16 into Equation 14.5.12:

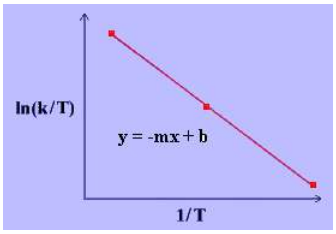
$$k = \frac{k_B T}{h} e^{-\frac{\Delta H^{\ddagger}}{RT}} e^{\frac{\Delta S^{\ddagger}}{R}} \tag{14.5.17}$$

Application of the Eyring Equation

The linear form of the Eyring Equation is given below:

$$\ln \frac{k}{T} = \frac{-\Delta H^{\dagger}}{R} \frac{1}{T} + \ln \frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R} \tag{14.5.18}$$

The values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be determined from kinetic data obtained from a $\ln \frac{k}{T}$ vs. $\frac{1}{T}$ plot. The Equation is a straight line with negative slope, $\frac{-\Delta H^{\ddagger}}{R}$, and a y-intercept, $\frac{\Delta S^{\ddagger}}{R} + \ln \frac{k_B}{h}$.



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CHAPTER OVERVIEW

15: Chemical Kinetics II- Reaction Mechanisms

15.1: A Mechanism is a Sequence of Elementary Reactions
15.2: The Steady-State Approximation
15.3: Rate Laws Do Not Imply Unique Mechanism
15.4: The Lindemann Mechanism
15.5: Some Reaction Mechanisms Involve Chain Reactions
15.6: A Catalyst Affects the Mechanism and Activation Energy
15.7: The Michaelis-Menten Mechanism for Enzyme Catalysis

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15.1: A Mechanism is a Sequence of Elementary Reactions

The mechanism of a reaction is a series of steps leading from the starting materials to the products. After each step, an intermediate is formed. The intermediate is short-lived, because it quickly undergoes another step to form the next intermediate. These simple steps are called elementary reactions. Because an overall reaction is composed of a series of elementary reaction, the overall rate of the reaction is somehow dependent on the rates of those smaller reactions. But how are the two related? Let's look at two cases. We'll keep it simple and both cases will be two-step reactions.

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15.2: The Steady-State Approximation

One of the most commonly used and most attractive approximations is the **steady state approximation**. This approximation can be applied to the rate of change of concentration of a highly reactive (short lived) intermediate that holds a constant value over a long period of time. The advantage here is that for such an intermediate (I),

$$\frac{d[I]}{dt} = 0$$

So long as one can write an expression for the rate of change of the concentration of the intermediate I, the steady state approximation allows one to solve for its constant concentration. For example, if the reaction

$$A + B \rightarrow C \tag{15.2.1}$$

is proposed to follow the mechanism

$$A + A \xrightarrow{k_1} A_2 \tag{15.2.2}$$

$$A_2 + B \xrightarrow{k_2} C + A \tag{15.2.3}$$

The time-rate of change of the concentration of the intermediate A_2 can be written as

$$\frac{d[A_2]}{dt} = k_1[A]^2 - k_2[A_2][B]$$

In the limit that the steady state approximation can be applied to A_2

$$\frac{d[A_2]}{dt} = k_1[A]^2 - k_2[A_2][B] \approx 0$$

or

$$[A_2] \approx \frac{k_1[A]^2}{k_2[B]}$$

So if the rate of the overall reaction is expressed as the rate of formation of the product C,

$$\frac{d[C]}{dt} = k_2[A_2][B]$$

the above expression for $[A_2]$ can be substituted

$$\frac{d[C]}{dt} = k_2\left(\frac{k_1[A]^2}{k_2[B]}\right)[B]$$

of

$$\frac{d[C]}{dt} = k_1[A]^2$$

and the reaction is predicted to be second order in $[A]$.

Alternatively, if the mechanism for Equation 15.2.1 is proposed to be

$$A \xrightarrow{k_1} A^* \tag{15.2.4}$$

$$A^* + B \xrightarrow{k_2} C \tag{15.2.5}$$

then the rate of change of the concentration of A^* is

$$\frac{[A^*]}{dt} = k_1[A] - k_2[A^*][B]$$

And if the steady state approximation holds, then

$$[A^*] \approx \frac{k_1[A]}{k_2[B]}$$

So the rate of production of C is

$$\frac{d[C]}{dt} = k_2[A^*][B] \tag{15.2.6}$$

$$= \cancel{k_2}\left(\frac{k_1[A]}{\cancel{k_2}\cancel{[B]}}\right)\cancel{[B]} \tag{15.2.7}$$

or

$$\frac{d[C]}{dt} = k_1[A]$$

and the rate law is predicted to be first order in A. In this manner, the plausibility of either of the two reaction mechanisms is easily deduced by comparing the predicted rate law to that which is observed. If the prediction cannot be reconciled with observation, then the scientific method eliminates that mechanism from consideration.

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15.3: Rate Laws Do Not Imply Unique Mechanism

Because a proposed mechanism can only be valid if it is consistent with the rate law found experimentally, the rate law plays a central role in the investigation of chemical reaction mechanisms. The discussion above introduces the problems and methods associated with collecting rate data and with finding an empirical rate law that fits experimental concentration-*versus*-time data. We turn now to finding the rate laws that are consistent with a particular proposed mechanism. For simplicity, we consider reactions in closed constant-volume systems.

In principle, numerical integration can be used to predict the concentration at any time of each of the species in any proposed reaction mechanism. This prediction can be compared to experimental observations to see whether they are consistent with the proposed mechanism. To do the numerical integration, it is necessary to know the initial concentrations of all of the chemical species and to know, or assume, values of all of the rate constants. The initial concentrations are known from the procedure used to initiate the reaction. However, the rate constants must be determined by some iterative procedure in which initial estimates of the rate constants are used to predict concentration-*versus*-time data that can be compared to the experimental results to produce refined estimates.

In practice, we tailor our choice of reaction conditions so that we can use various approximations to test whether a proposed mechanism can explain the data. We now consider the most generally useful of these approximations.

In this discussion, we assume that the overall reaction goes to completion; that is, at equilibrium the concentration of the reactant whose concentration is limiting has become essentially zero. If the overall reaction involves more than one elementary step, then an intermediate compound is involved. A valid mechanism must include this intermediate, and more than one differential equation may be needed to characterize the time rate of change of all of the species involved in the reaction. We focus on conditions and approximations under which the rate of appearance of the final products in a multi-step reaction mechanism can be described by a single differential equation, the rate law.

We examine the application of these approximations to a particular reaction mechanism. When we understand the application of these approximations to this mechanism, the ways in which they can be used in other situations are clear.

Consider the following sequence of elementary steps

$$\mathrm{A} + \mathrm{B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} \xrightarrow{k_3} \mathrm{D}$$

whose kinetics are described by the following simultaneous differential equations:

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k_1[A][B] + k_2[C]$$

$$\frac{d[C]}{dt} = k_1[A][B] - k_2[C] - k_3[C]$$

$$\frac{d[D]}{dt} = k_3[C]$$

The general analytical solution for this system of coupled differential equations can be obtained, but it is rather complex, because $[C]$ increases early in the reaction, passes through a maximum, and then decreases at long times. In principle, experimental data could be fit to these equations. The numerical approach requires that we select values for k_1, k_2, k_3, $[A]_0$, $[B]_0$, $[C]_0$, and $[D]_0$, and then numerically integrate to get $[A]$, $[B]$, $[C]$, and $[D]$ as functions of time. In principle, we could refine our estimates of k_1, k_2, and k_3 by comparing the calculated values of one or more concentrations to the experimental ones. In practice, the approximate treatments we consider next are more expedient.

When we begin a kinetic study, we normally have a working hypothesis about the reaction mechanism, and we design our experiments to simplify the differential equations that apply to it. For the present example, we will assume that we always arrange the experiment so that $[C]_0 = 0$ and $[D]_0 = 0$. In consequence, at all times:

$$[A]_0 = [A] + [C] + [D]\,.$$

Also, we restrict our considerations to experiments in which $[B]_0 \gg [A]_0$. This exemplifies the use of **flooding**. The practical effect is that the concentration of B remains effectively constant at its initial value throughout the entire reaction, which simplifies the

differential equations significantly. In the present instance, setting $[B]_0 \gg [A]_0$ means that the rate-law term $k_1[A][B]$ can be replaced, to a good approximation, by $k_{obs}[A]$, where $k_{obs} = k_1[B]_0$.

Once we have decided upon the reaction conditions we are going to use, whether the resulting concentration-*versus*-time data can be described by a single differential equation depends on the relative magnitudes of the rate constants in the several steps of the overall reaction. Particular combinations of relationships that lead to simplifications are often referred to by particular names; we talk about a combination that has a ***rate-determining step***, or one that involves a ***prior equilibrium***, or one in which a ***steady-state approximation*** is applicable. To see what we mean by these terms, let us consider some particular relationships that can exist among the rate constants in the mechanism above.

15.3.1: Case I

Suppose that $k_1[A][B] \gg k_2[C]$ and $k_3 \gg k_2$. We often describe this situation by saying, rather imprecisely, that the reaction to convert C to D is very fast and that the reaction to convert C back to A and B is very slow—compared to the reaction that forms C from A and B. When C is produced in these circumstances, it is converted to D so rapidly that we never observe a significant concentration of C in the reaction mixture. The formation of a molecule of C is tantamount to the formation of a molecule of D, and the reaction produces D at essentially the same rate that it consumes A or B. We say that the first step, $A + B \rightarrow C$, is the rate-determining step in the reaction. We have

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} \approx \frac{d[D]}{dt}$$

The assumption that $k_1[A][B] \gg k_2[C]$ means that we can neglect the smaller term in the equation for $d[A]/dt$, giving the approximation

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -\frac{d[D]}{dt} = -k_1[A][B]$$

Letting $[D] = x$ and recognizing that our assumptions make $[C] \approx 0$, the mass-balance condition, $[A]_0 = [A] + [C] + [D]$, becomes $[A] = [A]_0 - x$. Choosing $[B]_0 \gg [A]_0$ means that $k_1[B] \approx k_1[B]_0 = k_{I,obs}$. The rate equation becomes first-order:

$$\frac{dx}{dt} = k_{I,obs}\,([A]_0 - x)$$

Since $k_{I,obs}$ is not strictly constant, it is a pseudo-first-order rate constant. The disappearance of A is said to follow a pseudo-first-order rate equation.

The concept of a rate-determining step step is an **approximation**. In general, the consequence we have in mind when we invoke this approximation is that no intermediate species can accumulate to a significant concentration if it is produced by the rate-determining step or by a step that occurs after the rate-determining step. We do not intend to exclude the accumulation of a species that is at equilibrium with another product. Thus, in the mechanism

$$\mathrm{A} \xrightarrow{k} \mathrm{B} \rightleftharpoons \mathrm{C}$$

we suppose that the conversion of A to B is rate-determining and that the interconversion of B and C is so rapid that their concentrations always satisfy the equilibrium relationship

$$K = \frac{[C]}{[B]}.$$

For the purpose at hand, we do not consider B to be an intermediate; B is a product that happens to be at equilibrium with the co-product, C.

15.3.2: Case II

Suppose that $k_1[A][B] \gg k_3[C]$. In this case $A + B \rightarrow C$ is fast compared to the rate at which C is converted to D, and we say that $C \rightarrow D$ is the rate-determining step. We can now distinguish three sub-cases depending upon the way $[C]$ behaves during the course of the reaction.

Case IIa: Suppose that $k_1[A][B] \gg k_3[C]$ and $k_3 \gg k_2$. Then $A + B \rightarrow C$ is rapid and essentially quantitative. That is, within a short time of initiating the reaction, all of the stoichiometrically limiting reactant is converted to C. Letting $[D] = x$ and recognizing that our assumptions make $[A] \approx 0$, the mass-balance condition,

$$[A]_0 = [A] + [C] + [D]$$

becomes

$$[C] = [A]_0 - x.$$

After a short time, the rate at which D is formed becomes

$$\frac{d[D]}{dt} = k_3[C]$$

or

$$\frac{dx}{dt} = k_3([A]_0 - x)$$

The disappearance of C and the formation of D follow a first-order rate law.

Case IIb: If the forward and reverse reactions in the first elementary process are rapid, then this process may be effectively at equilibrium during the entire time that D is being formed. (This is the case that $k_1[A][B] \gg k_3[C]$ and $k_2 \gg k_3$.) Then, throughout the course of the reaction, we have

$$K_{eq} = [C]/[A][B]$$

Letting $[D] = x$ and making the further assumption that $[A] \gg [C] \approx 0$ throughout the reaction, the mass-balance condition, $[A]_0 = [A] + [C] + [D]$, becomes $[A] = [A]_0 - x$. Substituting into the equilibrium-constant expression, we find

$$[C] = K_{eq}[B]_0\ ([A]_0 - x)$$

Substituting into $d[D]/dt = k_3[C]$ we have

$$\frac{dx}{dt} = k_3K_{eq}[B]_0\ ([A]_0 - x) = k_{IIa,obs}([A]_0 - x)$$

where $k_{IIa,obs} = k_3K_{eq}[B]_0$. The disappearance of A and the formation of D follow a pseudo-first-order rate equation. The pseudo-first-order rate constant is a composite quantity that is directly proportional to $[B]_0$.

Case IIc: If we suppose that the first step is effectively at equilibrium during the entire time that D is being produced (as in case IIb) but that $[C]$ is not negligibly small compared to $[A]$, we again have $K_{eq} = [C]/[A][B]$. With $[D] = x$, the mass-balance condition becomes $[A] = [A]_0 - [C] - x$. Eliminating $[A]$ between the mass-balance and equilibrium-constant equations gives

$$[C] = \frac{K_{eq}[B]_0([A]_0 - x)}{1 + K_{eq}[B]_0}$$

so that $d[D]/dt = k_3[C]$ becomes

$$\frac{dx}{dt} = \left(\frac{k_3K_{eq}[B]_0}{1 + K_{eq}[B]_0}\right)([A]_0 - x) = k_{IIc,obs}([A]_0 - x)$$

The formation of D follows a pseudo-first-order rate equation. (The disappearance of A is also pseudo-first-order, but the pseudo-first-order rate constant is different.) As in Case IIb, the pseudo-first-order rate constant, $k_{IIc,obs}$, is a composite quantity, but now its dependence on $[B]_0$ is more complex. The result for Case IIc reduces to that for Case IIb if $K_{eq}[B]_0 \ll 1$.

15.3.3: Case III

In the cases above, we have assumed that one or more reactions are intrinsically much slower than others are. The differential equations for this mechanism can also become much simpler if all three reactions proceed at similar rates, but do so in such a way that the concentration of the intermediate is always very small, $[C] \approx 0$. If the concentration of C is always very small, then we expect the graph of $[C]$ versus time to have a slope, $d[C]/dt$, that is approximately zero. In this case, we have

$$\frac{d[C]}{dt} = k_1[A][B] - k_2[C] - k_3[C] \approx 0$$

so that

$$[C] = \frac{k_1[A][B]}{k_2 + k_3}$$

With $[D] = x$, $d[D]/dt = k_3[C]$ becomes

$$\frac{dx}{dt} = \left(\frac{k_1 k_3 [B]_0}{k_2 + k_3}\right)([A]_0 - x) = k_{III,obs}([A]_0 - x)$$

As in the previous cases, the disappearance of A and the formation of D follow a pseudo-first-order rate equation. The pseudo-first-order rate constant is again a composite quantity, which depends on $[B]_0$ and the values of all of the rate constants.

Case III illustrates the ***steady-state approximation***, in which we assume that the concentration of an intermediate species is much smaller than the concentrations of other species that affect the reaction rate. Under these circumstances, we can be confident that the time-derivative of the intermediate's concentration is negligible compared to the reaction rate, so that it is a good approximation to set it equal to zero. The idea is simply that, if the concentration is always small, its time-derivative must also be small. If the graph of the intermediate's concentration versus time is always much lower than that of other participating species, then its slope will be much less.

Equating the time derivative of the steady-state intermediate's concentration to zero produces an algebraic expression that involves the intermediate's concentration. Solving this expression for the concentration of the steady-state intermediate makes it possible to greatly simplify the set of simultaneous differential equations that is predicted by the mechanism. When there are multiple intermediates to which the approximation is applicable, remarkable simplifications can result. This often happens when the mechanism involves free-radical intermediates.

The name "steady-state approximation" is traditional. When we use it, we do so on the understanding that the "state" which is approximately "steady" is the concentration of the intermediate, not the state of the system. Since a net reaction is occurring, the state of the system is distinctly not constant.

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15.4: The Lindemann Mechanism

The Lindemann mechanism, sometimes called the Lindemann-Hinshelwood mechanism, is a schematic reaction mechanism. Frederick Lindemann discovered the concept in 1921 and Cyril Hinshelwood developed it. It breaks down a stepwise reaction into two or more elementary steps, then it gives a rate constant for each elementary step. The rate law and rate equation for the entire reaction can be derived from this information. Lindemann mechanisms have been used to model gas phase decomposition reactions. Although the net formula for a decomposition may appear to be first-order (unimolecular) in the reactant, a Lindemann mechanism may show that the reaction is actually second-order (bimolecular).

A Lindemann mechanism typically includes an activated reaction intermediate, labeled A* (where A can be any element or compound). The activated intermediate is produced from the reactants only after a sufficient activation energy is applied. It then either deactivates from A* back to A, or reacts with another (dis)similar reagent to produce yet another reaction intermediate or the final product.

15.4.1: General Mechanism

The schematic reaction $A + M \rightarrow P$ is assumed to consist of two elementary steps:

STEP 1: Bimolecular activation of A

$$A + M \rightleftharpoons A^* + M \tag{15.4.1}$$

with

- forward activation reaction rate: k_1
- reverse deactivation reaction rate: k_{-1}

STEP 2: Unimolecular reaction of $A*$

$$A^* \xrightarrow{k_2} P \tag{15.4.2}$$

with

- forward reaction rate: k_2

Assuming that the concentration of intermediate A^* is held constant according to the quasi steady-state approximation, what is the rate of formation of product P?

Solution

First, find the rates of production and consumption of intermediate A^*. The rate of production of A^* in the first elementary step (Equation 15.4.1) and A^* is consumed both in the reverse first step and in the forward second step. The respective rates of consumption of A^* are:

$$\frac{d[A^*]}{dt} = \underset{\text{(forward first step)}}{k_1[A][M]} - \underset{\text{(reverse first step)}}{k_{-1}[A^*][M]} - \underset{\text{(forward second step)}}{k_2[A^*]} \tag{15.4.3}$$

According to the steady-state approximation,

$$\frac{d[A^*]}{dt} \approx 0 \tag{15.4.4}$$

Therefore the rate of production of A^* (first term in Equation 15.4.3) equals the rate of consumption (second and third terms in Equation 15.4.3):

$$k_1[A][M] = k_{-1}[A^*][M] + k_2[A^*] \tag{15.4.5}$$

Solving for $[A^*]$, it is found that

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2} \tag{15.4.6}$$

The overall reaction rate is (Equation 15.4.2)

$$\frac{d[P]}{dt} = k_2[A^*] \tag{15.4.7}$$

Now, by substituting the calculated value for $[A^*]$ (Equation 15.4.6 into Equation 15.4.7), the overall reaction rate can be expressed in terms of the original reactants A and M as follows:

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2} \tag{15.4.8}$$

The rate law for the Lindemann mechanism is not a simple first or second order reaction. However, under certain conditions (discussed below), Equation 15.4.8 can be simplified.

Three Principles of the Lindemann Mechanism

1. Energy is transferred by collision (forward reaction of Equation 15.4.1)
2. There is a time delay Δt between collision and reaction (Equation 15.4.2)
3. Molecules may be de-activated by another collision during Δt (reverse reaction of Equation 15.4.1)

N_2O_5 Example 29.6.1 : Dissociation of

The decomposition of dinitrogen pentoxide to nitrogen dioxide and nitrogen trioxide

$$N_2O_5 \rightarrow NO_2 + NO_3$$

is postulated to take place via two elementary steps, which are similar in form to the schematic example given above:

1. $N_2O_5 + N_2O_5 \rightleftharpoons N_2O_5^* + N_2O_5$
2. $N_2O_5^* \rightarrow NO_2 + NO_3$

Using the quasi steady-state approximation soluioten (Equation 9) with $[M] = [N_2O_5]$, then rate equation is:

$$\text{Rate} = k_2[N_2O_5]^* = \frac{k_1 k_2 [N_2O_5]^2}{k_{-1}[N_2O_5] + k_2}$$

Experiment has shown that the rate is observed as first-order in the original concentration of N_2O_5 sometimes, and second order at other times.

- If $k_2 >> k_{-1}$, then the rate equation may be simplified by assuming that $k_{-1} \approx 0$. Then the rate equation is

  $$\text{Rate} = k_1[N_2O_5]^2$$

  which is *second order*.
- If $k_2 << k_{-1}$, then the rate equation may be simplified by assuming $k_2 \approx 0$. Then the rate equation is

  $$\text{Rate} = \frac{k_1 k_2 [N_2O_5]}{k_{-1}} = k_{obs}[N_2O_5]$$

  which is *first order* with

  $$k_{obs} = \frac{k_2 k_2}{k_{-1}}.$$

Exercise 29.6.1

The following first order rate constants for the gas phase decomposition of N_2O_5 have been obtained as a function of number density at 298 K.

$k_{obs}(s^{-1})$	7.81×10^{-3}	12.5×10^{-3}	15.6×10^{-3}
$[N_2O_5](mol/m^{-3})$	10	25	50

Confirm that these data are consistent with the Lindemann mechanism and derive a rate constant and a ratio of two rate constants for elementary reactions in the mechanism. What are the units of the two quantities.

15.4.2: Lindemann Mechanism

Consider the isomerization of methylisonitrile gas, CH_3NC, to acetonitrile gas, CH_3CN:

$$CH_3NC \xrightarrow{k} CH_3CN$$

If the isomerization is a unimolecular elementary reaction, we should expect to see 1^{st} order rate kinetics. Experimentally, however, 1^{st} order rate kinetics are only observed at high pressures. At low pressures, the reaction kinetics follow a 2^{nd} order rate law:

$$\frac{d\left[CH_3NC\right]}{dt} = -k\left[CH_3NC\right]^2 \tag{15.4.9}$$

To explain this observation, J.A. Christiansen and F.A. Lindemann proposed that gas molecules first need to be energized via intermolecular collisions before undergoing an isomerization reaction. The reaction mechanism can be expressed as the following two elementary reactions

$$\mathrm{A} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{M} \tag{15.4.10}$$

$$\mathrm{A}^* \xrightarrow{k_2} \mathrm{B} \tag{15.4.11}$$

where $\mathbf{M}$ can be a reactant molecule, a product molecule or another inert molecule present in the reactor. Assuming that the concentration of $\mathbf{A^*}$ is small, or $k_1 \ll k_2 + k_{-1}$, we can use a steady-state approximation to solve for the concentration profile of species $\mathbf{B}$ with time:

$$\frac{d\left[\mathrm{A}^*\right]}{dt} = k_1\left[\mathrm{A}\right]\left[\mathrm{M}\right] - k_{-1}\left[\mathrm{A}^*\right]_{ss}\left[\mathrm{M}\right] - k_2\left[\mathrm{A}^*\right]_{ss} \approx 0 \tag{15.4.12}$$

Solving for $[\mathbf{A^*}]$,

$$\left[\mathrm{A}^*\right] = \frac{k_1\left[\mathrm{M}\right]\left[\mathrm{A}\right]}{k_2 + k_{-1}\left[\mathrm{M}\right]} \tag{15.4.13}$$

The reaction rates of species $\mathbf{A}$ and $\mathbf{B}$ can be written as

$$-\frac{d\left[\mathrm{A}\right]}{dt} = \frac{d\left[\mathrm{B}\right]}{dt} = k_2\left[\mathrm{A}^*\right] = \frac{k_1 k_2\left[\mathrm{M}\right]\left[\mathrm{A}\right]}{k_2 + k_{-1}\left[\mathrm{M}\right]} = k_{\mathrm{obs}}\left[\mathrm{A}\right] \tag{15.4.14}$$

where

$$k_{\mathrm{obs}} = \frac{k_1 k_2\left[\mathrm{M}\right]}{k_2 + k_{-1}\left[\mathrm{M}\right]} \tag{15.4.15}$$

At high pressures, we can expect collisions to occur frequently, such that $k_{-1}\left[\mathrm{M}\right] \gg k_2$. Equation 15.4.14 then becomes

$$-\frac{d\left[\mathrm{A}\right]}{dt} = \frac{k_1 k_2}{k_{-1}}\left[\mathrm{A}\right] \tag{15.4.16}$$

which follows 1^{st} order rate kinetics.

At low pressures, we can expect collisions to occurs infrequently, such that $k_{-1}\left[\mathrm{M}\right] \ll k_2$. In this scenario, Equation 15.4.14 becomes

$$-\frac{d\left[\mathrm{A}\right]}{dt} = k_1\left[\mathrm{A}\right]\left[\mathrm{M}\right] \tag{15.4.17}$$

which follows second order rate kinetics, consistent with experimental observations.

15.4.3: References

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15.5: Some Reaction Mechanisms Involve Chain Reactions

A large number of reactions proceed through a series of steps that can collectively be classified as a **chain reaction**. The reactions contain steps that can be classified as

- **initiation step** – a step that creates the intermediates from stable species
- **propagation step** – a step that consumes an intermediate, but creates a new one
- **termination step** – a step that consumes intermediates without creating new ones

These types of reactions are very common when the intermediates involved are radicals. An example, is the reaction

$$H_2 + Br_2 \rightarrow 2HBr$$

The observed rate law for this reaction is

$$\text{rate} = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]} \tag{15.5.1}$$

A proposed mechanism is

$$Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Br^{\cdot} \tag{15.5.2}$$

$$2Br^{\cdot} + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HBr + H^{\cdot} \tag{15.5.3}$$

$$H^{\cdot} + Br_2 \xrightarrow{k_3} HBr + Br^{\cdot} \tag{15.5.4}$$

Based on this mechanism, the rate of change of concentrations for the intermediates ($H^{\cdot}$ and $Br^{\cdot}$) can be written, and the steady state approximation applied.

$$\frac{d[H^{\cdot}]}{dt} = k_2[Br^{\cdot}][H_2] - k_{-2}[HBr][H^{\cdot}] - k_3[H^{\cdot}][Br_2] = 0$$

$$\frac{d[Br^{\cdot}]}{dt} = 2k_1[Br_2] - 2k_{-1}[Br^{\cdot}]^2 - k_2[Br^{\cdot}][H_2] + k_{-2}[HBr][H^{\cdot}] + k_3[H^{\cdot}][Br_2] = 0$$

Adding these two expressions cancels the terms involving k_2, k_{-2}, and k_3. The result is

$$2k_1[Br_2] - 2k_{-1}[Br^{\cdot}]^2 = 0$$

Solving for $Br^{\cdot}$

$$Br^{\cdot} = \sqrt{\frac{k_1[Br_2]}{k_{-1}}}$$

This can be substituted into an expression for the $H^{\cdot}$ that is generated by solving the steady state expression for $d[H^{\cdot}]/dt$.

$$[H^{\cdot}] = \frac{k_2[Br^{\cdot}][H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

so

$$[H^{\cdot}] = \frac{k_2\sqrt{\frac{k_1[Br_2]}{k_{-1}}}[H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

Now, armed with expressions for $H^{\cdot}$ and $Br^{\cdot}$, we can substitute them into an expression for the rate of production of the product HBr:

$$\frac{d[HBr]}{dt} = k_2[Br^{\cdot}][H_2] + k_3[H^{\cdot}][Br_2] - k_{-2}[H^{\cdot}][HBr]$$

After substitution and simplification, the result is

$$\frac{d[HBr]}{dt} = \frac{2k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{1/2}}{1+\frac{k_{-1}}{k_3}\frac{[HBr]}{[Br_2]}}$$

Multiplying the top and bottom expressions on the right by $[Br_2]$ produces

$$\frac{d[HBr]}{dt} = \frac{2k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{3/2}}{[Br_2]+\frac{k_{-1}}{k_3}[HBr]}$$

which matches the form of the rate law found experimentally (Equation 15.5.1)! In this case,

$$k = 2k_2\sqrt{\frac{k_1}{k_{-1}}}$$

and

$$k' = \frac{k_{-2}}{k_3}$$

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15.6: A Catalyst Affects the Mechanism and Activation Energy

As can be seen from the Arrhenius equation, the magnitude of the activation energy, E_a, determines the value of the rate constant, k, at a given temperature and thus the overall reaction rate. Catalysts provide a means of reducing E_a and increasing the reaction rate. Catalysts are defined as substances that participate in a chemical reaction but are not changed or consumed. Instead they provide a new mechanism for a reaction to occur which has a lower activation energy than that of the reaction without the catalyst.

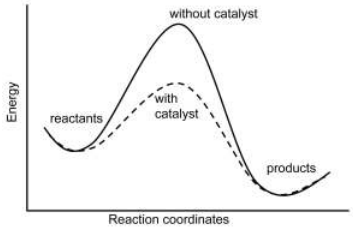


Figure 29.8.1 : Comparison of energy profiles with and without catalyst present.

Homogeneous catalysis refers to reactions in which the catalyst is in solution with at least one of the reactants whereas *heterogeneous catalysis* refers to reactions in which the catalyst is present in a different phase, usually as a solid, than the reactants. Figure 29.8.1 shows a comparison of energy profiles of a reaction in the absence and presence of a catalyst.

Consider a non-catalyzed elementary reaction

$$\mathrm{A} \xrightarrow{k} \mathrm{P}$$

which proceeds at rate k at a certain temperature. The reaction rate can be expressed as

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}]$$

In the presence of a catalyst C, we can write the reaction as

$$\mathrm{A} + \mathrm{C} \xrightarrow{k_{cat}} \mathrm{P} + \mathrm{C}$$

and the reaction rate as

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}] - k_{cat}[\mathrm{A}][\mathrm{C}]$$

where the first term represents the uncatalyzed reaction and the second term represents the catalyzed reaction. Because the reaction rate of the catalyzed reaction is often magnitudes larger than that of the uncatalyzed reaction (i.e. $k_{cat} \gg k$), the first term can often be ignored.

15.6.1: Example of Homogenous Catalysis: Acid Catalysis

A common example of homogeneous catalysts are acids and bases. For example, given an overall reaction is $\mathrm{S} \rightarrow \mathrm{P}$. If k is the rate, then

$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{S}]$$

The purpose of an enzyme is to enhance the rate of production of the product P. The equations of the acid-catalyzed reaction are

$$\mathrm{S} + \mathrm{A}H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{S}H^+ + \mathrm{A}^- \tag{15.6.1}$$

$$\mathrm{S}H^+ + H_2O \xrightarrow{k_2} \mathrm{P} + H_3O^+ \tag{15.6.2}$$

$$H_3O^+ + \mathrm{A}^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{A}H + H_2O \tag{15.6.3}$$

The full set of kinetic equations is

$$\frac{d[\mathrm{S}]}{dt} = -k_1[\mathrm{S}][\mathrm{A}H] + k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] \tag{15.6.4}$$

$$\frac{d[\mathrm{A}H]}{dt} = -k_1[\mathrm{S}][\mathrm{A}H] + k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] - k_{-3}[\mathrm{A}H] + k_3[H_3O^+][\mathrm{A}^-] \tag{15.6.5}$$

$$\frac{d[\mathrm{S}H^+]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] - k_2[\mathrm{S}H^+] \tag{15.6.6}$$

$$\frac{d[\mathrm{A}^-]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] - k_2[\mathrm{A}^-][H_3O^+] + k_{-3}[\mathrm{A}H] \tag{15.6.7}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{S}H^+] \tag{15.6.8}$$

$$\frac{d[H_3O^+]}{dt} = -k_2[\mathrm{S}H^+] - k_3[H_3O^+][\mathrm{A}^-] + k_{-3}[\mathrm{A}H] \tag{15.6.9}$$

We cannot easily solve these, as they are nonlinear. However, let us consider two cases $k_2 \gg k_{-1}[\mathrm{A}^-]$ and $k_2 \ll k_{-1}[\mathrm{A}^-]$. In both cases, $\mathrm{S}H^+$ is consumed quickly, and we can apply a steady-state approximation:

$$\frac{d[\mathrm{S}H^+]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[\mathrm{A}^-][\mathrm{S}H^+] - k_2[\mathrm{S}H^+] = 0$$

Rearranging in terms of $\mathrm{S}H^+$ yields

$$[\mathrm{S}H^+] = \frac{k_1[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-] + k_2}$$

and the rate of production of P can be written as

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{S}H^+] = \frac{k_1k_2[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-] + k_2}$$

In the case where $k_2 \gg k_{-1}[\mathrm{A}^-]$, Equation 29.8.17 can be written as

$$\frac{d[\mathrm{P}]}{dt} = k_1[\mathrm{S}][\mathrm{A}H]$$

which is known as a general acid-catalyzed reaction. On the other hand, if $k_2 \ll k_{-1}[\mathrm{A}^-]$, we can use an equilibrium approximation to write the rate of production of P as

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1k_2[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-]} = \frac{k_1k_2}{k_{-1}K}[\mathrm{S}][H^+]$$

where K is the acid dissociation constant:

$$K = \frac{[\mathrm{A}^-][H^+]}{[\mathrm{A}H]}$$

In this case, the reaction is hydrogen ion-catalyzed.

15.6.2: Example of Heterogeneous Catalysis: Surface Catalysis of Gas-Phase Reactions

Many gas-phase reactions are catalyzed on a solid surface. For a first-order, unimolecular reaction, the reaction mechanism can be written as

$$\mathrm{A}(g) + \mathrm{S}(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}(s)$$

$$\mathrm{AS}(s) \xrightarrow{k_2} \mathrm{P}(g) + \mathrm{S}(g)$$

where the first step is reversible adsorption of the gas molecule, A, onto active sites on the catalyst surface, S, to form a transition state, AS, and the second step is the conversion of adsorbed A molecules to species P. Applying the steady-state approximation to species AS, we can write

$$\frac{d[\mathrm{AS}]}{dt} = k_1[\mathrm{A}][\mathrm{S}] - k_{-1}[\mathrm{AS}]_{ss} - k_2[\mathrm{AS}]_{ss} = 0$$

Because the concentration of total active sites on the catalyst surface is fixed at $[\mathrm{S}]_0$, the concentration of adsorbed species on the catalyst surface, $[\mathrm{AS}]$ can be written as

$$[\mathrm{AS}] = \theta\,[\mathrm{S}]_0$$

and $[\mathrm{S}]$ can be written as

$$[\mathrm{S}] = (1-\theta)\,[\mathrm{S}]_0$$

where θ is the fractional surface coverage of species A on the catalyst surface. We can now write Equation 29.8.23 as

$$k_1\,[\mathrm{A}]\,(1-\theta)\,[\mathrm{S}]_0 - (k_{-1}+k_2)\,\theta\,[\mathrm{S}]_0 = 0$$

Rearranging the above equation in terms of θ yields

$$\theta = \frac{k_1\,[\mathrm{A}]}{k_1\,[\mathrm{A}] + k_{-1} + k_2}$$

The rate of production of P can be written as

$$\frac{d\,[\mathrm{P}]}{dt} = k_2\,[\mathrm{AS}]_{ss} = k_2\theta\,[\mathrm{S}]_0 = \frac{k_1 k_2}{k_1\,[\mathrm{A}] + k_{-1} + k_2}\,[\mathrm{A}]\,[\mathrm{S}]_0$$

From the above equation, we can observe the importance of having high surface areas for catalytic reactions.

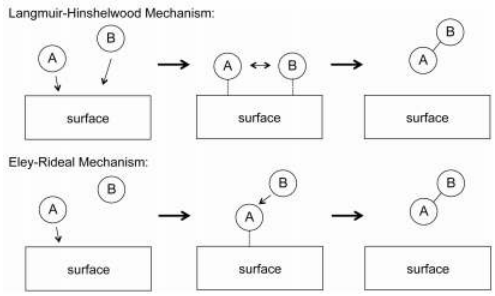


Figure 29.8.2 : Illustrations of the Langmuir-Hinshelwood and Eley-Rideal mechanisms for heterogeneous catalysis of bimolecular gas-phase reactions.

For bimolecular gas-phase reactions, two generally-used mechanisms to explain reactions kinetics are the Langmuir-Hinshelwood and Eley-Rideal mechanisms, shown in Figure 29.8.2 . In the Langmuir-Hinshelwood mechanism, A and B both adsorb onto the catalyst surface, at which they react to form a product. The reaction mechanism is

$$\mathrm{A}\,(g) + \mathrm{S}\,(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}\,(s)$$

$$\mathrm{B}\,(g) + \mathrm{S}\,(s) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{BS}\,(s)$$

$$\mathrm{AS}\,(s) + \mathrm{BS}\,(s) \xrightarrow{k_3} \mathrm{P}$$

The rate law for the Langmuir-Hinshelwood mechanism can be derived in a similar manner to that for unimolecular catalytic reactions by assuming that the total number of active sites on the catalyst surface is fixed. In the Eley-Rideal mechanism, only one species adsorbs onto the catalyst surface. An example of such a reaction is the partial oxidation of ethylene into ethylene oxide, as shown in Figure 29.8.3 . In this reaction, diatomic oxygen adsorbs onto the catalytic surface where it reacts with ethylene molecules in the gas phase.

The reactions for the Eley-Rideal mechanism can be written as

$$\mathrm{A}\,(g) + \mathrm{S}\,(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}\,(s)$$

$$\mathrm{AS}\,(s) + \mathrm{B}\,(g) \xrightarrow{k_2} \mathrm{P}\,(g) + \mathrm{S}\,(s)$$

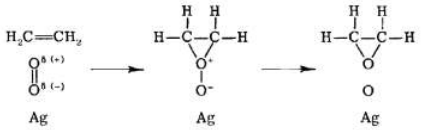


Figure 29.8.3 : Illustrations of the reaction mechanism for the partial oxidation of ethylene to ethylene oxide. [Reproduced from Kilty, PA and WMH Sacthler. Catal. Rev., 10, 1]

Assuming that $k_{-1} \gg k_1$, we can apply a steady-state approximation to species **AS**:

$$\frac{d[\mathrm{AS}]}{dt} = 0 = k_1[\mathrm{A}][\mathrm{S}] - k_{-1}[\mathrm{AS}]_{ss} - k_2[\mathrm{AS}]_{ss}[\mathrm{B}]$$

As in the case of unimolecular catalyzed reactions, we can express the concentrations of **AS** and **S** in terms of a fraction of the total number of active sites, $\mathbf{S_0}$ and rewrite the above equation as

$$0 = k_1[\mathrm{A}](1-\theta)[\mathrm{S}]_0 - k_{-1}[\mathrm{S}]_0 - k_2\theta[\mathrm{S}]_0[\mathrm{B}]$$

Solving for θ yields

$$\theta = \frac{k_1[\mathrm{A}]}{k_1[\mathrm{A}] + k_{-1} + k_2[\mathrm{B}]}$$

Furthermore, if $k_2 \ll k_1$ and k_{-1}, we can simplify θ to

$$\theta = \frac{k_1[\mathrm{A}]}{k_1[\mathrm{A}] + k_{-1}}$$

The rate of production of **P** can be expressed as

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{AS}]_{ss}[\mathrm{B}] = k_2\theta[\mathrm{S}]_0[\mathrm{B}] = \frac{k_1k_2[\mathrm{A}]}{k_1[\mathrm{A}] + k_{-1}}[\mathrm{S}]_0[\mathrm{B}]$$

We can also write the above expression in terms of the equilibrium constant, K, which is equal to k_1/k_{-1}

$$\frac{d[\mathrm{P}]}{dt} = Kk_2[\mathrm{B}]\frac{K[\mathrm{A}]}{K[\mathrm{A}] + 1}$$

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15.7: The Michaelis-Menten Mechanism for Enzyme Catalysis

Enzymes are biological catalysts and functional proteins. Enzymes contain specificity in its protein structure in order to have its specialized function. It usually contains more than one subunit and they are critical to sustain life. Enzymes can increase the chemical reactions in living cells. However, enzymes are not consumed in the reaction and their main function is to assist in bringing the substrates together so they can undergo normal reaction faster.

The first enzyme was found in the process of fermentation in milk and alcohol during the nineteenth century. Later in the early 1830s, the term enzyme was used to replace the term ferment. Some scientists believe that ferments must contain living cells and some think ferments could be non-living cells. Finally, in the 1920s, Sumner purified the structure of enzyme and then properties of enzyme then was more clearly understood. Until today, enzymes are still the popular research field that many people are subject to study.

15.7.1: Michaelis-Menten Kinetics

In biological systems, enzymes act as catalysts and play a critical role in accelerating reactions, anywhere from 10^3 to 10^{17} times faster than the reaction would normally proceed. Enzymes are high-molecular weight proteins that act on a substrate, or reactant molecule, to form one or more products. In 1913, Leonor Michaelis and Maude Menten proposed the following reaction mechanism for enzymatic reactions:

$$\mathbf{E} + \mathbf{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{ES} \xrightarrow{k_2} \mathbf{E} + \mathbf{P}$$

where $\mathbf{E}$ is the enzyme, $\mathbf{ES}$ is the enzyme-substrate complex, and $\mathbf{P}$ is the product. In the first step, the substrate binds to the active site of the enzyme. In the second step, the substrate is converted into the product and released from the substrate. For this mechanism, we can assume that the concentration of the enzyme-substrate complex, $\mathbf{ES}$, is small and employ a steady-state approximation:

$$\frac{d[\mathrm{ES}]}{dt} = k_1[\mathrm{E}][\mathrm{S}] - k_{-1}[\mathrm{ES}]_{ss} - k_2[\mathrm{ES}]_{ss} \approx 0 \tag{15.7.1}$$

Furthermore, because the enzyme is unchanged throughout the reaction, we express the total enzyme concentration as a sum of enzyme and enzyme-substrate complex:

$$[\mathrm{E}]_0 = [\mathrm{ES}] + [\mathrm{E}] \tag{15.7.2}$$

Plugging Equation 15.7.2 into Equation 15.7.1, we obtain

$$0 = k_1([\mathrm{E}]_0 - [\mathrm{ES}]_{ss})[\mathrm{S}] - k_{-1}[\mathrm{ES}]_{ss} + k_2[\mathrm{ES}]_{ss} \tag{15.7.3}$$

Solving for $[\mathrm{ES}]_{ss}$

$$[\mathrm{ES}]_{ss} = \frac{k_1[\mathrm{E}]_0[\mathrm{S}]}{k_1[\mathrm{S}] + k_{-1} + k_2} = \frac{[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + \frac{k_{-1} + k_2}{k_1}} \tag{15.7.4}$$

We can then write the reaction rate of the product as

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}]_{ss} = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + \frac{k_{-1} + k_2}{k_1}} = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + K_M} \tag{15.7.5}$$

where K_M is the Michaelis constant. Equation 15.7.5 is known as the Michaelis-Menten equation. The result for Michaelis-Menten kinetics equivalent to that for a unimolecular gas phase reaction catalyzed on a solid surface. In the limit where there is a large amount of substrate present ($[\mathrm{S}] \gg K_M$) Equation 15.7.5 reduces to

$$\frac{d[\mathrm{P}]}{dt} = r_{\max} = k_2[\mathrm{E}]_0 \tag{15.7.6}$$

which is a 0^{th} order reaction, since $[E]_0$ is a constant. The value $k_2 [E]_0$ represents the maximum rate, r_{max}, at which the enzymatic reaction can proceed. The rate constant, k_2, is also known as the *turnover number*, which is the number of substrate molecules converted to product in a given time when all the active sites on the enzyme are occupied. Figure 29.9.4 displays the dependence of the reaction rate on the substrate concentration, $[S]$. This plot is known as the Michaelis-Menten plot. Examining the figure, we can see that the reaction rate reaches a maximum value of $k_2 [E]_0$ at large values of $[S]$.

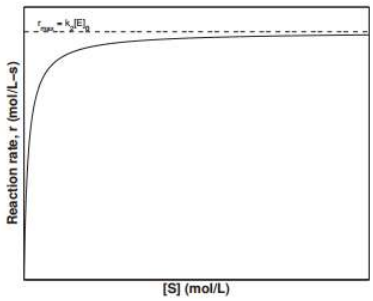


Figure 29.9.4 : Rate dependence on substrate concentration for an enzymatic reaction.

Another commonly-used plot in examining enzyme kinetics is the **Lineweaver-Burk plot**, in with the inverse of the reaction rate, $1/r$, is plotted against the inverse of the substrate concentration $1/[S]$. Rearranging Equation 15.7.5,

$$\frac{1}{r} = \frac{K_M + [S]}{k_2 [E]_0 [S]} = \frac{K_M}{k_2 [E]_0} \frac{1}{[S]} + \frac{1}{k_2 [E]_0} \tag{15.7.7}$$

The Lineweaver-Burk plot results in a straight line with the slope equal to $K_M / k_2 [E]_0$ and y-intercept equal to $1/k_2 [E]_0$.

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CHAPTER OVERVIEW

16: Math Chapters

16.1: Probability and Statistics
16.2: Spherical Coordinates
16.3: Partial Differentiation

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16.1: Probability and Statistics

A random variable X can have more than one value x as an outcome. Which value the variable has in a particular case is a matter of *chance* and cannot be predicted other than that we associate a probability to the outcome. **Probability** p is a number between 0 and 1 that indicates the likelihood that the variable X has a particular outcome x. The set of outcomes and their probabilities form a ***probability distribution***. There are two kinds of distributions:

1. discrete ones
2. continuous ones

Total probability should always add up to unity.

16.1.1: Discrete Distributions

A good example of a discrete distribution is a *true coin*. The random variable X can have two values:

1. heads (0)
2. tails (1)

Both have equal probability and as the sum must equal unity, the probability must be ½ for each. 'The probability that X=heads' is written formally as:

$$Pr(X = heads) = Pr(X = 0) = 0.5$$

The random function is written as a combination of three statements.

- Pr(X=0) = ½
- Pr(X=1) = ½
- elsewhere Pr = 0

16.1.2: Continuous Distributions

Now consider a spherical die. One could say it has an infinite number of facets that it can land on. Thus the number of outcomes $n = \infty$, this make each probability

$$p = 1/\infty = 0.$$

This creates a bit of a mathematical problem, because how can we get a total probability of unity by adding up zeros? Also, if we divide the sphere in a northern and a southern hemisphere clearly the probability that it lands on a point in say, the north should be ½. Still, p = 0 for all points. We introduce a new concept: **probability density** over which we *integrate* rather than *sum*. We assign an equal density to each point of the sphere and make sure that if we integrate over a hemisphere we get ½. (This involves two angles θ and φ and an integration over them and I won't go into that).

A bit simpler example of a continuous distribution than the spherical die is the 1D ***uniform*** distribution. It is the one that the Excel function =RAND() produces to good approximation. Its probability density is defined as

- f(x) = 1 for 0<1>
- f(x) = 0 elsewhere

The figure shows a (bivariate) uniform distribution.

The probability that the outcome is smaller than 0.5 is written as Pr(X<0.5) and is found by integrating from 0 to 0.5 over f(x).

$$\Pr(X<0.5) = \int \mathbf{f(x)}.dx \text{ from 0 to } 0.5 = \int \mathbf{1}.dx \text{ from 0 to } 0.5 = [x]^{0.5}\text{-}[x]_0 = 0.5$$

Notice that in each individual outcome b the probability is indeed zero because an integral from b to b is always zero, even if the probability density f(b) is not zero. Clearly the probability and the probability density are not the same. Unfortunately the distinction between probability and probability density is often not properly made in the physical sciences. Moments can also be computed for continuous distributions by integrating over the probability density

Another well-known continuous distribution is the ***normal*** (or ***Gaussian***) distribution, defined as:

\[f(x) = 1/[\sqrt{(2\pi)}\sigma] * \exp(-½[(x-\mu)/\sigma]^2) \nonumber \]

(Notice the normalization factor $1/[\sqrt{(2\pi)}\sigma]$)

We can also compute moments of continuous distribution. Instead of using a summation we now have to evaluate an integral:

$$\langle X \rangle = \int [f(x)^* x] dx$$

$$\langle X^2 \rangle = \int [f(x)^* x^2] dx$$

For the normal distribution $\langle X \rangle = \mu$

? Exercise

Compute ^{2}> and ^{3}> for the uniform distribution. answer>

16.1.3: Indistinguishable Outcomes

When flipping two coins we could get four outcomes: two heads (0), heads plus tails (1), tails plus heads (1), two tails (2)

Each outcome is equally likely, this implies a probability of ¼ for each:

X_{tot} = X1 + X2 = 0 + 0 = 0 p=¼
X_{tot} = X1 + X2 = 0 + 1 = 1 p=¼
X_{tot} = X1 + X2 = 1 + 0 = 1 p=¼
X_{tot} = X1 + X2 = 1 + 1 = 2 p=¼

The probability of a particular outcome is often abbreviated simply to p. The two middle outcomes collapse into one with p=¼+¼= ½ if the coins are **indistinguishable**. We will see that this concept has very important consequences in statistical thermodynamics.

If we cannot distinguish the two outcomes leading to X_{tot}=1 we get the following random function:

- Pr(X_{tot}=0) = ¼
- Pr(X_{tot}=1) = ½
- Pr(X_{tot}=2) = ¼
- elsewhere Pr = 0

Notice that it is quite possible to have a distribution where the probabilities differ from outcome to outcome. Often the p values are given as f(x), a function of x. An example:

X3 defined as:

- f(x) = (x+1)/6 for x=0,1,2;
- f(x) =0 elsewhere;

The factor 1/6 makes sure the probabilities add up to unity. Such a factor is known as a **normalization factor**. Again this concept is of prime importance in statistical thermodynamics.

Another example of a discrete distribution is a die. If it has 6 sides (the most common die) there are six outcomes, each with p= 1/6. There are also dice with n=4, 12 or 20 sides. Each outcome will then have p= 1/n.

16.1.4: Moments of Distributions

In important aspect of probability distributions are the **moments** of the distribution. They are values computed by summing over the whole distribution.

The **zero** order moment is simply the sum of all p and that is unity:

$^0> = \Sigma X^0 * p = \Sigma 1 * p = 1$

The **first** moment multiplies each outcome with its probability and sums over all outcomes:

$= \Sigma X * p$

This moment is known as the ***average*** or ***mean***. (It is what we have done to your grades for years...)

For one coin is ½, for two coins is 1. (Exercise: verify this)

The **second** moment is computed by summing the product of the square of X and p:

$^2> = \Sigma X^2 * p$

For one coin we have $^2> = ½$,
For two coins $^2> = [0*¼ + 1*½ + 4*¼] = 1.5$

What is $^2>$ for X3? answer

The notation is used a lot in quantum mechanics, often in the form <ψ*ψ> or <ψ*|h|ψ>. The <.. part is known as the ***bra***, the ..> part as the ***ket***. (Together ***bra***(c)***ket***)

Intermezzo: The strange employer

You have a summer job but your employer likes games of chance. At the end of every day he rolls a die and pays you the square of the outcome in dollars per hour. So on a lucky day you'd make $36.- per hour, but on a bad day $1.-. Is this a bad deal? What would you make on the average over a longer period?

To answer this we must compute the second moment $^2>$ of the distribution:

$^2> = 1/6 * [1+4+9+16+25+36] = 91/6 = \$15.17$ per hour.

(I have taken p=1/6 out of brackets because the value is the same for all six outcomes)

As you see in the intermezzo, the value of the second moment is in this case what you ***expect*** to be making on the long term. Moments are examples of what is know as **expectation values**. Another term you may run into that of a **functional**. A functional is a *number* computed by some operation (such as summation or integration) over a whole function. Moments are clearly an example of that too.

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Index

A

absolute entropy
8.3: Absolute Entropy
activity
12.1: Reaction Quotient and Equilibrium Constant
activity coefficient
11.7: Activities of Nonideal Solutions
Anharmonicity
1.8: The Harmonic Oscillator Approximates Molecular Vibrations
Arrhenius equation
14.4: Arrhenius Equation

B

Boltzman Distribution
5.2: The Boltzmann Distribution represents a Thermally Equilibrated Distribution
Boltzmann Factor
5.1: The Boltzmann Factor is used to Approximate the Fraction of Particles in a Large System

C

Carnot cycle
7.7: Thermodynamics Provides Insight into the Conversion of Heat into Work
catalyst
15.6: A Catalyst Affects the Mechanism and Activation Energy
chain reaction
15.5: Some Reaction Mechanisms Involve Chain Reactions
Clapeyron equation
10.3: The Chemical Potentials of a Pure Substance in Two Phases in Equilibrium
collision energy
13.3: Mean Free Path
collision frequency
13.4: Rates of Gas-Phase Chemical Reactions
collisional cross section
13.3: Mean Free Path
critical opalescence
10.1: A Phase Diagram Summarizes the Solid-Liquid-Gas Behavior of a Substance

D

de Broglie thermal wavelength
5.6: Translational Partition Functions of Monotonic Gases
degeneracy
5.10: Most Molecules are Rotationally Excited at Ordinary Temperatures
Diatomic Vibration
1.9: The Harmonic Oscillator and Infrared Spectra
diffusion equation
13.3: Mean Free Path

E

Einstein Solid Model
5.4: Heat Capacity at Constant Volume is the Change in Internal Energy with Temperature
Einstein temperature
5.4: Heat Capacity at Constant Volume is the Change in Internal Energy with Temperature
elementary reaction
15.1: A Mechanism is a Sequence of Elementary Reactions
equilibrium constant
12.1: Reaction Quotient and Equilibrium Constant
12.3: The Equilibrium Constant
exact differential
6.4: State Functions and Exact Differentials
16.3: Partial Differentiation
expansion coefficient
6.4: State Functions and Exact Differentials
Eyring equation
14.5: Eyring equation

H

Harmonic oscillator
1.8: The Harmonic Oscillator Approximates Molecular Vibrations
1.9: The Harmonic Oscillator and Infrared Spectra
heat pump
7.7: Thermodynamics Provides Insight into the Conversion of Heat into Work
Helmholtz function
9.1: Helmholtz Energy

I

inexact differential
6.4: State Functions and Exact Differentials
16.3: Partial Differentiation
infrared spectroscopy
1.9: The Harmonic Oscillator and Infrared Spectra
internal pressure
6.4: State Functions and Exact Differentials
IR spectra
1.9: The Harmonic Oscillator and Infrared Spectra
isolated system
7.2: The Second Law of Thermodynamics

K

Koopmans' Theorem
3.7: Photoelectron Spectroscopy

L

Lindemann mechanism
15.4: The Lindemann Mechanism

M

Margules Functions
11.6: Vapor Pressures of Volatile Binary Solutions
Maxwell relations
9.3: The Maxwell Relations
mean free path
13.3: Mean Free Path
Morse potential
1.8: The Harmonic Oscillator Approximates Molecular Vibrations
1.9: The Harmonic Oscillator and Infrared Spectra

N

natural variable
9.1: Helmholtz Energy

P

Particle in a box
1.6: Particle in a One-Dimensional Box
Partition Function (Rotational)
5.11: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number
photoelectron spectroscopy
3.7: Photoelectron Spectroscopy
principle of corresponding states
4.4: The Law of Corresponding States
probability
16.1: Probability and Statistics
probability density
16.1: Probability and Statistics
probability distribution
16.1: Probability and Statistics

R

reaction mechanism
15.1: A Mechanism is a Sequence of Elementary Reactions
reaction quotient
12.1: Reaction Quotient and Equilibrium Constant
reducing agent
1.9: The Harmonic Oscillator and Infrared Spectra

S

Selection rules
1.9: The Harmonic Oscillator and Infrared Spectra
Spherical Coordinates
16.2: Spherical Coordinates
steady state approximation
15.2: The Steady-State Approximation
symmetry number
5.11: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number

T

The Isothermal Compressibility
6.4: State Functions and Exact Differentials
Thermochemical Cycles
8.4: Evaluating Entropy Changes Using Thermochemical Cycles
thermodynamic stability
10.1: A Phase Diagram Summarizes the Solid-Liquid-Gas Behavior of a Substance
Third Law of Thermodynamics
8.2: The Third Law
Total Differentials
16.3: Partial Differentiation
translational partition function
5.6: Translational Partition Functions of Monotonic Gases

U

Ultraviolet Photoelectron Spectroscopy (UPS)
3.7: Photoelectron Spectroscopy

V

van der Waals equation

4.3: van der Waals and Redlich-Kwong Equations of State

van’t Hoff equation

12.7: The van 't Hoff Equation

van’t Hoff plot

12.7: The van 't Hoff Equation

vertical ionization energy

3.7: Photoelectron Spectroscopy

vibrational temperature

5.9: Most Molecules are in the Ground Vibrational State

Glossary

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- CHM 363: Physical Chemistry 1 (Grinnell College) - *Undeclared*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
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    - 2.1: The Schrödinger Wave Equation for the Hydrogen Atom - *Undeclared*
    - 2.2: Many-Electron Atoms and the Periodic Table - *Undeclared*
    - 2.3: Quantum-Mechanical Tunneling - *Undeclared*
  - 3: Chemical Bond - *Undeclared*
    - 3.1: Lewis Structures - *Undeclared*
    - 3.2: Valence Bond Theory - *Undeclared*
    - 3.3: Hybridization of Atomic Orbitals - *Undeclared*
    - 3.4: Molecular Orbital Theory - *Undeclared*
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    - 4.1: The Perfect Gas - *Undeclared*
    - 4.2: Real Gases (Deviations From Ideal Behavior) - *Undeclared*
    - 4.3: van der Waals and Redlich-Kwong Equations of State - *Undeclared*
    - 4.4: The Law of Corresponding States - *Undeclared*
    - 4.5: The Repulsive Term in the Lennard-Jones Potential - *CC BY 4.0*
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    - 5.6: Translational Partition Functions of Monotonic Gases - *Undeclared*
    - 5.7: Most Atoms are in the Ground Electronic State - *Undeclared*

- 5.8: The Energy of a Diatomic/Polyatomic Molecule Can Be Approximated as a Sum of Separate Terms - *Undeclared*
- 5.9: Most Molecules are in the Ground Vibrational State - *Undeclared*
- 5.10: Most Molecules are Rotationally Excited at Ordinary Temperatures - *Undeclared*
- 5.11: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number - *CC BY-NC-SA 4.0*

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  - 6.1: Internal Energy - *Undeclared*
  - 6.2: Enthalpy - *Undeclared*
  - 6.3: Thermochemistry - *Undeclared*
  - 6.4: State Functions and Exact Differentials - *Undeclared*
  - 6.5: Adiabatic Changes - *Undeclared*
- 7: Entropy and The Second Law of Thermodynamics - *Undeclared*
  - 7.1: Energy Does not Determine Spontaneity - *Undeclared*
  - 7.2: The Second Law of Thermodynamics - *Undeclared*
  - 7.3: We Must Always Devise a Reversible Process to Calculate Entropy Changes - *Undeclared*
  - 7.4: The Famous Equation of Statistical Thermodynamics is S=k ln W - *Undeclared*
  - 7.5: Entropy Can Be Expressed in Terms of a Partition Function - *Undeclared*
  - 7.6: The Statistical Definition of Entropy is Analogous to the Thermodynamic Definition - *Undeclared*
  - 7.7: Thermodynamics Provides Insight into the Conversion of Heat into Work - *Undeclared*
- 8: The Third Law, Absolute Entropy, and the Gibbs Free Energy of Formation - *CC BY-SA 4.0*
  - 8.1: Heat Capacity as a Function of Temperature - *CC BY-SA 4.0*
  - 8.2: The Third Law - *CC BY-SA 4.0*
  - 8.3: Absolute Entropy - *CC BY-SA 4.0*
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  - 9.1: Helmholtz Energy - *Undeclared*
  - 9.2: Gibbs Energy Determines the Direction of Spontaneity at Constant Pressure and Temperature - *Undeclared*
  - 9.3: The Maxwell Relations - *Undeclared*
  - 9.4: Thermodynamic Functions have Natural Variables - *Undeclared*
  - 9.5: The Enthalpy of an Ideal Gas is Independent of Pressure - *Undeclared*
  - 9.6: The Gibbs-Helmholtz Equation - *CC BY-NC-SA 4.0*
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  - 10.1: A Phase Diagram Summarizes the Solid-Liquid-Gas Behavior of a Substance - *Undeclared*
  - 10.2: Gibbs Energies and Phase Diagrams - *Undeclared*
  - 10.3: The Chemical Potentials of a Pure Substance in Two Phases in Equilibrium - *Undeclared*
  - 10.4: The Clausius-Clapeyron Equation - *CC BY 4.0*
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  - 11.1: A Mixture is a Combination of Two or More Substances - *Undeclared*
  - 11.2: The Gibbs-Duhem Equation Relates Chemical Potential and Composition at Equilibrium - *Undeclared*
  - 11.3: Chemical Potential of Each Component Has the Same Value in Each Phase in Which the Component Appears - *Undeclared*
  - 11.4: Ideal Solutions obey Raoult's Law - *CC BY-NC-SA 4.0*
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  - 12.1: Reaction Quotient and Equilibrium Constant - *CC BY-SA 4.0*
  - 12.2: Equilibrium Results when Gibbs Energy is Minimized - *Undeclared*
  - 12.3: The Equilibrium Constant - *Undeclared*
  - 12.4: An Equilibrium Constant is a Function of Temperature Only - *Undeclared*
  - 12.5: Reaction Quotient and Equilibrium Constant Ratio Determines Reaction Direction - *CC BY 4.0*
  - 12.6: The Sign of ΔG and not ΔG° Determines the Direction of Reaction Spontaneity - *Undeclared*
  - 12.7: The van 't Hoff Equation - *Undeclared*
  - 12.8: Equilibrium Constants in Terms of Partition Functions - *CC BY-SA 4.0*
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  - 14.2: First-Order Reactions Show an Exponential Decay of Reactant Concentration with Time - *Undeclared*
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  - 15.6: A Catalyst Affects the Mechanism and Activation Energy - *Undeclared*
  - 15.7: The Michaelis-Menten Mechanism for Enzyme Catalysis - *Undeclared*
- 16: Math Chapters - *Undeclared*
  - 16.1: Probability and Statistics - *Undeclared*
  - 16.2: Spherical Coordinates - *Undeclared*
  - 16.3: Partial Differentiation - *Undeclared*
- Back Matter - *Undeclared*
  - Index - *Undeclared*
  - Glossary - *Undeclared*
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    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
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    - 2.1: The Schrödinger Wave Equation for the Hydrogen Atom - *Undeclared*
    - 2.2: Many-Electron Atoms and the Periodic Table - *Undeclared*
    - 2.3: Quantum-Mechanical Tunneling - *Undeclared*
  - 3: Chemical Bond - *Undeclared*
    - 3.1: Lewis Structures - *Undeclared*
    - 3.2: Valence Bond Theory - *Undeclared*
    - 3.3: Hybridization of Atomic Orbitals - *Undeclared*
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    - 4.1: The Perfect Gas - *Undeclared*
    - 4.2: Real Gases (Deviations From Ideal Behavior) - *Undeclared*
    - 4.3: van der Waals and Redlich-Kwong Equations of State - *Undeclared*
    - 4.4: The Law of Corresponding States - *Undeclared*
    - 4.5: The Repulsive Term in the Lennard-Jones Potential - *CC BY 4.0*
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- 5.9: Most Molecules are in the Ground Vibrational State - *Undeclared*
- 5.10: Most Molecules are Rotationally Excited at Ordinary Temperatures - *Undeclared*
- 5.11: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number - *CC BY-NC-SA 4.0*

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  - 6.1: Internal Energy - *Undeclared*
  - 6.2: Enthalpy - *Undeclared*
  - 6.3: Thermochemistry - *Undeclared*
  - 6.4: State Functions and Exact Differentials - *Undeclared*
  - 6.5: Adiabatic Changes - *Undeclared*
- 7: Entropy and The Second Law of Thermodynamics - *Undeclared*
  - 7.1: Energy Does not Determine Spontaneity - *Undeclared*
  - 7.2: The Second Law of Thermodynamics - *Undeclared*
  - 7.3: We Must Always Devise a Reversible Process to Calculate Entropy Changes - *Undeclared*
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  - 9.3: The Maxwell Relations - *Undeclared*
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- 13.2: The Distribution of Molecular Speeds is Given by the Maxwell-Boltzmann Distribution - *Undeclared*
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14: Chemical Kinetics I - Rate Laws - *Undeclared*

- 14.1: The Time Dependence of a Chemical Reaction is Described by a Rate Law - *Undeclared*
- 14.2: First-Order Reactions Show an Exponential Decay of Reactant Concentration with Time - *Undeclared*
- 14.3: Different Rate Laws Predict Different Kinetics - *Undeclared*
- 14.4: Arrhenius Equation - *CC BY 4.0*
- 14.5: Eyring equation - *Undeclared*

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- 15.1: A Mechanism is a Sequence of Elementary Reactions - *Undeclared*
- 15.2: The Steady-State Approximation - *CC BY-NC-SA 4.0*
- 15.3: Rate Laws Do Not Imply Unique Mechanism - *Undeclared*
- 15.4: The Lindemann Mechanism - *Undeclared*
- 15.5: Some Reaction Mechanisms Involve Chain Reactions - *Undeclared*
- 15.6: A Catalyst Affects the Mechanism and Activation Energy - *Undeclared*
- 15.7: The Michaelis-Menten Mechanism for Enzyme Catalysis - *Undeclared*

16: Math Chapters - *Undeclared*

- 16.1: Probability and Statistics - *Undeclared*
- 16.2: Spherical Coordinates - *Undeclared*
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