CHEM 3212



Geoffrey Smith
University of Georgia

LibreTexts™

CHEM 3212 - 2019

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

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

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



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

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

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

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

This text was compiled on 06/07/2025

TABLE OF CONTENTS

Licensing

1: The Properties of Gases

- 1.1: The Empirical Gas Laws
- 1.2: The Ideal Gas Law
- 1.3: The Kinetic Molecular Theory of Gases
- 1.4: Kinetic Energy
- 1.5: Graham's Law of Effusion
- 1.6: Collisions with Other Molecules
- 1.7: Real Gases
- 1.8: Intermolecular Forces
  - 1.8.1: Van der Waals Forces
- 1.9: Specific Interactions
  - 1.9.1: Dipole-Dipole Interactions
  - 1.9.2: Dipole Moment
  - 1.9.3: Dipole moments
  - 1.9.4: Hydrogen Bonding
  - 1.9.5: Ion - Dipole Interactions
  - 1.9.6: Ion - Induced Dipole Interactions
  - 1.9.7: Ion - Ion Interactions
  - 1.9.8: Lennard-Jones Potential
  - 1.9.9: London Dispersion Interactions
  - 1.9.10: Polarizability
- 1.E: Gases (Exercises)
- 1.S: Gases (Summary)

2: The Boltzmann Factor and Partition Functions

- 2.1: The Boltzmann Factor
- 2.2: The Thermal Boltzman Distribution
- 2.3: The Average Ensemble Energy

3: Quantum Review

- 3.1: The Schrödinger Equation and a Particle in a Box
  - 3.1.1: The Schrödinger Equation
  - 3.1.2: Linear Operators in Quantum Mechanics
  - 3.1.3: The Schrödinger Equation is an Eigenvalue Problem
  - 3.1.4: Wavefunctions Have a Probabilistic Interpretation
  - 3.1.5: The Energy of a Particle in a Box is Quantized
  - 3.1.6: Wavefunctions Must Be Normalized
  - 3.1.7: The Average Momentum of a Particle in a Box is Zero
  - 3.1.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions
  - 3.1.9: A Particle in a Three-Dimensional Box
  - 3.1.E: The Schrödinger Equation and a Particle in a Box (Exercises)
- 3.2: The Harmonic Oscillator and the Rigid Rotor
  - 3.2.1: A Harmonic Oscillator Obeys Hooke's Law

- 3.2.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule
- 3.2.3: The Harmonic Oscillator Approximates Vibrations
- 3.2.4: The Harmonic Oscillator Energy Levels
- 3.2.5: The Harmonic Oscillator and Infrared Spectra
- 3.2.6: The Harmonic-Oscillator Wavefunctions involve Hermite Polynomials
- 3.2.7: Hermite Polynomials are either Even or Odd Functions
- 3.2.8: The Energy Levels of a Rigid Rotor
- 3.2.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule
- 3.2.E: The Harmonic Oscillator and the Rigid Rotor (Exercises)

4: Partition Functions of Model Systems

- 4.1: Translational Partition Functions of Monotonic Gases
- 4.2: Most Atoms are in the Ground Electronic State
- 4.3: The Energy of a Diatomic Molecule Can Be Approximated as a Sum of Separate Terms
- 4.4: Most Molecules are in the Ground Vibrational State
- 4.5: Most Molecules are Rotationally Excited at Ordinary Temperatures
- 4.6: Rotational Partition Functions of Diatomic Gases
- 4.7: Vibrational Partition Functions of Polyatomic Molecules
- 4.8: Rotational Partition Functions of Polyatomic Molecules
- 4.9: Molar Heat Capacities
- 4.E: Partition Functions and Ideal Gases (Exercises)
- 4.10: Ortho and Para Hydrogen
- 4.11: The Equipartition Principle
- Symmetry and Group Theory

5: Energy and Enthalpy

- 5.1: First Law of Thermodynamics (Summary)
- 5.2: Prelude to Thermodynamics
- 5.3: Work and Heat
- 5.4: Reversible and Irreversible Pathways
- 5.5: The Joule Experiment
- 5.6: Calorimetry
- 5.7: Reaction Enthalpies
- 5.8: Lattice Energy and the Born-Haber Cycle
- 5.E: First Law of Thermodynamics (Exercises)

6: Entropy, Part I

- 6.1: Introduction to the Second Law
- 6.2: Heat Engines and the Carnot Cycle
- 6.3: Entropy
- 6.4: Calculating Entropy Changes
- 6.5: Comparing the System and the Surroundings
- 6.6: Entropy and Disorder
- 6.7: The Third Law of Thermodynamics
- 6.8: Adiabatic Compressibility
- 6.E: The Second Law (Exercises)
- 6.S: The Second Law (Summary)

7: Entropy, Part II

- 7.1: Calculating Entropy Changes
- 7.2: Trouton's rule
- 7.3: The Third Law of Thermodynamics

8: Gibbs and Helmholtz Energies

- 8.1: Free Energy Functions
- 8.2: Combining the First and Second Laws - Maxwell's Relations
- 8.3: ΔA, ΔG, and Maximum Work
- 8.4: Volume Dependence of Helmholtz Energy
- 8.5: Pressure Dependence of Gibbs Energy
- 8.6: Temperature Dependence of A and G
- 8.7: When Two Variables Change at Once
- 8.8: The Difference between Cp and Cv
- 8.9: Putting the Second Law to Work (Exercises)
- 8.S: Putting the Second Law to Work (Summary)

9: Phase Equilibria

- 9.1: Thermodynamics of Mixing
- 9.2: Partial Molar Volume
- 9.3: Chemical Potential
- 9.4: The Gibbs-Duhem Equation
- 9.5: Non-ideality in Gases - Fugacity
- 9.6: Colligative Properties
- 9.7: Solubility
- 9.8: Non-ideality in Solutions - Activity
- 9.9: Prelude to Phase Equilibrium
- 9.E: Mixtures and Solutions (Exercises)
- 9.E: Phase Equilibrium (Exercises)
- 9.S: Mixtures and Solutions (Summary)
- 9.10: Single Component Phase Diagrams
- 9.11: Criterion for Phase Equilibrium
- 9.12: The Clapeyron Equation
- 9.13: The Clausius-Clapeyron Equation

10: Chemical Equilibrium

- 10.1: Prelude to Chemical Equilibria
- 10.2: Chemical Potential
- 10.3: Activities and Fugacities
- 10.4: Pressure Dependence of Kp - Le Châtelier's Principle
- 10.5: Degree of Dissociation
- 10.6: Temperature Dependence of Equilibrium Constants - the van’t Hoff Equation
- 10.7: The Dumas Bulb Method for Measuring Decomposition Equilibrium
- 10.8: Acid-Base Equilibria
- 10.9: Buffers
- 10.E: Chemical Equilibria (Exercises)
- 10.S: Chemical Equilibria (Summary)

11: Solutions- Liquid-Liquid Solutions

- 11.1: Phase Diagrams for Binary Mixtures
- 11.2: Liquid-Vapor Systems - Raoult’s Law
- 11.3: Non-ideality - Henry's Law and Azeotropes

Math Review

Index

Glossary

Detailed Licensing

Licensing

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

CHAPTER OVERVIEW

1: The Properties of Gases



1.1: The Empirical Gas Laws
1.2: The Ideal Gas Law
1.3: The Kinetic Molecular Theory of Gases
1.4: Kinetic Energy
1.5: Graham's Law of Effusion
1.6: Collisions with Other Molecules
1.7: Real Gases
1.8: Intermolecular Forces
1.8.1: Van der Waals Forces
1.9: Specific Interactions
1.9.1: Dipole-Dipole Interactions
1.9.2: Dipole Moment
1.9.3: Dipole moments
1.9.4: Hydrogen Bonding
1.9.5: Ion - Dipole Interactions
1.9.6: Ion - Induced Dipole Interactions
1.9.7: Ion - Ion Interactions
1.9.8: Lennard-Jones Potential
1.9.9: London Dispersion Interactions
1.9.10: Polarizability
1.E: Gases (Exercises)
1.S: Gases (Summary)

Thumbnail: Image used with permission (CC SA-BY 3.0; Greg L)

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

1.1: The Empirical Gas Laws

A number of important relationships describing the nature of gas samples have been derived completely empirically (meaning based solely on observation rather making an attempt to define the theoretical reason these relationships may exist. These are the **empirical gas laws**.

Boyle's Law

One of the important relationships governing gas samples that can be modeled mathematically is the relationship between pressure and volume. Robert Boyle (1627 – 1691) (Hunter, 2004) did experiments to confirm the observations of Richard Towneley and Henry Powers to show that for a fixed sample of gas at a constant temperature, pressure and volume are inversely proportional.

$$pV = \text{constant}$$

or

$$p_1V_2 = p_2V_2$$

Boyle used a glass u-tube that was closed at one end and with the lower portion filled with mercury (trapping a sample of air in the closed end.) By adding mercury to the open end, he was able to observe and quantify the compression of the trapped air.

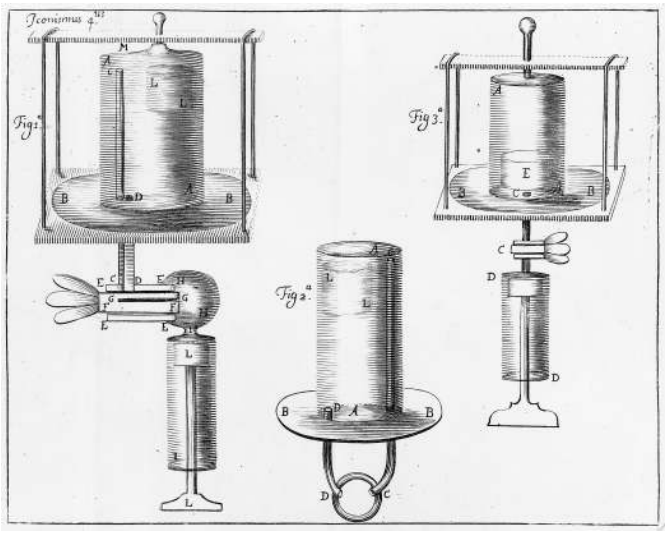


Figure 1.1.1: An apparatus similar to that used by Robert Boyle (1627 - 1691). Image taken from (Fazio, 1992).

Charles' Law

Charles' Law states that the volume of a fixed sample of gas at constant pressure is proportional to the temperature. For this law to work, there must be an absolute minimum to the temperature scale since there is certainly an absolute minimum to the volume scale!

$$\frac{V}{T} = \text{constant}$$

or

$$\frac{V_1}{T_2} = \frac{V_1}{T_2}$$

The second law of thermodynamics also predicts an absolute minimum temperature, but that will be developed in a later chapter.

Gay-Lussac's Law

Gay-Lussac's Law states that the pressure of a fixed sample of gas is proportional to the temperature. As with Charles' Law, this suggests the existence of an absolute minimum to the temperature scale since the pressure can never be negative.

$$\frac{p}{T} = \text{constant}$$

or

$$\frac{p_1}{T_2} = \frac{p_1}{T_2}$$

Combined Gas Law

Boyle's, Charles', and Gay-Lussac's Laws can be combined into a single empirical formula that can be useful. For a given amount of gas, the following relationship must hold:

$$\frac{pV}{T} = \text{constant}$$

or

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

Avogadro's Law

Amedeo Avogadro (1776-1856) (Encycolopedia, 2016) did extensive work with gases in his studies of matter. In the course of his work, he noted an important relationship between the number of moles in a gas sample. Avogadro's Law (Avogadro, 1811) states that at the same temperature and pressure, any sample of gas has the same number of molecules per unit volume.

$$\frac{n}{V} = \text{constant}$$

or

$$\frac{n_1}{V_1} = \frac{n_2}{V_2}$$



Figure 1.1.2: Amedeao Avogadro (1776 - 1856)

This page titled 1.1: The Empirical Gas Laws is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **2.1: The Empirical Gas Laws** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

1.2: The Ideal Gas Law

The **ideal gas law** combines the empirical laws into a single expression. It also predicts the existence of a single, universal gas constant, which turns out to be one of the most important fundamental constants in science.

[Math Processing Error]

The ideal gas law constant is of fundamental importance and can be expressed in a number of different sets of units.

Value	Units
0.08206	atm L mol^{-1} K^{-1}
8.314	J mol^{-1} K^{-1}
1.987	cal mol^{-1} K^{-1}

The ideal gas law, as derived here, is based entirely on empirical data. It represents “limiting ideal behavior.” As such, deviations from the behavior suggested by the ideal gas law can be understood in terms of what conditions are required for ideal behavior to be followed (or at least approached.) As such, it would be nice if there was a theory of gases that would suggest the form of the ideal gas law and also the value of the gas law constant. As it turns out, the kinetic molecular theory of gases does just that!

This page titled 1.2: The Ideal Gas Law is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **2.2: The Ideal Gas Law** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

1.3: The Kinetic Molecular Theory of Gases

Theoretical models attempting to describe the nature of gases date back to the earliest scientific inquiries into the nature of matter and even earlier! In about 50 BC, Lucretius, a Roman philosopher, proposed that macroscopic bodies were composed of atoms that continually collide with one another and are in constant motion, despite the observable reality that the body itself is as rest. However, Lucretius' ideas went largely ignored as they deviated from those of Aristotle, whose views were more widely accepted at the time.

In 1738, Daniel Bernoulli (Bernoulli, 1738) published a model that contains the basic framework for the modern Kinetic Molecular theory. Rudolf Clausius furthered the model in 1857 by (among other things) introducing the concept of mean free path (Clausius, 1857). These ideas were further developed by Maxwell (Maxwell, Molecules, 1873). But, because atomic theory was not fully embraced in the early 20th century, it was not until Albert Einstein published one of his seminal works describing Brownian motion (Einstein, 1905) in which he modeled matter using a kinetic theory of molecules that the idea of an atomic (or molecular) picture really took hold in the scientific community.

In its modern form, the Kinetic Molecular Theory of gasses is based on five basic postulates.

1. Gas particles obey Newton's laws of motion and travel in straight lines unless they collide with other particles or the walls of the container.
2. Gas particles are very small compared to the averages of the distances between them.
3. Molecular collisions are perfectly elastic so that kinetic energy is conserved.
4. Gas particles so not interact with other particles except through collisions. There are no attractive or repulsive forces between particles.
5. The average kinetic energy of the particles in a sample of gas is proportional to the temperature.

Qualitatively, this model predicts the form of the ideal gas law.

1. More particles means more collisions with the wall (\(p \propto n\))
2. Smaller volume means more frequent collisions with the wall (\(p \propto 1/V\))
3. Higher molecular speeds means more frequent collisions with the walls (\(p \propto T\))

Putting all of these together yields

$$p \propto \frac{nT}{V} = k\frac{nT}{V}$$

which is exactly the form of the ideal gas law! The remainder of the job is to derive a value for the constant of proportionality (k) that is consistent with experimental observation.

For simplicity, imagine a collection of gas particles in a fixed-volume container with all of the particles traveling at the same velocity. What implications would the kinetic molecular theory have on such a sample? One approach to answering this question is to derive an expression for the pressure of the gas.

The pressure is going to be determined by considering the collisions of gas molecules with the wall of the container. Each collision will impart some force. So the greater the number of collisions, the greater the pressure will be. Also, the larger force imparted per collision, the greater the pressure will be. And finally, the larger the area over which collisions are spread, the smaller the pressure will be.

$$p \propto \frac{(\text{number of collisions}) \times (\text{force imparted per collision})}{area}$$

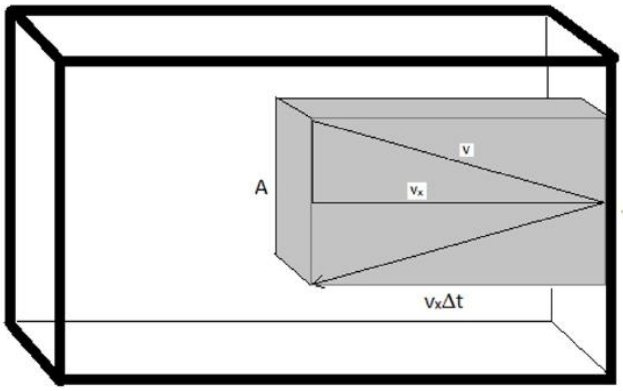


Figure 1.3.1: The "collision volume" is the subset of the total volume that contains molecules that will actually collide with area A in the time interval Δt.

First off, the pressure that the gas exerts on the walls of the container would be due entirely to the force imparted each time a molecule collides with the interior surface of the container. This force will be scaled by the number of molecules that hit the area of the wall in a given time. For this reason, it is convenient to define a “collision volume”.

$$V_{col} = (v_x \cdot \Delta t) \cdot A$$

where v_x is the speed the molecules are traveling in the x direction, \(\Delta t\) is the time interval (the product of $v_x \cdot \Delta T$ gives the length to the collision volume box) and A is the area of the wall with which the molecules will collide. Half of the molecules within this volume will collide with the wall since half will be traveling toward it and half will be traveling away from it. The number of molecules in this collision volume will be given by the total number of molecules in the sample and the fraction of the total volume that is the collision volume. And thus, the number of molecules that will collide with the wall is given by

$$N_{col} = \frac{1}{2} N_{tot} \frac{V_{col}}{V}$$

And thus the number of molecules colliding with the wall will be

$$N_{col} = \frac{1}{2} N_{tot} \frac{(v_x \cdot \Delta t) \cdot A}{V}$$

The magnitude of that force imparted per collision will be determined by the time-rate of change in momentum of each particle as it hits the surface. It can be calculated by determining the total momentum change and dividing by the total time required for the event. Since each colliding molecule will change its velocity from v_x to $-v_x$, the magnitude of the momentum change is $2(mv_x)$. Thus the force imparted per collision is given by

$$F = \frac{2(mv_x)}{\Delta t}$$

and the total force imparted is

$$F_{tot} = N_{col} \frac{2(mv_x)}{\Delta t} \tag{1.3.1}$$

$$= \frac{1}{2} N_{tot} \left[\frac{(v_x \Delta t) A}{V} \right] \left[\frac{2(mv_x)}{\Delta t} \right] \tag{1.3.2}$$

$$= N_{tot} \left(\frac{mv_x^2}{V} \right) A \tag{1.3.3}$$

Since the pressure is given as the total force exerted per unit area, the pressure is given by

$$p = \frac{F_{tot}}{A} = N_{tot} \left(\frac{mv_x^2}{V} \right) = \frac{N_{tot} m}{V} v_x^2$$

The question then becomes how to deal with the velocity term. Initially, it was assumed that all of the molecules had the same velocity, and so the magnitude of the velocity in the x-direction was merely a function of the trajectory. However, real samples of

gases comprise molecules with an entire distribution of molecular speeds and trajectories. To deal with this distribution of values, we replace (v_x^2) with the squared average of velocity in the x direction $\langle v_x \rangle^2$.

$$p = \frac{N_{tot} m}{V} \langle v_x \rangle^2 \tag{1.3.4}$$

The distribution function for velocities in the x direction, known as the **Maxwell-Boltzmann distribution**, is given by:

$$f(v_x) = \underbrace{\sqrt{\frac{m}{2\pi k_B T}}}_{\text{normalization term}} \underbrace{\exp\left(\frac{-mv_x^2}{2k_B T}\right)}_{\text{exponential term}}$$

This function has two parts: a **normalization constant** and an exponential term. The normalization constant is derived by noting that

$$\int_{-\infty}^{\infty} f(v_x) dv_x = 1 \tag{1.3.5}$$

Normalizing the Maxwell-Boltzmann Distribution

The Maxwell-Boltzmann distribution has to be normalized because it is a continuous probability distribution. As such, the sum of the probabilities for all possible values of v_x **must** be unity. And since vx can take any value between -∞ and ∞, then Equation 1.3.5 must be true. So if the form of $f(v_x)$ is assumed to be

$$f(v_x) = N \exp - \left(\frac{mv_x^2}{2k_B T}\right)$$

The normalization constant N can be found from

$$\int_{-\infty}^{\infty} f(v_x) dv_x = \int_{-\infty}^{\infty} N \exp\left(\frac{-mv_x^2}{2k_B T}\right) dv_x = 1$$

The expression can be simplified by letting $\alpha = m/2k_B T$. It is then more simply written

$$N \int_{-\infty}^{\infty} \exp\left(\frac{-mv_x^2}{2k_B T}\right) dv_x = 1$$

A table of definite integrals says that

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$

So

$$N\sqrt{\frac{\pi}{\alpha}} = \left(\frac{m}{2\pi k_B T}\right)^{1/2}$$

And thus the normalized distribution function is given by

$$f(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(\frac{mv_x^2}{2k_B T}\right) \tag{1.3.6}$$

Calculating an Average from a Probability Distribution

Calculating an average for a finite set of data is fairly easy. The average is calculated by

$$\bar{x} = \frac{1}{N} \sum_{i=1}^{N} x_i$$

But how does one proceed when the set of data is infinite? Or how does one proceed when all one knows are the probabilities for each possible measured outcome? It turns out that that is fairly simple too!

$$\bar{x} = \sum_{i=1}^{N} x_i P_i$$

where P_i is the probability of measuring the value x_i. This can also be extended to problems where the measurable properties are not discrete (like the numbers that result from rolling a pair of dice) but rather come from a continuous parent population. In this case, if the probability is of measuring a specific outcome, the average value can then be determined by

$$\bar{x} = \int x P(x) dx$$

where $P(x)$ is the function describing the probability distribution, and with the integration taking place across all possible values that x can take.

Calculating the average value of v_x

A value that is useful (and will be used in further developments) is the average velocity in the x direction. This can be derived using the probability distribution, as shown in the mathematical development box above. The average value of v_x is given by

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x (f(v_x) dx$$

This integral will, by necessity, be zero. This must be the case as the distribution is symmetric, so that half of the molecules are traveling in the +x direction, and half in the –x direction. These motions will have to cancel. So, a more satisfying result will be given by considering the magnitude of v_x, which gives the speed in the x direction. Since this cannot be negative, and given the symmetry of the distribution, the problem becomes

$$\langle |v_x| \rangle = 2 \int_{0}^{\infty} v_x (f(v_x) dx$$

In other words, we will consider only half of the distribution, and then double the result to account for the half we ignored.

For simplicity, we will write the distribution function as

$$f(v_x) = N \exp(-\alpha v_x^2)$$

where

$$N = \left(\frac{m}{2\pi k_B T} \right)^{1/2}$$

and

$$\alpha = \frac{m}{2k_B T}.$$

A table of definite integrals shows

$$\int_0^{\infty} x e^{-ax^2} dx = \frac{1}{2a}$$

so

$$\langle v_x \rangle = 2N \left(\frac{1}{2\alpha} \right) = \frac{N}{\alpha}$$

Substituting our definitions for N and α produces

$$\langle v_x \rangle = \left(\frac{m}{2\pi k_B T} \right)^{1/2} \left(\frac{2k_B T}{m} \right) = \left(\frac{2\pi k_B T}{\pi m} \right)^{1/2}$$

This expression indicates the average speed for motion of in one direction.

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 (Equation 1.3.4) 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. One of the first people to address this distribution was James Clerk Maxwell (1831-1879). In his 1860 paper (Maxwell, Illustrations of the dynamical theory of gases. Part 1. On the motions and collisions of perfectly elastic spheres, 1860), 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, and ignoring the angular part (since he was interested only in the speed) **Maxwell's distribution** (Equation 1.3.6) took the following form

$$f(v) = N v^2 \exp\left(\frac{m v^2}{2 k_B T}\right) \tag{1.3.7}$$

This function has three basic parts to it: **a normalization constant** (N), a velocity dependence (v^2), and an exponential term that contains the kinetic energy ($\frac{1}{2}mv^2$). Since 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

$$\int_0^\infty f(v) dv = 1$$

Choosing the normalization constant as

$$N = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3}$$

yields the final form of the Maxwell distribution of molecular speeds.

$$N = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} v^2 \exp\left(\frac{m v^2}{2 k_B T}\right) \tag{1.3.8}$$

At low velocities, the v^2 term causes the function to increase with increasing v, but then at larger values of v, the exponential term causes it to drop back down asymptotically to zero. The distribution will spread over a larger range of speed at higher temperatures, but collapse to a smaller range of values at lower temperatures (Table 2.3.1).

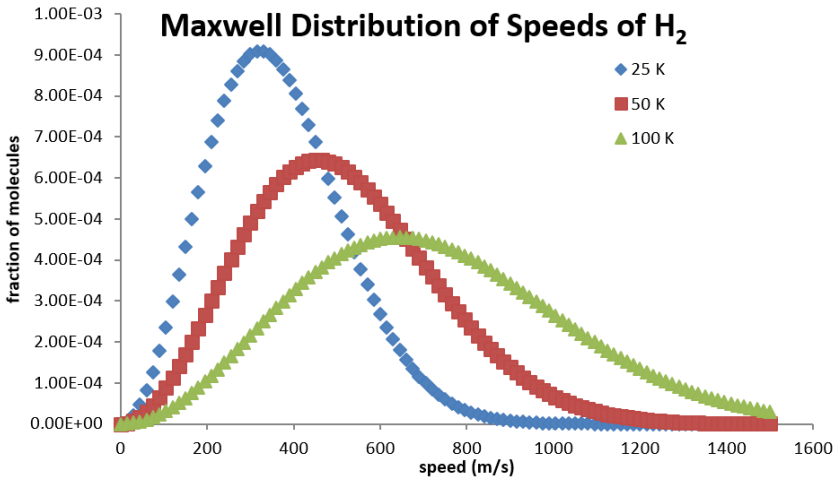


Figure 2.3.1: Maxwell Distribution of speeds for hydrogen molecules at differing temperatures.

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.

$$\langle v \rangle = \int_{-\infty}^{\infty} v\, f(v) dv \tag{1.3.9}$$

$$= \int_{-\infty}^{\infty} v\, 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} v^2 \exp\left(\frac{mv^2}{2k_B T}\right)\, dv \tag{1.3.10}$$

$$= 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \int_{-\infty}^{\infty} v^3 \exp\left(\frac{mv^2}{2k_B T}\right)\, dv \tag{1.3.11}$$

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 1.3.1:

What is the average value of the squared speed according to the Maxwell distribution law?

Solution

https://chem.libretexts.org/@go/page/199132

$$\langle v^2 \rangle = \int_{-\infty}^{\infty} v^2 \, f(v) dv \tag{1.3.12}$$

$$= \int_{-\infty}^{\infty} v^2 \, 4\pi \sqrt{\left(\frac{m}{2\pi k_B T} \right)^3} v^2 \exp\left(\frac{mv^2}{2k_B T} \right) \, dv \tag{1.3.13}$$

$$= 4\pi \sqrt{\left(\frac{m}{2\pi k_B T} \right)^3} \int_{-\infty}^{\infty} v^4 \exp\left(\frac{mv^2}{2k_B T} \right) \, dv \tag{1.3.14}$$

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

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \left(\frac{3k_B T}{m} \right)^{1/2}$$

The entire distribution is also affected by molecular mass. For lighter molecules, the distribution is spread across a broader range of speeds at a given temperature, but collapses to a smaller range for heavier molecules (Table 2.3.2).

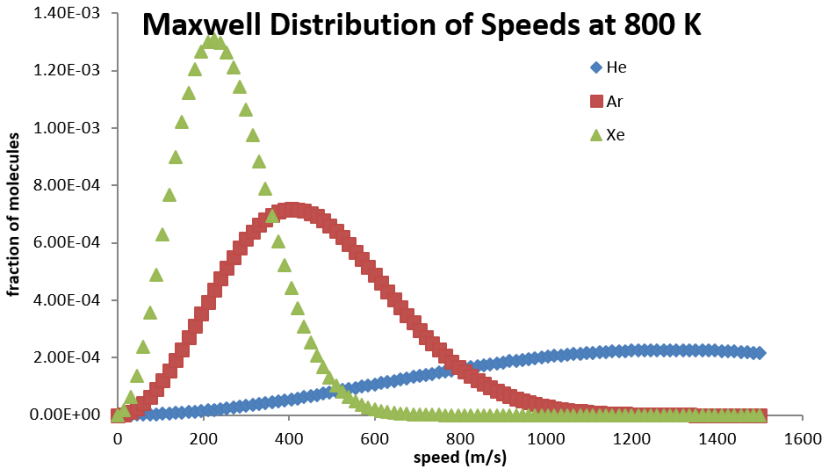


Figure 2.3.2: Maxwell Distribution of speeds at 800 K for different gasses of differing molecular masses.

The probability distribution function can also be used to derive an expression for the most probable speed (v_{mp}), the average (v_{ave}), and the root-mean-square (v_{rms}) speeds as a function of the temperature and masses of the molecules in the sample. The most probable speed is the one with the **maximum probability**. That will be the speed that yields the maximum value of $f(v)$. It is found by solving the expression

$$\frac{d}{dv} f(v) = 0$$

for the value of v that makes it true. This will be the value that gives the maximum value of $f(v)$ for the given temperature. Similarly, the average value can be found using the distribution in the following fashion

$$v_{ave} = \langle v \rangle$$

and the **root-mean-square** (RMS) speed by finding the square root of the average value of v^2. Both demonstrated above.

$$v_{rms} = \sqrt{\langle v^2 \rangle}$$

This page titled 1.3: The Kinetic Molecular Theory of Gases is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **2.3: The Kinetic Molecular Theory of Gases** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

1.4: Kinetic Energy

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 2.4.1). 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.

Table 2.4.1: 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	$\sqrt{\frac{3k_bT}{m}}$	$\frac{3}{2}k_BT$

The Ideal Gas Law

The expression for the root-mean-square molecular speed can be used to show that the Kinetic Molecular model of gases is consistent with the ideal gas law. Consider the expression for pressure

$$p = \frac{N_{tot}m}{3V}\langle v\rangle^2$$

Replacing $\langle v\rangle^2$ with the square of the RMS speed expression yields

$$p = \frac{N_{tot}m}{3V}\left(\frac{3k_BT}{m}\right)$$

which simplifies to

$$p = \frac{N_{tot}k_BT}{V}$$

Noting that $N_{tot} = n{\cdot}N_A$, where n is the number of moles and N_A is Avogadro's number

$$p = \frac{nN_Ak_BT}{V}$$

or

$$pV = nN_Ak_BT$$

Finally, noting that $N_A \bullet k_B = R$

$$pV = nRT$$

That's kind of cool, no? The only assumptions (beyond the postulates of the Kinetic Molecular Theory) is that the distribution of velocities for a thermalized sample of gas is described by the Maxwell-Boltzmann distribution law. The next development will be to use the Kinetic Molecular Theory to describe molecular collisions (which are essential events in many chemical reactions.)

Collisions with the Wall

In the derivation of an expression for the pressure of a gas, it is useful to consider the frequency with which gas molecules collide with the walls of the container. To derive this expression, consider the expression for the “collision volume”.

$$V_{col} = v_x \Delta t \cdot A$$

All of the molecules within this volume, and with a velocity such that the x-component exceeds v_x (and is positive) will collide with the wall. That fraction of molecules is given by

$$N_{col} = \frac{N}{V} \frac{\langle v \rangle \Delta t \cdot A}{2}$$

and the frequency of collisions with the wall per unit area per unit time is given by

$$Z_w = \frac{N}{V} \frac{\langle v \rangle}{2}$$

In order to expand this model into a more useful form, one must consider motion in all three dimensions. Considering that

$$\langle v \rangle = \sqrt{\langle v_x \rangle + \langle v_y \rangle + \langle v_z \rangle}$$

and that

$$\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle$$

it can be shown that

$$\langle v \rangle = 2 \langle v_x \rangle$$

or

$$\langle v_x \rangle = \frac{1}{2} \langle v \rangle$$

and so

$$Z_w = \frac{1}{4} \frac{N}{V} \langle v \rangle$$

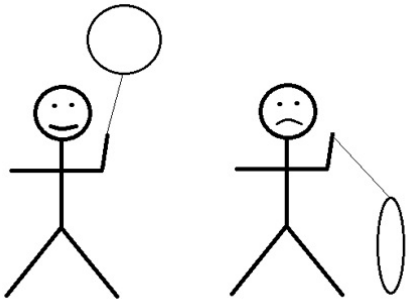
The factor of N/V is often referred to as the “number density” as it gives the number of molecules per unit volume. At 1 atm pressure and 298 K, the number density for an ideal gas is approximately 2.5 x 10^{19} molecule/cm^3. (This value is easily calculated using the ideal gas law.) By comparison, the average number density for the universe is approximately 1 molecule/cm^3.

This page titled 1.4: Kinetic Energy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **2.4: Kinetic Energy** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

1.5: Graham's Law of Effusion

An important consequence of the kinetic molecular theory is what it predicts in terms of *effusion* and *diffusion* effects. Effusion is defined as a loss of material across a boundary. A common example of effusion is the loss of gas inside of a balloon over time.



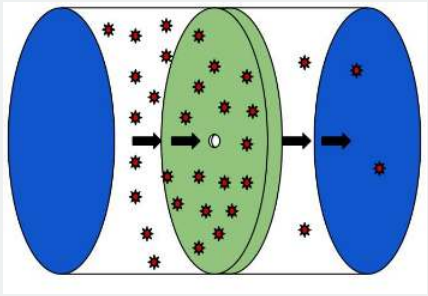
The rate at which gases will effuse from a balloon is affected by a number of factors. But one of the most important is the frequency with which molecules collide with the interior surface of the balloon. Since this is a function of the average molecular speed, it has an inverse dependence on the square root of the molecular weight.

$$\text{Rate of effusion} \propto \frac{1}{\sqrt{MW}}$$

This can be used to compare the relative rates of effusion for gases of different molar masses.

The Knudsen Cell Experiment

A Knudsen cell is a chamber in which a thermalized sample of gas is kept, but allowed to effuse through a small orifice in the wall. The gas sample can be modeled using the Kinetic Molecular Theory model as a collection of particles traveling throughout the cell, colliding with one another and also with the wall. If a small orifice is present, any molecules that would collide with that portion of the wall will be lost through the orifice.



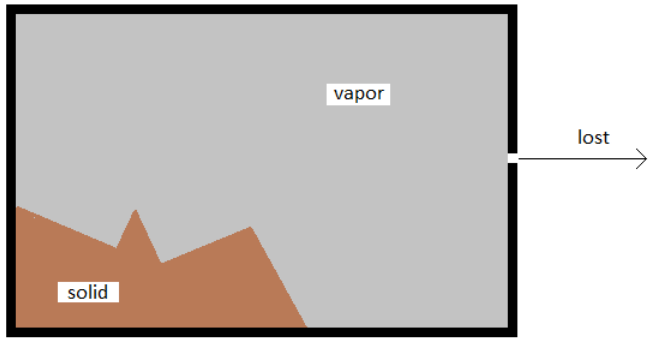
\

Figure 1.5.1: Effusion of gas particles through an orifice. (CC BY-SA 3.0; Astrang13).

This makes a convenient arrangement to measure the vapor pressure of the material inside the cell, as the total mass lost by effusion through the orifice will be proportional to the vapor pressure of the substance. The vapor pressure can be related to the mass lost by the expression

$$p = \frac{g}{A\Delta t}\sqrt{\frac{2\pi RT}{MW}}$$

where g is the mass lost, A is the area of the orifice, Δt is the time the effusion is allowed to proceed, T is the temperature and MW is the molar mass of the compound in the vapor phase. The pressure is then given by p. A schematic of what a Knudsen cell might look like is given below.



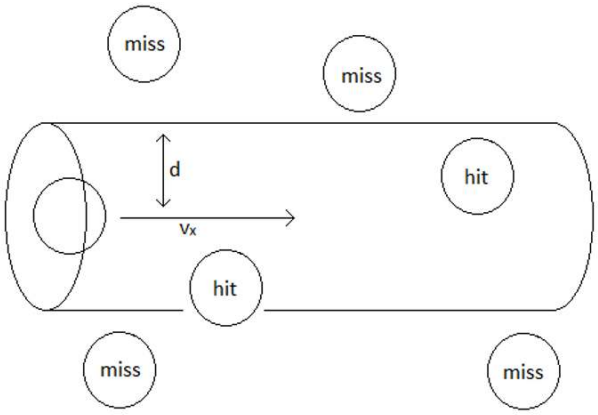
This page titled 1.5: Graham's Law of Effusion is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **2.5: Graham's Law of Effusion** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

1.6: Collisions with Other Molecules

A major concern in the design of many experiments is collisions of gas molecules with other molecules in the gas phase. For example, molecular beam experiments are often dependent on a lack of molecular collisions in the beam that could degrade the nature of the molecules in the beam through chemical reactions or simply being knocked out of the beam.

In order to predict the frequency of molecular collisions, it is useful to first define the conditions under which collisions will occur. For convenience, consider all of the molecules to be spherical and in fixed in position except for one which is allowed to move through a “sea” of other molecules. A molecular collision will occur every time the center of the moving molecule comes within one molecular diameter of the center of another molecule.



One can easily determine the number of molecules the moving molecule will “hit” by determining the number of molecules that lie within the “collision cylinder”. Because we fixed the positions of all but one of the molecules, we must use the relative speed of the moving molecule, which will be given by

$$v_{rel} = \sqrt{2} \times v$$

The volume of the collision cylinder is given by

$$V_{col} = \sqrt{2}\, v\, \Delta t\, A$$

The **collisional cross section**, which determined by the size of the molecule is given by

$$\sigma = \pi d^2$$

Some values of σ are given in the table below:

Table 2.6.1: Collisional cross-section of Select Species

Molecule	σ (nm^2)
He	0.21
Ne	0.24
N_2	0.43
CO_2	0.52
C_2H_4	0.64

Since the number of molecules within the collision cylinder is given by

$$N_{col} = \frac{N}{V} V_{col}$$

and since the number density (N/V) is given by

$$\frac{N}{V} = \frac{p}{k_B T}$$

the number of collisions is given by

$$N_{col} = \frac{p}{k_B T}(\sqrt{2}\, v \Delta t \sigma)$$

The frequency of collisions (number of collisions per unit time) is then given by

$$Z = \frac{\sqrt{2} p \sigma}{k_B T} \langle v \rangle$$

Perhaps a more useful value is the **mean free path** (λ), which is the distance a molecule can travel on average before it collides with another molecule. This is easily derived from the collision frequency. How far something can travel between collisions is given by the ratio of how fast it is traveling and how often it hits other molecules:

$$\lambda = \frac{\langle v \rangle}{Z}$$

Thus, the mean free path is given by

$$\lambda = \frac{k_B T}{\sqrt{2} p \sigma}$$

The mere fact that molecules undergo collisions represents a deviation from the kinetic molecular theory. For example, if molecules were infinitesimally small ($\sigma \approx 0$) then the mean free path would be infinitely long! The finite size of molecules represents one significant deviation from ideality. Another important deviation stems from the fact that molecules do exhibit attractive and repulsive forces between one another. These forces depend on a number of parameters, such as the distance between molecules and the temperature (or average kinetic energy of the molecules.)

This page titled 1.6: Collisions with Other Molecules is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **2.6: Collisions with Other Molecules** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

1.7: Real Gases

While the ideal gas law is sufficient for the prediction of large numbers of properties and behaviors for gases, there are a number of times that deviations from ideality are extremely important.

The van der Waals Equation

Several equations of state have been suggested to account for the deviations from ideality. One simple, but useful, expression is that proposed by Johannes Diderik van der Waals (1837 – 1923) (Johannes Diderik van der Waals - Biographical, 2014)

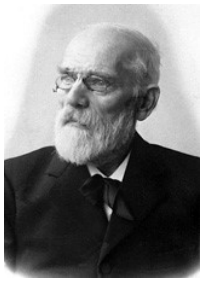


Figure 1.7.1: Johannes van der Waals (1837 – 1923)

van der Waals' equation introduced corrections to the pressure and volume terms of the ideal gas law in order to account for intermolecular interactions and molecular size respectively.

$$\left(p+\frac{a}{V_m^2}\right)(V_m-b)=RT \tag{1.7.1}$$

or

$$p=\frac{RT}{V_m-b}-\frac{a}{V_m^2} \tag{1.7.2}$$

In this expression, a and b are variables of a given substance which can be measured and tabulated. In general, molecules with large intermolecular forces will have large values of a, and large molecules will have large values of b. Some van der Waals constants are given in Table 1.7.1.

Table 1.7.1: van der Waals constants for select Species

Gas frequency of collisions	a (atm L^2 mol-2)	b (L/mol)
He	0.0341	0.0238
N_2	1.352	0.0387
CO_2	3.610	0.0429
C_2H_4	4.552	0.0305

The van der Walls model is useful because it makes it so simple to interpret the parameters in terms of molecular size and intermolecular forces. But it does have limitations as well (as is the case of every scientific model!) Some other useful two-parameter and three-parameter (or more) equations of state include the Redlich-Kwong, Dieterici, and Clausius models (Table 1.7.2). These have the advantage that they allow for temperature dependence on some of the parameters, which as will be seen later, is necessary to model certain behaviors of real gases.

Table 1.7.2: Other equations of State

Model	Equation of State
Ideal	$p=\frac{RT}{V_m}$
van der Waals (van der Waals J. D., 1867)	$p=\frac{RT}{V_m-b}-\frac{a}{V_m^2}$

Model	Equation of State
Redlich-Kwong (Redlich & Kwong, 1949)	$p = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m (V_m + b)}$
Dieterici (Dieterici, 1899)	$p = \frac{RT}{V_m - b} \exp\left(\frac{-a}{V_m RT}\right)$
Clausius	$p = \frac{RT}{V_m - b} - \frac{a}{T(V_m + c)^2}$
Virial Equations	$p = \frac{RT}{V_m}\left(1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m} \ldots\right)$

The Virial Equation

A very handy expression that allows for deviations from ideal behavior is the **Virial Equation** of state. This is a simple power series expansion in which the higher-order terms contain all of the deviations from the ideal gas law.

$$p = \frac{RT}{V_m}\left(1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} \ldots\right) \tag{1.7.3}$$

In the limit that $B(T)$ (the **Second Virial Coefficient**) and $C(T)$ are zero, the equation becomes the ideal gas law. Also, the molar volume of gases are small, the contributions from the third, fourth, etc. terms decrease in magnitude, allowing one to truncate the series at a convenient point. The second virial coefficient can be predicted from a theoretical intermolecular potential function by

$$B(T) = N_a \int_{r=0}^{\infty} \left[1 - \exp\left(\frac{U(r)}{k_B T}\right)\right] 2\pi r^2 \, dr$$

The quality of an intermolecular potential can be determined (partially) by the potential's ability to predict the value of the second virial coefficient, $B(T)$.

The Leonard-Jones Potential

An intermolecular potential function is used to describe the interactions between molecules. These interactions will have to include attractive forces, which will draw molecules together, and repulsive forces which will push them apart. If the molecules are hard spheres, lacking any attractive interactions, the potential function is fairly simple.

$$U(r) = \begin{cases} \infty & \text{for } r \leq \sigma \\ 0 & \text{for } r > \sigma. \end{cases}$$

In this function, σ is determined by the size of the molecules. If two molecules come within a distance r of one another, they collide, bouncing off in a perfectly elastic collision. Real molecules, however, with have a range of intermolecular separations through which they will experience attractive forces (the so-called "soft wall" of the potential surface.) And then at very small separations, the repulsive forces will dominate, pushing the molecules apart (the so-called "hard wall" of the potential surface.)

A commonly used intermolecular potential, $U(r)$, is the **Leonard-Jones potential**. This function has the form

$$U(r) = 4\epsilon \left[\underbrace{\left(\frac{\sigma}{r}\right)^{12}}_{\text{repulsive term}} - \underbrace{\left(\frac{\sigma}{r}\right)^{6}}_{\text{attractive term}}\right]$$

where σ governs the width of the potential well, and ϵ governs the depth. The distance between molecules is given by r. The repulsive interactions between molecules are contained in the first terms and the attractive interactions are found in the second term.

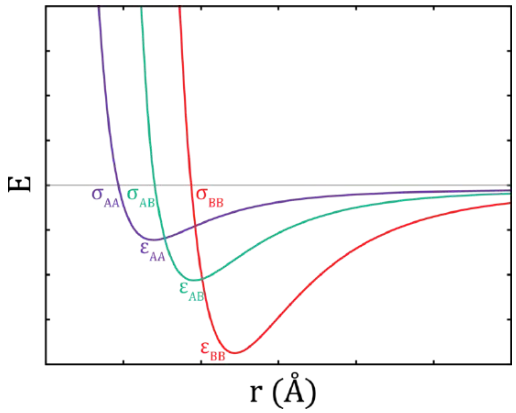


Figure 1.7.2: The estimation of Lennard-Jones potential parameters for mixed pairs of atoms. (CC BY-SA 4.0; Cnrowley).

Taylor Series Expansion

A commonly used method of creating a power series based on another equation is the **Taylor Series Expansion**. This is an expansion of a function about a useful reference point where each of the terms is generated by differentiating the original function.

For a function $f(x)$, the Taylor series $F(x)$ can be generated from the expression

$$F(x) = f(a) + \frac{d}{dx} f(x)\Big|_{x=a} (x-a) + \frac{1}{2!}\frac{d^2}{dx^2} f(x)\Big|_{x=a} (x-a)^2 + \dots$$

This can be applied to any equation of state to derive an expression for the virial coefficients in terms of the parameters of the equation of state.

Application to the van der Waals equation

The van der Waals equation can be written in terms of molar volume (Equation 1.7.2). When multiplying the right hand side by $\frac{u}{u}$ (where $u = 1/v$) yields:

$$p = \frac{RTu}{1-bu} - au^2$$

This expression can be "Talyor" expanded (to the first three terms) about $u = 0$ (which corresponds to an infinite molar volume.) The coefficient terms that are needed for the expansion are

$$p(u=0) = 0$$

$$\frac{dp}{du}|_{u=0} = \left[\frac{RT}{1-bu} + \frac{bRTu}{(1-bu)^2} - 2au\right]_{u=0} = RT$$

$$\frac{d^2p}{du^2}|_{u=0} = \frac{1}{2}\left[\frac{bRT}{(1-bu)^2} + \frac{bRT}{(1-bu)^2} - \frac{2b^2RTu}{(1-bu)^3} - 2au\right]_{u=0} = RT - a$$

$$\frac{d^3p}{du^3}|_{u=0} = RTb^2$$

And the virial equation can then be expressed in terms of the van der Waals parameters as

$$p = 0 + RT(u) + (bRT - a)(u)^2 + RTb^{2(u)^3}$$

Substituting $u = 1/V$ and simplifying gives the desired result:

$$p = RT\left[\frac{1}{V} + \frac{b - \frac{a}{RT}}{V^2} + \frac{b^2}{V^3} + \dots\right]$$

And the second virial coefficient is given by

$$B(T) = b - \frac{a}{RT}$$

The Boyle Temperature

A useful way in which deviations from ideality can be expressed is by defining the **compression factor** (Z) given by

$$Z = \frac{pV_m}{RT}$$

where V_m is the molar volume. For an ideal gas, $Z = 1$ under all combinations of P, V_m, and T. However, real gases will show some deviation (although all gases approach ideal behavior at low p, high V_m, and high T.) The compression factor for nitrogen at several temperatures is shown below over a range of pressures.

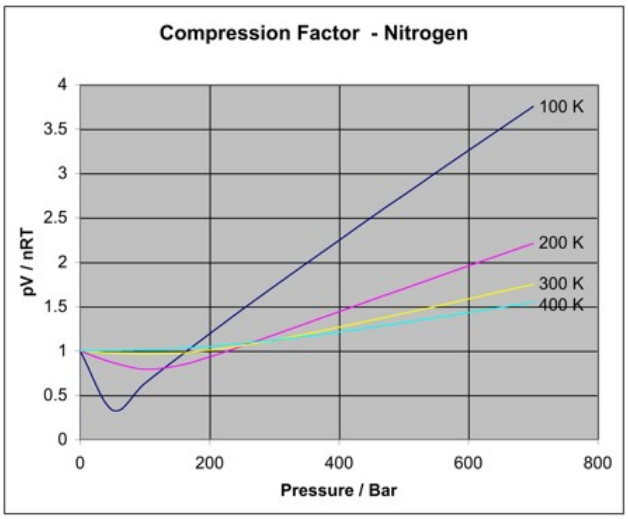


Figure 1.7.3: Compressibility of select gases as a function of applied pressure.

As can be seen, the gas behaves closer to ideally over a longer range of pressure at the higher temperatures. In general, there is one temperature, the **Boyle temperature**, at which a gas will approach ideal behavior as the pressure goes to zero asymptotically, and thus behave ideally over a broad range of lower pressures. The Boyle temperature is found by solving

$$\lim_{p \to 0} \left(\frac{\partial Z}{\partial p} \right) = 0$$

or

$$\lim_{1/V_m \to 0} \left(\frac{\partial Z}{\partial \left(\frac{1}{V_m} \right)} \right) = 0$$

Using the virial equation of state (Equation 1.7.3), the Boyle temperature can be expressed in terms of the virial coefficients. Starting with the compression factor

$$Z = 1 + \frac{B}{V_m} + \ldots$$

and then differentiating with respect to $1/V_m$ yields

\[\dfrac{\partial Z}{\partial \left(\frac{1}{V_m}\right)} = B \nonumber \]

So it can be concluded that at the Boyle temperature, the second virial coefficient B is equal to zero. This should make some sense given that the first virial coefficient provides most of the deviation from the ideal gas law, and so it must vanish as the gas behaves more ideally.

Critical Behavior

The isotherms (lines of constant temperature) of CO_2 reveal a very large deviation from ideal behavior. At high temperatures, CO_2 behaves according to Boyle's Law. However, at lower temperatures, the gas begins to condense to form a liquid at high pressures. At one specific temperature, the **critical temperature**, the isotherm begins to display this critical behavior. The temperature, pressure, and molar volume (p_c, T_c, and V_c) at this point define the **critical point**. In order to solve for expressions for the critical constants, one requires three equations. The equation of state provides one relationship. The second can be generated by recognizing that the slope of the isotherm at the critical point is zero. And finally, the third expression is derived by recognizing that the isotherm passes through an inflection point at the critical point. Using the van der Waals equation as an example, these three equations can be generated as follows:

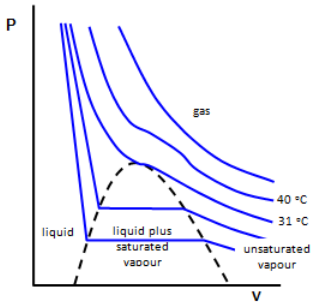


Figure 1.7.4: Condensation of a van der Waal gas.

Solving these expressions for p_c, T_c, and V_c yields

$$p_c = \frac{a}{27b^2}$$

$$T_c = \frac{8a}{27bR}$$

$$V_c = 3b$$

The critical variables can be used in this fashion to determine the values of the molecular parameters used in an equation of state (such as the van der Waals equation) for a given substance.

The Principle of Corresponding States

The **principle of corresponding states** was proposed by van der Waals in 1913 (van der Waals J. D., 1913). He noted that the compression factor at the critical point

$$Z_c = \frac{p_c V_c}{RT_c}$$

is very nearly the same for any substance. This is consistent with what is predicted by the van der Waals equation, which predicts $Z_c = 0.375$ irrespective of substance.

Further, it can be noted that based on **reduced variables** defined by

$$p_r = \frac{p}{p_c}$$

$$V_r = \frac{V}{V_c}$$

$$T_r = \frac{T}{T_c}$$

several physical properties are found to be comparable for real substances. For example (Guggenheim, 1945), for argon, krypton, nitrogen, oxygen, carbon dioxide and methane the reduced compressibility is

$$[\frac{p_c V_c}{RT_c} \approx 0.292$$

Also, the reduced compression factor can be plotted as a function of reduced pressure for several substances at several reduced isotherms with surprising consistency irrespective of the substance.

This page titled 1.7: Real Gases is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **2.7: Real Gases** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

SECTION OVERVIEW

1.8: Intermolecular Forces

Intermolecular forces are the attractive or repulsive forces between molecules. They are separated into two groups; short range and long range forces. Short range forces happen when the centers of the molecules are separated by three angstroms (10^{-8} cm) or less. Short range forces tend to be repulsive, where the long range forces that act outside the three angstroms range are attractive. Long range forces are also known as Van der Waals forces. They are responsible for surface tension, friction, viscosity and differences between actual behavior of gases and that predicted by the ideal gas law. Intermolecular forces are responsible for most properties of all the phases. The viscosity, diffusion, and surface tension are examples of physical properties of liquids that depend on intermolecular forces. Vapor pressure, critical point, and boiling point are examples of properties of gases. Melting and sublimation are examples of properties of solids that depend on intermolecular forces.

1.8.1: Van der Waals Forces

1.8: Intermolecular Forces is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

1.8.1: Van der Waals Forces

Van der Waals forces' is a general term used to define the attraction of intermolecular forces between molecules. There are two kinds of Van der Waals forces: weak London Dispersion Forces and stronger dipole-dipole forces.

Introduction

The chance that an electron of an atom is in a certain area in the electron cloud at a specific time is called the "electron charge density." Since there is no way of knowing exactly where the electron is located and since they do not all stay in the same area 100 percent of the time, if the electrons all go to the same area at once, a dipole is formed momentarily. Even if a molecule is nonpolar, this displacement of electrons causes a nonpolar molecule to become polar for a moment.

Since the molecule is polar, this means that all the electrons are concentrated at one end and the molecule is partially negatively charged on that end. This negative end makes the surrounding molecules have an instantaneous dipole also, attracting the surrounding molecules' positive ends. This process is known as the London Dispersion Force of attraction.

The ability of a molecule to become polar and displace its electrons is known as the molecule's "polarizability." The more electrons a molecule contains, the higher its ability to become polar. Polarizability increases in the periodic table from the top of a group to the bottom and from right to left within periods. This is because the higher the molecular mass, the more electrons an atom has. With more electrons, the outer electrons are easily displaced because the inner electrons shield the nucleus' positive charge from the outer electrons which would normally keep them close to the nucleus.

When the molecules become polar, the melting and boiling points are raised because it takes more heat and energy to break these bonds. Therefore, the greater the mass, the more electrons present, and the more electrons present, the higher the melting and boiling points of these substances.

London dispersion forces are stronger in those molecules that are not compact, but long chains of elements. This is because it is easier to displace the electrons because the forces of attraction between the electrons and protons in the nucleus are weaker. The more readily displacement of electrons means the molecule is also more “polarizable.”

Dipole-Dipole Forces

These forces are similar to London Dispersion forces, but they occur in molecules that are permanently polar versus momentarily polar. In this type of intermolecular interaction, a polar molecule such as water or H_2O attracts the positive end of another polar molecule with its negative end of its dipole. The attraction between these two molecules is the dipole-dipole force.

Van der Waals Equation

Van der Waals equation is required for special cases, such as non-ideal (real) gases, which is used to calculate an actual value. The equation consist of:

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \tag{1}$$

The V in the formula refers to the volume of gas, in moles *n*. The intermolecular forces of attraction is incorporated into the equation with the $\frac{n^2 a}{V^2}$ term where *a* is a specific value of a particular gas. P represents the pressure measured, which is expected to be lower than in usual cases. The variable *b* expresses the *eliminated volume per mole*, which accounts for the volume of gas molecules and is also a value of a particular gas. R is a known constant, 0.08206 L atm mol^{-1} K^{-1}, and T stands for temperature.

Unlike most equations used for the calculation of real, or ideal, gases, van der Waals equation takes into account, and corrects for, the volume of participating molecules and the intermolecular forces of attraction.

References

1. Petrucci, Ralph H., et al. General Chemistry: Principles and Modern Applications. Upper Saddle River, NJ: Prentice Hall, 2007

Contributors and Attributions

- Kathryn Rashe, Lisa Peterson, Seila Buth, Irene Ly

1.8.1: Van der Waals Forces is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Van der Waals Forces** is licensed CC BY-NC-SA 4.0.

SECTION OVERVIEW

1.9: Specific Interactions

Intermolecular forces are forces of attraction or repulsion which act between neighboring particles (atoms, molecules or ions). They are weak compared to the intramolecular forces, which keep a molecule together (e.g., covalent and ionic bonding).

Topic hierarchy

1.9.1: Dipole-Dipole Interactions

1.9.2: Dipole Moment

1.9.3: Dipole moments

1.9.4: Hydrogen Bonding

1.9.5: Ion - Dipole Interactions

1.9.6: Ion - Induced Dipole Interactions

1.9.7: Ion - Ion Interactions

1.9.8: Lennard-Jones Potential

1.9.9: London Dispersion Interactions

1.9.10: Polarizability

1.9: Specific Interactions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

1.9.1: Dipole-Dipole Interactions

Dipole-Dipole interactions result when two dipolar molecules interact with each other through space. When this occurs, the partially negative portion of one of the polar molecules is attracted to the partially positive portion of the second polar molecule. This type of interaction between molecules accounts for many physically and biologically significant phenomena such as the elevated boiling point of water.

Definition of a Dipole

Molecular dipoles occur due to the unequal sharing of electrons between atoms in a molecule. Those atoms that are more electronegative pull the bonded electrons closer to themselves. The buildup of electron density around an atom or discreet region of a molecule can result in a molecular dipole in which one side of the molecule possesses a partially negative charge and the other side a partially positive charge. Molecules with dipoles that are not canceled by their molecular geometry are said to be polar.

Example 1.9.1.1: Carbon Dioxide and Hydrogen Flouride

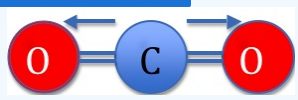


Figure 1.9.1.1.

In Figure 1 above, the more electronegative Oxygen atoms pull electron density towards themselves as demonstrated by the arrows. Carbon Dioxide is not polar however because of its linear geometry. A molecule's overall dipole is directional, and is given by the vector sum of the dipoles between the atoms. If we imagined the Carbon Dioxide molecule centered at 0 in the XY coordinate plane, the molecule's overall dipole would be given by the following equation:

$$\mu\cos(0)+-\mu\cos(0)=0. \tag{1.9.1.1}$$

Where μ is the dipole moment of the bond (given by μ=Q x r where Q is the charge and r is the distance of separation). Therefore, the two dipoles cancel each other out to yield a molecule with no net dipole.

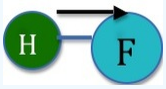


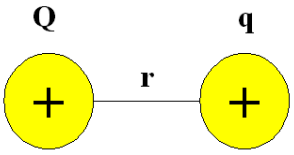
Figure 1.9.1.2.

In contrast, figure 2 demonstrates a situation where a molecular dipole does result. There is no opposing dipole moment to cancel out the one that is shown above. If we were to imagine the hydrogen flouride molecule placed so that the Hydrogen sat at the origin in the XY coordinate plane, the dipole would be given by $\mu\cos(0)=\mu$.

Potential Energy of Dipole Interaction

Potential energy is the maximum energy that is available for an object to do work. In physics, work is a quantity that describes the energy expended as a force operates over a distance. Potential energy is positional because it depends on the forces acting on an object at its position in space. For instance, we could say that an object held above the ground has a potential energy equal to its mass x acceleration due to gravity x its height above the ground (i.e., mgh). This potential energy that an object has as a result of its position can be used to do work. For instance we could use a pulley system with a large weight held above the ground to hoist a smaller weight into the air. As we drop the large weight it converts its potential energy to kinetic energy and does work on the rope which lifts the smaller weight into the air. It is important to remember that due to the second law of thermodynamics, the amount of work done by an object can never exceed (and is often considerably less) than the objects potential energy.

On a subatomic level, charged atoms have an electric potential which allows them to interact with each other. Electric potential refers to the energy held by a charged particle as a result of it's position relative to a second charged particle. Electric potential depends on charge polarity, charge strength and distance. Molecules with the same charge will repel each other as they come closer together while molecules with opposite charges will attract.



For two positively charged particles interacting at a distance r, the potential energy possessed by the system can be defined using Coulomb's Law:

$$V = \frac{kQq}{r} \tag{1.9.1.2}$$

where

- k is the Coulomb constant and
- Q and q refer to the magnitude of the charge for each particle in Coulombs.

The above equation can also be used to calculate the distance between two charged particles (r) if we know the potential energy of the system. While Coulomb's law is important, it only gives the potential energy between two point particles. Since molecules are much larger than point particles and have charge concentrated over a larger area, we have to come up with a new equation.

The potential energy possessed by two polar atoms interacting with each other depends on the dipole moment, μ, of each molecule, the distance apart, r, and the orientation in which the two molecules interact. For the case in which the partially positive area of one molecule interacts only with the partially negative area of the other molecule, the potential energy is given by:

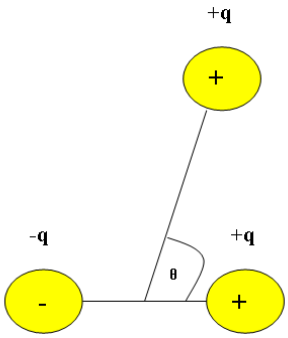
$$V(r) = -\frac{2\mu_1\mu_2}{4\pi\epsilon_o r^3} \tag{1.9.1.3}$$

where ϵ_o is the permeability of space. If it is not the case that the molecular dipoles interact in this straight end to end manor, we have to account mathematically for the change in potential energy due to the angle between the dipoles. We can add an angular term to the above equation to account for this new parameter of the system:

$$V(r) = -\frac{\mu_1\mu_2}{4\pi\epsilon_0 r_{12}^3}(\cos\theta_{12} - 3\cos\theta_1\cos\theta_2) \tag{1.9.1.4}$$

In this formula θ_{12} is the angle made by the two oppositely charged dipoles, and r_{12} is the distance between the two molecules. Also, θ_1 and θ_2 are the angles formed by the two dipoles with respect to the line connecting their centers.

It is also important to find the potential energy of the dipole moment for more than two interacting molecules. An important concept to keep in mind when dealing with multiple charged molecules interacting is that like charges repel and opposite charges attract. So for a system in which three charged molecules (2 positively charged molecules and 1 negatively charged molecule) are interacting, we need to consider the angle between the attractive and repellant forces.



The potential energy for the dipole interaction between multiple charged molecules is:

$$V = \frac{kp\cos\theta}{r^2} \tag{1.9.1.5}$$

where

- k is the Coulomb constant, and
- r is the distance between the molecules.

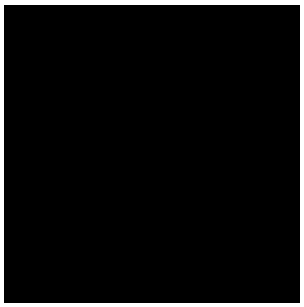


Figure 1.9.1.3: Dipole-Dipole Interaction in the Gas Phase. image used with permission (Gary L Bertrand).

Example 1.9.1.2

Calculate the potential energy of the dipole-dipole interaction between 2 HF molecules oriented along the x axis in an XY coordinate plane whose area of positive charge is separated by 5.00 Angstroms from the area of negative charge of the adjacent molecule:

Solution

The Dipole moment of the HF molecules can be found in many tables, μ=1.92 D. Assume the molecules exist in a vacuum such that $\epsilon_0 = 8.8541878 \times 10^{-12} C^2 N^{-1} m^{-2}$

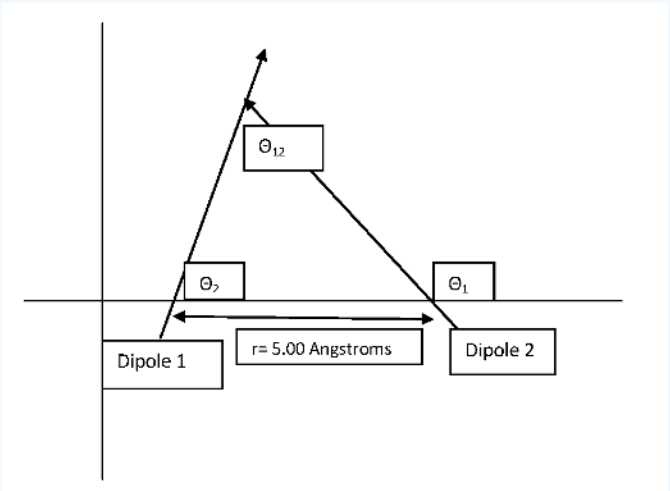
$$\mu = 1.92D \times 3.3356 \times 10^{-30} \frac{Cm}{D} = 6.4044 \times 10^{-30} Cm \tag{1.9.1.6}$$

Now use Equation 1.9.1.3to calculate the interaction energy

$$V = -\frac{2(6.4044 \times 10^{-30} Cm)^2}{4(8.8541878 \times 10^{-12} C^2 N^{-1} m^{-2})(5.0 \times 10^{-10})^3}$$
$$= 1.4745 \times 10^{-19} Nm$$

Example 1.9.1.3

Now imagine the same two HF molecules in the following orientation:



Given: $\theta_1 = \frac{3\pi}{4}$, $\theta_2 = \frac{\pi}{3}$ and $\theta_{12} = \frac{5\pi}{12}$

Solution

$$V = -\frac{(6.4044 \times 10^{-30} Cm)^2}{4\pi(8.8541878 \times 10^{-12} C^2 N^{-1} m^{-2}(5.00 \times 10^{-10} m)^3}(\cos\frac{5\pi}{12} - 3\cos\frac{3\pi}{4}\cos\frac{\pi}{3})$$
$$= -9.73 \times 10^{-20} Nm = 9.73 \times 10^{-20} J$$

Dipole-Dipole Interactions in Macroscopic Systems

It would seem, based on the above discussion, that in a system composed of a large number of dipolar molecules randomly interacting with one another, V should go to zero because the molecules adopt all possible orientations. Thus the negative potential energy of two molecular dipoles participating in a favorable interaction would be cancelled out by the positive energy of two molecular dipoles participating in a high potential energy interaction. Contrary to our assumption, in bulk systems, it is more probable for dipolar molecules to interact in such a way as to minimize their potential energy (i.e., dipoles form less energetic, more probable configurations in accordance with the Boltzmann's Distribution). For instance, the partially positive area of a molecular dipole being held next to the partially positive area of a second molecular dipole is a high potential energy configuration and few molecules in the system will have sufficient energy to adopt it at room temperature. Generally, the higher potential energy configurations are only able to be populated at elevated temperatures. Therefore, the interactions of dipoles in a bulk Solution are not random, and instead adopt more probable, lower energy configurations. The following equation takes this into account:

$$V = -\frac{2\mu_A^2\mu_B^2}{3(4\pi\epsilon_0)^2 r^6}\frac{1}{k_B T} \tag{1.9.1.7}$$

Example 1.9.1.4

Looking at Equation 1.9.1.7, what happens to the potential energy of the interaction as temperature increases.

Solution

The potential energy of the dipole-dipole interaction decreases as T increases. This can be seen from the form of the above equation, but an explanation for this observation is relatively simple to come by. As the temperature of the system increases, more molecules have sufficient energy to occupy the less favorable configurations. The higher, less favorable, configurations are those that give less favorable interactions between the dipoles (i.e., higher potential energy configurations).

Example 1.9.1.5

Calculate the average energy of HF molecules interacting with one another in a bulk Solution assuming that the molecules are 4.00 Angstroms apart in room temperature Solution.

Solution

Using Equation 1.9.1.7to calculate the bulk potential energy:

$$V = -\frac{2}{3}\frac{(6.4044 \times 10^{-30} Cm)^4}{(4\pi(8.8541878 \times 10^{-12} C^2 N^{-1} m^{-2})^2 (4.00 \times 10^{-10} m)^6}\frac{1}{(1.381 \times 10^{-23} Jk^{-1})(298k)}$$
$$= -5.46 \times 10^{-21} J$$

Example 1.9.1.6

What is the amount of energy stabilization that is provided to the system when 1 mole of HF atoms interact through dipole-dipole interactions.

Solution

Since we have already calculated above the average potential energy of the HF dipole-dipole interaction this problem can be easily solved.

$$V = -5.46 \times 10^{-21} J \times (6.022 \times 10^{23} mol^{-1})$$
$$= -3288\frac{J}{mol} = 3.29\frac{kJ}{mol}$$

Biological Importance of Dipole Interactions

The potential energy from dipole interactions is important for living organisms. The biggest impact dipole interactions have on living organisms is seen with protein folding. Every process of protein formation, from the binding of individual amino acids to secondary structures to tertiary structures and even the formation of quaternary structures is dependent on dipole-dipole interactions.

A prime example of quaternary dipole interaction that is vital to human health is the formation of erythrocytes. Erythrocytes, commonly known as red blood cells are the cell type responsible for the gas exchange (i.e. respiration). Inside the erythrocytes, the molecule involved in this crucial process, is 'hemoglobin', formed by four protein subunits and a heme group'. For an heme to form properly, multiple steps must occur, all of which involve dipole interactions. The four protein subunits—two alpha chains, two beta chains—and the heme group, interact with each other through a series of dipole-dipole interactions which allow the erythrocyte to take its final shape. Any mutation that destroys these dipole-dipole interactions prevents the erythrocyte from forming properly, and impairs their ability to carry oxygen to the tissues of the body. So we can see that without the dipole-dipole interactions, proteins would not be able to fold properly and all life as we know it would cease to exist.

References

1. Le Fèvre, R. J. W. (1953). Dipole moments; their measurement and application in chemistry. London, Methuen.
2. Atkins, P. W. and J. De Paula (2006). Physical chemistry for the life sciences. New York, Oxford University Press ; Freeman.
3. Petrucci, R. H., W. S. Harwood, et al. (2002). General chemistry : principles and modern applications. Upper Saddle River, N.J., Prentice Hall.
4. Bloomfield, M. M. (1992). Chemistry and the living organism. New York, Wiley.
5. Silbey, R. J., R. A. Alberty, et al. (2005). Physical chemistry. Hoboken, NJ, Wiley.
6. HyperPhysics. http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html Georgia State University, Department of Physics and Astronomy. 2008.
7. Campbell, N. A. and J. B. Reece (2005). Biology. San Francisco, Pearson Benjamin Cummings.
8. Chang, Raymond. (2005). Physical Chemistry for the Biosciences. Sausalito, California, University Science Books.

1.9.1: Dipole-Dipole Interactions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Dipole-Dipole Interactions** by David Johns, Gary L Bertrand, Joel Guess is licensed CC BY-NC-SA 4.0.

1.9.2: Dipole Moment

Let's go back to that first ion pair which was formed when the positive ion and the negative ion came together. If the electronegativities of the elements are sufficiently different (like an alkali metal and a halide), the charges on the paired ions will not change appreciably - there will be a full electron charge on the blue ion and a full positive charge on the red ion. The bond formed by the attraction of these opposite charges is called an ionic bond. If the difference in electronegativity is not so great, however, there will be some degree of sharing of the electrons between the two atoms. The result is the same whether two ions come together or two atoms come together:

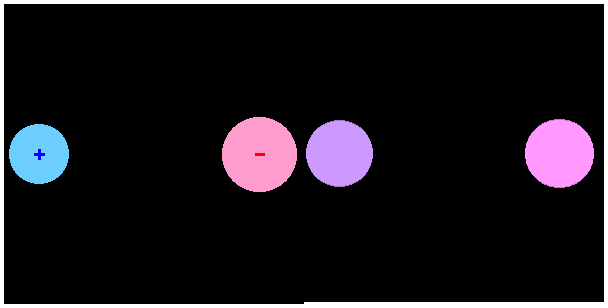


Figure 1.9.2.1: Polar Molecule

The combination of atoms or ions is no longer a pair of ions, but rather a polar molecule which has a measureable dipole moment. The dipole moment (D) is defined as if there were a positive (+q) and a negative (-q) charge separated by a distance (r):

$$D = qr \tag{1.9.2.1}$$

If there is no difference in electronegativity between the atoms (as in a diatomic molecule such as O_2 or F_2) there is no difference in charge and no dipole moment. The bond is called a covalent bond, the molecule has no dipole moment, and the molecule is said to be non-polar. Bonds between different atoms have different degrees of ionicity depending on the difference in the electronegativities of the atoms. The degree of ionicity may range from zero (for a covalent bond between two atoms with the same electronegativity) to one (for an ionic bond in which one atom has the full charge of an electron and the other atom has the opposite charge).

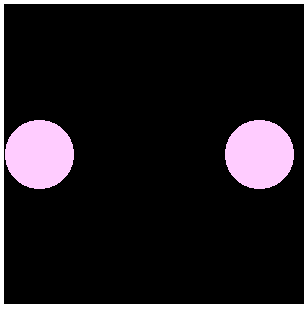


Figure 1.9.2.1: Non-polar Molecule

In some cases, two or more partially ionic bonds arranged symmetrically around a central atom may mutually cancel each other's polarity, resulting in a non-polar molecule. An example of this is seen in the carbon tetrachloride (CCl_4) molecule. There is a substantial difference between the electronegativities of carbon (2.55) and chlorine (3.16), but the four chlorine atoms are arranged symmetrically about the carbon atom in a tetrahedral configuration, and the molecule has zero dipole moment. Saturated hydrocarbons (C_nH_{n+2}) are non-polar molecules because of the small difference in the electronegativities of carbon and hydrogen plus the near symmetry about each carbon atom.

1.9.2: Dipole Moment is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Dipole Moment** by Gary L Bertrand is licensed CC BY-NC-SA 4.0. Original source: https://web.mst.edu/~gbert/links.html.

1.9.3: Dipole moments

The intermolecular forces have important contribution in helping us to understand the interaction between atoms in same or different kind of molecules. The interaction can involve polar or non polar molecules and ions. There are three common intermolecular forces and this module will focus more in-depth the interaction involving polar molecules and interaction between polar molecules and ions.

Introduction

Dipole moment (μ) is the measure of net molecular polarity, which is the magnitude of the charge Q at either end of the molecular dipole times the distance r between the charges.

$$\mu = Q \times r \tag{1.9.3.1}$$

Dipole moments tell us about the charge separation in a molecule. The larger the difference in electronegativities of bonded atoms, the larger the dipole moment. For example, NaCl has the highest dipole moment because it has an ionic bond (i.e. highest charge separation).

Example 1: Chloromethane

In the Chloromethane molecule (CH_3Cl), chlorine is more electronegative than carbon, thus attracting the electrons in the C—Cl bond toward itself (Figure 1). As a result, chlorine is slightly negative and carbon is slightly positive in C—Cl bond. Since one end of C-Cl is positive and the other end is negative, it is described as a polar bond. To indicate the increased in electron density, the dipole is represented by an arrow with a cross at one end. The cross end of the arrow represents the positive end and the point of the arrow represents the negative end of the dipole.

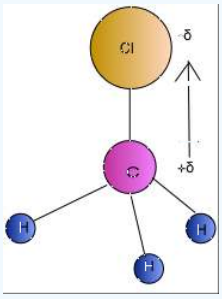


Figure 1

The vector will point from plus to minus charge and run parallel with the bond between 2 atoms. The symbol δ indicates the partial charge of an individual atom. In addition, the direction of vector implies the physical movement of electrons to an atom that has more electronegativity when 2 atoms are separated by a distance of r. In other words, the electrons will spend more time around atom that has larger electronegativity.

Table 1: Dipole Moments of Some Compounds

Compound	Dipole Moment (Debyes)
NaCl	9.0 (measured in the gas phase)
CH_3Cl	1.87
H_2O	1.85
NH_3	1.47
CO_2	0
CCl_4	0

Polar molecules and Dipole-Dipole Interaction

A polar molecule is a molecule where one end has a positive electrical charge and the other end has a negative charge due to the arrangement or geometry of its atoms. Because polar molecules have a positive and negative charge ends, the positive charge end of a molecule will attract to the negative end of adjacent molecule with the same or different kind of molecule. The attraction beween two polar molecules is called *dipole-dipole interaction*. The attraction between two dipoles create a very strong intermolecular force, which have great influence in the evaporation of liquid and condensation of gas.

Example

Since water are polar molecules, the interaction between water molecules are so strong that it takes a lot of energy to break the bond between the water molecules. Therefore, the boiling point of polar substances are higher than those of nonpolar substance due to stronger intermolecular force among polar molecules.

Polar molecules and Ions Interaction

When a polar molecule is mixed with ion, the positive charge end of the polar molecule will be attracted to the negative charge called anion on the ion. Also, the positive charge called cation on the ion will be attracted to the negative charge end of the polar molecule. This *ion-dipole interaction* is stronger than the dipole-dipole interaction between polar molecules, but is weaker than the ion-ion interaction.

Since ions and polar molecule have positive and negative charge, we can use **Coulomb's law** to evaluate the force between them

$$F = k_e \frac{q_1 q_2}{r^2} \tag{1.9.3.2}$$

with

- q_1 and q_2 are the charges on atoms
- k_e is the proportionality constant
- r_{12} is the distance between 2 separated charges

The strength of ion-dipole interaction is based on the distance between ion and polar molecule, the charge of the ion, and dipole magnitude. The closer ion and polar molecule are, the stronger the intermolecular force is between polar molecule and ion. An ion with higher charge will make the attraction stronger. Last, a greater magnitude of dipole will cause stronger attraction.

References

1. Fay, McMurry. Chemistry Fourth Edition, Pearson Education, New Jersey, 2004
2. Kotz, Treichel, Weaver. Chemistry and Chemical Reactivity, Thomson Brooks/Cole, 2006

1.9.3: Dipole moments is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Dipole moments** by Farah Yasmeen is licensed CC BY-NC-SA 4.0.

1.9.4: Hydrogen Bonding

A hydrogen bond is an intermolecular force (IMF) that forms a special type of dipole-dipole attraction when a hydrogen atom bonded to a strongly electronegative atom exists in the vicinity of another electronegative atom with a lone pair of electrons. Intermolecular forces (IMFs) occur between molecules. Other examples include ordinary dipole-dipole interactions and dispersion forces. Hydrogen bonds are are generally stronger than ordinary dipole-dipole and dispersion forces, but weaker than true covalent and ionic bonds.

The evidence for hydrogen bonding

Many elements form compounds with hydrogen. If you plot the boiling points of the compounds of the group 14 elements with hydrogen, you find that the boiling points increase as you go down the group.

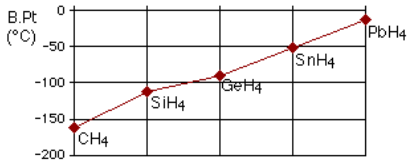


Figure 1: Boiling points of group 14 elemental halides.

The increase in boiling point happens because the molecules are getting larger with more electrons, and so van der Waals dispersion forces become greater. If you repeat this exercise with the compounds of the elements in groups 15, 16, and 17 with hydrogen, something odd happens.

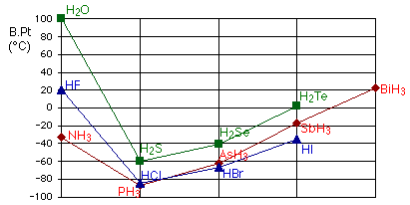


Figure 2: Boiling points of group 15-17 elemental halides.

Although the same reasoning applies for group 4 of the periodic table, the boiling point of the compound of hydrogen with the first element in each group is abnormally high. In the cases of NH_3, H_2O and HF there must be some additional intermolecular forces of attraction, requiring significantly more heat energy to break the IMFs. These relatively powerful intermolecular forces are described as hydrogen bonds.

Origin of Hydrogen Bonding

The molecules capable of hydrogen bonding include the following:

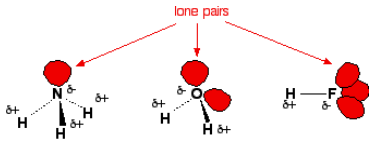


Figure 3: The lone pairs responsible for hydrogen bonding in NH_3, H_2O, and HF. The solid line represents a bond in the plane of the screen or paper. Dotted bonds are going back into the screen or paper away from you, and wedge-shaped ones are coming out towards you.

Notice that in each of these molecules:

- The hydrogen is attached directly to a highly electronegative atoms, causing the hydrogen to acquire a highly positive charge.
- Each of the highly electronegative atoms attains a high negative charge and has at least one "active" lone pair. Lone pairs at the 2-level have electrons contained in a relatively small volume of space, resulting in a high negative charge density. Lone pairs at higher levels are more diffuse and, resulting in a lower charge density and lower affinity for positive charge.

> *If you are not familiar with electronegativity, you should follow this link before you go on.*

Consider two water molecules coming close together.

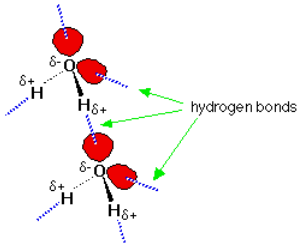


Figure 4: Hydrogen bonding in water

The δ^+ hydrogen is so strongly attracted to the lone pair that it is almost as if you were beginning to form a co-ordinate (dative covalent) bond. It doesn't go that far, but the attraction is significantly stronger than an ordinary dipole-dipole interaction. Hydrogen bonds have about a tenth of the strength of an average covalent bond, and are constantly broken and reformed in liquid water. If you liken the covalent bond between the oxygen and hydrogen to a stable marriage, the hydrogen bond has "just good friends" status.

Water is an ideal example of hydrogen bonding. Notice that each water molecule can potentially form four hydrogen bonds with surrounding water molecules: two with the hydrogen atoms and two with the with the oxygen atoms. There are exactly the right numbers of δ^+ hydrogens and lone pairs for every one of them to be involved in hydrogen bonding.

This is why the boiling point of water is higher than that of ammonia or hydrogen fluoride. In the case of ammonia, the amount of hydrogen bonding is limited by the fact that each nitrogen only has one lone pair. In a group of ammonia molecules, there are not enough lone pairs to go around to satisfy all the hydrogens. In hydrogen fluoride, the problem is a shortage of hydrogens. In water, two hydrogen bonds and two lone pairs allow formation of hydrogen bond interactions in a lattice of water molecules. Water is thus considered an ideal hydrogen bonded system.

More complex examples of hydrogen bonding

The hydration of negative ions

When an ionic substance dissolves in water, water molecules cluster around the separated ions. This process is called hydration. Water frequently attaches to positive ions by co-ordinate (dative covalent) bonds. It bonds to negative ions using hydrogen bonds.

> *If you are interested in the bonding in hydrated positive ions, you could follow this link to co-ordinate (dative covalent) bonding.*

The diagram shows the potential hydrogen bonds formed with a chloride ion, Cl-. Although the lone pairs in the chloride ion are at the 3-level and would not normally be active enough to form hydrogen bonds, they are made more attractive by the full negative charge on the chlorine in this case.

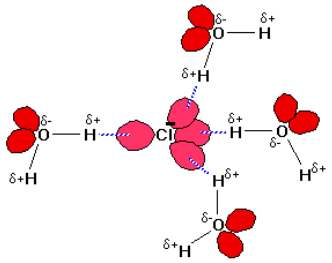


Figure 5: Hydrogen bonding between chloride ions and water.

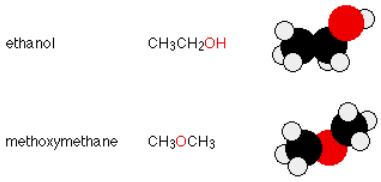
However complicated the negative ion, there will always be lone pairs that the hydrogen atoms from the water molecules can hydrogen bond to.

Hydrogen bonding in alcohols

An alcohol is an organic molecule containing an -OH group. Any molecule which has a hydrogen atom attached directly to an oxygen or a nitrogen is capable of hydrogen bonding. Hydrogen bonds also occur when hydrogen is bonded to fluorine, but the HF group does not appear in other molecules. Molecules with hydrogen bonds will always have higher boiling points than similarly sized molecules which don't have an -O-H or an -N-H group. The hydrogen bonding makes the molecules "stickier," such that more

heat (energy) is required to separate them. This phenomenon can be used to analyze boiling point of different molecules, defined as the temperature at which a phase change from liquid to gas occurs.

Ethanol, CH_3CH_2-O-H, and methoxymethane, CH_3-O-CH_3, both have the same molecular formula, C_2H_6O.

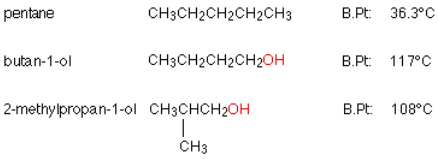


They have the same number of electrons, and a similar length. The van der Waals attractions (both dispersion forces and dipole-dipole attractions) in each will be similar. However, ethanol has a hydrogen atom attached directly to an oxygen; here the oxygen still has two lone pairs like a water molecule. Hydrogen bonding can occur between ethanol molecules, although not as effectively as in water. The hydrogen bonding is limited by the fact that there is only one hydrogen in each ethanol molecule with sufficient $\delta+$ charge.

In methoxymethane, the lone pairs on the oxygen are still there, but the hydrogens are not sufficiently $\delta+$ for hydrogen bonds to form. Except in some rather unusual cases, the hydrogen atom has to be attached directly to the very electronegative element for hydrogen bonding to occur. The boiling points of ethanol and methoxymethane show the dramatic effect that the hydrogen bonding has on the stickiness of the ethanol molecules:

ethanol (with hydrogen bonding)	78.5°C
methoxymethane (without hydrogen bonding)	-24.8°C

The hydrogen bonding in the ethanol has lifted its boiling point about 100°C. It is important to realize that hydrogen bonding exists in addition to van der Waals attractions. For example, all the following molecules contain the same number of electrons, and the first two have similar chain lengths. The higher boiling point of the butan-1-ol is due to the additional hydrogen bonding.



Comparing the two alcohols (containing -OH groups), both boiling points are high because of the additional hydrogen bonding; however, the values are not the same. The boiling point of the 2-methylpropan-1-ol isn't as high as the butan-1-ol because the branching in the molecule makes the van der Waals attractions less effective than in the longer butan-1-ol.

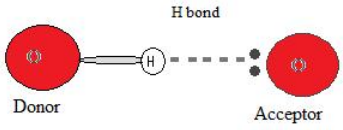
Hydrogen bonding in organic molecules containing nitrogen

Hydrogen bonding also occurs in organic molecules containing N-H groups; recall the hydrogen bonds that occur with ammonia. Examples range from simple molecules like CH_3NH_2 (methylamine) to large molecules like proteins and DNA. The two strands of the famous double helix in DNA are held together by hydrogen bonds between hydrogen atoms attached to nitrogen on one strand, and lone pairs on another nitrogen or an oxygen on the other one.

Donors and Acceptors

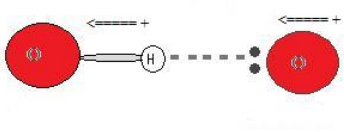
In order for a hydrogen bond to occur there must be both a hydrogen donor and an acceptor present. The donor in a hydrogen bond is usually a strongly electronegative atom such as N, O, or F that is covalently bonded to a hydrogen bond.

The hydrogen acceptor is an electronegative atom of a neighboring molecule or ion that contains a lone pair that participates in the hydrogen bond.



Why does a hydrogen bond occur?

Since the hydrogen donor (N, O, or F) is strongly electronegative, it pulls the covalently bonded electron pair closer to its nucleus, and away from the hydrogen atom. The hydrogen atom is then left with a partial positive charge, creating a dipole-dipole attraction between the hydrogen atom bonded to the donor and the lone electron pair of the acceptor. This results in a hydrogen bond.(see Interactions Between Molecules With Permanent Dipoles)

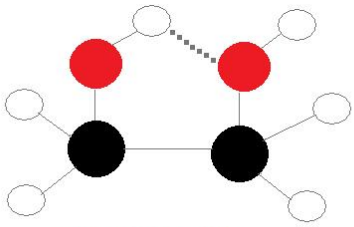


Types of hydrogen bonds

Although hydrogen bonds are well-known as a type of IMF, these bonds can also occur within a single molecule, between two identical molecules, or between two dissimilar molecules.

Intramolecular hydrogen bonds

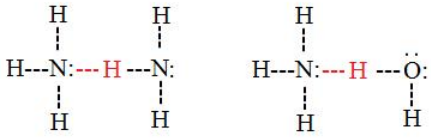
Intramolecular hydrogen bonds are those which occur *within* one single molecule. This occurs when two functional groups of a molecule can form hydrogen bonds with each other. In order for this to happen, both a hydrogen donor a hydrogen acceptor must be present within one molecule, and they must be within close proximity of each other in the molecule. For example, intramolecular hydrogen bonding occurs in ethylene glycol ($C_2H_4(OH)_2$) between its two hydroxyl groups due to the molecular geometry.



Intramolecular h-bonding in Ethylene Glycol molecule

Intermolecular hydrogen bonds

Intermolecular hydrogen bonds occur *between* separate molecules in a substance. They can occur between any number of like or unlike molecules as long as hydrogen donors and acceptors are present in positions where they can interact with one another. For example, intermolecular hydrogen bonds can occur between NH_3 molecules alone, between H_2O molecules alone, or between NH_3 and H_2O molecules.



Properties and effects of hydrogen bonds

On Boiling Point

When we consider the boiling points of molecules, we usually expect molecules with larger molar masses to have higher normal boiling points than molecules with smaller molar masses. This, without taking hydrogen bonds into account, is due to greater dispersion forces (see Interactions Between Nonpolar Molecules). Larger molecules have more space for electron distribution and thus more possibilities for an instantaneous dipole moment. However, when we consider the table below, we see that this is not always the case.

Compound	Molar Mass	Normal Boiling Point
H_2O	18 g/mol	373 K
HF	20 g/mol	292.5 K
NH_3	17 g/mol	239.8 K
H_2S	34 g/mol	212.9 K
HCl	36.4 g/mol	197.9 K
PH_3	34 g/mol	185.2 K

We see that H_2O, HF, and NH_3 each have higher boiling points than the same compound formed between hydrogen and the next element moving down its respective group, indicating that the former have greater intermolecular forces. This is because H_2O, HF, and NH_3 all exhibit hydrogen bonding, whereas the others do not. Furthermore, H_2O has a smaller molar mass than HF but partakes in more hydrogen bonds per molecule, so its boiling point is higher.

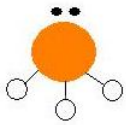
On Viscosity

The same effect that is seen on boiling point as a result of hydrogen bonding can also be observed in the viscosity of certain substances. Substances capable of forming hydrogen bonds tend to have a higher viscosity than those that do not form hydrogen bonds. Generally, substances that have the possibility for multiple hydrogen bonds exhibit even higher viscosities.

Factors preventing Hydrogen bonding

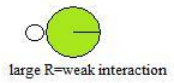
Electronegativity

Hydrogen bonding cannot occur without significant electronegativity differences between hydrogen and the atom it is bonded to. Thus, we see molecules such as PH_3, which do not participate in hydrogen bonding. PH_3 exhibits a trigonal pyramidal molecular geometry like that of ammonia, but unlike NH_3 it cannot hydrogen bond. This is due to the similarity in the electronegativities of phosphorous and hydrogen. Both atoms have an electronegativity of 2.1, and thus, there is no dipole moment. This prevents the hydrogen atom from acquiring the partial positive charge needed to hydrogen bond with the lone electron pair in another molecule. (see Polarizability)



Atom Size

The size of donors and acceptors can also affect the ability to hydrogen bond. This can account for the relatively low ability of Cl to form hydrogen bonds. When the radii of two atoms differ greatly or are large, their nuclei cannot achieve close proximity when they interact, resulting in a weak interaction.

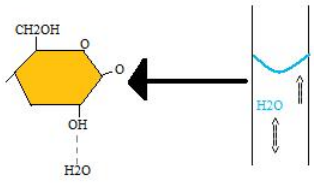


Hydrogen Bonding in Nature

Hydrogen bonding plays a crucial role in many biological processes and can account for many natural phenomena such as the Unusual properties of Water. In addition to being present in water, hydrogen bonding is also important in the water transport system of plants, secondary and tertiary protein structure, and DNA base pairing.

Plants

The cohesion-adhesion theory of transport in vascular plants uses hydrogen bonding to explain many key components of water movement through the plant's xylem and other vessels. Within a vessel, water molecules hydrogen bond not only to each other, but also to the cellulose chain that comprises the wall of plant cells. Since the vessel is relatively small, the attraction of the water to the cellulose wall creates a sort of capillary tube that allows for capillary action. This mechanism allows plants to pull water up into their roots. Furthermore, hydrogen bonding can create a long chain of water molecules, which can overcome the force of gravity and travel up to the high altitudes of leaves.



Proteins

Hydrogen bonding is present abundantly in the secondary structure of proteins, and also sparingly in tertiary conformation. The secondary structure of a protein involves interactions (mainly hydrogen bonds) between neighboring polypeptide backbones which contain nitrogen-hydrogen bonded pairs and oxygen atoms. Since both N and O are strongly electronegative, the hydrogen atoms bonded to nitrogen in one polypeptide backbone can hydrogen bond to the oxygen atoms in another chain and vice-versa. Though they are relatively weak, these bonds offer substantial stability to secondary protein structure because they repeat many times and work collectively.

In tertiary protein structure, interactions are primarily between functional R groups of a polypeptide chain; one such interaction is called a hydrophobic interaction. These interactions occur because of hydrogen bonding between water molecules around the hydrophobe that further reinforces protein conformation.

References

1. Brown, et al. Chemistry:The Central Science. 11th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2008.
2. Chang, Raymond. General Chemistry:The Essential Concepts. 3rd ed. New York: Mcgraw Hill, 2003
3. Petrucci, et al. General Chemistry: Principles & Modern Applications. 9th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2007.

1.9.4: Hydrogen Bonding is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Hydrogen Bonding** by Jim Clark, Jose Pietri is licensed CC BY-NC-SA 4.0.

1.9.5: Ion - Dipole Interactions

Polar molecules can interact with ions:

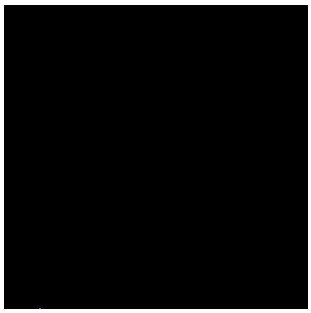


*Figure 1: Ion-Dipole Interactions (*Gary L Bertrand)

1.9.5: Ion - Dipole Interactions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Ion - Dipole Interactions** by Gary L Bertrand is licensed CC BY-NC-SA 4.0.

1.9.6: Ion - Induced Dipole Interactions

The charges on ions and the charge separation in polar molecules explain the fairly strong interactions between them, with very strong ion - ion interactions, weaker ion - dipole interactions, and considerably weaker dipole-dipole interactions. Even in a non-polar molecule, however, the valence electrons are moving around and there will occasionally be instances when more are on one side of the molecule than on the other. This gives rise to fluctuating or instantaneous dipoles:

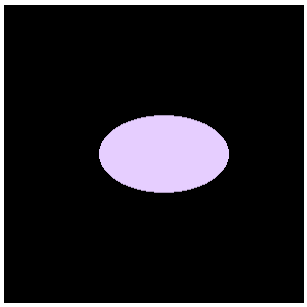


***Figure 1**: Fluctuating Dipole in a Non-polar Molecule*

These instantaneous dipoles may be induced and stabilized as an ion or a polar molecule approaches the non-polar molecule.

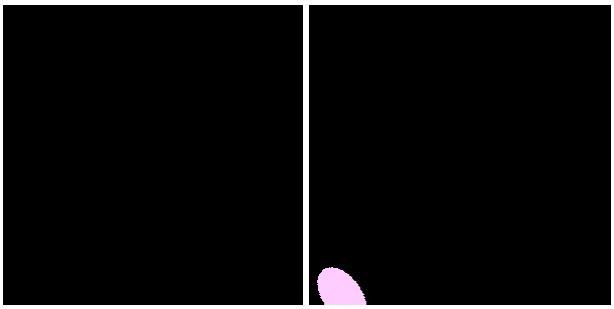


***Figure 2**: (Left) Ion - Induced Dipole Interaction. (Right) Dipole - Induced Dipole Interaction*

Contributors and Attributions

- Gary L Bertrand, Professor of Chemistry, University of Missouri-Rolla

1.9.6: Ion - Induced Dipole Interactions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Ion - Induced Dipole Interactions** is licensed CC BY-NC-SA 4.0.

1.9.7: Ion - Ion Interactions

The interactions between ions (ion - ion interactions) are the easiest to understand: like charges repel each other and opposite charges attract. These Coulombic forces operate over relatively long distances in the gas phase. The force depends on the product of the charges (Z_1, Z_2) divided by the square of the distance of separation (d^2):

$$F \propto \frac{-Z_1 Z_2}{d^2} \tag{1}$$

Two oppositely-charged particles flying about in a vacuum will be attracted toward each other, and the force becomes stronger and stronger as they approach until eventually they will stick together and a considerable amount of energy will be required to separate them.

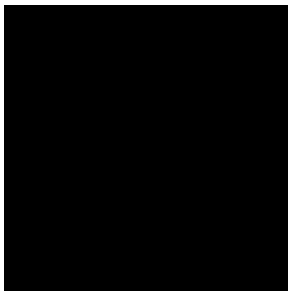


Figure 1: *Ion - Ion Interactions in the Gas Phase*

They form an *ion-pair*, a new particle which has a positively-charged area and a negatively-charged area. There are fairly strong interactions between these ion pairs and free ions, so that these the clusters tend to grow, and they will eventually fall out of the gas phase as a liquid or solid (depending on the temperature).

Contributors and Attributions

- Gary L Bertrand, Professor of Chemistry, University of Missouri-Rolla

1.9.7: Ion - Ion Interactions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Ion - Ion Interactions** is licensed CC BY-NC-SA 4.0.

1.9.8: 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.

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.

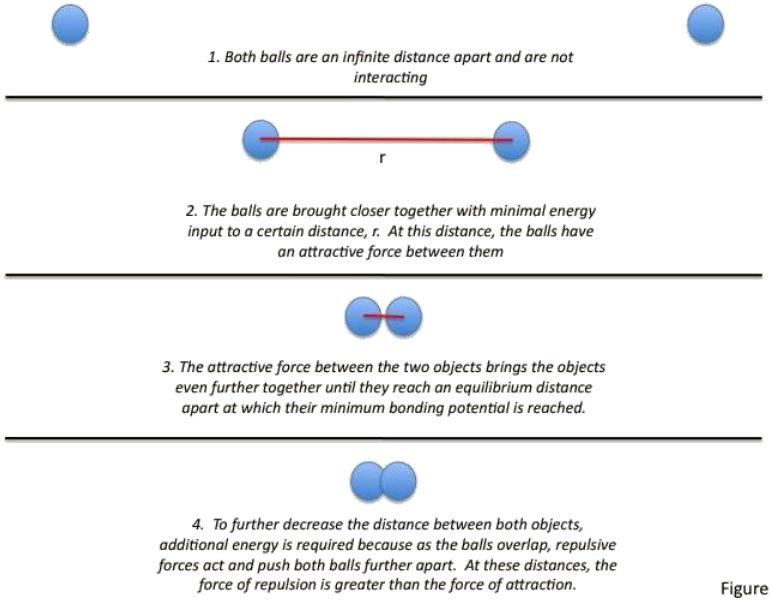


Figure A

This scenario is similar to that which takes place in neutral atoms and molecules and is often described by the **Lennard-Jones potential**.

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:

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{1.9.8.1}$$

or is sometimes expressed as:

$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}} \tag{1.9.8.2}$$

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 $1.9.8.1$). 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 $r = r_{min}$.

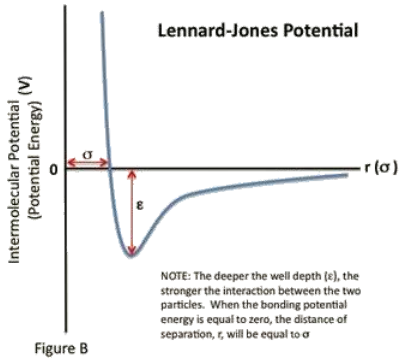


Figure 1.9.8.1: The Lennard-Jones potential describes both the attraction and repulsion between nonionic particles. The first part of the equation, the short-ranged $\sigma/r)^{12}$ term describes the repulsive forces between particles while the latter part of the equation and the longer-ranged σ/r^{6} term denotes the attraction.

Example 1.9.8.1: 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:

$$r = \sigma/2 = 4.10 \text{ Angstroms}/2 = 2.05 \text{ Angstroms}$$

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 1.9.8.2

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:

- $\epsilon = 0.997\ \text{kJ/mol}$,
- $\sigma = 3.40$ Angstroms, and
- the distance of separation, $r = 4.0$ Angstroms.

We plug these values into Equation 1.9.8.1 and solve as follows:

$$\begin{aligned} V &= 4(0.997\ \text{kJ/mol})\left[\left(\frac{3.40\ \text{Angstroms}}{4.0\ \text{Angstroms}}\right)^{12} - \left(\frac{3.40\ \text{Angstroms}}{4.0\ \text{Angstroms}}\right)^{6}\right] \\ &= 3.988(0.14 - 0.38) \\ &= 3.988(-0.24) \\ &= -0.96 kJ/mol \end{aligned}$$

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.

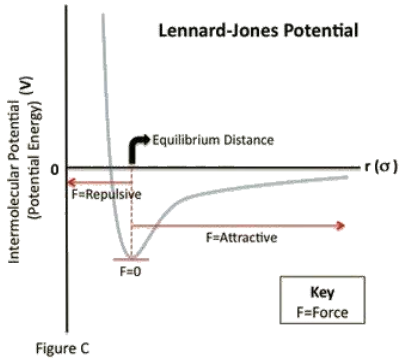


Figure C

Example 1.9.8.3

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 1.9.8.1

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 1.9.8.2

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.

References

1. Atkins, Peter and de Paula, Julio. *Physical Chemistry for the Life Sciences*. New York, N.Y. W. H. Freeman Company, 2006. (469-472).
2. Royer, Donald J. *Bonding Theory*. New York, NY.:McGraw-Hill, Inc., 1968.
3. Chang, Raymond. *Physical Chemistry for the Biosciences.* Sausalito, CA. University Science Books, 2005. (498-500)

1.9.8: Lennard-Jones Potential is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Lennard-Jones Potential** by Rabia Naeem is licensed CC BY 4.0.

1.9.9: London Dispersion Interactions

1.9.9: London Dispersion Interactions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

1.9.10: Polarizability

The term **polarizability** refers to the tendency of molecules to generate induced electric dipole moments when subjected to an electric field. It originates from the fact that nuclei and electrons are generally not fixed in space and that when molecules are subject to an electric field, the negatively charged electrons and positively charged atomic nuclei are subject to opposite forces and undergo charge separation. Polarizability allows us to better understand the interactions between nonpolar atoms and molecules and other electrically charged species, such as ions or polar molecules with dipole moments.

Introduction

Neutral nonpolar species have spherically symmetric arrangements of electrons in their electron clouds. When in the presence of an electric field, their electron clouds can be distorted (Figure 1.9.10.1). The ease of this distortion is the polarizability of the atom or molecule. The created distortion of the electron cloud causes the originally nonpolar molecule or atom to acquire a dipole moment. This induced dipole moment is related to the polarizability of the molecule or atom and the strength of the electric field by the following equation:

$$\mu_{ind} = \alpha E \tag{1.9.10.1}$$

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

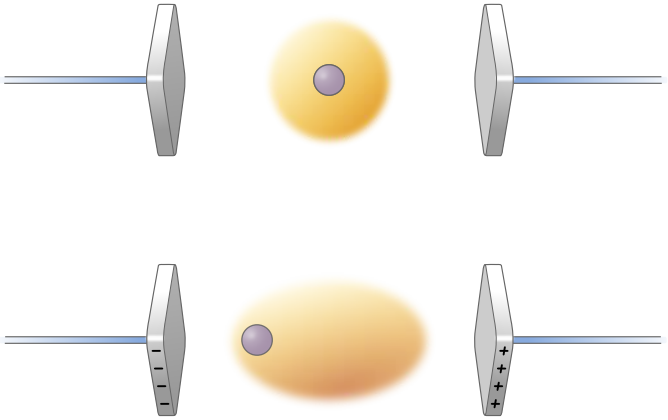


Figure 1.9.10.1: A neutral nonpolar species's electron cloud is distorted by an externally applied electric field. (top) Before the electric field is turned on the electron cloud is isotropically distributed. (bottom) Once the electric field is turned on, an induced dipole moment is generated. If we turn off the electric field, the dipole moment goes away (not shown). (CC BY-NC 4.0; Ümit Kaya via LibreTexts).

In general, polarizability correlates with the interaction between electrons and the nucleus. The amount of electrons in a molecule affects how tight the nuclear charge can control the overall charge distribution. Atoms with fewer electrons will have smaller, denser electron clouds, as there is a strong interaction between the few electrons in the atoms' orbitals and the positively charged nucleus. There is also less shielding in atoms with fewer electrons contributing to the stronger interaction of the outer electrons and the nucleus. With the electrons held tightly in place in these smaller atoms, these atoms are typically not easily polarized by external electric fields. In contrast, large atoms with many electrons, such as negative ions with excess electrons, are easily polarized. These atoms typically have very diffuse electron clouds and large atomic radii that limit the interaction of their external electrons and the nucleus.

Factors that Influence Polarizability

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

1. The greater the number of electrons, the less control the nuclear charge has on charge distribution, and thus the increased polarizability of the atom.

2. The greater the distance of electrons from nuclear charge, the less control the nuclear charge has on the charge distribution, and thus the increased polarizability of the atom.
3. Molecular orientation with respect to an electric field can affect polarizability (labeled Orientation-dependent), except for molecules that are: tetrahedral, octahedral or icosahedral (labeled Orientation-independent). This factor is more important for unsaturated molecules that contain areas of electron-dense regions, such as 2,4-hexadiene. Greatest polarizability in these molecules is achieved when the electric field is applied parallel to the molecule rather than perpendicular to the molecule.

Polarizability Influences Dispersion Forces

The dispersion force is the weakest intermolecular force. It is an attractive force that arises from surrounding temporary dipole moments in nonpolar molecules or species. These temporary dipole moments arise when there are instantaneous deviations in the electron clouds of the nonpolar species. Surrounding molecules are influenced by these temporary dipole moments and a sort of chain reaction results in which subsequent weak, dipole-induced dipole interactions are created (Figure 1.9.10.2).

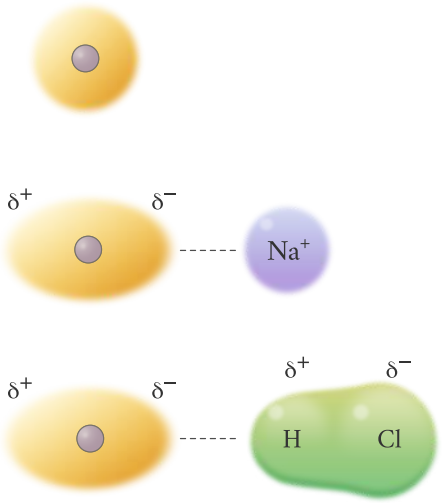


Figure 1.9.10.2: A neutral nonpolar species's electron cloud (yellow) can be distorted by the electric field of a nearby ion (e.g., sodium cation) or polar molecule (e.g., hydrogen chloride) to induce a dipole moment. (CC BY-NC 4.0; Ümit Kaya via LibreTexts).

These cumulative dipole-induced dipole interactions create attractive dispersion forces. Dispersion forces are the forces that make nonpolar substances condense to liquids and freeze into solids when the temperature is low enough.

Polarizability affects dispersion forces in the following ways:

- As polarizability *increases*, the dispersion forces also become *stronger*. Thus, molecules attract one another more *strongly* and melting and boiling points of covalent substances *increase* with *larger* molecular mass.
- Polarizability also affects dispersion forces through the molecular shape of the affected molecules. Elongated molecules with electrons that are delocalized (e.g., with double or triple bonds) will have some of those electrons easily shifted over a greater distance. This is manifested in an greater polarizability and thus greater dispersion forces.

Structure Dependence to Dispersion Forces

The influence of polarizability on the strength of the dispersion forces is also modulated by the 3-D structure of the molecules. For example, neo-pentane and n-pentane (Figure 1.9.10.3) exhibit comparable polarizabilities, but have different boiling points. The lack of polar bonding in both indicates that dispersion is the dominant interaction responsible in both substances. The higher boiling point of n-pentane indicates there are stronger intermolecular interactions.

Table 1.9.10.3: Properties of neopentane and n-pentane

molecule	Boiling Points (ºC)	α (Å^3)

molecule	Boiling Points (ºC)	α (Å^3)
neopentane	9.5	10.24
n-pentane	36.0	9.879

Both neopentane and n-pentane would be expected to exhibits comparable dispersion forces since they have comparable polarizabilities. However, the structure of the n-pentane molecule facilitates greater dispersion forces due to more contacts between n-pentane molecules. In contrast, neopentane has a smaller dispersion force since the interactions between neopentane are reduced since neopentane is more compact and symmetrical.

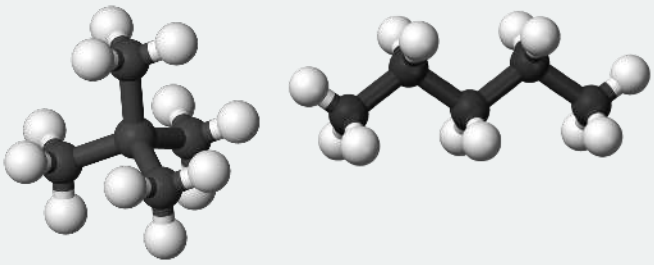


Figure 1.9.10.3: (left) Neopentane, an isomer of n-pentane, is an example of a more compact and less polarizable molecule. (right) n-Pentane is an example of an elongated molecule that is more easily polarized.

The relationship between polarizability and dispersion forces can be seen in the following equation, which can be used to quantify the interaction between two like nonpolar atoms or molecules (e.g., A with A):

$$V(r) = \frac{-3}{4}\frac{\alpha^2 I}{r^6} \tag{1.9.10.2}$$

where r is the distance between the atoms or molecules, I is the **first ionization energy** of the atom or molecule, and α is the polarizability constant expressed in units of m^3.

This expression of α is related to α' by the following equation:

$$\alpha' = \frac{\alpha}{4\pi\epsilon_o} \tag{1.9.10.3}$$

To quantify the interaction between unlike atoms or molecules (A and B), Equation 1.9.10.2becomes:

$$V(r) = \frac{-3}{2}\frac{I_A I_B}{I_A + I_B}\frac{\alpha_A \alpha_B}{r^6} \tag{1.9.10.4}$$

References

1. Petrucci, Ralph H., et al. General Chemistry: Principles and Modern Applications.Upper Saddle River, NJ: Prentice Hall, 2007
2. Chang, Raymond. "Chapter 13: Intermolecular Forces/ Ion-Induced Dipole and Dipole-Induced Dipole Interactions/ Dispersion, or London, Interactions." *Physical Chemistry for the Biosciences*. Sansalito, CA: University Science, 2005. 495-98. Print.
3. Housecroft, Catherine E., and Alan G. Sharpe. "Chapter 6: Structures and Energetics of Metallic and Ionic Solids." *Inorganic Chemistry*. Harlow [etc.: Prentice Hall, 2008. 173-74. Print.
4. Miessler, Gary L., and Donald A. Tarr. "Chapter 6: Acid-Base and Donor-Acceptor Chemistry." *Inorganic Chemistry*. Upper Saddle River, NJ: Pearson Education, 2004. 183-86. Print

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

- **Polarizability** by Dana Reusser, Delmar Larsen, Kelly Cox is licensed CC BY 4.0.

1.E: Gases (Exercises)

This page titled 1.E: Gases (Exercises) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

1.S: Gases (Summary)

Learning Objectives

After mastering the material covered in this chapter, one will be able to:

1. Understand the relationships demonstrated by and perform calculations using the empirical gas laws (Boyle's Law, Charles' Law, Gay-Lussac's Law, and Avogadro's Law, as well as the combined gas law.)
2. Understand and be able to utilize the ideal gas law in applications important in chemistry.
3. State the postulates of the Kinetic Molecular theory of gases.
4. Utilize the Maxwell and Maxwell-Boltzmann distributions to describe the relationship between temperature and the distribution of molecular speeds.
5. Derive an expression for pressure based on the predictions of the kinetic molecular theory for the collisions of gas molecules with the walls of a container.
6. Derive and utilize an expression for the frequency with which molecules in a gas sample collide with other molecules.
7. Derive and utilize an expression for the mean-free-path of molecules based on temperature, pressure, and collisional cross section.
8. Explain how the van der Waals (and other) model(s) allow for deviations from ideal behavior of gas samples.
9. Derive an expression for the Boyle temperature and interpret the results based on how a gas's behavior approaches that of an ideal gas.
10. Explain and utilize the Principle of Corresponding States.

Vocabulary and Concepts

- average
- Boyle temperature
- collisional cross section
- compression factor
- critical point
- critical temperature
- diffusion
- effusion
- empirical
- empirical gas laws
- frequency of collisions
- frequency of collisions with the wall
- gas law constant
- ideal gas law
- intermolecular potential
- isotherm
- Kinetic Molecular Theory
- Knudsen cell
- Leonard-Jones potential
- maximum probability
- Maxwell's distribution
- Maxwell-Boltzmann distribution
- mean free path
- normalization constant
- number density
- principle of corresponding states
- reduced variables
- root-mean-square
- Second Virial Coefficient
- Taylor Series Expansion

- van der Waals' equation
- Virial Equation

References

1. Avogadro, A. (1811). Essay on a Manner of Determining the Relative Masses of the Elementary Molecules of Bodies, and the Proportions in Which They Enter into These Compounds. *Journal de Physique, 73*, 58-76.
2. Bernoulli, D. (1738). *Hydronamica.*
3. Clausius, R. (1857). Ueber die Art der Bewegung, welche wir Wärme nennen. *Annalen der Physik, 176*(3), 353–379. doi:10.1002/andp.18571760302
4. Dieterici, C. (1899). *Ann. Phys. Chem., 69*, 685.
5. Einstein, A. (1905). Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen. *Annalen der Physik, 17*(8), 549-560. doi:10.1002/andp.19053220806
6. Encycolopedia, N. W. (2016). *Amedeao Avogadro*. Retrieved April 13, 2016, from New World Encycolpedia: http://www.newworldencyclopedia.org/...medeo_Avogadro
7. Fazio, F. (1992). Using Robert Boyle's Original Data in the Physics and Chemistry Classrooms. *Journal of College Science Teaching*, 363-365.
8. Guggenheim, E. A. (1945). Corresponding State for Perfect Liquids. *Journal of Chemical Physics, 13*, 253-261.
9. Hunter, M. (2004). *Robert Boyle (1627 - 91)*. Retrieved March 10, 2016, from The Robert Boyle Project: http://www.bbk.ac.uk/boyle/
10. *Johannes Diderik van der Waals - Biographical*. (2014). Retrieved March 12, 2016, from Nobelprize.org: http://www.nobelprize.org/nobel_priz...waals-bio.html
11. Maxwell, J. C. (1860). Illustrations of the dynamical theory of gases. Part 1. On the motions and collisions of perfectly elastic spheres. *Phil. Mag., XIX*, 19-32.
12. Maxwell, J. C. (1873). Molecules. *Nature, 417*, 903-915. doi:10.1038/417903a
13. Redlich, O., & Kwong, J. N. (1949). On the Thermodynamics of Solutions. V. An Equation of State. Fugacities of Gaseous Solutions. *Chemical Reviews, 44*(1), 233-244.
14. van der Waals, J. D. (1913). The law of corresponding states for different substances. *Proceedings of the Koninklijke Nederlandse Akademie van Wetenschappen*, (pp. 971-981).
15. van der Waals, J. D. (1967). The equation of state for gases and liquids. *Nobel Lectures in Physics 1901 - 1921*, 254-265.

This page titled 1.S: Gases (Summary) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **2.S: Gases (Summary)** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

2: The Boltzmann Factor and Partition Functions



2.1: n Factor
2.2: The Thermal Boltzman Distribution
2.3: The Average Ensemble Energy

Thumbnail: Image used with permission (Mysterioso [CC BY-SA 3.0 (https://creativecommons.org/licenses/by-sa/3.0)])

2: The Boltzmann Factor and Partition Functions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

2.1: The Boltzmann Factor

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.

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 $\left(v_{x_i}, v_{y_i}, v_{z_i}\right)$ 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:

$$\mathbf{v}_i(t) = \frac{d\mathbf{r}_i}{dt} = \dot{\mathbf{r}}_i \tag{2.1.2}$$

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:

$$\mathbf{F}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{2.1.3}$$

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.

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:

$$\frac{3}{2}NkT = \sum_{i=1}^{N} \frac{1}{2} m_i \mathbf{v}_i^2 \tag{2.1.4}$$

which can be solved to give:

$$T = \frac{2}{3k}\left(\frac{1}{N}\sum_{i=1}^{N} \frac{1}{2} m_i \mathbf{v}_i^2\right) \tag{2.1.5}$$

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.

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:

$$e^{-\beta E_i} \tag{2.1.6}$$

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 2.1.6 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.

References

1. Hakala, R.W. (1961). A new derivation of the Boltzmann distribution law. *Journal of Chemical Education.* **doi:** 10.1021/ed038p33.
2. Claudio Fazio, Onofrio R Battaglia, Ivan Guastella. (2012).Two experiments to approach the Boltzmann factor: chemical reaction and viscous flow. *European Journal of Physics*, *33*, *2*, *359*.doi:10.1088/0143-0807/33/2/359.

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?

2.1: The Boltzmann Factor is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **17.1: The Boltzmann Factor is used to Approximate the Fraction of Particles in a Large System** by Mark Tuckerman is licensed CC BY 4.0.

2.2: The Thermal Boltzman 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.

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:

$$W(a_1, a_2, \dots) = \frac{A!}{a_1! a_2! \dots}$$

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:

$$\begin{aligned} P_j &= \frac{\langle a_j \rangle}{A} \\ &= \frac{1}{A} \frac{\sum_a W(a) a_j(a)}{\sum_a W(a)} \end{aligned}$$

where the angle brackets indicate an ensemble average. Using this definition we can calculate any average property (i.e. any thermodynamic property):

$$\langle M \rangle = \sum_j M_j P_j \tag{2.2.1}$$

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:

$$E_{total} = \sum_j a_j e_j \tag{2.2.2}$$

where e_j is the energy of the jth quantum state.

- Constraint 2: Conservation of mass requires:

$$A = \sum_j a_j \tag{2.2.3}$$

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.

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 2.2.3):

$$A = \sum_j a_j$$

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:

$$\frac{a_j}{A} = e^a \sum_j e^{-\beta e_j} \tag{2.2.4}$$

Now we need to find the undetermined multipliers α and β.

The left hand side of Equation 2.2.4 is 1. Thus, we have:

$$P_j = \frac{a_j}{A} = \frac{e^{-\beta e_j}}{\sum_j e^{-\beta e_j}}$$

This determines a 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).

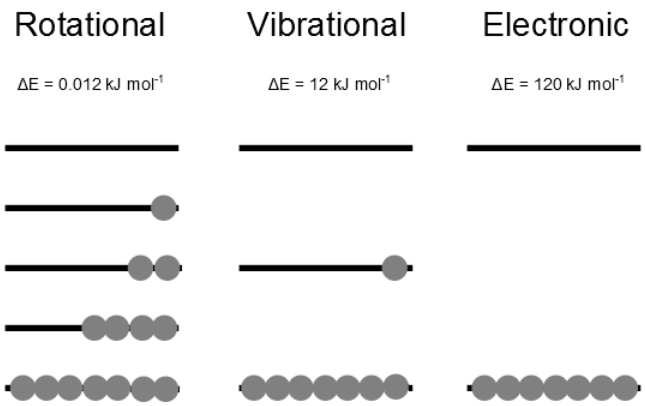


Figure 17.2.1 : At lower temperatures, the lower energy states are more greatly populated. At higher temperatures, there are more higher energy states populated, but each is populated less. k_BT 2.5 $kJ\ mol^{-1}$ at 300 K. (CC SA-BY 3.0; Mysterioso via Wikiversity).

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 2.2.1). 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.*

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).

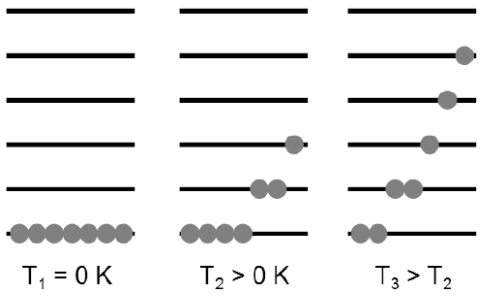


Figure 17.2.2 : At lower temperatures, the lower energy states are more greatly populated. At higher temperatures, there are more higher energy states populated, but each is populated less. (CC SA-BY 3.0; Mysterioso via Wikiversity).

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.

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

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?

2.2: The Thermal Boltzman Distribution is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **17.2: The Boltzmann Distribution represents a Thermally Equilibrated Distribution** by Jerry LaRue is licensed CC BY 4.0.

2.3: The Average Ensemble Energy

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:

$$P_i = \frac{n_i}{N} = \frac{e^{-E_i/kT}}{Q} \tag{2.3.2}$$

The average energy is obtained by multiplying E_i with its probability and summing over all i:

$$\langle E \rangle = \sum_i E_i P_i \tag{2.3.3}$$

> Equation 2.3.3 is the standard average over a distribution commonly found in quantum mechanics as expectation values. The quantum mechanical version of this Equation is
>
> $$\langle \psi | \hat{H} | \psi \rangle$$
>
> 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 2.3.3 can be solved by plugging in the Boltzmann distribution (Equation 2.3.2):

$$\langle E \rangle = \sum_i \frac{E_i e^{-E_i/kT}}{Q} \tag{2.3.4}$$

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:

$$\left(\frac{\partial \ln Q}{\partial T}\right) = \frac{1}{kT^2} \sum_i \frac{E_i e^{-E_i/kT}}{Q} \tag{2.3.5}$$

Comparing Equation 2.3.4 with 2.3.5, 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 $\langle E \rangle$.

2.3: The Average Ensemble Energy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **17.3: The Average Ensemble Energy is Equal to the Observed Energy of a System** by Jerry LaRue is licensed CC BY 4.0.

CHAPTER OVERVIEW

3: Quantum Review

3.1: The Schrödinger Equation and a Particle in a Box

3.1.1: The Schrödinger Equation

3.1.2: Linear Operators in Quantum Mechanics

3.1.3: The Schrödinger Equation is an Eigenvalue Problem

3.1.4: Wavefunctions Have a Probabilistic Interpretation

3.1.5: The Energy of a Particle in a Box is Quantized

3.1.6: Wavefunctions Must Be Normalized

3.1.7: The Average Momentum of a Particle in a Box is Zero

3.1.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions

3.1.9: A Particle in a Three-Dimensional Box

3.1.E: The Schrödinger Equation and a Particle in a Box (Exercises)

3.2: The Harmonic Oscillator and the Rigid Rotor

3.2.1: A Harmonic Oscillator Obeys Hooke's Law

3.2.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule

3.2.3: The Harmonic Oscillator Approximates Vibrations

3.2.4: The Harmonic Oscillator Energy Levels

3.2.5: The Harmonic Oscillator and Infrared Spectra

3.2.6: The Harmonic-Oscillator Wavefunctions involve Hermite Polynomials

3.2.7: Hermite Polynomials are either Even or Odd Functions

3.2.8: The Energy Levels of a Rigid Rotor

3.2.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule

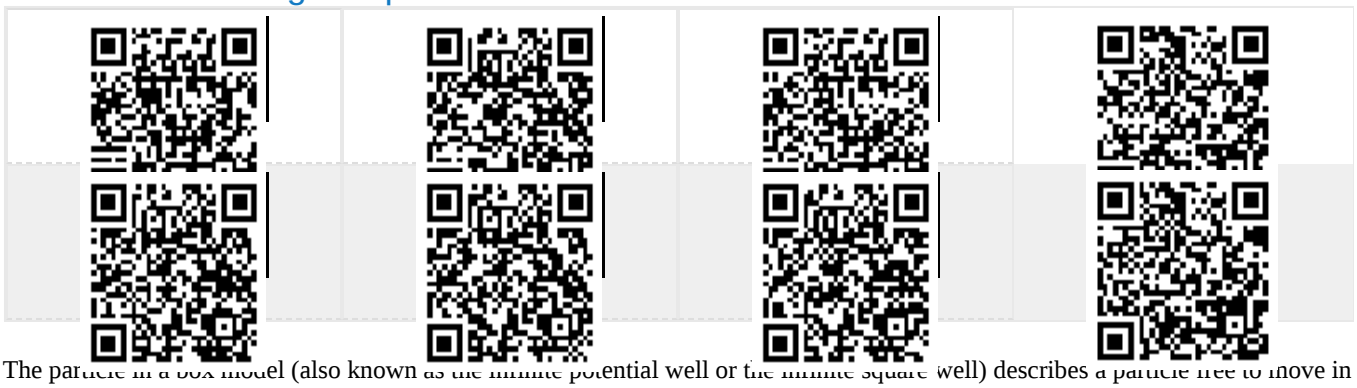
3.2.E: The Harmonic Oscillator and the Rigid Rotor (Exercises)

Thumbnail: Image used with permission (Darekk2 [CC BY-SA 3.0 (https://creativecommons.org/licenses/by-sa/3.0)])

3: Quantum Review is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

3.1: The Schrödinger Equation and a Particle in a Box



The particle in a box model (also known as the infinite potential well or the infinite square well) describes a particle free to move in a small space surrounded by impenetrable barriers. The model is mainly used as a hypothetical example to illustrate the differences between classical and quantum systems. In classical systems, for example a ball trapped inside a large box, the particle can move at any speed within the box and it is no more likely to be found at one position than another. However, when the well becomes very narrow (on the scale of a few nanometers), quantum effects become important. The particle may only occupy certain positive energy levels. The particle in a box model provides one of the very few problems in quantum mechanics which can be solved analytically, without approximations. This means that the observable properties of the particle (such as its energy and position) are related to the mass of the particle and the width of the well by simple mathematical expressions. Due to its simplicity, the model allows insight into quantum effects without the need for complicated mathematics. It is one of the first quantum mechanics problems taught in undergraduate physics courses, and it is commonly used as an approximation for more complicated quantum systems.

3.1.1: The Schrödinger Equation
3.1.2: Linear Operators in Quantum Mechanics
3.1.3: The Schrödinger Equation is an Eigenvalue Problem
3.1.4: Wavefunctions Have a Probabilistic Interpretation
3.1.5: The Energy of a Particle in a Box is Quantized
3.1.6: Wavefunctions Must Be Normalized
3.1.7: The Average Momentum of a Particle in a Box is Zero
3.1.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions
3.1.9: A Particle in a Three-Dimensional Box
3.1.E: The Schrödinger Equation and a Particle in a Box (Exercises)

Thumbnail: The quantum wavefunction of a particle in a 2D infinite potential well of dimensions L_x and L_y. The wavenumbers are $n_x = 2$ and $n_y = 2$. Image used with permission (Public Domain; Inductiveload).

3.1: The Schrödinger Equation and a Particle in a Box is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

3.1.1: The Schrödinger Equation

Learning Objectives

- To be introduced to the general properties of the Schrödinger equation and its solutions.

De Broglie's doctoral thesis, defended at the end of 1924, created a lot of excitement in European physics circles. Shortly after it was published in the fall of 1925 Pieter Debye, Professor of Theoretical Physics at Zurich and Einstein's successor, suggested to Erwin Schrödinger that he give a seminar on de Broglie's work. Schrödinger gave a polished presentation, but at the end Debye remarked that he considered the whole theory rather childish: why should a wave confine itself to a circle in space? It wasn't as if the circle was a waving circular string, real waves in space diffracted and diffused, in fact they obeyed three-dimensional wave equations, and that was what was needed. This was a direct challenge to Schrödinger, who spent some weeks in the Swiss mountains working on the problem and constructing his equation. There is no rigorous derivation of Schrödinger's equation from previously established theory, but it can be made very plausible by thinking about the connection between light waves and photons, and construction an analogous structure for de Broglie's waves and electrons (and, later, other particles).

The Schrödinger Equation: A Better Approach

While the Bohr model is able to predict the allowed energies of any single-electron atom or cation, it by no means, a general approach. Moreover, it relies heavily on classical ideas, clumsily grafting quantization onto an essentially classical picture, and therefore, provides no real insights into the true quantum nature of the atom. Any rule that might be capable of predicting the allowed energies of a quantum system must also account for the *wave-particle duality* and implicitly include a wave-like description for particles. Nonetheless, we will attempt a heuristic argument to make the result at least plausible. In classical electromagnetic theory, it follows from Maxwell's equations that each component of the electric and magnetic fields in vacuum is a solution of the 3-D wave equation for electronmagnetic waves:

$$\nabla^2 \Psi(x,y,z,t) - \frac{1}{c^2}\frac{\partial^2 \Psi(x,y,z,t)}{\partial t^2} = 0 \tag{3.1.1.1}$$

The wave equation in Equation 3.1.1.1 is the three-dimensional analog to the wave equation presented earlier (Equation 2.1.1) with the velocity fixed to the known speed of light: c. Instead of a partial derivative $\dfrac{\partial^2}{\partial x^2}$ in one dimension, the Laplacian (or "del-squared") operator is introduced:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{3.1.1.2}$$

Corresponding, the solution to this 3D equation wave equation is a function of *four* independent variables: x, y, z, and t and is generally called the **wavefunction** ψ.

We will attempt now to create an analogous equation for de Broglie's matter waves. Accordingly, let us consider a only 1-dimensional wave motion propagating in the *x*-direction. At a given instant of time, the form of a wave might be represented by a function such as

$$\Psi(x) = f\left(\frac{2\pi x}{\lambda}\right) \tag{3.1.1.3}$$

where $f(\theta)$ represents a sinusoidal function such as $\sin\theta$, $\cos\theta$, $e^{i\theta}$, $e^{-i\theta}$ or some linear combination of these. The most suggestive form will turn out to be the complex exponential, which is related to the sine and cosine by Euler's formula

$$e^{\pm i\theta} = \cos\theta \pm i\sin\theta \tag{3.1.1.4}$$

Each of the above is a periodic function, its value repeating every time its argument increases by 2π. This happens whenever x increases by one wavelength λ. At a fixed point in space, the time-dependence of the wave has an analogous structure:

$$T(t) = f(2\pi\nu t) \tag{3.1.1.5}$$

where ν gives the number of cycles of the wave per unit time. Taking into account both x and t dependence, we consider a wavefunction of the form

$$\Psi(x,t) = exp\left[2\pi i\left(\frac{x}{\lambda} - \nu t\right)\right] \tag{3.1.1.6}$$

representing waves traveling from left to right. Now we make use of the Planck formula ($E = h\nu$) and de Broglie formulas ($p = \frac{h}{\lambda}$) to replace ν and λ by their particle analogs. This gives

$$\Psi(x,t) = \exp\left[\frac{i(px - Et)}{\hbar}\right] \tag{3.1.1.7}$$

where

$$\hbar \equiv \frac{h}{2\pi} \tag{3.1.1.8}$$

Since Planck's constant occurs in most formulas with the denominator 2π, the $\hbar$ symbol was introduced by Paul Dirac. Equation 3.1.1.5represents in some way the wavelike nature of a particle with energy E and momentum p. The time derivative of Equation 3.1.1.7gives

$$\frac{\partial \Psi}{\partial t} = -\left(\frac{iE}{\hbar}\right)\exp\left[\frac{i(px - Et)}{\hbar}\right] \tag{3.1.1.9}$$

Thus from a simple comparison of Equations 3.1.1.7and 3.1.1.9

$$i\hbar\frac{\partial \Psi}{\partial t} = E\Psi \tag{3.1.1.10}$$

or analogously differentiation of Equation 3.1.1.9with respect to x

$$-i\hbar\frac{\partial \Psi}{\partial x} = p\Psi \tag{3.1.1.11}$$

and then the second derivative

$$-\hbar^2\frac{\partial^2 \Psi}{\partial x^2} = p^2\Psi \tag{3.1.1.12}$$

The energy and momentum for a *nonrelativistic* free particle (i.e., all energy is kinetic with no potential energy involved) are related by

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \tag{3.1.1.13}$$

Substituting Equations 3.1.1.12and 3.1.1.10into Equation 3.1.1.13shows that $\Psi(x,t)$ satisfies the following partial differential equation

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} \tag{3.1.1.14}$$

Equation 3.1.1.14is the applicable differential equation describing the wavefunction of a *free particle* that is not bound by any external forces or equivalently not in a region where its potential energy $V(x,t)$ varies.

For a particle with a non-zero potential energy $V(x)$, the total energy E is then a sum of kinetics and potential energies

$$E = \frac{p^2}{2m} + V(x) \tag{3.1.1.15}$$

we postulate that Equation 3.1.1.3for matter waves can be generalized to

$$\underbrace{i\hbar\frac{\partial \Psi(x,t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\Psi(x,t)}_{\text{time-dependent Schrödinger equation in 1D}} \tag{3.1.1.16}$$

For matter waves in three dimensions, Equation 3.1.1.6is then expanded

$$\underbrace{i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t)=\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\Psi(\vec{r},t)}_{\text{time-dependent Schrödinger equation in 3D}} \tag{3.1.1.17}$$

Here the potential energy and the wavefunctions Ψ depend on the three space coordinates x, y, z, which we write for brevity as $\vec{r}$. Notice that the potential energy is assumed to depend on position only and not time (i.e., particle motion). This is applicable for conservative forces that a potential energy function $V(\vec{r})$ can be formulated.

The Laplacian Operator

The three second derivatives in parentheses together are called the Laplacian operator, or del-squared,

$$\begin{aligned}\nabla^2 &= \nabla\cdot\nabla \\ &= \left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\end{aligned} \tag{3.1.1.18}$$

with the del operator,

$$\nabla=\left(\vec{x}\frac{\partial}{\partial x}+\vec{y}\frac{\partial}{\partial y}+\vec{z}\frac{\partial}{\partial z}\right) \tag{3.1.1.19}$$

Remember from basic calculus that when the del operator is direclty operates on a field (e.g, $\nabla f(x,y,x)$), it denotes the gradient (i.e, the locally steepest slope) of the field. The symbols with arrows in Equation 3.1.1.19 are unit vectors.

Equation 3.1.1.17 is the *time-dependent Schrödinger* equation describing the wavefunction amplitude $\Psi(\vec{r},t)$ of matter waves associated with the particle within a specified potential $V(\vec{r})$. Its formulation in 1926 represents the start of modern quantum mechanics (Heisenberg in 1925 proposed another version known as matrix mechanics).

For *conservative* systems, the energy is a constant, and the time-dependent factor from Equation 3.1.1.7 can be separated from the space-only factor (via the *Separation of Variables* technique discussed in Section 2.2)

$$\Psi(\vec{r},t)=\psi(\vec{r})e^{-iEt/\hbar} \tag{3.1.1.20}$$

where $\psi(\vec{r})$ is a wavefunction dependent (or time-independent) wavefuction that only depends on space coordinates. Putting Equation 3.1.1.20 into Equation 3.1.1.17 and cancelling the exponential factors, we obtain the time-independent Schrödinger equation:

$$\underbrace{\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\psi(\vec{r})=E\psi(\vec{r})}_{\text{time-independent Schrödinger equation}} \tag{3.1.1.21}$$

The overall form of the Equation 3.1.1.21 is not unusual or unexpected as it uses the principle of the **conservation of energy**. Most of our applications of quantum mechanics to chemistry will be based on this equation (with the exception of spectroscopy). The terms of the time-independent Schrödinger equation can then be interpreted as total energy of the system, equal to the system kinetic energy plus the system potential energy. In this respect, it is just the same as in classical physics.

Time Dependence to the Wavefunctions

Notice that the wavefunctions used with the time-independent Schrödinger equation (i.e., $\psi(\vec{r})$) do not have explicit t dependences like the wavefunctions of time-dependent analog in Equation 3.1.1.17 (i.e., $\Psi(\vec{r},t)$). That does **not imply** that there is no time dependence to the wavefunction. Equation 3.1.1.20 argues that the time-dependent (i.e., full spatial and temporal) wavefunction ($\Psi(\vec{r},t)$) differs from from the time-independent (i.e., spatial only) wavefunction $\psi(\vec{r})$ by a "phase factor" of constant magnitude. Using the Euler relationship in Equation 3.1.1.4, the total wavefunction above can be expanded

$$\Psi(\vec{r},t)=\psi(\vec{r})\left(\cos\frac{Et}{\hbar}-i\,\sin\frac{Et}{\hbar}\right) \tag{3.1.1.22}$$

This means the total wavefunction has a **complex behavior** with a real part and an imaginary part. Moreover, using the trigonometry identity $\sin(\theta) = \cos(\theta - \pi/2)$ Equation 3.1.1.22can further simplified to

$$\Psi(\vec{r},t) = \psi(\vec{r}) \cos\left(\frac{Et}{\hbar}\right) - i\psi(\vec{r}) \cos\left(\frac{Et}{\hbar} - \frac{\pi}{2}\right)$$

This shows that both the real and the imaginary components of the total wavefunction oscillate, the imaginary part of the total wavefunction oscillates **out of phase** by $\frac{\pi}{2}$ with respect to the real part.

Note that while all wavefunctions have a time-dependence, that dependence may not impact in simple quantum problems as the next sections discuss and can often be ignored.

Before we embark on this, however, let us pause to comment on the validity of quantum mechanics. Despite its weirdness, its abstractness, and its strange view of the universe as a place of randomness and unpredictability, quantum theory has been subject to intense experimental scrutiny. It has been found to agree with experiments to better than $10^{-10}\%$ for all cases studied so far. When the Schrödinger Equation is combined with a quantum description of the electromagnetic field, a theory known as *quantum electrodynamics*, the result is one of the most accurate theories of matter that has ever been put forth. Keeping this in mind, let us forge ahead in our discussion of the quantum universe and how to apply quantum theory to both model and real situations.

3.1.1: The Schrödinger Equation is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **3.1: The Schrödinger Equation** by Michael Fowler is licensed CC BY-NC-SA 4.0.

3.1.2: Linear Operators in Quantum Mechanics

Learning Objectives

- Classical-Mechanical quantities are represented by linear operators in Quantum Mechanics
- Understand that "algebra" of scalars and functions do not always to operators (specifically the commutative property)

The bracketed object in the time-independent Schrödinger Equation (in 1D)

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \tag{3.1.2.1}$$

is called an *operator*. An operator is a generalization of the concept of a function applied to a function. Whereas a function is a rule for turning one number into another, an operator is a rule for turning one function into another. For the time-independent Schrödinger Equation, the operator of relevance is the Hamiltonian operator (often just called the Hamiltonian) and is the most ubiquitous operator in quantum mechanics.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})$$

We often (but not always) indicate that an object is an operator by placing a 'hat' over it, eg, $\hat{H}$. So time-independent Schrödinger Equation can then be simplified from Equation 3.1.2.1 to

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r}) \tag{3.1.2.2}$$

Equation 3.1.2.2 says that the Hamiltonian operator operates on the wavefunction to produce the energy, which is a scalar (i.e., a number, a quantity and observable) times the wavefunction. Such an equation, where the operator, operating on a function, produces a constant times the function, is called an **eigenvalue equation**. The function is called an eigenfunction, and the resulting numerical value is called the eigenvalue. Eigen here is the German word meaning self or own. We will discuss this in detail in later Sections.

Fundamental Properties of Operators

Most properties of operators are straightforward, but they are summarized below for completeness.

1. The sum and difference of two operators $\hat{A}$ and $\hat{B}$ are given by

$$(\hat{A} \pm \hat{B})f = \hat{A}f \pm \hat{B}f$$

2. The product of two operators is defined by

$$\hat{A}\hat{B}f \equiv \hat{A}[\hat{B}f]$$

3. Two operators are equal if

$$\hat{A}f = \hat{B}f$$

for **all** functions f.

4. The identity operator $\hat{1}$ does nothing (or multiplies by 1)

$$\hat{1}f = f$$

5. The n-th power of an operator $\hat{A}^n$ is defined as n successive applications of the operator, e.g.

$$\hat{A}^2 f = \hat{A}\hat{A}f$$

6. The *associative law* holds for operators

$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C}$$

7. The *commutative law* does **not** generally hold for operators. In general, but not always,

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}. \tag{3.1.2.3}$$

To help identify if the inequality in Equation 3.1.2.3 holds for any two specific operators, we define the commutator.

Definition: The Commutator

It is convenient to define the **commutator** of $\hat{A}$ and $\hat{B}$

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

If $\hat{A}$ and $\hat{B}$ commute, then

$$[\hat{A}, \hat{B}] = 0.$$

If the commutator is not zero, the order of operating matters and the operators are said to "not commute." Moreover, this property applies

$$[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}].$$

Linear Operators

The action of an operator that turns the function $f(x)$ into the function $g(x)$ is represented by

$$\hat{A}f(x) = g(x) \tag{3.1.2.4}$$

The most common kind of operator encountered are *linear operators* which satisfies the following two conditions:

$$\underset{\text{Condition A}}{\hat{O}(f(x)+g(x)) = \hat{O}f(x) + \hat{O}g(x)} \tag{3.1.2.5}$$

and

$$\underset{\text{Condition B}}{\hat{O}cf(x) = c\hat{O}f(x)} \tag{3.1.2.6}$$

where

- $\hat{O}$ is a linear operator,
- c is a constant that can be a complex number ($c = a + ib$), and
- $f(x)$ and $g(x)$ are functions of x

If an operator fails to satisfy either Equations 3.1.2.5 or 3.1.2.6 then it is not a linear operator.

Example 3.2.1

Is this operator $\hat{O} = -i\hbar\dfrac{d}{dx}$ linear?

Solution

To confirm is an operator is linear, both conditions in Equation 3.1.2.6 must be demonstrated.

Condition A (Equation 3.1.2.5):

$$\hat{O}(f(x)+g(x)) = -i\hbar\frac{d}{dx}(f(x)+g(x))$$

From basic calculus, we know that we can use the **sum rule for differentiation**

$$\begin{aligned}\hat{O}(f(x)+g(x)) &= -i\hbar\frac{d}{dx}f(x) - i\hbar\frac{d}{dx}g(x) \\ &= \hat{O}f(x) + \hat{O}g(x) \quad \checkmark\end{aligned}$$

Condition A is confirmed. Does Condition B (Equation 3.1.2.6) hold?

$$\hat{O}cf(x) = -i\hbar\frac{d}{dx}cf(x)$$

Also from basic calculus, this can be factored out of the derivative

$$\hat{O}cf(x) = -ci\hbar\frac{d}{dx}f(x)$$
$$= c\hat{O}f(x) \quad \checkmark$$

Yes. This operator is a linear operator (this is the linear momentum operator).

? Exercise 3.2.1

Confirm if the square root operator $\sqrt{f(x)}$ linear or not?

Answer

To confirm is an operator is linear, both conditions in Equations 3.1.2.5and 3.1.2.6must be demonstrated. Let's look first at Condition B.

Does Condition B (Equation 3.1.2.6) hold?

$$\hat{O}cf(x) = c\hat{O}f(x)$$
$$\sqrt{cf(x)} \neq c\sqrt{f(x)}$$

Condition B does not hold, therefore the square root operator is not linear.

The most operators encountered in quantum mechanics are *linear operators*.

Hermitian Operators

An important property of operators is suggested by considering the Hamiltonian for the particle in a box:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

Let $f(x)$ and $g(x)$ be arbitrary functions which obey the same boundary values as the eigenfunctions of $\hat{H}$ (e.g., they vanish at $x = 0$ and $x = a$). Consider the integral

$$\int_0^a f(x)\,\hat{H}\,g(x)\,\mathrm{d}x = -\frac{\hbar^2}{2m}\int_0^a f(x)\,g''(x)\,\mathrm{d}x$$

Now, using integration by parts,

$$\int_0^a f(x)\,g''(x)\,\mathrm{d}x = -\int_0^a f'(x)\,g'(x)\,\mathrm{d}x + f(x)\,g'(x)\Big|_0^a \tag{3.1.2.7}$$

The boundary terms vanish by the assumed conditions on f and g. A second integration by parts transforms Equation 3.1.2.7to

$$\int_0^a f''(x)\,g(x)\,\mathrm{d}x \; - \; f'(x)\,g(x)\Big|_0^a$$

It follows therefore that

$$\int_0^a f(x)\,\hat{H}\,g(x)\,\mathrm{d}x = \int_0^a g(x)\,\hat{H}\,f(x)\,\mathrm{d}x$$

An obvious generalization for complex functions will read

$$\int_0^a f^*(x)\,\hat{H}\,g(x)\,\mathrm{d}x = \left(\int_0^a g^*(x)\,\hat{H}\,f(x)\,\mathrm{d}x\right)^*$$

In mathematical terminology, an operator $\hat{A}$ for which

$$\int f^* \, \hat{A} \, g \, \mathrm{d}\tau = \left(\int g^* \, \hat{A} \, f \, \mathrm{d}\tau \right)^*$$

for all functions f and g which obey specified boundary conditions is classified as *Hermitian* or *self-adjoint*. Evidently, the Hamiltonian is a **Hermitian operator**. It is postulated that *all* quantum-mechanical operators that represent dynamical variables are Hermitian. The term is also used for specific times of matrices in linear algebra courses.

> *All quantum-mechanical operators that represent dynamical variables are Hermitian.*

3.1.2: Linear Operators in Quantum Mechanics is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **3.2: Linear Operators in Quantum Mechanics** by S. M. Blinder is licensed CC BY-NC-SA 4.0.

3.1.3: The Schrödinger Equation is an Eigenvalue Problem

Learning Objectives

- To recognize that each quantum mechanical observable is determined by solve by an eigenvalue problem with different operators for different observable
- Confirm if a specific wavefunction is an eigenfunction of a specific operation and extract the corresponding obserable (the eigenvalue)
- To recognize that the Schrödinger equation, just like all measurable, is also an eigenvalue problem with the eigenvalue ascribed to total energy
- Identity and manipulate several common quantum mechanical operators

As per the definition, an operator acting on a function gives another function, however a special case occurs when the generated function is proportional to the original

$$\hat{A}\psi \propto \psi \tag{3.1.3.1}$$

This case can be expressed in terms of a equality by introducing a proportionality constant k

$$\hat{A}\psi = k\psi \tag{3.1.3.2}$$

Not all functions will solve an equation like in Equation 3.1.3.2 If a function does, then ψ is known as an **eigenfunction** and the constant k is called its **eigenvalue** (these terms are hybrids with German, the purely English equivalents being "characteristic function" and "characteristic value", respectively). Solving eigenvalue problems are discussed in most linear algebra courses.

In quantum mechanics, every experimental measurable a is the eigenvalue of a specific operator ($\hat{A}$):

$$\hat{A}\psi = a\psi \tag{3.1.3.3}$$

The a eigenvalues represents the possible measured values of the $\hat{A}$ operator. Classically, a would be allowed to vary continuously, but in quantum mechanics, a typically has only a sub-set of allowed values (hence the quantum aspect). Both time-dependent and time-independent Schrödinger equations are the best known instances of an eigenvalue equations in quantum mechanics, with its eigenvalues corresponding to the allowed energy levels of the quantum system.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \tag{3.1.3.4}$$

The object on the left that acts on $\psi(x)$ is an example of an **operator**.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right] \tag{3.1.3.5}$$

In effect, what is says to do is "take the second derivative of $\psi(x)$, multiply the result by $-(\hbar^2/2m)$ and then add $V(x)\psi(x)$ to the result of that." Quantum mechanics involves many different types of operators. This one, however, plays a special role because it appears on the left side of the Schrödinger equation. It is called the **Hamiltonian** *operator* and is denoted as

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \tag{3.1.3.6}$$

Therefore, the time-dependent Schrödinger equation can be (and it more commonly) written as

$$\hat{H}\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t) \tag{3.1.3.7}$$

and the time-independent Schrödinger equation

$$\hat{H}\psi(x) = E\psi(x) \tag{3.1.3.8}$$

Note that the functional form of Equation 3.1.3.8 is the same as the general eigenvalue equation in Equation 3.1.3.2 where the eigenvalues are the (allowed) total energies (E).

The Hamiltonian, named after the Irish mathematician Hamilton, comes from the formulation of Classical Mechanics that is based on the total energy, $H = T + V$, rather than Newton's second law, $F = ma$. Equation 3.1.3.8 says that the Hamiltonian operator operates on the wavefunction to produce the energy E, which is a scalar (e.g., expressed in Joules) times the wavefunction.

Correspondence Principle

Note that $\hat{H}$ is derived from the classical energy $p^2/2m + V(x)$ simply by replacing $p \rightarrow -i\hbar(d/dx)$. This is an example of the **Correspondence Principle** initially proposed by Niels Bohr that states that the behavior of systems described by quantum theory reproduces classical physics in the limit of large quantum numbers.

It is a general principle of Quantum Mechanics that there is an operator for every physical observable. A physical observable is anything that can be measured. If the wavefunction that describes a system is an eigenfunction of an operator, then the value of the associated observable is extracted from the eigenfunction by operating on the eigenfunction with the appropriate operator. The value of the observable for the system is then the eigenvalue, and the system is said to be in an eigenstate. Equation 3.1.3.8 states this principle mathematically for the case of energy as the observable. If the wavefunction is not the eigenfunction of the operation, then the measurement will give an eigenvalue (by definition), but not necessarily the same one for each measurement (this will be discussed in more detail in later section).

Common Operators

Although we could theoretically come up with an infinite number of operators, in practice there are a few which are much more important than any others.

- **Linear Momentum:**

  The linear momentum operator of a particle moving in one dimension (the x-direction) is

  $$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{3.1.3.9}$$

  and can be generalized in three dimensions:

  $$\hat{\vec{p}} = -i\hbar\nabla \tag{3.1.3.10}$$

- **Position**

  The position operator of a particle moving in one dimension (the x-direction) is

  $$\hat{x} = x \tag{3.1.3.11}$$

  and can be generalized in three dimensions:

  $$\hat{\vec{r}} = \vec{r} \tag{3.1.3.12}$$

  where $\vec{r} = (x, y, z)$.

- **Kinetic Energy**

  Classically, the kinetic energy of a particle moving in one dimension (the x-direction), in terms of momentum, is

  $$KE_{classical} = \frac{p_x^2}{2m} \tag{3.1.3.13}$$

  Quantum mechanically, the corresponding kinetic energy operator is

  $$\hat{KE}_{quantum} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{3.1.3.14}$$

  and can be generalized in three dimensions:

  $$\hat{KE}_{quantum} = -\frac{\hbar^2}{2m}\nabla^2 \tag{3.1.3.15}$$

- **Angular Momentum:**

Angular momentum requires a more complex discussion, but is the cross product of the position operator $\hat{\vec{r}}$ and the momentum operator $\hat{p}$

$$\hat{\vec{L}} = -i\hbar(\vec{r} \times \nabla) \tag{3.1.3.16}$$

- **Hamiltonian:**

  The Hamiltonian operator corresponds to the total energy of the system

  $$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{3.1.3.17}$$

  and it represents the total energy of the particle of mass m in the potential $V(x)$. The Hamiltonian in three dimensions is

  $$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \tag{3.1.3.18}$$

- **Total Energy:**

  The energy operator from the time-dependent Schrödinger equation

  $$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hat{H}\Psi(x,t) \tag{3.1.3.19}$$

  The right hand side of Equation 3.1.3.6 is the Hamiltonian Operator. In addition determining system energies, the Hamiltonian operator dictates the time evolution of the wavefunction

  $$\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \tag{3.1.3.20}$$

  This aspect will be discussed in more detail elsewhere.

Eigenstate, Eigenvalues, Wavefunctions, Measurables, and Observables

In general, the **wavefunction** gives the "state of the system" for the system under discussion. It stores all the information available to the observer about the system. Often in discussions of quantum mechanics, the terms *eigenstate* and *wavefunction* are used interchangeably. The term eigenvalue is used to designate the value of measurable quantity associated with the wavefunction.

- If you want to measure the energy of a particle, you have to operate on the wavefunction with the Hamiltonian operator (Equation 3.1.3.6).
- If you want to measure the momentum of a particle, you have to operate on wavefunction with the momentum operator (Equation 3.1.3.9).
- If you want to measure the position of a particle, you have to operate on wavefunction with the position operator (Equation 3.1.3.11).
- If you want to measure the kinetic energy of a particle, you have to operate on wavefunction with the kinetic energy operator (Equation 3.1.3.14).

When discussing the eigenstates of the Hamiltonian ($\hat{H}$), the associated eigenvalues represent energies and within the context of the momentum operators, the associated eigenvalues refer to the momentum of the particle. However, not all wavefunctions (ψ) are eigenstates of an operator (ϕ) – and if they are not, they can be usually be written as superpositions of eigenstates.

$$\psi = \sum_i c_i\phi_i$$

This will be discussed in more detail in later sections.

While the wavefunction may not be the eigenstate of an observable, when that operator operates on that wavefunction, the wavefunction **becomes** an eigenstate of that observable and only eigenvalues can be observed. Another way to say this is that the wavefunction "collapses" into an eigenstate of the observable. Because quantum mechanical operators have different forms, their associated eigenstates are similarly often (i.e., most of the time) different. For example, when a wavefunction is an eigenstate of total energy, it will **not** be an eigenstate of momentum.

> *If a wavefunction is an eigenstate of one operator, (e.g., momentum), that state is not necessarily an eigenstate of a different operator (e.g., energy), although not always.*

The wavefunction immediately after a measurement is an eigenstate of the operator associated with this measurement. What happens to the wavefunction after the measurement is a different topic.

Example 3.3.1

Confirm that the following wavefunctions are eigenstates of linear momentum and kinetic energy (or neither or both):

a. $\psi = A\sin(ax)$
b. $\psi = Ne^{-ix/\hbar}$

Strategy

This question is asking if the eigenvalue equation holds for the operators and these wavefunctions. This is just asking if these wavefunctions are solutions to Equation 3.1.3.2using the operators in Equations 3.1.3.9and 3.1.3.14, i.e., are these equations true:

$$\hat{p}_x\psi = p_x\psi \tag{3.1.3.21}$$

$$\hat{KE}\psi = KE\psi \tag{3.1.3.22}$$

where p_x and KE are the measurables (eigenvalues) for these operators.

Solution a

Let's evaluate the left side of the linear momentum eigenvalue problem (Equation 3.1.3.21)

$$-i\hbar\frac{\partial}{\partial x}A\sin(ax) = -i\hbar Aa\cos(ax)$$

and compare to the the right side of Equation 3.1.3.21

$$p_x A\sin(ax)$$

These are **not** the same so this wavefunction is not an eigenstate of momentum.

Let's look at the left side of the kinetic energy eigenvalue problem (Equation 3.1.3.22)

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}A\sin(ax) &= -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}Aa\cos(ax) \\ &= +\frac{\hbar^2}{2m}Aa^2\sin(ax) \end{aligned}$$

and compare to the right side

$$KEA\sin(ax)$$

These are same, so this specific wavefunction is an eigenstate of kinetic energy. Moreover, the measured kinetic energy will be

$$KE = +\frac{\hbar^2}{2m}a^2$$

Solution b

Let's look at the left side of Equation 3.1.3.21for linear momentum

$$-i\hbar\frac{\partial}{\partial x}Ne^{-ix/\hbar} = -Ne^{-ix/\hbar}$$

and the right side of Equation 3.1.3.21

$$p_x Ne^{-ix/\hbar}$$

These are the same so this wavefunction is an eigenstate of momentum with momentum $p_x = -N$.

Let's look at the left side of Equation 3.1.3.22 for kinetic energy

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}Ne^{-ix/\hbar} = +i\frac{\hbar}{2m}\frac{\partial}{\partial x}Ne^{-ix/\hbar}$$
$$= +\frac{1}{2m}Ne^{-ix/\hbar}$$

and the right side

$$KENe^{-ix/\hbar}$$

These are same so this wavefunction is an eigenstate of kinetic energy. And the measured kinetic energy will be

$$KE = \frac{1}{2m}$$

This wavefunction is an eigenstate of both momentum and kinetic energy.

Exercise 3.3.1

Are $\psi = Me^{-bx}$ functions eigenstates of linear momentum and kinetic energy (or neither or both)?

Answer

ψ is an eigenstate of linear momentum with a eigenvalue of $bi\hbar$ and also an eigenstate of kinetic energy with an eigenvalue of b^2.

3.1.3: The Schrödinger Equation is an Eigenvalue Problem is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **3.3: The Schrödinger Equation is an Eigenvalue Problem** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

3.1.4: Wavefunctions Have a Probabilistic Interpretation

Learning Objectives

- To understand that wavefunctions can have probabilistic interpretations.
- To calculate the probabilities directly from a wavefunctions

For a single-particle system, the wavefunction $\Psi(\vec{r},t)$, or $\psi(\vec{r})$ for the time-independent case, represents the amplitude of the still vaguely defined matter waves. 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** (also called absolute value).

$$P(\vec{r},t) = \Psi^*(\vec{r},t)\Psi(\vec{r},t) \tag{3.1.4.1}$$

$$= |\Psi(\vec{r},t)|^2 \tag{3.1.4.2}$$

where $\vec{r}$ 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.

Born proposed in 1926, the most commonly accepted interpretation of the wavefunction **that the square of the modulus** (Equation 3.1.4.2) is **proportional** to the **probability density** (probability per unit volume) that the electron is in the volume $d\tau$ located at r_i. Since the wavefunction represents the wave properties of matter, the probability amplitude $P(x,t)$ will also exhibit wave-like behavior. Probability density is the three-dimensional analog of the diffraction pattern that appears on the two-dimensional screen in the double-slit diffraction experiment for electrons. 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.

> *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 P*

The probability that a single quantum particle moving in one spatial dimension will be found in a region $x \in [a,b]$ if a measurement of its location is performed is

$$P(x \in [a,b]) = \int_a^b |\psi(x)|^2 dx \tag{3.1.4.3}$$

In three dimensions, Equation 3.1.4.3is represented differently

$$P(x \in [a,b]) = \int_V |\psi(\vec{r})|^2 d\tau \tag{3.1.4.4}$$

This integration extends over a specified volume (V) with the symbol $d\tau$ designating the appropriate volume element (including a Jacobian) of the coordinate system adopted:

- Cartesian:

$$d\tau = dx\, dy\, dz$$

- Spherical:

$$d\tau = r^2 \sin\phi\, dr\, d\theta\, d\phi$$

- Cylindrical:

$$d\tau = r\, dr\, d\phi\, dz.$$

For rectilinear Cartesian space, Equation 3.1.4.4can be is expanded with dimension explicitly indicated

$$P(x \in [a,b]) = \int_{a_x}^{b_x} \int_{a_y}^{b_y} \int_{a_z}^{b_z} |\psi(x,y,z)|^2 dx\, dy\, dz \tag{3.1.4.5}$$

where the limits of integration are selected to encompass the volume V of consideration.

The Born interpretation (Equation 3.1.4.2) of relating the wavefunction to probability forces certain demands on its mathematical behavior of wavefunctions and not any mathematical function can be a valid wavefunction.

Required Properties of Wavefunction

- The wavefunction must be a *single-valued function* of all its coordinates, since the probability density ought to be *uniquely determined* at each point in space.
- The wavefunction should be both *finite* as an infinite probability has no meaning.
- The wavefunction should be *continuous everywhere*, as expected for a physically-meaningful probability density.

The conditions that the wavefunction be single-valued, finite and continuous--in short, "well behaved"-- lead to restrictions on solutions of the Schrödinger equation such that only certain values of the energy and other dynamical variables are allowed. This is called *quantization* and is in the feature that gives *quantum* mechanics its name.

It is important to note that this interpretation implies the wavefunction does **not** mean the particle is distributed over a large region as a sort of "charge cloud". The wavefunction is used to describe the electron motion that behaves like waves and satisfies a wave equation. This is akin to how a grade distribution in a large class does not represent a smearing of grades for a single student, but only makes sense when taking into account that the distribution is the result of many measurables (e.g., student performances).

Example 3.4.1

Show that the square of the modulus of $\Psi(\vec{r},t) = \psi(\vec{r})e^{-i\omega t}$ is time independent. What insight regarding stationary states do you gain from this proof?

Example 3.4.2

According to the Born interpretation, what is the physical significance of $e\psi^*(r_0)(r_0)d\tau$?

3.1.4: Wavefunctions Have a Probabilistic Interpretation is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **3.4: Wavefunctions Have a Probabilistic Interpretation** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

3.1.5: The Energy of a Particle in a Box is Quantized

Learning Objectives

- Solve the particle-in-a-box model used to describing a trapped particle in 1 D well
- Characterize the particle-in-a-box eigenstates (i.e., wavefunctions) and the eigenenergies as a function of the quantum number
- Demonstrate that the eigenstates are orthogonal

The *particle in the box* model system is the simplest non-trivial application of the Schrödinger equation, but one which illustrates many of the fundamental concepts of quantum mechanics. For a particle moving in one dimension (again along the x- axis), the Schrödinger equation can be written

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

Assume that the particle can move freely between two endpoints $x=0$ and $x=L$, but cannot penetrate past either end. This is equivalent to a potential energy dependent on x with

$$V(x)=\begin{cases}0 & 0\le x\le L\\ \infty & x<0\ and\ x>L\end{cases}$$

This potential is represented in Figure 3.5.1 . The infinite potential energy constitutes an impenetrable barrier since the particle would have an infinite potential energy if found there, which is clearly impossible.

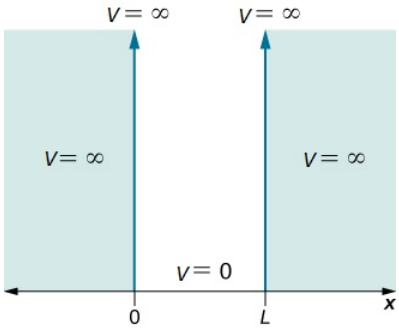


Figure 3.5.1 : The barriers outside a one-dimensional box have infinitely large potential, while the interior of the box has a constant, zero potential. (CC-BY 4.0; OpenStax).

The particle is thus bound to a *"potential well"* since the particle cannot penetrate beyond $x=0$ or $x=L$

$$\psi(x)=0 \quad for\ \ x<0\ \ and\ \ x>L \tag{3.1.5.1}$$

By the requirement that the wavefunction be continuous, it must be true as well that

$$\psi(0)=0 \quad and \quad \psi(L)=0 \tag{3.1.5.2}$$

which constitutes a pair of boundary conditions on the wavefunction within the box. Inside the box, $V(x)=0$, so the Schrödinger equation reduces to the free-particle form:

$$-\frac{\hbar^2}{2m}\psi''(x)=E\psi(x) \tag{3.1.5.3}$$

with $0\le x\le L$.

We again have the differential equation

$$\psi''(x)+k^2\psi(x)=0 \tag{3.1.5.4}$$

with

$$k^2 = \frac{2mE}{\hbar^2} \tag{3.1.5.5}$$

The general solution can be written

$$\psi(x) = A\ \sin\ kx\ +\ B\ \cos\ kx \tag{3.1.5.6}$$

where A and B are constants to be determined by the boundary conditions in Equation 3.1.5.2 By the first condition, we find

$$\psi(0) = A\ \sin\ 0\ +\ B\ \cos\ 0\ =\ B\ = 0 \tag{3.1.5.7}$$

The second boundary condition at $x = L$ then implies

$$\psi(a) = A\ \sin\ kL\ =\ 0 \tag{3.1.5.8}$$

It is assumed that $A \neq 0$, for otherwise $\psi(x)$ would be zero everywhere and the particle would disappear (i.e., the trivial solution). The condition that $\sin kx = 0$ implies that

$$kL\ =\ n\pi \tag{3.1.5.9}$$

where n is a integer, positive, negative or zero. The case $n = 0$ must be excluded, for then $k = 0$ and again $\psi(x)$ would vanish everywhere. Eliminating k between Equation 3.1.5.4and 3.1.5.9, we obtain

$$E_n = \frac{\hbar^2\pi^2}{2mL^2}\ n^2 = \frac{h^2}{8mL^2}n^2 \tag{3.1.5.10}$$

with $n = 1, 2, , 3\ldots$

These are the only values of the energy which allows solutions of the Schrödinger Equation 3.1.5.3consistent with the boundary conditions in Equation 3.1.5.2 The integer n, called a **quantum number**, is appended as a subscript on E to label the allowed energy levels. Negative values of n add nothing new because the energies in Equation 3.1.5.10depends on n^2.

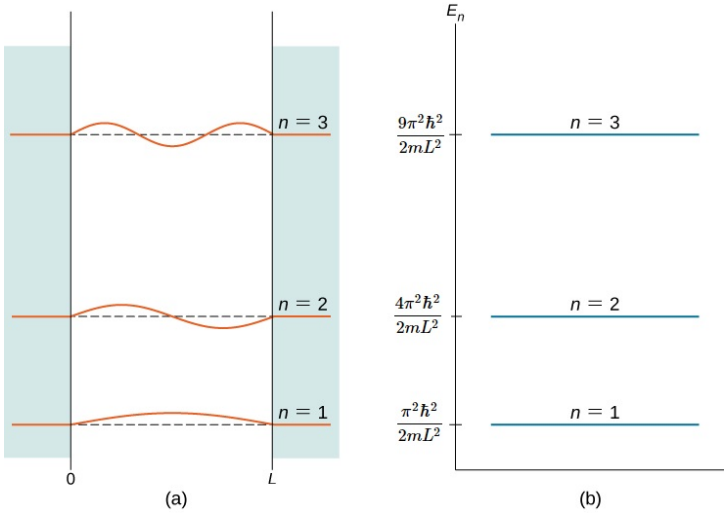


Figure 3.5.2 : A plot of $\psi_n(x)$ for the first four wavefunctions. (CC-BY 4.0; OpenStax).

Figure 3.5.2 shows part of the energy-level diagram for the particle in a box. The occurrence of discrete or quantized energy levels is characteristic of a bound system, that is, one confined to a finite region in space. For the free particle, the absence of confinement allowed an energy continuum. Note that, in both cases, the number of energy levels is infinite-denumerably infinite for the particle in a box, but nondenumerably infinite for the free particle.

The particle in a box assumes its lowest possible energy when $n = 1$, namely

$$E_1 = \frac{h^2}{8mL^2} \tag{3.1.5.11}$$

The state of lowest energy for a quantum system is termed its *ground state*.

Zero Point Energy

An interesting point is that $E_1 > 0$, whereas the corresponding classical system would have a minimum energy of zero. This is a recurrent phenomenon in quantum mechanics. The residual energy of the ground state, that is, the energy in excess of the classical minimum, is known as **zero point energy**. In effect, the kinetic energy, hence the momentum, of a bound particle cannot be reduced to zero. The minimum value of momentum is found by equating E_1 to $p^2/2m$, giving $p_{min} = \pm h/2L$. This can be expressed as an *uncertainty* in momentum given by $\Delta p \approx h/L$. Coupling this with the uncertainty in position, $\Delta x \approx L$, from the size of the box, we can write

$$\Delta x \Delta p \approx h \tag{3.1.5.12}$$

This is in accord with the *Heisenberg uncertainty principle*.

The particle-in-a-box eigenfunctions are given by Equation 3.1.5.13, with $B = 0$ and $k = n\pi/L = a$, in accordance with Equation 3.1.5.9

$$\psi_n(x) = A \sin \frac{n\pi x}{L} \tag{3.1.5.13}$$

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

These, like the energies, can be labeled by the quantum number n. The constant A, thus far arbitrary, can be adjusted so that $\psi_n(x)$ is normalized. The normalization condition is, in this case,

$$\int_0^a [\,\psi_n(x)\,]^2\, dx = 1 \tag{3.1.5.14}$$

the integration running over the domain of the particle $0 \le x \le L$. Substituting Equation 3.1.5.13into Equation 3.1.5.14,

$$A^2 \int_0^L \sin^2 \frac{n\pi x}{L} dx = A^2 \frac{L}{n\pi} \int_0^{n\pi} \sin^2 \theta\, d\theta \tag{3.1.5.15}$$

$$= A^2 \frac{L}{2} = 1 \tag{3.1.5.16}$$

We have made the substitution $\theta = n\pi x/L$ and used the fact that the average value of $\sin^2\theta$ over an integral number of half wavelengths equals 1/2 (alternatively, one could refer to standard integral tables). From Equation 3.1.5.16, we can identify the general normalization constant

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

for all values of n. Finally we can write the normalized eigenfunctions:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \tag{3.1.5.17}$$

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

The first few eigenfunctions and the corresponding probability distributions are plotted in Figure 3.5.3 . There is a close analogy between the states of this quantum system and the modes of vibration of a violin string. The patterns of standing waves on the string are, in fact, identical in form with the wavefunctions in Equation 3.1.5.17.

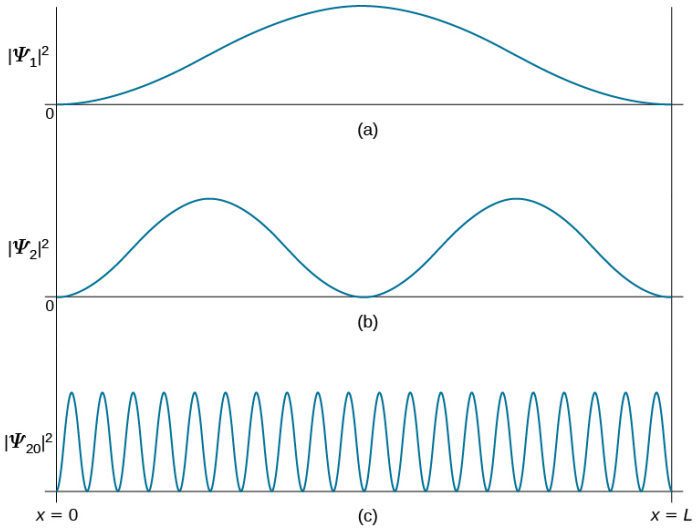


Figure 3.5.3 : The probability density distribution $|\psi_n(x)|^2$ for a quantum particle in a box for: (a) the ground state, $n = 1$; (b) the first excited state, $n = 2$; and, (c) the nineteenth excited state, $n = 20$. (CC-BY 4.0; OpenStax).

Nodes and Curvature

A significant feature of the particle-in-a-box quantum states is the occurrence of *nodes*. These are points, other than the two end points (which are fixed by the boundary conditions), at which the wavefunction vanishes. At a node there is exactly zero probability of finding the particle. The *n*th quantum state has, in fact, $n - 1$ nodes. It is generally true that the number of nodes increases with the energy of the quantum state, which can be rationalized by the following qualitative argument. As the number of nodes increases, so does the number and the steepness of the 'wiggles' in the wavefunction. It's like skiing down a slalom course. Accordingly, the average curvature, given by the second derivative, must increase. But the second derivative is proportional to the kinetic energy operator. Therefore, the more nodes, the higher the energy. This will prove to be an invaluable guide in more complex quantum systems.

Example 3.5.1 : Excited State Probabilities

For a particle in a one-dimensional box of length L, the second excited state wavefunction ($n = 3$) is

$$\psi_3 = \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L}$$

a. What is the probability that the particle is in the left half of the box?
b. What is the probability that the particle is in the middle third of the box?

Strategy

Probability that the particle will be found between a and b is

$$P(a,b) = \int_a^b \psi^2 \, dx$$

For this problem,

$$\psi_3 = \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L}$$

therefore,

$$P(a,b) = \frac{2}{L}\int_a^b \sin^2\frac{3\pi x}{L}\,dx$$
$$= \frac{2}{L}\left(\frac{x}{2} - \frac{L\sin\left(\frac{6\pi x}{L}\right)}{12\pi}\right)\Bigg|_a^b$$
$$= \frac{b-a}{L} - \frac{1}{6\pi}\left[\sin\left(\frac{6\pi b}{L}\right) - \sin\left(\frac{6\pi a}{L}\right)\right]$$

Solution a

The probability that the particle is in the left half of the box is

$$P\left(0,\frac{L}{2}\right) = \frac{\frac{L}{2}-0}{L} - \frac{1}{6\pi}\left[\sin\left(\frac{6\pi\left(\frac{L}{2}\right)}{L}\right) - \sin\left(\frac{6\pi(0)}{L}\right)\right]$$
$$= \frac{1}{2}$$

Solution b

The probability that the particle is in the middle third of the box

$$P\left(\frac{L}{3},\frac{2L}{3}\right) = \frac{\frac{2L}{3}-\frac{L}{3}}{L} - \frac{1}{6\pi}\left[\sin\frac{6\pi\left(\frac{2L}{3}\right)}{L} - \sin\frac{6\pi\left(\frac{L}{3}\right)}{L}\right]$$
$$= \frac{1}{3}$$

Exercise 3.5.1 : Ground State Probability

For a particle in a one-dimensional box, the ground state wavefunction is

$$\psi_1 = \sqrt{\frac{2}{L}}\sin\frac{x\pi}{L}$$

What is the probability that the particle is in the left half of the box in the ground state?

Answer

$$P\left(0,\frac{L}{2}\right) = \frac{2}{L}\int_0^{\frac{L}{2}} \sin^2\frac{x\pi}{L}dx$$
$$= \frac{2}{L}\frac{\frac{L\pi}{L} + \sin 0 + \sin\frac{L\pi}{L}}{\frac{4\pi}{L}}$$
$$= \frac{1}{2}$$

This is the same answer as for the ψ_3 state in Example 3.5.1 . This is because the eigenstate squared (.e., probability density) for the particle in a 1D box will always be symmetric around the center of the box. So there will be equal probability to be on either side (i.e., no side is favored).

Time Dependence and Complex Nature of Wavefunctions

Recall that the time-dependence of the wavefunction with time-independent potential was discussed in Section 3.1 and is expressed as

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

so for the particle in a box, these are

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}e^{-iE_nt/\hbar} \tag{3.1.5.18}$$

with E_n given by Equation 3.1.5.10.

The phase part of Equation 3.1.5.18 can be expanded into a real part and a complex components. So the total wavefunction for a particle in a box is

$$\Psi(x,t) = \underbrace{\left(\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\right)\left(\cos\frac{E_nt}{\hbar}\right)}_{\text{real part}} - \underbrace{i\left(\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\right)\left(\sin\frac{E_nt}{\hbar}\right)}_{\text{imaginary part}}$$

which can be simplified (slightly) to

$$\Psi(x,t) = \underbrace{\left(\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\right)\left(\cos\frac{E_nt}{\hbar}\right)}_{\text{real part}} - \underbrace{i\left(\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\right)\left(\cos\frac{E_nt}{\hbar}-\frac{\pi}{2}\right)}_{\text{imaginary part}}$$

As discussed previously, the imaginary part of the total wavefunction oscillates out of phase by $\pi/2$ with respect to the real part (we call this "out of phase"). This is demonstrated in the time-dependent behavior of the first three eigenfunctions in Figure 3.5.4 .

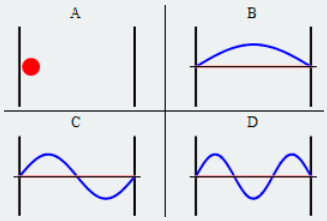


Figure 3.5.4 : Some trajectories of a particle in a box according to Newton's laws of classical mechanics (A), and according to the Schrödinger equation of quantum mechanics (B-D). In (B-D), the horizontal axis is position, and the vertical axis is the real part (blue) and imaginary part (red) of the wavefunction. The states (B, C, D) are energy eigenstates. (Public Domain; Sbyrnes321 via Wikipedia).

Note that as n increased, the energy of the wavefunction increases (Equation 3.1.5.10) and both the number of nodes and antinodes increase and the frequency of oscillation of the wavefunction increases.

> *It is generally true in quantum systems (not just for particles in boxes) that the number of nodes in a wavefunction increases with the energy of the quantum state.*

Orthonormality of the Eigenstates

Another important property of the eigenfunctions in Equation 3.1.5.17 applies to the integral over a product of two *different* eigenfunctions (Equation 3.1.5.17). It is easy to see from Figure 3.5.5 that the integral

$$\int_0^L \psi_2(x)\psi_1(x)dx = 0 \tag{3.1.5.19}$$

The integral in Equation 3.1.5.19 is zero when the two eignestates differ and when integrated over the entire range of the system (from $-\infty$ to ∞ for a 1-D particle in the box, but this can be a narrow region of 0 to L since the eigenstates are zero outside of the box).

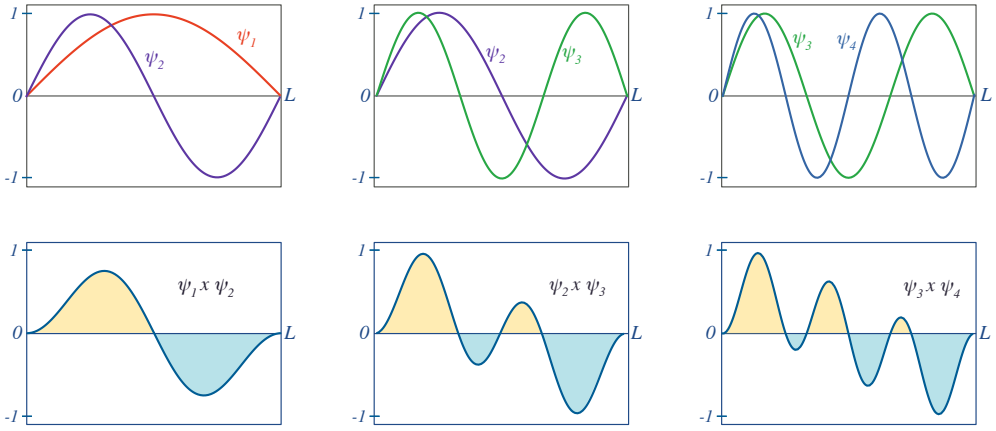


Figure 3.5.5 : (Top Row): Select plots of the $n = 1$ (red curves), $n = 2$ (purple curves), $n = 3$ (green curves), and $n = 4$ (blue curves) eigenfunctions. (Bottom Row): Product of different eigenstates with positive (tan) and negative (cyan) areas emphasized. Note that the negative and positive areas perfectly cancel when added together. Created via fooplot (CC BY-NC; Ümit Kaya via LibreTexts)

To prove Equation 3.1.5.19for a particle in a box model, we can use the trigonometric identity

$$\sin\,\alpha\,\sin\,\beta = \frac{1}{2}[\,\cos(\alpha-\beta) - \cos(\alpha+\beta)\,] \tag{3.1.5.20}$$

to show that

$$\int_0^L \psi_m(x)\psi_n(x)dx = 0 \quad if \quad m \neq n \tag{3.1.5.21}$$

This property is called **orthogonality**. We will show in the next chapter, that this is a general result from quantum-mechanical eigenfunctions. The normalization (Equation 3.1.5.19) together with the orthogonality (Equation 3.1.5.21) can be combined into a single relationship

$$\int_0^L \psi_m(x)\psi_n(x)dx = \delta_{mn} \tag{3.1.5.22}$$

In terms of the *Kronecker delta*

$$\delta_{mn} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases} \tag{3.1.5.23}$$

A set of functions $\{\,\psi_n\,\}$ which obeys Equation 3.1.5.22is called *orthonormal*.

Example 3.5.2

Evaluate

a. $\langle\psi_3|\psi_3\rangle$
b. $\langle\psi_4|\psi_4\rangle$
c. $\langle\psi_3|\psi_4\rangle$
d. $\langle\psi_4|\psi_3\rangle$

for the normalized wavefunctions:

$$|\psi_3\rangle = \sqrt{\frac{2}{L}}\,\sin\frac{3\pi x}{L}$$

and

$$|\psi_4\rangle = \sqrt{\frac{2}{L}} \sin \frac{4\pi x}{L}$$

Strategy

These are four different integrals and we can solve them directly or use orthonormality (Equation 3.1.5.23) to evaluate.

Solution a

$$\begin{aligned}\langle \psi_3 | \psi_3 \rangle &= \int_{-\infty}^{+\infty} \left(\sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L} \right) \left(\sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L} \right) dx \\ &= \frac{2}{L} \int_{-\infty}^{+\infty} \sin^2 \frac{3\pi x}{L} \, dx\end{aligned}$$

This is an integration over an even function, so it cannot be tossed out via symmetry. We can use the Trigonometry relationship in Equation 3.1.5.20to get

$$\frac{2}{L} \int_{-\infty}^{+\infty} \sin^2 \frac{3\pi x}{L} \, dx = \frac{2}{L} \int_{-\infty}^{+\infty} \frac{1}{2} \left(1 - \cos \frac{6\pi x}{L} \right) dx$$

and we can continue the fun. However, there is no need. Since the we can recognize that $\langle \psi_3 | \psi_3 \rangle$ is 1 by the normalization criteria which is folded into the orthonormal criteria (Equation 3.1.5.23).

Therefore $\langle \psi_3 | \psi_3 \rangle = 1$.

Solution b

$$\begin{aligned}\langle \psi_4 | \psi_4 \rangle &= \int_{-\infty}^{+\infty} \left(\sqrt{\frac{2}{L}} \sin \frac{4\pi x}{L} \right) \left(\sqrt{\frac{2}{L}} \sin \frac{4\pi x}{L} \right) dx \\ &= \frac{2}{L} \int_{-\infty}^{+\infty} \sin^2 \frac{4\pi x}{L} \, dx\end{aligned}$$

We can expand and solve, but again there is no need. The wavefunctions are normalized therefore $\langle \psi_4 | \psi_4 \rangle = 1$.

Solution c

$$\begin{aligned}\langle \psi_3 | \psi_4 \rangle &= \int_{-\infty}^{+\infty} \left(\sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L} \right) \left(\sqrt{\frac{2}{L}} \sin \frac{4\pi x}{L} \right) dx \\ &= \frac{2}{L} \int_{-\infty}^{+\infty} \sin\left(\frac{3\pi x}{L} \right) \sin\left(\frac{4\pi x}{L} \right) dx\end{aligned}$$

We can expand this integral and evaluate, but since the integrand is odd (and even function times an odd), this integral is zero. Alternatively, we can use the orthogonality criteria into the greater orthonormal criteria (Equation 3.1.5.23).

Solution d

$$\begin{aligned}\langle \psi_4 | \psi_3 \rangle &= \int_{-\infty}^{+\infty} \left(\sqrt{\frac{2}{L}} \sin \frac{4\pi x}{L} \right) \left(\sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L} \right) dx \\ &= \frac{2}{L} \int_{-\infty}^{+\infty} \sin\left(\frac{4\pi x}{L} \right) \sin\left(\frac{3\pi x}{L} \right) dx\end{aligned}$$

We can expand this integral and evaluate, but since the integrand is odd (and even function times an odd function), this integral is zero. Alternatively, we can use the orthogonality criteria into the greater orthonormal criteria (Equation 3.1.5.23).

However, since the wavefunctions are real, then

$$\langle \psi_4 | \psi_3 \rangle = \langle \psi_3 | \psi_4 \rangle$$

which also means

$$\langle \psi_4 | \psi_3 \rangle = 0$$

from the results of section c.

3.1.5: The Energy of a Particle in a Box is Quantized is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **3.5: The Energy of a Particle in a Box is Quantized** by S. M. Blinder is licensed CC BY-NC-SA 4.0.

3.1.6: Wavefunctions Must Be Normalized

Learning Objectives

- Calculate the probability of an event from the wavefunction
- Understand the utility and importance of normalizing wavefunctions
- Demonstrate how to normalize an arbitrary wavefunction

Extracting Probabilities

Since wavefunctions can in general be complex functions, the physical significance of wavefunctions cannot be found from the functions themselves 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**.

$$\Psi^*(r,t)\Psi(r,t) = |\Psi(r,t)|^2 \tag{3.1.6.1}$$

where r is a vector 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. Remember that the Born interpretation is that $\psi^*(r_i)\psi(r_i)\,d\tau$ is the **probability** that the electron is in the volume $d\tau$ 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.

Since the squared magnitude $|\psi|^2$ of the wavefunction of a particle can be interpreted as the probability density, then the probability for a one-dimensional wavefunction between the points $x = a$ and $x = b$ can be calculated by

$$P_{1D} = \int_a^b |\psi(x)|^2 \mathrm{d}x \tag{3.1.6.2}$$

This is just the area under the under the $|\psi|^2$ curve (Figure 3.6.1).

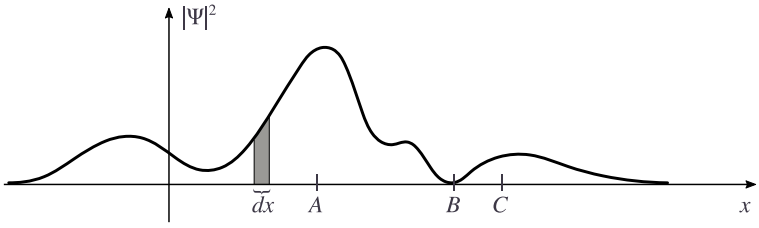


Figure 3.6.1 : The probability can be interpreted as an area under the probability density $|\psi|^2$. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

If the probability of a two-dimensional wavefunction is being evaluated, then Equation 3.1.6.2 will be amended to included a double integral:

$$P_{2D} = \int_{a_1,a_2}^{b_1,b_2} |\psi(x,y)|^2 \mathrm{d}x\mathrm{d}y$$

and similarly a triple integral would be used for calculating probabilities of three-dimensional wavefunctions:

$$P_{3D} = \int_{a_1,a_2,a_3}^{b_1,b_2,b_3} |\psi(x,y,z)|^2 \mathrm{d}x\mathrm{d}y\mathrm{d}z$$

Example 3.6.1 : Probability of a Particle in a Box

Calculate the probability of finding an electron at $L/2$ in a box of infinite height within an interval ranging from $\frac{L}{2}-\frac{L}{200}$ to $\frac{L}{2}+\frac{L}{200}$ for the $n=1$ and $n=2$ states. Since the length of the interval, $L/100$, is small compared to L, you can get an approximate answer without explicitly integrating.

Solution

The wavefunction for the particle in a box is

$$\psi(x)=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

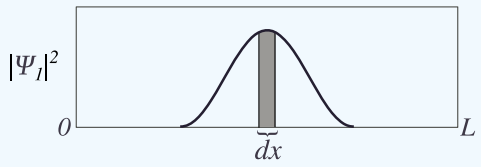
and the wavefunction for the $n=1$ state is

$$\psi_{n=1}=\sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)$$

From the interpretation that the wavefunction modulus squared is the probability density, we can establish the following integral to solve the problem (note the limits of integration)

$$|\psi_{n=1}|^2=\frac{2}{L}\int_{\frac{99L}{200}}^{\frac{101L}{200}}\sin^2\left(\frac{\pi x}{L}\right)dx \tag{3.1.6.3}$$

We can solve this, but we can also recognize that Equation 3.1.6.3 is just calculating an area that can be approximated as the area of a rectangle with a height ($\frac{2}{L}\sin^2\left(\frac{\pi x}{L}\right)$ at $x=L/2$) and width $\Delta x=L/100$ (Figure 3.6.2).



(a)

Figure 3.6.2 : The probability can be interpreted as an area under the probability density $|\psi_1|^2$. (CC BY-NC; Ümit Kaya via LibreTexts)

This area can be computed:

$$\begin{aligned}|\psi_{n=1}|^2 &\approx \frac{2}{L}\sin^2\left(\frac{\pi(L/2)}{L}\right)^{1}\Delta x\\ &\approx\left(\frac{2}{L}\right)(L/100)\\ &\approx 1/50=0.02\end{aligned}$$

Given that the wavefunction is sinusoidal, the actual probability of finding an electron within the given interval at $\frac{L}{2}$ should be slightly less because of the behavior of the sinusoid at $\frac{L}{2}$ is at its peak of the wavefunction (Figure 3.6.2).

The wavefunction for the $n=2$ state

$$\psi_{n=2}=\sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{L}\right)$$

so the integral that we need to construct and solve is

$$|\psi_{n=2}|^2=\frac{2}{L}\int_{\frac{99L}{200}}^{\frac{101L}{200}}\sin^2\left(\frac{2\pi x}{L}\right)dx$$

We can use the same graphical interpretation as above, but using the probability density of the ψ_2 wavefunction (Figure 3.6.3).

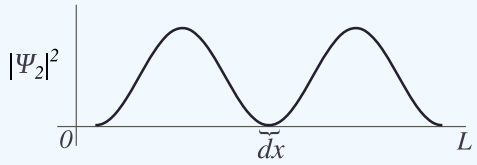


Figure 3.6.3 : The probability can be interpreted as an area under the probability density $|\psi_2|^2$. (CC BY-NC Copyright; Ümit Kaya via LibreTexts)

$$|\psi_{n=1}|^2 \approx \frac{2}{L}\sin^2\left(\frac{2\pi(L/2)}{L}\right)^{0}\Delta x$$

$$\approx 0$$

The probability of finding an electron in a box at $\frac{L}{2}$ for $n = 2$ is approximately zero.

? Exercise 3.6.1

Show that the square of the modulus of $\Psi(r,t) = \psi(r)e^{-i\omega t}$ is time independent. What insight regarding stationary states do you gain from this proof?

Solution

The square of the modulus of a wavefunction is $\Psi(r,t)^*\Psi(r,t)$ so for wavefunctions of this form, the square of the modulus is

$$\Psi(r,t)^*\Psi(r,t) = \psi(r)\, e^{+i\omega t}\psi(r)\, e^{-i\omega t}$$

$$= \psi(r)^2$$

Hence, there is no time dependence to the modulus of wavefunctions of this work, which from the probability interpretation of the wavefunction means that the probability density is time-independent.

Normalizing of the Wavefunction

A probability is a real number between 0 and 1, inclusive. 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. According to Equation 3.1.6.1, the probability of a measurement of x yielding a result between $-\infty$ and $+\infty$ is

$$P_{x\in-\infty:\infty}(t) = \int_{-\infty}^{\infty}|\psi(x,t)|^2 dx. \tag{3.1.6.4}$$

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

$$\int_{-\infty}^{\infty}|\psi(x,t)|^2 dx = 1, \tag{3.1.6.5}$$

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

✓ Example 3.6.2 : Normalizing a Gaussian Wavepacket

Normalize the wavefunction of a Gaussian wave packet, centered on $x = x_o$ with characteristic width σ:

$$\psi(x) = \psi_0 \mathrm{e}^{-(x-x_0)^2/(4\sigma^2)}. \tag{3.1.6.6}$$

Solution

To determine the normalization constant ψ_0, we simply substitute Equation 3.1.6.6 into Equation 3.1.6.5, to obtain

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

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

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

However, from an integral table we know

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

which implies that

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

Hence, a general normalized Gaussian wavefunction takes the form

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

where ϕ is an arbitrary real phase-angle.

? Exercise 3.6.2

Normalize this wavefunction for a particle in a harmonic well:

$$\psi = xe^{-x^2}$$

Answer

$$\psi = 2\left(\frac{2}{\pi}\right)^{1/4} xe^{-x^2}$$

Time Dependence to the Wavefunction

Now, it is important to demonstrate that if a wavefunction is initially normalized then it stays normalized as it evolves in time according to the time-dependent Schrödinger's equation. If this is not the case then the probability interpretation of the wavefunction is untenable, since it does not make sense for the probability that a measurement of x yields *any* possible outcome (which is, manifestly, unity) to change in time. Hence, we require that

$$\frac{d}{dt} \int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = 0$$

for wavefunctions satisfying the time-dependent Schrödinger's equation (this results from the time-dependent Schrödinger's equation and Equation 3.1.6.5). The above equation gives

$$\frac{d}{dt} \int_{-\infty}^{\infty} \psi^* \psi \, dx = \int_{-\infty}^{\infty} \left(\frac{\partial \psi^*}{\partial t} \psi + \psi^* \frac{\partial \psi}{\partial t} \right) dx = 0. \tag{3.1.6.7}$$

Now, multiplying Schrödinger's equation by $\psi^*/(\mathrm{i}\hbar)$, we obtain

$$\psi^* \frac{\partial \psi}{\partial t} = \frac{\mathrm{i}}{2m} \psi^* \frac{\partial^2 \psi}{\partial x^2} - \frac{\mathrm{i}}{\hbar} V |\psi|^2 \tag{3.1.6.8}$$

The complex conjugate of this expression yields

$$\psi \frac{\partial \psi^*}{\partial t} = -\frac{\mathrm{i}}{2m} \psi \frac{\partial^2 \psi^*}{\partial x^2} + \frac{\mathrm{i}}{\hbar} V |\psi|^2 \tag{3.1.6.9}$$

since

- $(AB)^* = A^* B^*$,
- $A^{**} = A$, and
- $i^* = -i$.

Summing Equation 3.1.6.8 and 3.1.6.9 results in

$$\frac{\partial \psi^*}{\partial t}\psi + \psi^* \frac{\partial \psi}{\partial t} = \frac{\mathrm{i}}{2m}\left(\psi^* \frac{\partial^2 \psi}{\partial x^2} - \psi \frac{\partial^2 \psi^*}{\partial x^2}\right) \tag{3.1.6.10}$$

$$= \frac{\mathrm{i}}{2m}\frac{\partial}{\partial x}\left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right). \tag{3.1.6.11}$$

Equations 3.1.6.7 and 3.1.6.11 can be combined to produce

$$\frac{d}{dt}\int_{-\infty}^{\infty} |\psi|^2 dx = \frac{\mathrm{i}}{2m}\left[\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right]_{-\infty}^{\infty} = 0. \tag{3.1.6.12}$$

The above equation is satisfied provided the wavefunction converges

$$\lim_{|x|\to\infty} |\psi| = 0 \tag{3.1.6.13}$$

However, this is a necessary condition for the integral on the left-hand side of Equation 3.1.6.5 to converge. Hence, we conclude that all wavefunctions which are *square-integrable* [i.e., are such that the integral in Equation 3.1.6.5 converges] have the property that if the normalization condition Equation 3.1.6.5 is satisfied at one instant in time then it is satisfied at all subsequent times.

Not all Wavefunctions can be Normalized

Not all wavefunctions can be normalized according to the scheme set out in Equation 3.1.6.5. For instance, a planewave wavefunction for a quantum free particle

$$\Psi(x,t) = \psi_0 \mathrm{e}^{\mathrm{i}(kx-\omega t)}$$

is not square-integrable, and, thus, cannot be normalized. For such wavefunctions, the best we can say is that

$$P_{x\in a:b}(t) \propto \int_a^b |\Psi(x,t)|^2 dx.$$

In the following, all wavefunctions are assumed to be square-integrable and normalized, unless otherwise stated.

3.1.6: Wavefunctions Must Be Normalized is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **3.6: Wavefunctions Must Be Normalized** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

3.1.7: The Average Momentum of a Particle in a Box is Zero

Learning Objectives

- Calculate the expectation value for a measurement
- Apply the expectation value concept to calculate average properties of a participle in a box model
- Understand the origin of a zero-point energy/zero-point motion.
- Extend the concept of orthogonality from vectors to mathematical functions (and wavefunctions).

Now that we have mathematical expressions for the wavefunctions and energies for the particle-in-a-box, we can answer a number of interesting questions. The answers to these questions use quantum mechanics to predict some important and general properties for electrons, atoms, molecules, gases, liquids, and solids. Key to addressing these questions is the formulation and use of expectation values. This is demonstrated below and used in the context of evaluating average properties (momentum of the particle in a box for the case below).

Classical Expectation Values

The expectation value is the probabilistic expected value of the result (measurement) of an experiment. It is not the most probable value of a measurement; indeed the expectation value may even have zero probability of occurring. The expected value (or expectation, mathematical expectation, mean, or first moment) refers to the value of a variable one would "expect" to find if one could repeat the random variable process an infinite number of times and take the average of the values obtained. More formally, the expected value is a weighted average of all possible values.

Example 3.7.1 : Classical Expectation Value of Exam Scores (a discretized example)

A classical example is calculating the expectation value (i.e. average) of the exam grades in the class. For example if the class scores for an exam were

65	67	94	43	67	76	94	67

The discrete way is to sum up all scores and divide by the number of students:

$$\langle s \rangle = \frac{\sum_{i}^{N} s(i)}{N} \tag{3.1.7.1}$$

which of this example of scores is

$$\begin{aligned} \langle s \rangle &= \frac{65+67+94+43+67+76+94+76}{8} \\ &= 71.625 \end{aligned}$$

Notice that the average is not an allowable score on an individual exam. Equation 3.1.7.1 can be rewritten with "probability" or "probability weights"

$$\langle s \rangle = \sum_{i}^{N} s(i) P_s(i) \tag{3.1.7.2}$$

where $P_s(i)$ is the probability of observing a score of s. This is just the number of times it occurs in a dataset divided by the number of elements in that data set. Applying Equation 3.1.7.2 to the set of scores, we need to calculate these weights:

Score	65	67	94	43	76
P_s	1/8	3/8	2/8	1/8	1/8

As with all probabilities, the sum of all probabilities possible must be one. These confirm that for the weights here:

$$\frac{1}{8}+\frac{3}{8}+\frac{2}{8}+\frac{1}{8}+\frac{1}{8}=\frac{8}{8}=1$$

This is the discretized "normalization" criterion (the same as why we normalize wavefunctions).

So, now we can use Equation 3.1.7.2 properly

$$\begin{aligned}\langle s\rangle &= 65\times\frac{1}{8}+67\times\frac{3}{8}+94\times\frac{2}{8}+43\times\frac{1}{8}+76\times\frac{1}{8}\\ &= 71.625\end{aligned}$$

Hence, Equation 3.1.7.2 gives the same result, as expected, from Equation 3.1.7.1.

Quantum Expectation Values

The extension of the classical expectation (average) approach in Example 3.7.1 using Equation 3.1.7.2 to evaluating quantum mechanical expectation values requires three small changes:

1. Switch from descretized to continuous variables
2. Substitute the wavefunction squared for the probability weights (i.e., the probability distribution)
3. Use an operator instead of the scalar

Hence, the quantum mechanical expectation value $\langle o\rangle$ for an observable, o, associated with an operator, $\hat{O}$, is given by

$$\langle o\rangle=\int_{-\infty}^{+\infty}\psi^{*}\hat{O}\psi\,dx \tag{3.1.7.3}$$

where x is the range of space that is integrated over (i.e., an integration over all possible probabilities). The expectation value changes as the wavefunction changes and the operator used (i.e, which observable you are averaging over).

> *In general, changing the wavefunction changes the expectation value for that operator for a state defined by that wavefunction.*

Average Energy of a Particle in a Box

If we generalize this conclusion, such integrals give the average value for any physical quantity by using the operator corresponding to that physical observable in the integral in Equation 3.1.7.3. In the equation below, the symbol $\langle H\rangle$ is used to denote the average value for the total energy.

$$\langle H\rangle=\int_{-\infty}^{\infty}\psi^{*}(x)\hat{H}\psi(x)dx \tag{3.1.7.4}$$

$$=\int_{-\infty}^{\infty}\psi^{*}(x)\hat{KE}\psi(x)dx+\int_{-\infty}^{\infty}\psi^{*}(x)\hat{V}\psi(x)dx \tag{3.1.7.5}$$

$$=\underbrace{\int_{-\infty}^{\infty}\psi^{*}(x)\left(\frac{-\hbar^{2}}{2m}\right)\frac{\partial^{2}}{\partial x^{2}}\psi(x)dx}_{\text{average kinetic energy}}+\underbrace{\int_{-\infty}^{\infty}\psi^{*}(x)\hat{V}(x)\psi(x)dx}_{\text{average potential energy}} \tag{3.1.7.6}$$

The Hamiltonian operator consists of a kinetic energy term and a potential energy term. The kinetic energy operator involves differentiation of the wavefunction to the right of it. This step must be completed before multiplying by the complex conjugate of the wavefunction. The potential energy, however, usually depends only on position and not momentum (i.e., it involves conservative forces). The potential energy operator therefore only involves the coordinates of a particle and does not involve differentiation. For this reason we do not need to use a caret over V in Equation 3.1.7.6.

Equation 3.1.7.6 can be simplified

$$\langle H\rangle=\langle KE\rangle+\langle V\rangle \tag{3.1.7.7}$$

The potential energy integral then involves only products of functions, and the order of multiplication does not affect the result, e.g. 6×4 = 4×6 = 24. This property is called the **commutative property**. The average potential energy therefore can be written as

$$\langle V \rangle = \int_{-\infty}^{\infty} V(x)\psi^*(x)\psi(x)dx \tag{3.1.7.8}$$

This integral is telling us to take the probability that the particle is in the interval dx at x, which is $\psi^*(x)\psi(x)dx$, multiply this probability by the potential energy at x, and sum (i.e., integrate) over all possible values of x. This procedure is just the way to calculate the average potential energy $\langle V \rangle$ of the particle.

Exercise 3.7.2 : Particle in Box

Evaluate the two integrals in Equation 3.1.7.6 for the PIB wavefunction $\psi(x) = \sqrt{\frac{2}{L}}\sin(kx)$ with the potential function $V(x) = 0$ from 0 to the length of a box L with $k = \frac{\pi}{L}$.

Solution

The *average kinetic energy* is

$$\langle KE \rangle = \int_0^L \left(\sqrt{\frac{2}{L}}\right)\sin(kx)\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\left(\sqrt{\frac{2}{L}}\right)\sin(kx)dx$$

$$= \left(\frac{2}{L}\right)\int_0^L \sin(kx)\left(\frac{-\hbar^2}{2m}\right)\frac{\partial}{\partial x}\cos(kx)(k)dx$$

$$= \left(\frac{2}{L}\right)\int_0^L \sin(kx)\left(\frac{-\hbar^2}{2m}\right)\sin(kx)(k)(-k)dx$$

$$= \left(\frac{2}{L}\right)\left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \sin^2(kx)dx$$

We can solve this intergral using the standard half-angle representation from an integral table. Or we can recognize that we already did this integral when we normalized the PIB wavefunction by rewriting this integral:

$$\langle KE \rangle = \left(\frac{2}{L}\right)\left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \sin^2(kx)dx$$

$$= \left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \left(\frac{2}{L}\right)\sin^2(kx)dx$$

$$= \left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \psi^*(x)\psi(x)dx \quad (\text{the integral} = 1)$$

$$= \frac{k^2\hbar^2}{2m}$$

Thus, the average value for the total energy of this particular system is

$$\langle KE \rangle = \frac{k^2\hbar^2}{2m} = \frac{\pi^2\hbar^2}{2mL^2}$$

Hence, the average kinetic energy of the wavefunction is dependent on the n quantum number

The *average potential energy* is

$$\langle V \rangle = \int_{-\infty}^{\infty} \sin(kx) 0 \sin(kx) dx = 0$$

Thus, the average potential energy of the PIB is 0 irrespective of the wavefunction.

Hence via Equation 3.1.7.7for this system and set of wavefunctions

$$\langle H \rangle = \frac{\pi^2 \hbar^2}{2mL^2}$$

This is the same result obtained from solving the eigenvalue equation for the PIB. However, if the wavefunctions used were NOT eigenstates of energy, then we cannot use the eigenvalue approach and need to rely on the expectation values to describe the energy of the system.

What is the lowest energy for a particle in a box? The lowest energy level is E_1, and it is important to recognize that this lowest energy of a particle in a box is not zero. This finite energy is called the **zero-point energy**, and the motion associated with this energy is called the zero-point motion. Any system that is restricted to some region of space is said to be bound. The zero-point energy and motion are manifestations of the wave properties and the Heisenberg Uncertainty Principle, and are general properties of bound quantum mechanical systems.

? Exercise 3.7.2 : Progressing to the Classical Limit

What happens to the energy level spacing for a particle-in-a-box when mL^2 becomes much larger than h^2? What does this result imply about the relevance of quantization of energy to baseballs in a box between the pitching mound and home plate? What implications does quantum mechanics have for the game of baseball in a world where h is so large that baseballs exhibit quantum effects?

Answer

As mL^2 becomes much larger than h^2, as everyday objects are, the spacing between energy levels becomes much smaller. This shows how the quantizations of energy levels become irrelevant for an everyday object, as the quantizations of the energy of baseballs in a box between the pitching mound and home plate would appear particularly continuous for such a relatively large mass and box length. If h were so large that a baseball experiences quantum effects then a game of baseball would be far less predictable, in a classical world the position of a baseball can be easily predicted by the everyday understanding of projectile motion, however, in such a quantum world the baseball would not behave with expected projectile motion but instead behave wave-like with a probability of being in a certain position.

The first derivative of a function is the rate of change of the function, and the second derivative is the rate of change in the rate of change, also known as the curvature. A function with a large second derivative is changing very rapidly. Since the second derivative of the wavefunction occurs in the Hamiltonian operator that is used to calculate the energy by using the Schrödinger equation, a wavefunction that has sharper curvatures than another, i.e. larger second derivatives, should correspond to a state having a higher energy. A wavefunction with more nodes than another over the same region of space must have sharper curvatures and larger second derivatives, and therefore should correspond to a higher energy state.

? Exercise 3.7.3 : Nodes and Energies

Identify a relationship between the number of nodes in a wavefunction and its energy by examining the graphs you made above. A node is the point where the amplitude passes through zero. What does the presence of many nodes mean about the shape of the wavefunction?

Average Position of a Particle in a Box

We can calculate the most probable position of the particle from knowledge of probability distribution, $\psi^*\psi$. For the ground-state particle in a box wavefunction with $n = 1$ (Figure 3.1.7.1*a*)

$$\psi_{n=1} = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \tag{3.1.7.9}$$

This state has the following probability distribution (Figure 3.1.7.1*b*):

$$\psi^*_{n=1}\psi_{n=1} = \frac{2}{L}\sin^2\left(\frac{\pi x}{L}\right)$$

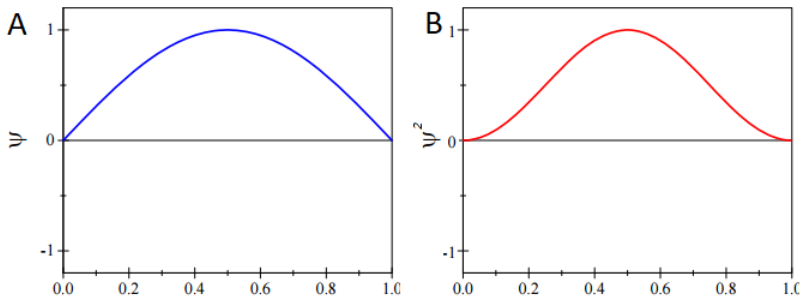


Figure 3.7.1 : (left) The ground-state ($n = 1$) wavefunction for a particle in a box. (right) The ground-state ($n = 1$) probability for a particle in a box.

The expectation value for position with the $\hat{x} = x$ operation for any wavefunction (Equation 3.1.7.3) is

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi^* x \psi \, dx$$

which for the ground-state wavefunction (Equation 3.1.7.9) shown in Figure 3.7.1 is

$$\langle x \rangle = \int_{-\infty}^{+\infty} \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) x \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx \tag{3.1.7.10}$$

$$= \frac{2}{L} \int_{-\infty}^{+\infty} x \sin^2\left(\frac{\pi x}{L}\right) \tag{3.1.7.11}$$

Solution by Inspection

Without even having to evaluate Equation 3.1.7.11, we can get the expectation value from simply inspecting $\psi^*_{n=1}\psi_{n=1}$ in (Figure 3.1.7.1; *right*). This is a symmetric distribution around the center of the box ($L/2$) so it is just as likely to be found in the left half than the right half. Moreover, specifically at any point a fixed distance away from the mean, i.e.

$$\psi^*_{n=1}\psi_{n=1}(L/2 + \Delta x) = \psi^*_{n=1}\psi_{n=1}(L/2 - \Delta x)$$

Therefore, the particle is most likely to be found at the center of the box. So

$$\langle x \rangle = \frac{L}{2}$$

Exercise 3.7.4

Use the general form of the particle-in-a-box wavefunction for any n to find the mathematical expression for the position expectation value $\langle x \rangle$ for a box of length L. How does $\langle x \rangle$ depend on n?

Average Momentum of a Particle in a Box

What is the average momentum of a particle in the box? We start with Equation 3.1.7.3and use the momentum operator

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{3.1.7.12}$$

We note that the particle-in-a-box wavefunctions are **not** eigenfunctions of the momentum operator (Exercise 3.7.4). However, this does not mean that Equation 3.1.7.3is inapplicable as Example 3.7.2 demonstrates.

Example 3.7.3 : The Average Momentum of a Particle in a Box is Zero

Even though the wavefunctions are not momentum eigenfunctions, we can calculate the expectation value for the momentum. Show that the expectation or average value for the momentum of an electron in the box is zero in every state (i.e., arbitrary values of n).

Strategy

First write the expectation value integral (Equation 3.1.7.3) with the momentum operator. Then insert the expression for the wavefunction and evaluate the integral as shown here.

Solution

$$\begin{aligned}
\langle p \rangle &= \int_0^L \psi_n^*(x)\left(-i\hbar\frac{d}{dx}\right)\psi_n(x)dx \\
&= \int_0^L \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)\left(-i\hbar\frac{d}{dx}\right)\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)dx \\
&= -i\hbar\left(\frac{2}{L}\right)\int_0^L \sin\left(\frac{n\pi x}{L}\right)\left(\frac{d}{dx}\right)\sin\left(\frac{n\pi x}{L}\right)dx \\
&= -i\hbar\left(\frac{2}{L}\right)\left(\frac{n\pi}{L}\right)\int_0^L \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)dx \\
&= 0
\end{aligned}$$

Note that this makes sense since the particles spends an equal amount of time traveling in the $+x$ and $-x$ direction.

Interpretation

It may seem that this means the particle in a box does not have any momentum, which is incorrect because we know the energy is never zero. In fact, the energy that we obtained for the particle-in-a-box is entirely kinetic energy because we set the potential energy at 0. Since the kinetic energy is the momentum squared divided by twice the mass, it is easy to understand how the average momentum can be zero and the kinetic energy finite

Exercise 3.7.5

Show that the particle-in-a-box wavefunctions are not eigenfunctions of the momentum operator (Equation 3.1.7.12).

Answer

The easiest way to address this question is asking if the PIB wavefunction also satisfies the eigenvalue equation using the momentum operation instead of the Hamiltonian operator (3rd postulate of QM). That is

$$\hat{p}_x\psi(n) = p\psi(n)$$

with the following PIB wavefunctions

$$\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

and

$$\hat{p} = -i\hbar\frac{d}{dx}$$

and p is a real scalar (since it is a measurable).

$$\begin{aligned}\hat{p}_x\psi_n &= -i\hbar\frac{d}{dx}\left[\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\right] \\ &= -i\hbar\sqrt{\frac{2}{L}}\cos\left(\frac{n\pi x}{L}\right)\left(\frac{n\pi}{L}\right) \\ &\neq p\psi_n\end{aligned}$$

Hence, the PIB wavefunctions are NOT eigenfunctions of the momentum operator.

Alternative Solution

An alternative, albeit more complicated, approach is to recognize that the uncertainty of p must be zero if the wavefunction is an eigenstate of the momentum operator. Hence

$$\sqrt{\langle p^2\rangle - \langle p\rangle^2} = 0$$

This requires calculating the $\langle p^2\rangle$ and $\langle p\rangle$ expectation values:

$$\begin{aligned}\langle p\rangle &= \int_0^L \psi^*\left[-i\hbar\frac{d}{dx}\right]\psi dx \\ &= -i\hbar\int_0^L \frac{2}{L}\sin\left(\frac{n\pi x}{L}\right)\frac{d}{dx}x\sin\left(\frac{n\pi x}{L}\right)dx \\ &= -i\frac{\mathrm{h}^2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)dx \\ &= 0\end{aligned}$$

This integral is zero via orthonormality of the sine and cosine functions (although you can expand the integrand and confirm this).

$$\begin{aligned}\langle p^2\rangle &= \int_0^L \psi^*\left[-i\hbar\frac{d}{dx}\right]^2\psi dx \\ &= \frac{\mathrm{h}^2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\frac{d^2}{dx^2}\sin\left(\frac{n\pi x}{L}\right)dx \\ &= \frac{-\mathrm{h}^2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx \\ &= -\frac{\mathrm{h}^2}{L}\end{aligned}$$

Now the integral above is 1 using orthonormality (although you can expand the integrand and confirm this). Now we calculate the uncertainty in momentum in the PIB wavefunctions:

$$\begin{aligned}\sqrt{\langle p^2\rangle - \langle p\rangle^2} &= \sqrt{\frac{-\mathrm{h}^2}{L} - 0^2} \\ &= \sqrt{\frac{-\mathrm{h}^2}{L}} \\ &\neq 0 \rightarrow\end{aligned}$$

Since the uncertainty is not 0, different measurements (experiments) will results in different values of momentum being quantified. Hence, the PIB wavefunctions are **not** eigenfunctions of the momentum operator.

It must be equally likely for the particle-in-a-box to have a momentum $-p$ as $+p$. The average of $+p$ and $-p$ is zero, yet p^2 and the average of p^2 are not zero. The information that the particle is equally likely to have a momentum of $+p$ or $-p$ is contained in the wavefunction. In fact, the sine function is a representation of the two momentum eigenfunctions e^{+ikx} and e^{-ikx} (Figure 3.7.2).

? Exercise 3.7.6

Write the particle-in-a-box wavefunction as a normalized linear combination of the momentum eigenfunctions e^{ikx} and e^{-ikx} by using Euler's formula. Show that the momentum eigenvalues for these two functions are $p = +\hbar k$ and $-\hbar k$.

The interpretation of the results of Exercise 3.7.6 is physically interesting. The exponential wavefunctions in the linear combination for the sine function represent the two opposite directions in which the electron can move. One exponential term represents movement to the left and the other term represents movement to the right (Figure 3.7.2).

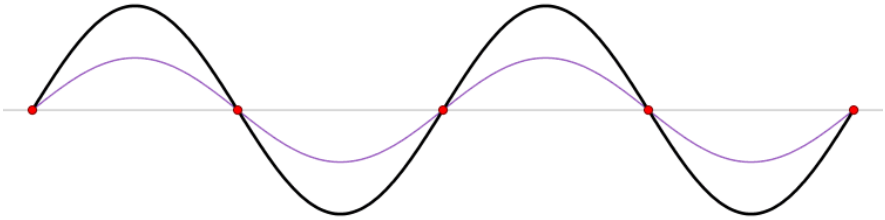


Figure 3.7.2 : Two waves traveling in opposite directions across the same medium combine linearly. In this animation, both waves have the same wavelength and the sum of amplitudes results in a standing wave. (Public Domain; LucasVB).

> *The electrons are moving, they have kinetic energy and momentum, yet the average momentum is zero.*

Did we just Violate the Uncertainty Principle?

Does the fact that the average momentum of an electron is zero and the average position is $L/2$ violate the Heisenberg Uncertainty Principle? No, because the Heisenberg Uncertainty Principle pertains to the uncertainty in the momentum and in the position, not to the average values. Quantitative values for these uncertainties can be obtained to compare with the limit set by the Heisenberg Uncertainty Principle for the product of the uncertainties in the momentum and position. However, to do this we need a quantitative definition of uncertainty, which is discussed in the following Section.

Orthogonality

In vector calculus, *orthogonality* is the relation of two lines at right angles to one another (i.e., perpendicularity), but is generalized into n dimensions via zero amplitude "dot products" or "inner products." Hence, orthogonality is thought of as describing **non-overlapping**, **uncorrelated**, or **independent** objects of some kind. The concept of orthogonality extends to functions (wavefunctions or otherwise) too. Two functions ψ_A and ψ_B are said to be orthogonal if

$$\int_{allspace} \psi_A^* \psi_B d\tau = 0 \tag{3.1.7.13}$$

In general, eigenfunctions of a quantum mechanical operator with different eigenvalues are orthogonal. Are the eigenfunctions of the particle-in-a-box Hamiltonian orthogonal?

? Exercise 3.7.7

Evaluate the integral $\int \psi_1^* \psi_3 dx$ for all possible pairs of particle-in-a-box eigenfunctions from $n = 1$ to $n = 3$ (use symmetry arguments whenever possible) and explain what the results say about orthogonality of the functions.

3.1.7: The Average Momentum of a Particle in a Box is Zero is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **3.7: The Average Momentum of a Particle in a Box is Zero** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

3.1.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions

Learning Objectives

- Expand on the introduction of Heisenberg's Uncertainty Principle by calculating the Δx or Δp directly from the wavefunction

As will be discussed in Section 4.6, the operators $\hat{x}$ and $\hat{p}$ are not compatible and there is **no** measurement that can precisely determine the coresponding observables (x and p) simultaneously. Hence, there must be an uncertainty relation between them that specifies how uncertain we are about one quantity given a definite precision in the measurement of the other. Presumably, if one can be determined with infinite precision, then there will be an infinite uncertainty in the other. The uncertainty in a general quantity A is

$$\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2} \tag{3.1.8.1}$$

where $\langle A^2 \rangle$ and $\langle A \rangle$ are the expectation values of $\hat{A}^2$ and $\hat{A}$ operators for a specific wavefunction. Extending Equation 3.1.8.1 to x and p results in the following uncertainties

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \tag{3.1.8.2}$$

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} \tag{3.1.8.3}$$

These quantities can be expressed explicitly in terms of the (time-dependent) wavefunction $\Psi(x,t)$ using the fact that

$$\langle x \rangle = \langle \Psi(t) | \hat{x} | \Psi(t) \rangle \tag{3.1.8.4}$$

$$= \int \Psi^*(x,t) x \Psi(x,t)\, dx \tag{3.1.8.5}$$

and

$$\langle x^2 \rangle = \langle \Psi(t) | \hat{x}^2 | \Psi(t) \rangle \tag{3.1.8.6}$$

$$= \int \Psi^*(x,t) x^2 \Psi(x,t)\, dx \tag{3.1.8.7}$$

The middle terms in both Equations 3.1.8.4 and 3.1.8.6 are the integrals expressed in Dirac's Bra-ket notation. Similarly using the definition of the linear momentum operator:

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}.$$

So

$$\langle p \rangle = \langle \Psi(t) | \hat{p} | \Psi(t) \rangle \tag{3.1.8.8}$$

$$= \int \Psi^*(x,t) - i\hbar \frac{\partial}{\partial x} \Psi(x,t)\, dx \tag{3.1.8.9}$$

and

$$\langle p^2 \rangle = \langle \Psi(t) | \hat{p}^2 | \Psi(t) \rangle \tag{3.1.8.10}$$

$$= \int \Psi^*(x,t) \left(-\hbar^2 \frac{\partial^2}{\partial x^2} \right) \Psi(x,t)\, dx \tag{3.1.8.11}$$

Time-dependent vs. time-independent wavefunction

The expectation values above are formulated with the total time-dependence wavefunction $\psi(x,t)$ that are functions of x and t. However, it is easy to show that the same expectation value would be obtained if the time-independent wavefunction $\psi(x)$ that are functions of only x are used. If $V(x)$ in $\hat{H}$ is time independent, then the wavefunctions are stationary and the

expectation value are time-independent. You can easily confirm that by comparing the expectation values using the general formula for a stationary wavefunction

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

and for $\psi(x)$.

The Heisenberg uncertainty principle can be quantitatively connected to the properties of a wavefunction, i.e., calculated via the expectation values outlined above:

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{3.1.8.12}$$

This essentially states that the greater certainty that a measurement of x or p can be made, the greater will be the *uncertainty* in the other. Hence, as Δp approaches 0, Δx must approach ∞, which is the case of the free particle (e.g, with $V(x) = 0$) where the momentum of a particles can be determined precisely.

Example 3.8.1 : Uncertainty with a Gaussian wavefunction

A particle is in a state described by the wavefunction

$$\psi(x) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} \tag{3.1.8.13}$$

where a is a constant and $-\infty \leq x \leq \infty$. Verify that the value of the product $\Delta p\, \Delta\, x$ is consistent with the predictions from the uncertainty principle (Equation 3.1.8.12).

Solution

Let's calculate the average of x:

$$\begin{aligned}
\langle x \rangle &= \int_{-\infty}^{\infty} \psi^* x \psi \, dx \\
&= \int_{-\infty}^{\infty} (2a/\pi)^{\frac{1}{4}} e^{-ax^2} x (2a/\pi)^{\frac{1}{4}} e^{-ax^2} \, dx \\
&= \int_{-\infty}^{\infty} x (2a/\pi)^{\frac{1}{2}} e^{-2ax^2} \, dx \\
&= 0
\end{aligned}$$

since the integrand is an odd function (an even function times an odd function is an odd function). This makes sense given that the gaussian wavefunction is symmetric around $x = 0$.

Let's calculate the average of x^2:

$$\begin{aligned}
\langle x^2 \rangle &= \int_{-\infty}^{\infty} \psi^* x^2 \psi \, dx \\
&= \int_{-\infty}^{\infty} (2a/\pi)^{\frac{1}{4}} e^{-ax^2} (x^2) (2a/\pi)^{\frac{1}{4}} e^{-ax^2} \, dx \\
&= \int_{-\infty}^{\infty} x^2 (2a/\pi)^{\frac{1}{2}} e^{-2ax^2} \, dx \\
&= \frac{1}{4a}
\end{aligned}$$

Let's calculate the average in p:

$$\begin{aligned}\langle p\rangle &= \int_{-\infty}^{\infty} \psi^* p \psi \, dx \\ &= \int_{-\infty}^{\infty} \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} - i\hbar \frac{d}{dx}\left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} \, dx \\ &= \int_{-\infty}^{\infty} \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} (-i\hbar)\left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} (-2ax) \, dx \\ &= 0\end{aligned}$$

since the integrand is an odd function.

Let's calculate the average of p^2:

$$\begin{aligned}\langle p^2\rangle &= \int_{-\infty}^{\infty} \psi^* p^2 \psi dx \\ &= -\hbar^2 \left(\frac{2a}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} 2a(ax^2 - 1) e^{-2ax^2} dx \\ &= -4\hbar^2 a^2 \left(\frac{2a}{\pi}\right)^{1/2} \int_0^{\infty} x^2 e^{-2ax^2} dx + 4\hbar^2 a \left(\frac{2a}{\pi}\right)^{1/2} \int_0^{\infty} e^{-2ax^2} dx \\ &= a\hbar^2\end{aligned}$$

We use Equation 3.1.8.1to check on the uncertainty

$$\begin{aligned}\Delta x^2 &= \langle x^2\rangle - \langle x\rangle^2 = \frac{1}{4a} - 0 \\ \Delta x &= \sqrt{\Delta x^2} = \frac{1}{2\sqrt{a}} \\ \Delta p^2 &= \langle p^2\rangle - \langle p\rangle^2 = a\hbar^2 - 0 \\ \Delta p &= \sqrt{\Delta p^2} = \hbar\sqrt{a}\end{aligned}$$

Finally we have

$$\Delta p \Delta x = \left(\frac{1}{2\sqrt{a}}\right)(\hbar\sqrt{a}) = \frac{\hbar}{2}$$

Not only does the Heisenburg uncertainly principle hold (Equation 3.1.8.12), but the equality is established for this wavefunction. This is because the Gaussian wavefunction (Equation 3.1.8.13) is special as discussed later.

? Exercise 3.8.1

A particle is in a state described by the ground state wavefunction of a particle in a box

$$\psi = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

where L is the length of the box and $0 \le x \le L$. Verify that the value of the product $\Delta p \, \Delta x$ is consistent with the predictions from the uncertainty principle (Equation 3.1.8.12).

The uncertainty principle is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space.

3.1.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **3.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

3.1.9: A Particle in a Three-Dimensional Box

Learning Objectives

- To demonstrate how the particle in 1-D box problem can extend to a particle in a 3D box
- Introduction to nodal surfaces (e.g., nodal planes)

The quantum particle in the 1D box problem can be expanded to consider a particle within a higher dimensions as demonstrated elsewhere for a quantum particle in a 2D box. Here we continue the expansion into a particle trapped in a 3D box with three lengths L_x, L_y, and L_z. As with the other systems, there is NO FORCE (i.e., no potential) acting on the particles *inside* the box (Figure 3.9.1).

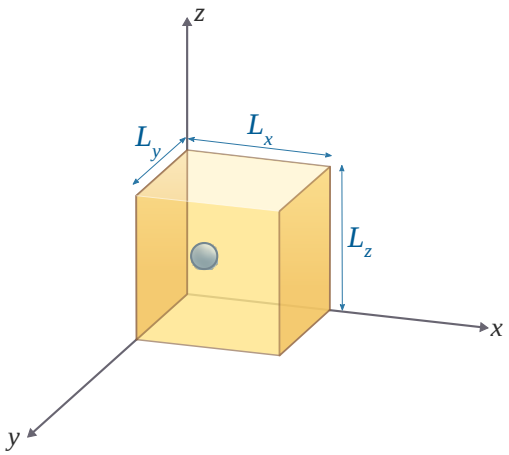


Figure 3.9.1 : A particle in 3D box with three lengths L_x, L_y, and L_z. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

The potential for the particle inside the box

$$V(\vec{r}) = 0$$

- $0 \leq x \leq L_x$
- $0 \leq y \leq L_y$
- $0 \leq z \leq L_z$
- $L_x < x < 0$
- $L_y < y < 0$
- $L_z < z < 0$

$\vec{r}$ is the vector with all three components along the three axes of the 3-D box: $\vec{r} = L_x\hat{x} + L_y\hat{y} + L_z\hat{z}$. When the potential energy is infinite, then the wavefunction equals zero. When the potential energy is zero, then the wavefunction obeys the Time-Independent Schrödinger Equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r) = E\psi(r) \tag{3.1.9.1}$$

Since we are dealing with a 3-dimensional figure, we need to add the 3 different axes into the Schrondinger equation:

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\psi(r)}{dx^2} + \frac{d^2\psi(r)}{dy^2} + \frac{d^2\psi(r)}{dz^2}\right) = E\psi(r) \tag{3.1.9.2}$$

The easiest way in solving this partial differential equation is by having the wavefunction equal to a **product** of individual function for each independent variable (e.g., the Separation of Variables technique):

$$\psi(x,y,z) = X(x)Y(y)Z(z) \tag{3.1.9.3}$$

Now each function has its own variable:

- $X(x)$ is a function of variable x only

- $Y(y)$ is a function of variable y only
- $Z(z)$ is a function of variable z only

Now substitute Equation 3.1.9.3into Equation 3.1.9.2and divide it by the xyzproduct:

$$\frac{d^2\psi}{dx^2} = YZ\frac{d^2X}{dx^2} \Rightarrow \frac{1}{X}\frac{d^2X}{dx^2}$$

$$\frac{d^2\psi}{dy^2} = XZ\frac{d^2Y}{dy^2} \Rightarrow \frac{1}{Y}\frac{d^2Y}{dy^2}$$

$$\frac{d^2\psi}{dz^2} = XY\frac{d^2Z}{dz^2} \Rightarrow \frac{1}{Z}\frac{d^2Z}{dz^2}$$

$$\left(-\frac{\hbar^2}{2mX}\frac{d^2X}{dx^2}\right) + \left(-\frac{\hbar^2}{2mY}\frac{d^2Y}{dy^2}\right) + \left(-\frac{\hbar^2}{2mZ}\frac{d^2Z}{dz^2}\right) = E \tag{3.1.9.4}$$

E is an energy constant, and is the sum of x, y, and z. For this to work, each term must equal its own constant. For example,

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}\varepsilon_x X = 0$$

Now separate each term in Equation 3.1.9.4to equal zero:

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}\varepsilon_x X = 0$$

$$\frac{d^2Y}{dy^2} + \frac{2m}{\hbar^2}\varepsilon_y Y = 0$$

$$\frac{d^2Z}{dz^2} + \frac{2m}{\hbar^2}\varepsilon_z Z = 0$$

Now we can add all the energies together to get the total energy:

$$\varepsilon_x + \varepsilon_y + \varepsilon_z = E \tag{3.1.9.5}$$

Do these equations look familiar? They should because we have now reduced the 3D box into three particle in a 1D box problems!

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}E_x X = 0 \approx \frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi \tag{3.1.9.6}$$

Now the equations are very similar to a 1-D box and the boundary conditions are identical, i.e.,

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

Use the normalization wavefunction equation for each variable:

$$\psi(x) = \begin{cases} \sqrt{\frac{2}{L_x}}\sin\frac{n\pi x}{L_x} & \text{if } 0 \le x \le L \\ 0 & \text{if } L < x < 0 \end{cases}$$

Normalization wavefunction equation for each variable (that substitute into Equation 3.1.9.3):

$$X(x) = \sqrt{\frac{2}{L_x}}\sin\left(\frac{n_x\pi x}{L_x}\right) \tag{3.1.9.7}$$

$$Y(y) = \sqrt{\frac{2}{L_y}}\sin\left(\frac{n_y\pi y}{L_y}\right) \tag{3.1.9.8}$$

$$Z(z) = \sqrt{\frac{2}{L_z}}\sin\left(\frac{n_z\pi z}{L_z}\right) \tag{3.1.9.9}$$

The limits of the three quantum numbers

- $n_x = 1, 2, 3, \ldots \infty$
- $n_y = 1, 2, 3, \ldots \infty$
- $n_z = 1, 2, 3, \ldots \infty$

For each constant use the de Broglie Energy equation:

$$\varepsilon_x = \frac{n_x^2 h^2}{8mL_x^2} \tag{3.1.9.10}$$

with $n_x = 1 \ldots \infty$

Do the same for variables n_y and n_z. Combine Equation 3.1.9.3 with Equations 3.1.9.7-3.1.9.9 to find the wavefunctions inside a 3D box.

$$\psi(r) = \sqrt{\frac{8}{V}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right) \tag{3.1.9.11}$$

with

$$V = \underbrace{L_x \times L_y \times L_z}_{\text{volume of box}}$$

To find the Total Energy, add Equation 3.1.9.10 and Equation 3.1.9.5

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \tag{3.1.9.12}$$

Notice the similarity between the energies a particle in a 3D box (Equation 3.1.9.12) and a 1D box.

Degeneracy in a 3D Cube

The energy of the particle in a 3-D cube (i.e., $L_x = L_y = L$) in the *ground state* is given by Equation 3.1.9.12 with $n_x = 1$, $n_y = 1$, and $n_z = 1$. This energy ($E_{1,1,1}$) is hence

$$E_{1,1,1} = \frac{3h^2}{8mL^2}$$

The ground state has only one wavefunction and no other state has this specific energy; the ground state and the energy level are said to be **non-degenerate**. However, in the 3-D cubical box potential the energy of a state depends upon the sum of the squares of the quantum numbers (Equation 3.1.9.11). The particle having a particular value of energy in the excited state *MAY* has several different stationary states or wavefunctions. If so, these states and energy eigenvalues are said to be **degenerate**.

For the first excited state, three combinations of the quantum numbers $(n_x,\ n_y,\ n_z)$ are $(2,\ 1,\ 1)$, $(1, 2, 1)$, $(1, 1, 2)$ The sum of squares of the quantum numbers in each combination is same (equal to 6). Each wavefunction has same energy:

$$E_{2,1,1} = E_{1,2,1} = E_{1,1,2} = \frac{6h^2}{8mL^2}$$

Corresponding to these combinations three different wavefunctions and **three** different states are possible. Hence, the first excited state is said to be three-fold or triply degenerate. The number of independent wavefunctions for the stationary states of an energy level is called as the **degree of degeneracy** of the energy level. The value of energy levels with the corresponding combinations and sum of squares of the quantum numbers

$$n^2 \ = n_x^2 + n_y^2 + n_z^2$$

as well as the degree of degeneracy are depicted in Table 3.9.1 .

Table 3.9.1 : Degeneracy properties of the particle in a 3-D cube with $L_x = L_y = L$.

$n_x^2 + n_y^2 + n_z^2$	Combinations of Degeneracy (n_x, n_y, n_z)	Total Energy (E_{n_x, n_y, n_z})	Degree of Degeneracy

$n_x^2+n_y^2+n_z^2$	Combinations of Degeneracy (n_x, n_y, n_z)						Total Energy (E_{n_x,n_y,n_z})	Degree of Degeneracy
3	(1,1,1)						$\frac{3h^2}{8mL^2}$	1
6	(2,1,1)	(1,2,1)	(1,1,2)				$\frac{6h^2}{8mL^2}$	3
9	(2,2,1)	(1,2,2)	(2,1,2)				$\frac{9h^2}{8mL^2}$	3
11	(3,1,1)	(1,3,1)	(1,1,3)				$\frac{11h^2}{8mL^2}$	3
12	(2,2,2)						$\frac{12h^2}{8mL^2}$	1
14	(3,2,1)	(3,1,2)	(2,3,1)	(2,1,3)	(1,3,2)	(1,2,3)	$\frac{14h^2}{8mL^2}$	6
17	(2,2,3)	(3,2,2)	(2,3,2)				$\frac{17h^2}{8mL^2}$	3
18	(1,1,4)	(1,4,1)	(4,1,1)				$\frac{18h^2}{8mL^2}$	3
19	(1,3,3)	(3,1,3)	(3,3,1)				$\frac{19h^2}{8mL^2}$	3
21	(1,2,4)	(1,4,2)	(2,1,4)	(2,4,1)	(4,1,2)	(4,2,1)	$\frac{21h^2}{8mL^2}$	6

Example 3.9.1 : Accidental Degeneracies

When is there degeneracy in a 3-D box when none of the sides are of equal length (i.e., $L_x \neq L_y \neq L_z$)?

Solution

From simple inspection of Equation 3.1.9.12 or Table 3.9.1 , it is clear that degeneracy originates from different combinations of n_x^2/L_x^2, n_y^2/L_y^2 and n_z^2/L_z^2 that give the same value. These will occur at common multiples of at least two of these quantities (the Least Common Multiple is one example). For example

if

$$\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2}$$

there will be a degeneracy. Also degeneracies will exist if

$$\frac{n_y^2}{L_y^2} = \frac{n_z^2}{L_z^2}$$

or if

$$\frac{n_x^2}{L_x^2} = \frac{n_z^2}{L_z^2}$$

and especially if

$$\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2} = \frac{n_z^2}{L_z^2}.$$

There are two general kinds of degeneracies in quantum mechanics: degeneracies due to a symmetry (i.e., $L_x = L_y$) and accidental degeneracies like those above.

Exercise 3.9.1

The 6th energy level of a particle in a 3D Cube box is 6-fold degenerate.

a. What is the energy of the 7th energy level?
b. What is the degeneracy of the 7th energy level?

Answer a

$$\frac{17h^2}{8mL^2}$$

Answer b

three-fold (i.e., there are three wavefunctions that share the same energy.

References

1. Atkins, Peter. Physical Chemistry 5th Ed. USA. 1994.
2. Fitts, Donald. Principles of Quantum Mechanics. United Kingdom, Cambridge. University Press. 1999
3. McQuarrie. Donald. Physical Chemistry A Molecular Approach. Sausalito, CA. University Science Books. 1997.
4. Riggs. N. V. Quantum Chemistry. Toronto, Ontario. The Macmillan Company. 1969
5. C. A. Hollingsworth, Accidental Degeneracies of the Particle in a Box, J. Chem. Educ., 1990, 67 (12), p 999

3.1.9: A Particle in a Three-Dimensional Box is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **3.9: A Particle in a Three-Dimensional Box** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

3.1.E: The Schrödinger Equation and a Particle in a Box (Exercises)

Solutions to select questions can be found online.

3.2

Determine from the following operators which are linear and nonlinear:

a. $\hat{A}f(x) = f(x)^2$ [square f(x)]
b. $\hat{A}f(x) = f^*(x)$ [form the complex conjugate of f(x)]
c. $\hat{A}f(x) = 0$ [multiply f(x) by zero]
d. $\hat{A}f(x) = [f(x)]^{-1}$ [take the reciprocal of f(x)]
e. $\hat{A}f(x) = f(0)$ [evaluate f(x) at x=0]
f. $\hat{A}f(x) = \ln f(x)$ [take the log of f(x)]

Solution

It is important to note that an operator $\hat{A}$ is *linear* if

$$\underbrace{\hat{A}[c_1 f(x) + c_2 f_2(x)]}_{\text{left side}} = \underbrace{c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)}_{\text{right side}}$$

and the operator is *nonlinear* if

$$\underbrace{\hat{A}[c_1 f_1(x) + c_2 f_2(x)]}_{\text{left side}} \neq \underbrace{c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)}_{\text{right side}}$$

a)

Evaluate the left side

$$\begin{aligned} \hat{A}[c_1 f(x) + c_2 f_2(x)] &= [c_1 f_1(x) + c_2 f_2(x)]^2 \\ &= c_1^2 f_1(x)^2 + 2c_1 f_1(x) c_2 f_2(x) + c_2^2 f_2(x)^2 \end{aligned}$$

Evaluate the right side

$$c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) = c_1 [f_1(x)]^2 + c_2 [f_2(x)]^2 \neq \hat{A}[c_1 f_1(x) + c_2 f_2(x)]$$

This operator is nonlinear

b)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1^* f_1^*(x) + c_2^* f_2^*(x)$$

Evaluate the right side

$$\begin{aligned} c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) &= c_1 f_1^*(x) + c_2 f_2^*(x) \\ &= \hat{A}[c_1 f_1(x) + c_2 f_2(x)] \end{aligned}$$

This operator is linear

c)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = 0$$

Evaluate the right side

$$\begin{aligned} c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) = c_1 f_1(x) + c_2 f_2(x) = 0 \\ = \hat{A}[c_1 f_1(x) + c_2 f_2(x)] \end{aligned}$$

This operator is linear

d)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = \frac{1}{c_1 f_1(x) + c_2 f_2(x)}$$

Evaluate the right side

$$c_1\hat{A}f_1(x)+c_2\hat{A}f_2(x)=\frac{c_1}{f_1(x)}+\frac{c_2}{f_2(x)}$$

$$\neq \hat{A}[c_1f_1(x)+c_2f_2(x)]$$

This operator is nonlinear

e)

Evaluate the left side

$$\hat{A}[c_1f_1(x)+c_2f_2(x)]=c_1f_1(0)+c_2f_2(0)$$

Evaluate the right side

$$=c_1\hat{A}f_1(x)+c_2\hat{A}f_2(x)$$

This operator is linear

f)

Evaluate the left side

$$\hat{A}[c_1f_1(x)+c_2f_2(x)]=\ln[c_1f_1(x)+c_2f_2(x)]$$

Evaluate the right side

$$c_1\hat{A}f_1(x)+c_2\hat{A}f_2(x)=c1\ln f_1(x)+c_2\ln f_2(x)$$

$$\neq \hat{A}[c_1f_1(x)+c_2f_2(x)]$$

This operator is nonlinear

3.8

Show that for a particle in a box with length a with state $n = 3$ that there are 3 locations along the x axis where the probability density is at a maximum.

Solution

The probability density for a particle in a box for state $n = 3$ is

$$\psi^* \psi = \frac{2}{a} \sin^2 \frac{3px}{a}$$

To maximize the probability density, take its derivative and set it equal to zero and solve for x .

$$\frac{d}{dx}\left[\frac{2}{a} \sin^2 \frac{3\pi x}{a}\right] = \frac{2}{a} \cdot 2 \cdot \sin \frac{3\pi x}{a} \cdot \cos \frac{3\pi x}{a} \cdot \frac{3\pi}{a} = 0$$

$$\sin \frac{3\pi x}{a} \cos \frac{3\pi x}{a} = 0$$

We want to not choose values of x that make $\sin \frac{3\pi x}{a} = 0$, as that means that the probability density will be zero. We will only choose the zeros of $\cos \frac{3\pi x}{a}$. So the possible values for x which make

$$\cos \frac{3\pi x}{a} = 0$$

are

$$\frac{3px}{a} = \frac{2m+1}{2} p \qquad m = 0, 1, 2, \ldots$$

$$x = \frac{(2m+1)\, a}{6}$$

We only choose $m = 0, 1, 2$ and not 3 because $m = 3$ would give $x = \frac{7a}{6}$ which is outside the box. So the locations are

$$x = \frac{a}{6}$$

$$x = \frac{a}{2}$$

$$x = \frac{5a}{6}$$

3.13

What range for L is possible for σ_x given:

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

where L is the length of the 1-D box? Hint: Remember that σ_x is the uncertainty in the position of a particle in a box.

Solution

For a particle in a box:

$$\langle x \rangle = \frac{\mathrm{L}}{2}$$

and

$$\langle x^2 \rangle = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}$$

$$\sigma_x = \sqrt{\frac{L^2}{3} - \frac{L^2}{2n^2\pi^2} - (\frac{\mathrm{L}}{2})^2}$$

By inspection, only values of σ_x less than L will make this statement true.

3.14

Using the trigonometric identity

$$\cos(2x) = 2\cos^2 x - 1$$

show that

$$\int_0^a 2\cos^2 \frac{n\pi x}{a} - 1 dx = 0$$

$$\int_0^a \cos \frac{2n\pi x}{a} dx = 0$$

$$\frac{a}{2n\pi} \sin(2n\pi) = 0$$

3.18

Is the wavefunction $\phi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$ orthonormal over $0 \leq x \leq L$. Explain your reasoning.

Solution

For a wavefunction to be orthonormal, it has to satisfy these conditions 1.) it has to be orthogonal and 2.) it has to be normalized.

To show that it is orthogonal:

$$\int_0^L \phi_m \phi *_n \, dx = 0$$

when $m \neq$ n

To show that that the wavefunction is normalized it must follow that

$$\int_0^L \phi_n \phi *_n \, dx = 1$$

when m=n

Because our wavefunction satisfies both conditions, it is an orthonormal function.

We find that

$$\langle \psi_3 | \psi_3 \rangle = \int_{-\infty}^{\infty} \frac{2}{L} (\sin \frac{3\pi x}{L})^2 dx = 1$$

and

$$\langle \psi_4 | \psi_4 \rangle = \int_{-\infty}^{\infty} \frac{2}{L} (\sin \frac{3\pi x}{L})(\sin \frac{4\pi x}{L}) dx = 0$$

From orthogonality, we can learn that if n is not equal to m, our dot product will always be zero. But if n = m our dot product will equal 1.

3.22

What is the Heisenberg Uncertainty Principle? Do position and momentum follow the uncertainty principle; why or why not? If they do, what is the minimum uncertainty in the velocity of an electron if it is known to be within 1.5nm of a nucleus?

Solution

The Heisenberg Uncertainty Principle states that two properties that follow cannot be **simultaneously** measured to **arbitrary** precision. Position and momentum follow the principle. If one were to try and commute these two operators, one would not get zero and therefore the properties do not commute. If they do not commute then they cannot be measured to arbitrary precision.

We know that

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

And that p = mv. This gives

$$m \Delta x \Delta v \geq \frac{\hbar}{2}$$

The mass of an electron is known is $m_e \approx 9.1 \times 10^{-31}\ kg$. The problem also gives Δx to be 1.5 nm. From here, it becomes a plug and chug to solve for Δv.

$$\Delta v = 3.86 \times 10^{4}$$

3.23

Describe the degeneracies of a two-dimensional box whose two sides have different lengths.

Solution

The energies of a two-dimensional box is given by,

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$$

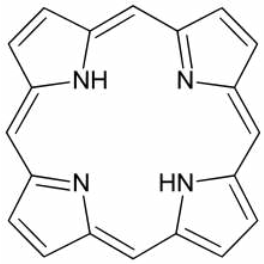
We can see that even if $a \neq b$, the energy levels will not necessarily be degenerate.

3.26

How many degenerate states do the first three energy levels for a three-dimensional particle in a box have if $a = b = c$?

3.27

Metal porphyrin molecules are commonly in many proteins and it has the general structure.



This molecule is planar, so we can approximate π electrons as being confined inside a square. What are energy levels and corresponding degeneracies of a particle in a square of side m? Porphyrin molecules have 18 π electrons. If the length of the molecule is 850 pm, what is the lowest energy absorption of the porphyrin molecules? (the experimental value ≈ 17,000 cm^{-1})

Solution

The first energy level is $E_{(1,1,1)}$ which has no degeneracy.

The second energy state is $E_{(2,1,1)}=E_{(1,2,1)}=E_{(1,1,2)}$, therefore it has three degenerate states.

The third energy state is $E_{(2,2,1)}=E_{(2,1,2)}=E_{(1,2,2)}$, therfeore it has three degenerate states.

3.26

For a two dimensional box of width w and height $h = \sqrt{a}w$, calculate all possible energy combinations between E_{11} and E_{33} note any degeneracy.

Solution

The energy of a two dimensional particle in the box has the form,

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{w^2} + \frac{n_y^2}{h^2}\right)$$

In this specific case $h = \sqrt{a}w$ so we can simplify the problem to,

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{w^2} + \frac{2n_y^2}{w^2}\right)$$

Now we can tabulate the energy level indicating degeneracy.

E_{xy}	**Degeneracy**	$\frac{E8mw^2}{h^2}$
E_{11}	1	3
$E_{12}. E_{31}$	2	5
E_{21}	1	4
E_{22}	1	6
$E_{13}. E_{32}$	2	7
E_{23}	1	8
E_{33}	1	9

3.32

In this problem, we will explore the quantum-mechanical problem of a free particle that is not restricted to a finite region. Remember quantized energies of a particle in a box is a direct result from the boundary conditions set by the confines of the box.

When the potential energy $V(x)$ is equal to zero and the Schrodinger equation become

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi(x) = 0$$

The two solutions to this Schrodinger equation are

$$\psi_1(x) = A_1 e^{ikx}$$

$$\psi_2(x) = A_2 e^{-ikx}$$

where

$$k = \frac{(2mE)^(1/2)}{\hbar}$$

Show that $\psi_1(x)$ and $\psi_2(x)$ are solution to the Schrodinger equation where the potential energy $V(x)$ is equal to zero

Solution

In order to prove that $\psi_1(x)$ and $\psi_2(x)$ are solutions we need to mention a few values

$$p = \hbar k \rightarrow k = p/\hbar \rightarrow k = \frac{(2mE)^{1/2}}{\hbar}$$

Now we have

$$\frac{d^2 Ae^{\pm ikx}}{dx^2} + \frac{2mE}{\hbar^2} Ae^{\pm ikx} = 0$$

$$A(\pm ik)^2 e^{\pm ikx} + \frac{2mE}{\hbar^2} Ae^{\pm ikx} = 0 \rightarrow -k^2 + \frac{2mE}{\hbar^2} = 0$$

Cancel the like terms

Thus, $k = \frac{(2mE)^{1/2}}{\hbar}$, which equals the original k value

3.32

Show that E had to be a positive value, since when E is negative the wave function become unbounded for large x values

Solution

If E < 0 then k becomes imaginary, $k = ik$

$\psi = Ae^{\pm ikx} = Ae^{\pm i(ik)x} Ae^{\pm kx}$

For $\psi_1(x) = A_1 e^{-kx}$ this will blow up for x → - ∞

For $\psi_2(x) = A_2 e^{kx}$ this will blow up for x → ∞

3.32

With $\hat{P}\ \psi_1(x)$ and $\hat{P}\ \psi_2(x)$ as eigenvalue equations, show that

$$\hat{P}\psi_1(x) = -i\hbar\frac{d\psi_1}{dx} = \hbar k\psi_1$$

and

$$\hat{P}\psi_2(x) = -i\hbar\frac{d\psi_2}{dx} = -\hbar k\psi_2$$

Solution

$$\hat{P}\psi_1(x) = -i\hbar\frac{d\psi_1}{dx} = -i\hbar\frac{d}{dx}A_1e^{+ikx} = -i\hbar A_1(ik)e^{ikx} = +\hbar kA_1e^{ikx} = +\hbar k\psi_1$$

$$\hat{P}\psi_2(x) = -i\hbar\frac{d\psi_2}{dx} = -i\hbar\frac{d}{dx}A_2e^{-ikx} = -i\hbar A_2(-ik)e^{ikx} = -\hbar kA_1e^{-ikx} = -\hbar k\psi_2$$

Now we can show that

$$E = \frac{p^2}{2m} = \frac{\pm(\hbar)^2}{2m} = \frac{\hbar^2k^2}{2m}$$

3.32

Show that $\psi_1^*\psi_1(x) = A_1^*A_1 = |A_1|^2$ and that $\psi_2^*\psi_2(x) = A_2^*A_2 = |A_2|^2$

Solution

$$\begin{aligned}\psi_1^*\psi_1(x) &= (A_1e^{ikx})^*A_1e^{ikx}\\ &= A_1^*A_1e^{-ikx}e^{ikx}\\ &= A_1^*A_1e^{-ikx+ikx} = A_1^*A_1e^0\\ &= A_1^*A_1\\ \psi_2^*\psi_2(x) &= (A_2e^{-ikx})^*A_2e^{-ikx}\\ &= A_2^*A_2e^{ikx-ikx}\\ &= A_2^*A_2e^0 = A_2^*A_2\end{aligned}$$

ψ has equal probability to be everywhere when $\Delta x = \infty$ and $\Delta p = 0$

3.33A

Assuming that a particle is characterized by a standing de Broglie wave, come up with an equation for the allowed energies of a particle in a one-dimensional box.

Solution

The de Broglie relationship is

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

Because the waves are standing waves, an integral number of half wave-lengths will fit in the box or:

$$a = \frac{n\lambda}{2}$$

and

$$a = \frac{nh}{2p}$$

Solving for p yields

$$p = \frac{nh}{2a}$$

and the corresponding energy is

$$E = \frac{mv^2}{2} = \frac{p^2}{2m} = \frac{1}{2m}\frac{n^2h^2}{4a^2} = \frac{n^2h^2}{8ma^2}$$

3.33B

Derive the lowest allowed velocity for a proton in a box of length 10^{-14} m (approximate size of nucleus), assuming the particle is described by a standing deBroglie wave.

Solution

The de Broglie wavelength is

$$\lambda = \frac{h}{p} = \frac{h}{m_p v}$$

For a one dimensional wave that has nodes on both ends of a box, an integer number of half wavelengths can fit, so

$$n\left(\frac{\lambda}{2}\right) = L$$

Substituting this wavelength in the de Broglie relationship, one gets

$$\nu = \frac{hn}{2m_L}$$

lowest allowed velocity will have $n = 1$

$$\nu = \frac{(6.626 \times 10^{-34})(1)}{2 \times (1.67 \times 10^{-27})(10^{-14})}$$

$$= 19.8 \times 10^{6} m/s$$

3.33C

If a particle in a one-dimensional box is described by standing de Broglie waves within the box, derive an equation for the allowed energies. Then use that equation to find the transition energy from n=1 to n=2 given the length of the box is 350 pm and the mass of an electron is $9.109 \times 10^{-31} kg$.

Solution

The de Broglie formula is

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

An integral number of half-wavelengths will fit in the box because the waves are standing waves so

$$\frac{n\lambda}{2} = a$$

$$\frac{nh}{2p} = a$$

Then solving for p

$$p = \frac{nh}{2a}$$

Therefore the energy equation is

$$E = \frac{mv^2}{2} = \frac{p^2}{2,m} = \frac{1}{2m}\frac{n^2h^2}{4a^2} = \frac{n^2h^2}{8ma^2}$$

Just plug into the equation to find the transition energy

$$\Delta E = \frac{h^2}{8m_e a^2}(2^2 - 1^2)$$

$$\Delta E = \frac{(6.626 \times 10^{-34} J\cdot s)^2(3)}{8(9.109 \times 10^{-31} kg)(350 \times 10^{-12} m)^2}$$

$$\Delta E = 1.47 \times 10^{-18} J$$

3.35A

Consider the two wavefunctions

$$\psi_n(x) = \sin \frac{n\pi x}{a}$$

with even n numbers and

$$\psi_n(x) = \cos \frac{n\pi x}{a}$$

with odd n numbers.

Prove that the wavefunctions can be symmetric and antisymmetric by using the operation x to -x, a is a constant.

Given that the Schrödinger equation has the expression:

$$\hat{H}(x)\psi_n(x) = E_n\psi_n(x)$$

Through the operation x to -x, the equation now becomes:

$$\hat{H}(-x)\psi_n(-x) = E_n\psi_n(-x)$$

Show that

$$\hat{H}(x) = \hat{H}(-x)$$

is true to prove the Schrödinger equation.

Solution

Substituting x by $-x$, for odd n numbers,

$$\hat{\psi}_n(-x) = \cos \frac{-n\pi x}{a} = \cos \frac{n\pi x}{a} = \hat{\psi}_n(x) \tag{3.1.E.1}$$

For even n numbers,

$$\hat{\psi}_n(-x) = sin\frac{-n\pi x}{a} = -sin\frac{n\pi x}{a} = -\hat{\psi}_n(x) \tag{3.1.E.2}$$

Thus, the wavefunction for odd n number is symmetric and even n numbers is antisymmetric.

And,

$$\hat{H}(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} = \hat{H}(x) \tag{3.1.E.3}$$

$$\hat{H}(-x) = -\frac{\hbar^2}{2m}\frac{d^2}{d(-x)^2} = \hat{H}(x) \tag{3.1.E.4}$$

Thus,

$$\hat{H}(x) = \hat{H}(-x)$$

and

$$\hat{H}(x)$$

is an even function of x.

3.35B

Show that the Hamiltonian for a Rigid Rotor Model is odd.

Solution

$$\hat{H}(x) = \hat{H}(-x)$$

so

$$\hat{H} = -\frac{h^2}{4\pi\mu}\nabla^2$$

$$\nabla^2 = \frac{d^2y}{dx^2}\frac{d^2y}{dy^2}\frac{d^2y}{dz^2}$$

so

$$\frac{d^2y}{dx^2}(x) = 0$$

and

$$\frac{d^2y}{dx^2}(-x) = 0$$

so

$$\hat{H}(x) = 0$$

and

$$\hat{H}(-x) = 0$$

so

$$\hat{H}(x) = \hat{H}(-x)$$

3.1.E: The Schrödinger Equation and a Particle in a Box (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

3.2: The Harmonic Oscillator and the Rigid Rotor



The harmonic oscillator is common: It appears in many everyday examples. Pendulums, springs, electronics (such as the RLC circuit), standing waves on a string, etc. It's trivial to set up demonstrations of these phenomena, and we see them constantly. **The harmonic oscillator is intuitive:** We can picture the forces on systems such as pendulum or a plucked string. This makes it simple to study in the classroom. In contrast, there are many "everyday" examples that are not intuitive. **The harmonic oscillator is mathematically simple:** Math is part of physics. In studying simple harmonic motion, students can immediately use the formulas that describe its motion. These formulas are understandable: for example, the equation for frequency shows the intuitive result that increasing spring stiffness increases frequency.

3.2.1: A Harmonic Oscillator Obeys Hooke's Law
3.2.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule
3.2.3: The Harmonic Oscillator Approximates Vibrations
3.2.4: The Harmonic Oscillator Energy Levels
3.2.5: The Harmonic Oscillator and Infrared Spectra
3.2.6: The Harmonic-Oscillator Wavefunctions involve Hermite Polynomials
3.2.7: Hermite Polynomials are either Even or Odd Functions
3.2.8: The Energy Levels of a Rigid Rotor
3.2.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule
3.2.E: The Harmonic Oscillator and the Rigid Rotor (Exercises)

3.2: The Harmonic Oscillator and the Rigid Rotor is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

3.2.1: A Harmonic Oscillator Obeys Hooke's Law

The motion of two atoms in a diatomic molecule can be separated into translational, vibrational, and rotational motions. Both rotation and vibrational motions are internal motions that do not change the center of mass for the molecule (Figure 5.1.1), which is described by translational motion. Quantum translational motions can be modeled with the particle in a box model discussed previously and rotation and vibration can be modeled via the **rigid rotor** and **harmonic oscillator** models, respectively.



Figure 5.1.1 : Two atoms connected by a vibrating bond. There is a rotation around the common center of mass, and oscillation in bond distance. (CC SA-BY, 3.0; www.cleonis.nl).

Before delving into the quantum mechanical harmonic oscillator, we will introduce the classical harmonic oscillator (i.e., involving classical mechanics) to build an intuition that we will extend to the quantum world. A classical description of the vibration of a diatomic molecule is needed because the quantum mechanical description begins with replacing the classical energy with the Hamiltonian operator in the Schrödinger equation. It also is interesting to compare and contrast the classical description with the quantum mechanical picture.

The Classical Harmonic Oscillator

Simple harmonic oscillators about a potential energy minimum can be thought of as a ball rolling frictionlessly in a curved dish or a pendulum swinging frictionlessly back and forth (Figure 5.1.2). The restoring forces are precisely the same in either horizontal direction.

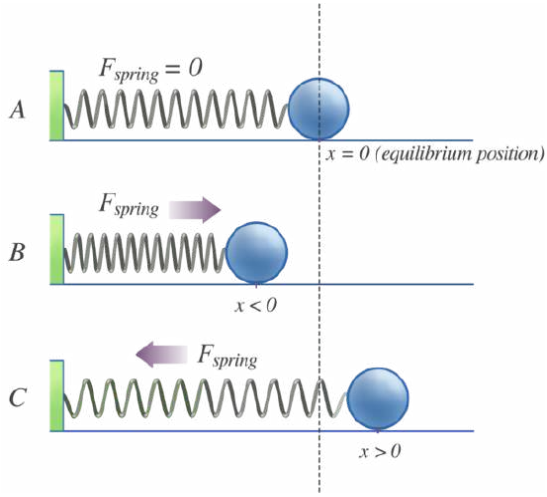


Figure 5.1.2 : A mass connected to a spring that follows Hooke's law is a system that, when displaced from its equilibrium position ($x_o = 0$), experiences a restoring force, F that is proportional to the displacement, x from the equilibrium length (x_o). (CC BY-NC; Ümit Kaya via LibreTexts)

If we consider the bond to behave like a mass on a spring (Figure 5.1.2), then this restoring force (F) is proportional to the displacement (x) from the equilibrium length (x_o) - this is *Hooke's Law*:

$$F = -kx \tag{3.2.1.1}$$

where k is the force constant. Hooke's Law says that the force is proportional to, but in opposite direction to, the displacement (x). The force constant reflects the **stiffness** of the spring. The idea incorporated into the application of Hooke's Law to a diatomic molecule is that when the atoms move away from their equilibrium positions, a restoring force is produced that increases proportionally with the displacement from equilibrium. The potential energy for such a system increases *quadratically* with the displacement.

$$V(x) = \frac{1}{2}kx^2 \tag{3.2.1.2}$$

Hooke's Law or the harmonic (i.e. quadratic) potential given by Equation 3.2.1.2is an excellent *approximation* for the vibrational oscillations of molecules. The magnitude of the force constant k depends upon the nature of the chemical bond in molecular systems just as it depends on the nature of the spring in mechanical systems. The larger the force constant, the stiffer the spring or the stiffer the bond. Since it is the electron distribution between the two positively charged nuclei that holds them together, a double bond with more electrons has a larger force constant than a single bond, and the nuclei are held together more tightly.

Caution

A stiff bond with a large force constant is not necessarily a strong bond with a large dissociation energy. A harmonic oscillator has no dissociation energy since it CANNOT be broken - there is always a restoring force to keep the molecule together. This is one of many deficiencies in using the harmonic oscillator model to describe molecular vibrations.

Two atoms or one?

You may have questioned the applicability of the harmonic oscillator model involving one moving mass bound to a fix wall via a spring like in Figure 5.1.2 for the vibration of a diatomic molecule with two moving masses like in Figure 5.1.1 . It turned out the two are mathematically the same with internal vibration motion described by a single reduced particle with a reduced mass μ.

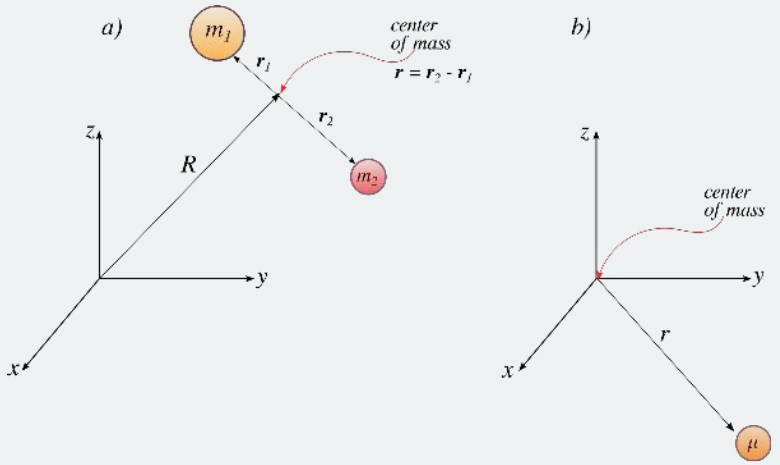


Figure 5.1.3 : Diagrams of the coordinate systems and relevant vectors for the motion of (a) a two-particle diatomic molecule with atoms of mass m_1 and m_2 and (b) the equivalent one-particle pseudo-particle of reduced mass μ. (CC BY-NC; Ümit Kaya via LibreTexts)

For a diatomic molecule, Figure 5.1.3 , the vector $\vec{r}$ corresponds to the internuclear axis. The magnitude or length of r is the bond length, and the orientation of r in space gives the orientation of the internuclear axis in space. Changes in the orientation correspond to rotation of the molecule, and changes in the length correspond to vibration. The change in the bond length from the equilibrium bond length is the **vibrational coordinate** for a diatomic molecule.

Example 5.1.1

a. Show that minus the first derivative of the harmonic potential energy function in Equation 3.2.1.2with respect to x is the Hooke's Law force in Equation 3.2.1.1.
b. Show that the second derivative is the force constant, k.
c. At what value of x is the potential energy a minimum; at what value of x is the force zero?
d. Sketch graphs to compare the potential energy and the force for a system with a large force constant to one with a small force constant.

Solution a

Hooke's Law for a spring entails that the force applied on a spring F is equal to the force constant, $-k$ times the distance compressed or stretched, x (Equation 3.2.1.1). The derivative of $V(x) = 0.5kx^2$ is

$$V'(x) = (2)\left(\frac{1}{2}\right)kx = kx.$$

The negative of this is $-V'(x) = -kx$ which is exactly equal to Hooke's Law.

Solution b

The second derivative

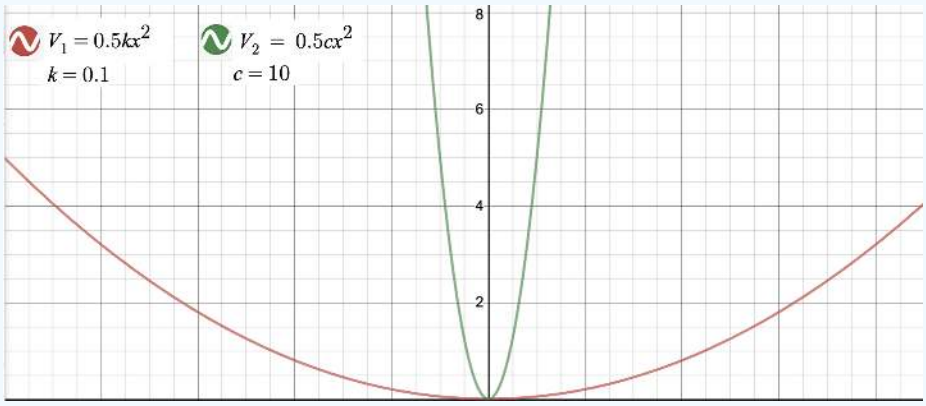
$$V\text{''}(x) = \frac{d}{dx}kx = k$$

Thus, the second derivative of this equation for potential energy is equal to the force constant, k.

Solution c

To find the minimum potential energy, it is easiest to set the first derivative equal to zero and solve for x. When $V'(x) = kx = 0$ then x must be equal to zero. Thus, the minimum potential energy is when x=0. Plugging this into Hooke's Law, $F(0) = -k(0) = 0$ so this is also the value for x when the force is zero.

Solution d



The force constant has a drastic effect on both the potential energy and the force. A system with a large force constant requires minimal change in x to have a drastic change in potential energy or force, whereas a system with a small force constant is the exact opposite phenomenon.

Solving the Harmonic Oscillator Model

The classical equation of motion for a one-dimensional simple harmonic oscillator with a particle of mass m attached to a spring having spring constant k is

$$m\frac{d^2x(t)}{dt^2} = -kx(t) \tag{3.2.1.3}$$

which can be rewritten in the standardform:

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0 \tag{3.2.1.4}$$

Equation 3.2.1.3 is a linear second-order differential equation that can be solved by the standard method of factoring and integrating. The resulting solution to Equation 3.2.1.3is

$$x(t) = x_o \sin(\omega t + \phi) \tag{3.2.1.5}$$

with

$$\omega = \sqrt{\frac{k}{m}} \tag{3.2.1.6}$$

and the momentum has time dependence

$$\begin{aligned} p &= mv \\ &= mx_o\omega\cos(\omega t + \phi) \end{aligned}$$

Figure 5.1.4 show the displacement of the bond from its equilibrium length as a function of time. Such motion is called **harmonic**.

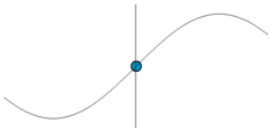


Figure 5.1.4 : Solution to the Harmonic Oscillator. Displacement (y-axis) is plotted as a function of time.

Example 5.1.2

Substitute the following functions into Equation 3.2.1.4 to demonstrate that they are both possible solutions to the classical equation of motion.

a. $x(t) = x_0 e^{i\omega t}$
b. $x(t) = x_0 e^{-i\omega t}$

where

$$\omega = \sqrt{\frac{k}{m}}$$

Note that the Greek symbol ω for frequency represents the angular frequency $2\pi\nu$.

Solution a

This requires simply placing the given function $x(t) = x_0 e^{i\omega t}$ into Equation 3.2.1.4

$$\begin{aligned} \frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) &= 0 \\ \frac{d^2}{dt^2}\left(x_o e^{i\omega t}\right) + \frac{k}{m}x_o e^{i\omega t} &= 0 \\ x_o\frac{d^2}{dt^2}\left(e^{i\omega t}\right) + \frac{k}{m}x_o e^{i\omega t} &= 0 \\ x_o i^2\omega^2\left(e^{i\omega t}\right) + \frac{k}{m}x_o e^{i\omega t} &= 0 \\ x_o i^2\omega^2 e^{i\omega t} + \frac{k}{m}x_o e^{i\omega t} &= 0 \\ x_o i^2\omega^2 + \frac{k}{m}x_o &= 0 \\ -x_o\frac{k}{m} + \frac{k}{m}x_o = 0 \;\text{ with }\; \omega &= \sqrt{\frac{k}{m}} \end{aligned}$$

Solution b

This requires simply placing the given function $x(t) = x_0 e^{-i\omega t}$ into Equation 3.2.1.4

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0$$

$$\frac{d^2}{dt^2}\left(x_o e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o\frac{d^2}{dt^2}\left(e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2\left(e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2 e^{-i\omega t} + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2 + \frac{k}{m}x_o = 0$$

$$-x_o\frac{k}{m} + \frac{k}{m}x_o = 0 \text{ with } \omega = \sqrt{\frac{k}{m}}$$

Exercise 5.1.1

Show that sine and cosine functions also are solutions to Equation 3.2.1.4

Answer

Using Equation 3.2.1.4

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0$$

with $\omega = \sqrt{\frac{k}{m}}$.

For

$$x(t) = x_o\sin(\omega t + \phi)$$

Take the second derivative of $x(t)$

$$\begin{aligned}\frac{d^2x(t)}{dt} &= -\omega^2 x_o\sin(\omega t + \phi)\\ &= \omega^2 x_o\sin(\omega t + \phi)\\ &= -\frac{k}{m}x_o\sin\left(\sqrt{\frac{k}{m}}t + \phi\right)\end{aligned}$$

Plug in $x(t)$ and the second derivative of $x(t)$ into Equation 3.2.1.4

$$-\frac{k}{m}x_o\sin\left(\sqrt{\frac{k}{m}}t + \phi\right) + \frac{k}{m}x_o\sin\left(\sqrt{\frac{k}{m}}t + \phi\right) = 0$$

Hence, the sine equation is a solution to Equation 3.2.1.4

We do the same for the cosine function

$$x(t) = x_o\cos(\omega t + \phi)$$

Take the second derivative of $x(t)$

$$\begin{aligned}\frac{d^2x(t)}{dt} &= -\omega^2 x_o \cos(\omega t + \phi) \\ &= -\omega^2 x_o \cos(\omega t + \phi) \\ &= -\frac{k}{m} x_o \cos\left(\sqrt{\frac{k}{m}} t + \phi\right)\end{aligned}$$

Plug in $x(t)$ and the second derivative of $x(t)$ into Equation 3.2.1.4

$$-\frac{k}{m} x_o \cos\left(\sqrt{\frac{k}{m}} t + \phi\right) + \frac{k}{m} x_o \cos\left(\sqrt{\frac{k}{m}} t + \phi\right) = 0$$

The cosine equation is also a solution to Equation 3.2.1.4

? Exercise 5.1.2

Identify what happens to the frequency of the motion as the force constant increases in one case and as the mass increases in another case. If the force constant is increased 9-fold and the mass is increased by 4-fold, by what factor does the frequency change?

Answer

This is a simple application of Equation 3.2.1.6 As the force constant increases, the frequency of the motion increases, while as the mass increases, the frequency of the motion decreases. If the force constant increased 9-fold and the mass increased 4-fold,

$$\omega = \sqrt{\frac{9k}{4m}} = \frac{3}{2}\left(\frac{k}{m}\right)$$

The entire frequency of motion would increase by a factor of 3/2.

Harmonic Oscillator Energies

The energy of the vibration is the sum of the kinetic energy and the potential energy. The momentum associated with the harmonic oscillator is

$$p = m\frac{dx}{dt} \tag{3.2.1.7}$$

so combining Equations 3.2.1.7and 3.2.1.2, the total energy can be written as

$$E = T + V \tag{3.2.1.8}$$

$$= \frac{p^2}{2m} + \frac{k}{2}x^2 \tag{3.2.1.9}$$

The total energy of the harmonic oscillator is equal to the maximum potential energy stored in the spring when $x = \pm A$, called the *turning points (*Figure 5.1.5). The total energy (Equation 3.2.1.9) is continuously being shifted between potential energy stored in the spring and kinetic energy of the mass.

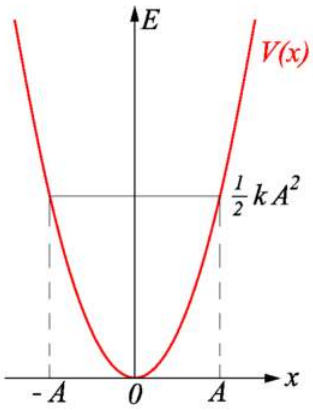


Figure 5.1.5 : The potential $V(x)$ for a harmonic oscillator. Vertical axis energy; horizontal axis displacement x. The potential energy $V(x) = ½kx^2$ is shown in red. (Paul Wormer Wikipedia).

The motion of a classical oscillator is confined to the region where its kinetic energy is nonnegative, which is what the energy relation Equation 3.2.1.9 says. Physically, it means that a classical oscillator can never be found beyond its turning points, and its energy depends only on how far the turning points are from its equilibrium position. The energy of a classical oscillator changes in a continuous way. The lowest energy that a classical oscillator may have is zero, which corresponds to a situation where an object is at rest at its equilibrium position. The zero-energy state of a classical oscillator simply means no oscillations and no motion at all (a classical particle sitting at the bottom of the potential well in Figure 5.1.5). When an object oscillates, no matter how big or small its energy may be, it spends the longest time near the turning points, because this is where it slows down and reverses its direction of motion. Therefore, the probability of finding a classical oscillator between the turning points is highest near the turning points and lowest at the equilibrium position. (Note that this is not a statement of preference of the object to go to lower energy. It is a statement about how quickly the object moves through various regions.)

Example5.1.3

a. What happens to the frequency of the oscillation as the vibration is excited with more and more energy?
b. What happens to the maximum amplitude of the vibration as it is excited with more and more energy?

Solution

a. Frequency

The energy of the harmonic oscillator can be written as

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

and the frequency of oscillation is $\omega = \sqrt{\frac{k}{m}}$. Notice that the frequency depends only on the stiffness (k) and reduced mass (μ) of the oscillator and not on the energy. Hence, increasing the energy of the vibrations does not affects its frequency.

b. Amplitude

The kinetic and potential terms for energy of the harmonic oscillator can be written as

$$\begin{aligned} E &= K + V \\ &= \frac{1}{2}m\omega^2 A^2 \sin^2 \omega t + \frac{1}{2}kA^2 \cos^2 \omega t \end{aligned}$$

with $\omega = \sqrt{\frac{k}{m}}$ so

$$\begin{aligned} E &= \frac{1}{2}kA^2\left(\sin^2 \omega t + \cos^2 \omega t\right) \\ &= \frac{1}{2}kA^2 \end{aligned}$$

The maximum amplitude of the vibration will **increase** as the energy **increases.**

Exercise 5.1.3

If a molecular vibration is excited by collision with another molecule and is given a total energy E_{hit} as a result, what is the maximum amplitude of the oscillation? Is there any constraint on the magnitude of energy that can be introduced?

Answer

The equation that defines the energy of a molecular vibration can be approximated is:

$$E_{hit} = T + V = \frac{p^2}{2m} + \frac{k}{2}x$$

The maximum amplitude of a harmonic oscillator is equal to x when the kinetic energy term of total energy equals zero

$$E_{hit} = \frac{k}{2}x$$

Solving for x gives the maximum amplitude:

$$x = \sqrt{\frac{2}{k}E_{hit}}$$

The constraint for the energy that can be introduced cannot be greater than the energy required to break the bond between atoms.

3.2.1: A Harmonic Oscillator Obeys Hooke's Law is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.1: A Harmonic Oscillator Obeys Hooke's Law** by Michael Fowler is licensed CC BY-NC-SA 4.0.

3.2.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule

For studying the energetics of molecular vibration we take the simplest example, a diatomic heteronuclear molecule AB. Let the respective masses of atoms A and B be m_A and m_B. For diatomic molecules, we define the reduced mass μ_{AB} by:

$$\mu_{AB} = \frac{m_A\, m_B}{m_A + m_B} \tag{3.2.2.1}$$

Reduced mass is the representation of a two-body system as a single-body one. When the motion (displacement, vibrational, rotational) of two bodies are only under mutual interactions, the inertial mass of the moving body with respect to the body at rest can be simplified to a reduced mass.

Reduced Mass

Viewing the multi-body system as a single particle allows the separation of the motion: vibration and rotation, of the particle from the displacement of the center of mass. This approach greatly simplifies many calculations and problems.

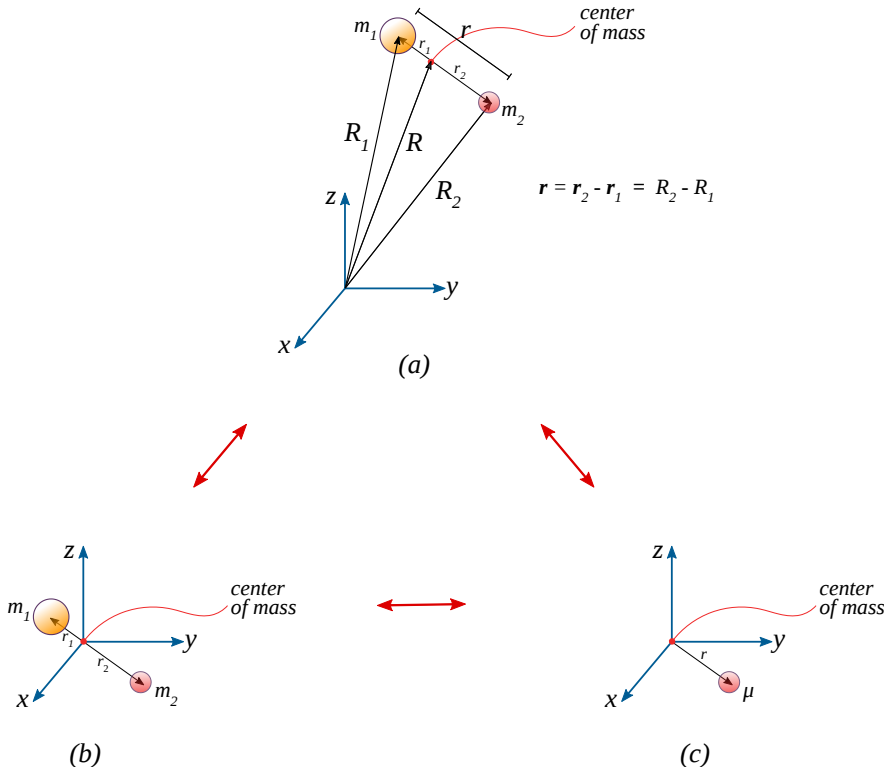


Figure 5.2.1 : a) the individual vectors to the particles m_1 and m_2 in the coordinate space and the resultant vector. b) center of mass. c) reduced mass. (CC BY-NC; Ümit Kaya via LibreTexts)

This concept is readily used in the general motion of diatomics, i.e. simple harmonic oscillator (vibrational displacement between two bodies, following Hooke's Law), the rigid rotor approximation (the moment of inertia about the center of mass of a two-body system), spectroscopy, and many other applications.

Example 5.2.1 : Reduced Mass

Determine the reduced mass of the two body system of a proton and electron with $m_{proton} = 1.6727 \times 10^{-27}\ kg$ and $m_{electron} = 9.110 \times 10^{-31}\ kg$).

Answer

$$\mu_{pe} = \frac{(1.6727 \times 10^{-27})(9.110 \times 10^{-31})}{1.6727 \times 10^{-27} + 9.110 \times 10^{-31}}$$
$$= 9.105 \times 10^{-31} kg$$

The Quantum Harmonic Oscillator

The classical Harmonic Oscillator approximation is a simple yet powerful representation of the energetics of an oscillating spring system. Central to this model is the formulation of the quadratic potential energy

$$V(x) \approx \frac{1}{2}kx^2 \tag{3.2.2.2}$$

One problem with this classical formulation is that it is not general. We cannot use it, for example, to describe vibrations of diatomic molecules, where quantum effects are important. This require the formulation for Schrödinger Equation using Equation 3.2.2.2

$$\hat{H}|\psi\rangle = \left[\frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right]|\psi\rangle = E|\psi\rangle$$

Solving this quantum harmonic oscillator is appreciably harder than solving the Schrödinger Equation for the simpler particle-in-the-box model and is outside the scope of this text. However, as with most quantum modules (and in contrast to the classical harmonic oscillator), the energies are quantized in terms of a quantum number (v in this case):

$$E_v = \hbar\left(\sqrt{\frac{k}{\mu}}\right)\left(v + \frac{1}{2}\right) \tag{3.2.2.3}$$
$$= h\nu\left(v + \frac{1}{2}\right) \tag{3.2.2.4}$$

with the natural vibrational frequency of the system given as

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{3.2.2.5}$$

and the mass, μ, is the reduced mass of the system (Equation 3.2.2.1).

Warning

Be careful to distinguish ν, the symbol for the natural frequency (as a Greek nu) from v the quantum harmonic oscillator quantum number (Latin v).

Caution: Do Not Use Atomic Weights to Calculate Reduced Masses

The vibrational frequencies given by Equation 3.2.2.5depend on the force constants (k) and the atomic masses of the vibrating nuclei via the reduced mass (μ). It should be clear that the substitution of one isotope of an atom in a molecule for another isotope will affect the atomic masses and therefore the reduced mass (via Equation 3.2.2.1) and therefore the vibrational frequencies (via Equation 3.2.2.5).

It is important to remember that the Periodic Table gives only atomic weights of elements, which are scaled averages of atoms normally encountered in the laboratory (Table 5.2.1). To properly discuss vibrational frequencies of molecules, we need to know (or denote) the specific isotopes in the molecule. Check Table A4 for that information.

Table 5.2.1: Atomic Mass and Isotope Composition. Consult Table A4 for more extensive table.

isotope	atomic mass (in amu)	isotopic abundance (%)
^{1}H	1.007825	99.985
^{2}H	2.0140	0.015

isotope	atomic mass (in amu)	isotopic abundance (%)
^{35}Cl	35.968852	75.77
^{37}Cl	36.965903	24.23
^{79}Br	78.918336	50.69
^{81}Br	80.916289	49.31

Example 5.2.1 : Isotope Effect

What are the reduced mass for $^{1}H^{35}Cl$ and $^{1}H^{37}Cl$? If the spring constants for vibrations of both molecules are equal and estimated at $478\ N/m$, what are the natural vibrational frequencies of these two molecules?

Solution

The periodic table gives an atomic weight of 35.45 amu for chlorine, but remember this is the the average of the natural abundances of different chlorine isotopes which is dictated primary by two isotopes: ^{35}Cl and ^{37}Cl. For this problem, we need the exact mass of the ^{1}H, ^{35}Cl, and ^{37}Cl isotopes. Check Table A4 for that information.

For $^{1}H^{35}Cl$:

$$\begin{aligned}\text{Reduced mass} &= \frac{m_1 m_2}{m_1 + m_2} \\ &= \frac{m_{\text{H}} m_{^{35}\text{Cl}}}{m_{\text{H}} + m_{^{35}\text{Cl}}} \\ &= \frac{(1.0078)(34.9688)}{1.0078 + 34.9688)}\, amu \\ &= 0.9796\, amu\end{aligned}$$

or when converted into kg is $1.629 \times 10^{-27}\ kg$.

For $^{1}H^{37}Cl$:

$$\begin{aligned}\text{Reduced mass} &= \frac{m_1 m_2}{m_1 + m_2} \\ &= \frac{m_{\text{H}} m_{^{37}\text{Cl}}}{m_{\text{H}} + m_{^{37}\text{Cl}}} \\ &= \frac{(1.0078)(36.965)}{1.0078 + 36.965)}\, amu \\ &= 0.9810\, amu\end{aligned}$$

or when converted into kg is $1.6291 \times 10^{-27}\ kg$. This is only 0.29% bigger.

Equation 3.2.2.5 is used to predict the respective vibrational frequencies of these two molecules.

For $^{1}H^{35}Cl$:

$$\begin{aligned}\nu &= \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \\ &= \frac{1}{2\pi}\sqrt{\frac{478\ N/m}{1.629 \times 10^{-27}\ kg}} \\ &= 8.6394 \times 10^{13} s^{-1}\end{aligned}$$

For $^{1}H^{37}Cl$:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$= \frac{1}{2\pi}\sqrt{\frac{478\ N/m}{1.629 \times 10^{-27}\ kg}}$$

$$= 8.621 \times 10^{13} s^{-1}$$

As with the differences in the reduced masses, the differences in the vibrational frequencies of these two molecules is quite small. However, high resolution IR spectroscopy can easily distinguish the vibrations between these two molecules. Exercise 5.2.1 will demonstrate that this "**isotope effect**" is not always a small effect.

? Exercise 5.2.1 : Hydrogen Chloride

The force constant is weakly sensitive to the specific isotopes in a molecule (and we typically assume it is isotope independent). If the $k = 478\ N/m$ for both $H^{35}Cl$ and $H^{37}Cl$. What are the vibration frequencies in these two diatomic molecules.

Answer

$H^{35}Cl$: 2886 cm^{-1}

$D^{35}Cl$: 2081 cm^{-1}

3.2.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule** by Eugene Lee is licensed CC BY-NC-SA 4.0.

3.2.3: The Harmonic Oscillator Approximates 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

$$V(x) = V(x_0) + \frac{dV(x)}{dx}\bigg|_{x_0}^{x}(x - x_0) + \frac{1}{2!}\frac{d^2V(x)}{dx^2}\bigg|_{x_0}^{x}(x - x_0)^2 + \ldots + \frac{1}{n!}\frac{d^nV(x)}{dx^n}\bigg|_{x_0}^{x}(x - x_0)^n \qquad (3.2.3.1)$$

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

$$V(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 \qquad (3.2.3.2)$$

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).

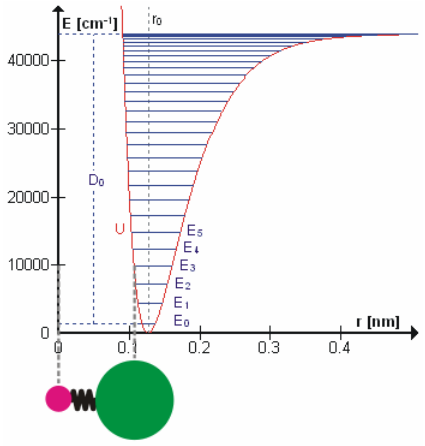


Figure 5.3.1 : The vibration of the HCl molecule is really an anharmonic oscillator, but can be approximated as a harmonic oscillator at low energies. In this animation, HCl is vibrating at the E_3 energy level. D_0 is dissociation energy here, r_0 bond length, V potential energy. Energy is expressed 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 3.2.3.2) 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.

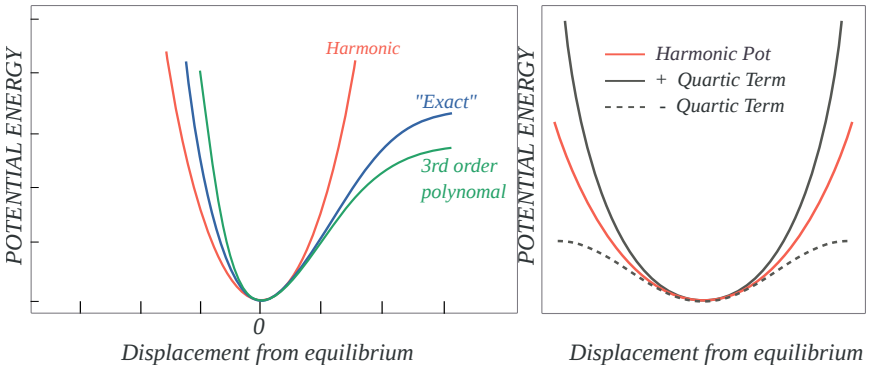


Figure 5.3.2 : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

Naturally, adding higher order anharmonic terms, like quartic terms (Figure $3.2.3.2; right$) improve the approximation. Almost all diatomics have experimentally determined potentials for their lowest energy states. H_2, Li_2, O_2, N_2, and F_2 with terms up to $n < 10$ determined of Equation 3.2.3.1.

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).

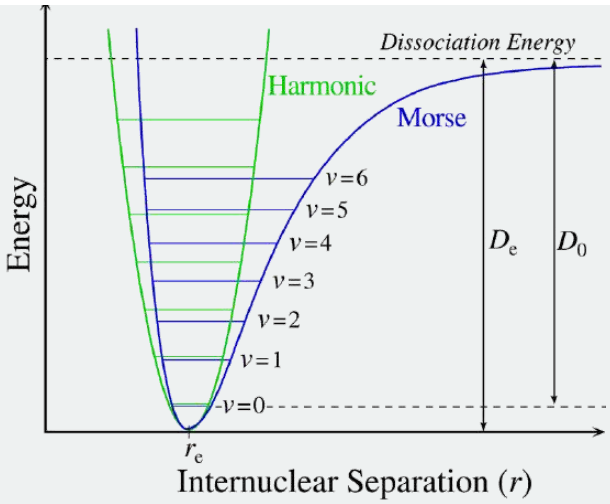


Figure 5.3.4 : The Morse potential (blue) and harmonic oscillator potential (green). Unlike the energy levels of the harmonic oscillator potential, which are evenly spaced by ħω, the Morse potential level spacing decreases as the energy approaches the dissociation energy. The dissociation energy D_e 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:

$$V(x) = D(1 - e^{-\beta(x-x_0)})^2 \tag{3.2.3.3}$$

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 3.2.3.3) 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.

3.2.3: The Harmonic Oscillator Approximates Vibrations is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.3: The Harmonic Oscillator Approximates Molecular Vibrations** by Peter Kelly is licensed CC BY 4.0.

3.2.4: The Harmonic Oscillator Energy Levels

For a classical oscillator, we know exactly the position, velocity, and momentum as a function of time. The frequency of the oscillator (or normal mode) is determined by the reduced mass μ and the effective force constant k of the oscillating system and does not change unless one of these quantities is changed. There are no restrictions on the energy of the oscillator, and changes in the energy of the oscillator produce changes in the amplitude of the vibrations experienced by the oscillator.

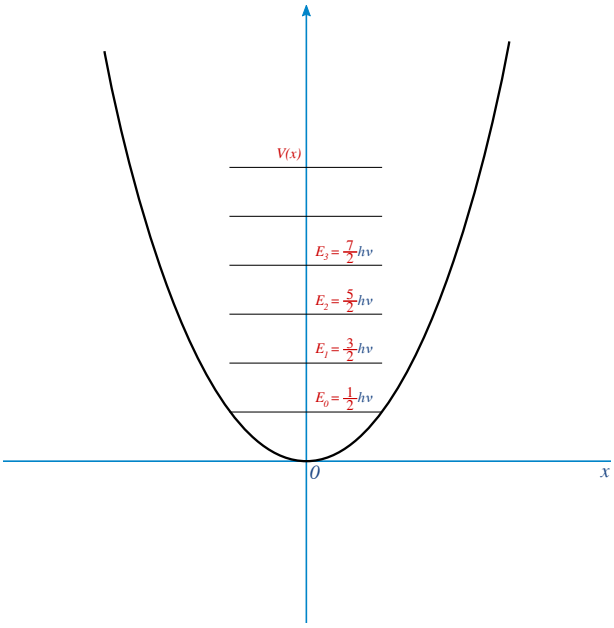


Figure 5.4.1 : Potential energy function and first few energy levels for harmonic oscillator. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

For the quantum mechanical oscillator, the oscillation frequency of a given normal mode is still controlled by the mass and the force constant (or, equivalently, by the associated potential energy function). However, the energy of the oscillator is limited to certain values. The allowed quantized energy levels are equally spaced and are related to the oscillator frequencies as given by Equation 3.2.4.1and Figure 5.4.1 .

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega = \left(v + \frac{1}{2}\right)h\nu \tag{3.2.4.1}$$

with

$$v = 0, 1, 2, 3, \cdots \infty$$

In a quantum mechanical oscillator, we cannot specify the position of the oscillator (the exact displacement from the equilibrium position) or its velocity as a function of time; we can only talk about the probability of the oscillator being displaced from equilibrium by a certain amount. This probability is given by

$$P_{Q \to Q+dQ} = \int_{Q}^{Q+dQ} \psi_v^*(Q)\psi_v(Q)dQ \tag{3.2.4.2}$$

We can, however, calculate the average displacement and the mean square displacement of the atoms relative to their equilibrium positions. This average is just $\langle Q \rangle$, the expectation value for Q, and the mean square displacement is $\left\langle Q^2 \right\rangle$, the expectation value for Q^2. Similarly we can calculate the average momentum $\langle P_Q \rangle$, and the mean square momentum $\left\langle P_Q^2 \right\rangle$, but we cannot specify the momentum as a function of time.

Physically what do we expect to find for the average displacement and the average momentum? Since the potential energy function is *symmetric* around $Q = 0$, we expect values of $Q > 0$ to be equally as likely as $Q < 0$. The average value of Q therefore should be zero.

These results for the average displacement and average momentum do not mean that the harmonic oscillator is sitting still. As for the particle-in-a-box case, we can imagine the quantum mechanical harmonic oscillator as moving back and forth and therefore having an average momentum of zero. Since the lowest allowed harmonic oscillator energy, E_0, is $\frac{\hbar\omega}{2}$ and not 0, the atoms in a molecule must be moving even in the lowest vibrational energy state. This phenomenon is called the zero-point energy or the zero-point motion, and it stands in direct contrast to the classical picture of a vibrating molecule. Classically, the lowest energy available to an oscillator is zero, which means the momentum also is zero, and the oscillator is not moving.

? Exercise 5.4.1

Compare the quantum mechanical harmonic oscillator to the classical harmonic oscillator at $v = 1$ and $v = 50$.

Answer

At v=1 the classical harmonic oscillator poorly predicts the results of quantum mechanical harmonic oscillator, and therefore reality. At v=1 the particle will be near the ground state and the classical model will predict the particle to spend most it's time on the outer edges when the KE goes to zero and PE is at a maximum, while the quantum model says the opposite and that the particle will be more likely to be found in the center. At v=50 the quantum model will begin to match the classical much more closely, with the particle most likely to be found at the edges. The quantum model looking more like the classical at higher quantum numbers can be referred to as the correspondence principle.

Since the average values of the displacement and momentum are all zero and do not facilitate comparisons among the various normal modes and energy levels, we need to find other quantities that can be used for this purpose. We can use the root mean square deviation (see also root-mean-square displacement) (also known as the standard deviation of the displacement) and the root-mean-square momentum as measures of the uncertainty in the oscillator's position and momentum.

For a molecular vibration, these quantities represent the standard deviation in the bond length and the standard deviation in the momentum of the atoms from the average values of zero, so they provide us with a measure of the relative displacement and the momentum associated with each normal mode in all its allowed energy levels. These are important quantities to determine because vibrational excitation changes the size and symmetry (or shape) of molecules. Such changes affect chemical reactivity, the absorption and emission of radiation, and the dissipation of energy in radiationless transitions.

The harmonic oscillator wavefunctions form an orthonormal set; this means that all functions in the set are normalized individually

$$\int_{-\infty}^{\infty} \psi_v^*(x)\psi_v(x)dx = 1 \tag{3.2.4.3}$$

and are orthogonal to each other.

$$\int_{-\infty}^{\infty} \psi_{v'}^*(x)\psi_v(x)dx = 0 \quad \text{for} \quad v' \neq v \tag{3.2.4.4}$$

The fact that a family of wavefunctions forms an orthonormal set is often helpful in simplifying complicated integrals. We will use these properties when we determine the harmonic oscillator selection rules for vibrational transitions in a molecule and calculate the absorption coefficients for the absorption of infrared radiation.

Finally, we can calculate the probability that a harmonic oscillator is in the classically forbidden region. What does this tantalizing statement mean? Classically, the maximum extension of an oscillator is obtained by equating the total energy of the oscillator to the potential energy, because at the maximum extension all the energy is in the form of potential energy. If all the energy weren't in the form of potential energy at this point, the oscillator would have kinetic energy and momentum and could continue to extend further away from its rest position. Interestingly, as we show below, the wavefunctions of the quantum mechanical oscillator extend beyond the classical limit, i.e. beyond where the particle can be according to classical mechanics.

The lowest allowed energy for the quantum mechanical oscillator is called the **zero-point energy,** $E_0 = \frac{\hbar\omega}{2}$. Using the classical picture described in the preceding paragraph, this total energy must equal the potential energy of the oscillator at its maximum

extension. We define this classical limit of the amplitude of the oscillator displacement as Q_0. When we equate the zero-point energy for a particular normal mode to the potential energy of the oscillator in that normal mode, we obtain

$$\frac{\hbar\omega}{2} = \frac{kQ_0^2}{2} \tag{3.2.4.5}$$

> *The zero-point energy is the **lowest** possible energy that a quantum mechanical physical system may have. Hence, it is the energy of its ground state.*

Recall that k is the effective force constant of the oscillator in a particular normal mode and that the frequency of the normal mode is given by Equation 3.2.4.1which is

$$\omega = \sqrt{\frac{k}{\mu}} \tag{3.2.4.6}$$

3.2.4: The Harmonic Oscillator Energy Levels is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.4: The Harmonic Oscillator Energy Levels** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

3.2.5: 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.

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 vth eigenstate of a harmonic oscillator can be written as

$$E_v = \left(v + \frac{1}{2}\right) \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \tag{3.2.5.1}$$

where h is Planck's constant and v is the vibrational quantum number and ranges from 0, 1, 2, 3,..., ∞. Equation 3.2.5.1 is often rewritten as

$$E_v = \left(v + \frac{1}{2}\right) h\nu_m \tag{3.2.5.2}$$

where ν_m is the vibrational frequency of the vibration. Equation 3.2.5.2 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

$$\begin{aligned} h\nu_{photon} &= \Delta E_{vv'} \\ &= E_{v'} - E_v \\ &= \left(v' + \frac{1}{2}\right) h\nu_m - \left(v + \frac{1}{2}\right) h\nu_m \\ &= (v' - v)\, h\nu_m \end{aligned} \tag{3.2.5.3}$$

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 3.2.5.3 simplifies to

$$h\nu_{photon} = h\nu_m$$
$$= \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \tag{3.2.5.4}$$

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:

$$\bar{\nu}(cm^{-1}) = \frac{1}{\lambda(\mu m)} \times 10^4 \left(\frac{\mu m}{cm}\right) \tag{3.2.5.5}$$
$$= \frac{\nu\,(Hz)}{c\,(cm/s)} \tag{3.2.5.6}$$

Equation 3.2.5.3can be modified so that the radiation can be expressed in wavenumbers

$$\tilde{\nu}_m = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \tag{3.2.5.7}$$

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 ($\text{rad} \cdot s^{-1}$)
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

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

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

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

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

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

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

$$\text{Percent bond length} = \frac{Q_0}{x_{eq}} \times 100\%$$
$$= \frac{0.110\, nm}{0.127\, nm} \times 100\%$$
$$= 86.6\%$$

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:

$$\mu_T = \langle \psi_{v'} | \hat{\mu}(x) | \psi_v \rangle \tag{3.2.5.8}$$
$$= \int_{-\infty}^{\infty} \psi_{v'}^*(x)\hat{\mu}(x)\psi_v(x)dx \tag{3.2.5.9}$$

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.

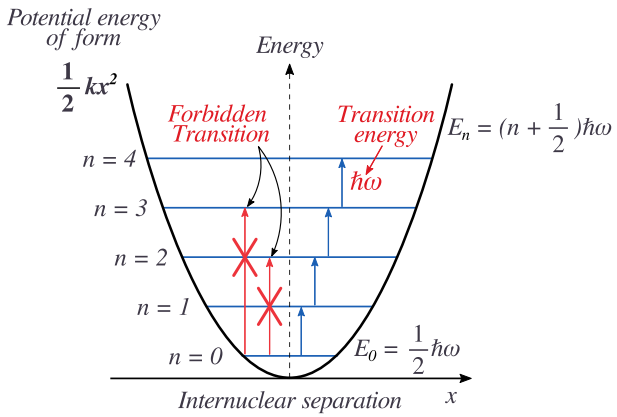


Figure 5.5.1: Possible transitions for a harmonic oscillator. Allowed transitions are labeled with blue arrows and forbidden transitions are labeled with red arrows. (CC BY-NC; Ümit Kaya via LibreTexts)

To evaluate Equation 3.2.5.9, 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

$$\hat{\mu} = \sum_{electrons} e\vec{r} + \sum_{nuclei} q\vec{R} \tag{3.2.5.10}$$

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 ($x = 0$).

$$\hat{\mu}(x) = \mu_{x=0} + \left.\frac{d\mu(x)}{dx}\right|_{x=0} x + \left.\frac{d^2\mu(x)}{dx^2}\right|_{x=0} x^2 + \cdots \tag{3.2.5.11}$$

Retaining only the first two terms and substituting into Equation 3.2.5.9 produces

$$\mu_T = \mu_{x=0} \int_{-\infty}^{\infty} \psi_{v'}(x)\psi_v(x)dx + \left.\frac{d\mu(x)}{dx}\right|_{x=0} \int_{-\infty}^{\infty} x\psi^*_{v'}(x)\psi_v(x)dx \tag{3.2.5.12}$$

where $\mu_{x=0} = 0$ 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 3.2.5.11. 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 3.2.5.12 is 0 because any two harmonic oscillator wavefunctions are *orthogonal*. The integral in the second term of Equation 3.2.5.12 is zero except when $v' = v \pm 1$ as demonstrated in Exercise 5.5.1 . Also note that the second term is zero if

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0} = 0 \tag{3.2.5.13}$$

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 3.2.5.12 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 3.2.5.13 **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

$$\underbrace{\Delta v = \pm 1}_{\text{For allowed transitions}} \tag{3.2.5.14}$$

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 3.2.5.4 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}.

3.2.5: The Harmonic Oscillator and Infrared Spectra is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.5: The Harmonic Oscillator and Infrared Spectra** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

3.2.6: The Harmonic-Oscillator Wavefunctions involve Hermite Polynomials

Learning Objectives

- The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule

For a diatomic molecule, there is only one vibrational mode, so there will be only a single set of vibrational wavefunctions with associated energies for this system. For polytatomic molecules, there will be a set of wavefunctions with associated energy associated with each vibrational mode.

The Hamiltonian operator, the general quantum mechanical operator for energy, includes both a kinetic energy term, $\hat{T}$, and a potential energy term, $\hat{V}$.

$$\hat{H} = \hat{T} + \hat{V} \tag{3.2.6.1}$$

For the free particle and the particle in a box, the potential energy term used in the Hamiltonian was zero. As shown in Equation 3.2.6.1, the classical expression for the energy of a harmonic oscillator includes both a kinetic energy term and the harmonic potential energy term. Transforming this equation into the corresponding Hamiltonian operator gives,

$$\hat{H}(q) = \frac{1}{2\mu}\hat{P}_q^2 + \frac{k}{2}\hat{q}^2 \tag{3.2.6.2}$$

where $\hat{q}$ is the operator for the length of the normal coordinate, and $\hat{P}_q$ is the momentum operator associated with the normal coordinate. μ is an effective (reduced) mass, and k is an effective force constant, and these quantities will be different for each of the normal modes (vibrations).

Substituting the definitions for the operators yields

$$\hat{H}(q) = -\frac{\hbar^2}{2\mu}\frac{d^2}{dq^2} + \frac{k}{2}q^2 \tag{3.2.6.3}$$

since the operator for position or displacement is just the position or displacement. The time-independent Schrödinger Equation then becomes

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi_v(q)}{dq^2} + \frac{k}{2}q^2\psi_v(q) = E_v\psi_v(q) \tag{3.2.6.4}$$

or upon rearranging

$$\frac{d^2\psi_v(q)}{dq^2} + \frac{2\mu}{\hbar^2}\left(E_v - \frac{k}{2}q^2\right)\psi_v(q) = 0 \tag{3.2.6.5}$$

This differential equation is not straightforward to solve. Rather than fully develop the details of the solution, we will outline the method used because it represents a common strategy for solving differential equations. The steps taken to solve Equation 3.2.6.5 are to simplify the equation by collecting constants in the parameter β

$$\beta^2 = \frac{\hbar}{\sqrt{\mu k}} \tag{3.2.6.6}$$

and then changing the variable from q to x where

$$x = \frac{q}{\beta} \tag{3.2.6.7}$$

so that

$$\frac{d^2}{dq^2} = \frac{1}{\beta^2}\frac{d^2}{dx^2} \tag{3.2.6.8}$$

After substituting Equations 3.2.6.6 and 3.2.6.8 into Equation 3.2.6.5, the differential equation for the harmonic oscillator becomes

$$\frac{d^2\psi_v(x)}{dx^2} + \left(\frac{2\mu\beta^2 E_v}{\hbar^2} - x^2\right)\psi_v(x) = 0 \tag{3.2.6.9}$$

? Exercise 5.6.1

Make the substitutions given in Equations 3.2.6.6 and 3.2.6.8 into Equation 3.2.6.5 to get Equation 3.2.6.9.

Solving for the Quantum Wavefunctions

A common strategy for solving differential equations, which is employed here, is to find a solution that is valid for large values of the variable and then develop the complete solution as a product of this asymptotic solution and a power series. Since the potential energy approaches infinity as x and the coordinate q approach infinity, the wavefunctions must approach zero (this is, the wavefunctions must **converge to zero**):

$$\lim_{x\to\infty} \psi_v(x) = 0 \tag{3.2.6.10}$$

The function that has this property and satisfies the differential equation for large values of x is the exponential function, i.e.,

$$\lim_{x\to\infty} \phi_v(x)\exp\left(\frac{-x^2}{2}\right) = 0 \tag{3.2.6.11}$$

where the wavefunctions are

$$\psi_v(x) \propto \phi_v(x)\exp\left(\frac{-x^2}{2}\right)$$

The general expression for a power series of $\phi_v(x)$ is

$$\begin{aligned}\phi_v(x) &= \sum_{n=0}^{\infty} c_n(v)x^n \\ &= c_n(v)x + c_n(v)x^2 + c_n(v)x^3 + \cdots\end{aligned}$$

which can be truncated after the first term, after the second term, after the third term, etc. to produce a set of polynomials. There is one polynomial for each value of v where v can be equal to any integer value including zero.

$$\sum_{n=0}^{v} c_n x^n \tag{3.2.6.12}$$

Each of the truncations of the power series in Equation 3.2.6.12 can be multiplied by the exponential function in Equation 3.2.6.11 to create a family of valid solutions to the differential equation in Equation 3.2.6.9.

$$\psi_v(x) = \sum_{n=0}^{v} c_n x^n \exp\left(\frac{-x^2}{2}\right) \tag{3.2.6.13}$$

? Exercise 5.6.2

Write the first four polynomials, $v = 0$ to $v = 1$, $v = 12$, $v = 13$, $v = 14$ for Equation 3.2.6.12 and use suitable software to prepare plots of these polynomials. Identify the curves in the plots.

? Exercise 5.6.3

Confirm that the wavefunction given by Equation 3.2.6.13 is a solution to the harmonic oscillator Schrödinger Equation in Equation 3.2.6.9 for $v = 0$ and $v = 1$.

Hermite Polynomials

While polynomials in general approach ∞ (or $-\infty$) as x approaches ∞, the decreasing exponential term overpowers the polynomial term so that the overall wavefunction exhibits the desired approach to zero at large values of x or $-x$. The exact forms

of polynomials that solve Equation 3.2.6.9 are the **Hermite polynomials**, which are standard mathematical functions known from the work of Charles Hermite. The first eight Hermite polynomials, $H_v(x)$, are given below.

- $H_0 = 1$
- $H_1 = 2x$
- $H_2 = -2 + 4x^2$
- $H_3 = -12x + 8x^3$
- $H_4 = 12 - 48x^2 + 16x^4$
- $H_5 = 120x - 160x^3 + 32x^5$
- $H_6 = -120 + 720x^2 - 480x^4 + 64x^6$
- $H_7 = -1680x + 3360x^3 - 1344x^5 + 128x^7$

The first six Hermite polynomials are plotted in Figure 5.6.1 . Hermite polynomials will be discussed in more detail in the following Section.

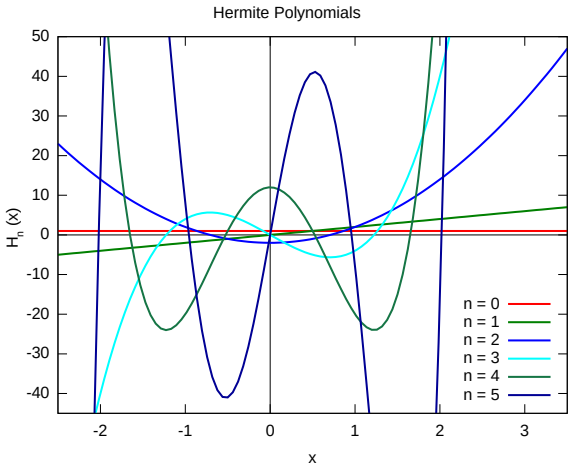


Figure 5.6.1 : The first six Hermite polynomials $H_n(x)$. (CC BY-SA 3.0 Unported; Alessio Damato, Vulpecula and others via Wikipedia)

? Exercise 5.6.4

Determine the units of β and the units of x in the Hermite polynomials.

Because of the association of the wavefunction with a probability density, it is necessary for the wavefunction to include a normalization constant, N_v.

$$N_v = \frac{1}{(2^v v! \sqrt{\pi})^{1/2}} \tag{3.2.6.14}$$

The final form of the harmonic oscillator wavefunctions is thus

$$\psi_v(x) = N_v H_v(x) e^{-x^2/2} \tag{3.2.6.15}$$

Alternative and More Common Formulation of Harmonic Oscillator Wavefunctions

The harmonic oscillator wavefunctions are often written in terms of Q, the unscaled displacement coordinate (Equation 3.2.6.7) and a different constant α:

$$\alpha = 1/\sqrt{\beta} = \sqrt{\frac{k\mu}{\hbar^2}}$$

so Equation 3.2.6.15 becomes

$$\psi_v(x) = N_v'' H_v(\sqrt{\alpha} Q) e^{-\alpha Q^2/2}$$

with a slightly different normalization constant

$$N_v'' = \sqrt{\frac{1}{2^v v!}} \left(\frac{\alpha}{\pi}\right)^{1/4}$$

Exercise 5.6.5

Compute the normalization factor for $\psi_v(x)$ where $v = 0$ and $v = 4$. What is the purpose of N_v?

The energy eigenvalues for a quantum mechanical oscillator also are obtained by solving the Schrödinger equation. The energies are restricted to discrete values

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega \tag{3.2.6.16}$$

with $v = 0, 1, 2, 3, \cdots$.

The energies depend both on the quantum number, v, and the oscillator frequency

$$\omega = \sqrt{\frac{k}{\mu}}$$

which in turn depends on the spring constant k and the reduced mass of the vibration μ.

Exercise 5.6.6

Determine the energy for the first ten harmonic oscillator energy levels in terms of $\hbar\omega$. Sketch an energy level diagram of these energies.

1. What insights do you gain from Equation 3.2.6.16, your calculations, and your diagram?
2. Is it possible to have a molecule that is not vibrating?
3. In terms of $\hbar\omega$, what is the energy of the photon required to cause a transition from one vibrational state to the next higher one?
4. If a transition from energy level $v = 9$ to $v = 10$ were observed in a spectrum, where would that spectral line appear relative to the one for the transition from level $v = 0$ to $v = 1$?
5. If a vibrational transition is observed at 3000 cm-1 in an infrared spectrum, what is the value of $\hbar\omega$ for the normal mode?
6. Identify all the possible meanings of $\Delta E = h\nu$ and the definition of the frequency, ν, in each case.

The normalized wavefunctions for the first four states of the harmonic oscillator are shown in Figure 5.6.2 , and the corresponding probability densities are shown in Figure 5.6.3 . You should remember the mathematical and graphical forms of the first few harmonic oscillator wavefunctions, and the correlation of v with E_v. The number of nodes in the wavefunction will help you to remember these characteristics. Also note that the functions fall off exponentially and that the symmetry alternates. For v equal to an even number, ψ_v is gerade; for v equal to an odd number, ψ_v is ungerade.

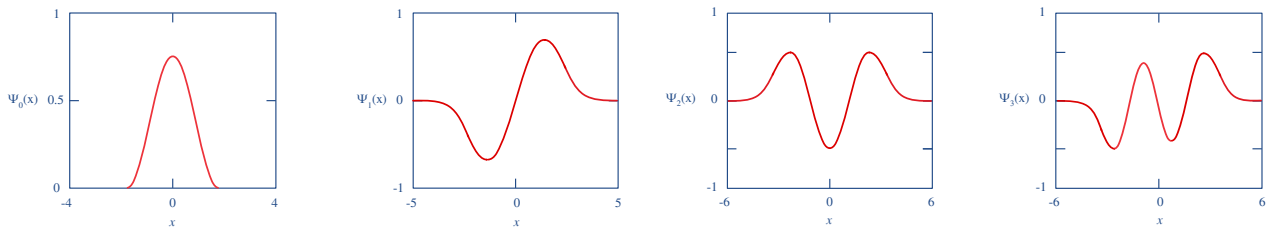


Figure 5.6.2 : The harmonic oscillator wavefunctions describing the four lowest energy states.

Exercise 5.6.7

Write a few sentences describing and comparing the plots in Figure 5.6.2 . How many nodes are there as a function of v? Do the wavefunctions converge at extreme displacement? Where is the most likely displacements for the oscillator to be found?

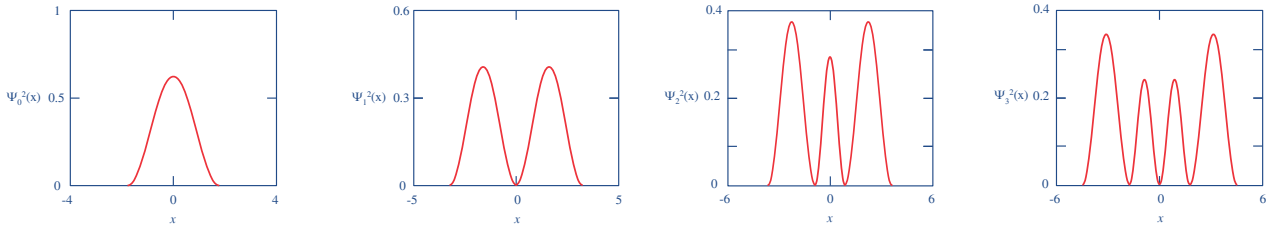


Figure 5.6.3 : The probability densities for the four lowest energy states of the harmonic oscillator.

Exercise 5.6.8

Explain how Figure 5.6.3 is related to Figure 5.6.2 . Explain the physical significance of the plots in Figure 5.6.3 in terms of the magnitude of the normal coordinate Q. Couch your discussion in terms of the HCl molecule. How would you describe the location of the atoms in each of the states? How does the oscillator position correspond to the energy of a particular level?

Answer

Figure 5.6.2 is simply the wavefunction in Figure 5.6.1 squared. The normal coordinate is the linear combination of the atomic cartesian coordinates. As Q is often in relation to the energy (kinetic and potential), they would be displaced by a certain amount dependent on Q (energy) along with an increase in nodes. This displacement is apparent when comparing the ascending energy levels of each of the wavefunctions. In the n=0 (first) energy state, it is most probable to be found between -2, 2. (in a range of -4, 4) In the second energy state, it is likely to be between -2.5, 2.5 (range -5, 5), third level: (-3,3) (range -6,6), fourth level (-4,4) (range -6,6).

Exercise 5.6.9

Plot the probability density for energy level 10 of the harmonic oscillator. How many nodes are present? Plot the probability density for energy level 20. Compare the plot for level 20 with that of level 10 and level 1. Compare these quantum mechanical probability distributions to those expected for a classical oscillator. What conclusion can you draw about the probability of the location of the oscillator and the length of a chemical bond in a vibrating molecule? Extend your analysis to include a very high level, like level 50.

In completing Exercise 5.6.9 , you should have noticed that as the quantum number increases and becomes very large, the probability distribution approaches that of a classical oscillator. This observation is very general. It was first noticed by Bohr, and is called the Bohr Correspondence Principle. This principle states that classical behavior is approached in the limit of large values for a quantum number. A classical oscillator is most likely to be found in the region of space where its velocity is the smallest. This situation is similar to walking through one room and running through another. In which room do you spend more time? Where is it more likely that you will be found?

Examination of the quantum mechanical wavefunction for the lowest-energy state reveals that the wavefunction $\psi_0(x)$ extends beyond the classical limit (i.e., outside of the harmonic oscillator well, albeit slightly). Higher energy states have higher total energies, so the classical limits to the amplitude of the displacement will be larger for these states.

Tunneling in the Quantum Harmonic Oscillator

The observation that the wavefunctions are not zero at the classical limit means that the quantum mechanical oscillator has a finite probability of having a displacement that is larger than what is classically possible. The oscillator can be in a region of space where the potential energy is greater than the total energy. Classically, when the potential energy equals the total energy, the kinetic energy and the velocity are zero, and the oscillator cannot pass this point. A quantum mechanical oscillator, however, has a finite probability of passing this point. For a molecular vibration, this property means that the amplitude of the vibration is larger than

what it would be in a classical picture. In some situations, a larger amplitude vibration could enhance the chemical reactivity of a molecule.

? Exercise 5.6.10

Plot the probability density for $v = 0$ and $v = 1$ states. Mark the classical limits on each of the plots, since the limits are different because the total energy is different for $v = 0$ and $v = 1$. Shade in the regions of the probability densities that extend beyond the classical limit.

We should be able to calculate the probability that the quantum mechanical harmonic oscillator is in the classically forbidden region for the lowest energy state of the harmonic oscillator, the state with $v = 0$. The classically forbidden region is shown by the shading of the regions beyond Q_0 in the graph you constructed for Exercise 5.6.3 . The area of this shaded region gives the probability that the bond oscillation will extend into the forbidden region (Figure 5.6.3). To calculate this probability, we use

$$P[\text{forbidden}] = 1 - P[\text{allowed}] \tag{3.2.6.17}$$

because the integral from 0 to Q_0 for the allowed region can be found in integral tables and the integral from Q_0 to ∞ cannot. The form of the integral, $P[\text{allowed}]$, to evaluate is

$$P[\text{allowed}] = 2\int_0^{Q_0} \psi_0^*(Q)\psi_0(Q)dQ \tag{3.2.6.18}$$

The factor 2 appears in Equation 3.2.6.18 from the chancing the limits of integration from $-Q_0$ to $+Q_0$ into 0 to $+Q_0$; we can do this since the integrand is an even function, i. e., $f(-x) = f(x)$. To evaluate the integral in Equation 3.2.6.18, use the wavefunction and do the integration in terms of x. Recall that for $v = 0$, $Q = Q_0$ corresponds to $x = 1$. Including the normalization constant, Equation 3.2.6.18 produces

$$P[\text{allowed}] = \frac{2}{\sqrt{\pi}}\int_0^1 \exp(-x^2)dx \tag{3.2.6.19}$$

The integral in Equation 3.2.6.19 is called an error function (ERF) and can only be evaluated numerically. Values can be found in books of mathematical tables. When the limit of integration is 1, ERF(l) = 0.843 and P[forbidden] = 0.157. This result means that the quantum mechanical oscillator can be found in the forbidden region 16% of the time. This effect is substantial and leads to the phenomenon called *quantum mechanical tunneling*.

? Exercise 5.6.11

Numerically verify that $P[\text{allowed}]$ in Equation 3.2.6.19 equals 0.843. To obtain a value for the integral do not use symbolic integration or symbolic equals.

3.2.6: The Harmonic-Oscillator Wavefunctions involve Hermite Polynomials is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.6: The Harmonic Oscillator Wavefunctions involve Hermite Polynomials** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

3.2.7: Hermite Polynomials are either Even or Odd Functions

Learning Objectives

- Understand key properties of the Hermite polynomials including orthogonality and symmetry.
- Be proficient at using symmetries of integrands to quickly solve integrals.

Hermite polynomials were defined by Laplace (1810) though in scarcely recognizable form, and studied in detail by Chebyshev (1859). Chebyshev's work was overlooked and they were named later after Charles Hermite who wrote on the polynomials in 1864 describing them as new. They were consequently not new although in later 1865 papers Hermite was the first to define the multidimensional polynomials. The first six Hermite polynomial are plotted in Figure 5.7.1 .

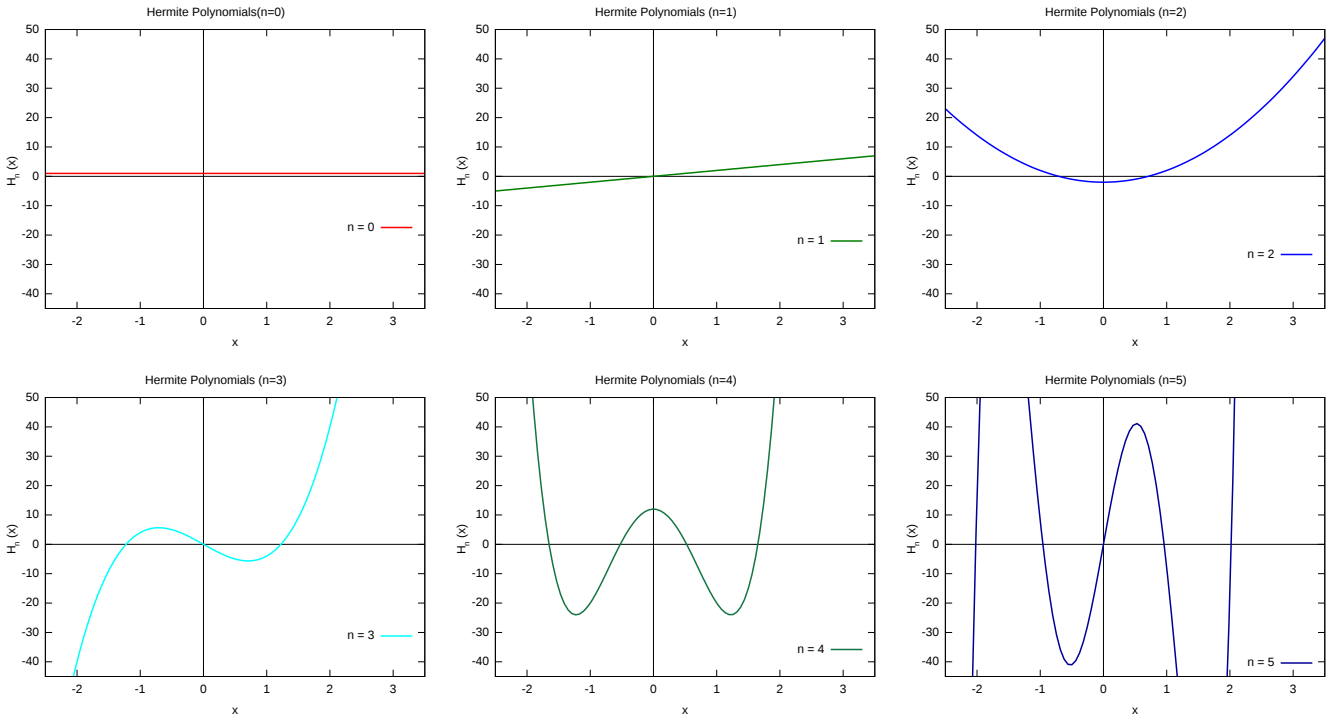


Figure 5.7.1 : The first six Hermite polynomials *[Math Processing Error]*. (CC BY-SA 3.0 Unported; Alessio Damato, Vulpecula and others via Wikipedia)

Generating Formula

Any Hermite polynomial *[Math Processing Error]* can be generated from a previous one *[Math Processing Error]* via the following using the recurrence relation

[Math Processing Error]

Hermite Polynomials are Symmetric

Let *[Math Processing Error]* be a real-valued function of a real variable.

- Then *[Math Processing Error]* is **even** if the following equation holds for all x and -x in the domain of f *[Math Processing Error]*
- Then *[Math Processing Error]* is **odd** if the following equation holds for all x and -x in the domain of f *[Math Processing Error]*

Even and odd are terms used to describe particularly well-behaved functions. An *even* function is symmetric about the y-axis (Figure 5.7.2 ; left). That is, if we reflect the graph of the function in the *[Math Processing Error]*-axis, then it does not change.

Formally, we say that *[Math Processing Error]* is even if, for all *[Math Processing Error]* and *[Math Processing Error]* in the domain of *[Math Processing Error]*, we have

[Math Processing Error]

Two examples of even functions are *[Math Processing Error]* and *[Math Processing Error]*.

An *odd* function has rotational symmetry of order two about the origin (Figure 5.7.2 ; middle). That is, if we rotate the graph of the function 180° about the origin, then it does not change. Formally, we say that ff is odd if, for all *[Math Processing Error]* and *[Math Processing Error]* in the domain of *[Math Processing Error]*, we have

[Math Processing Error]

Examples of odd functions are *[Math Processing Error]* and *[Math Processing Error]*.

Naturally, not all functions can be classified as even or odd. For example *[Math Processing Error]* shown in the right side of Figure 5.7.2 , is neither.

> You can also think of these properties as symmetry conditions at the origin. More symmetries in 3D space are discussed in Group Theory.

Without proof, we can identify several key features involving multiplication properties of even and odd functions:

- The product of two **even** functions is an **even** function.
- The product of two **odd** functions is an **even** function.
- The product of an **even** function and an **odd** function is an odd function.

This can be shown graphically as a product table like that in Table 5.7.1 .

Table 5.7.1 : Product table of 1D Functions

Product table	Odd Function (anti-symmetric)	Even Function (symmetric)	No symmetry (neither)
Odd Function (anti-symmetric)	Even Function (symmetric)	Odd Function (anti-symmetric)	who knows
Even Function (symmetric)	Odd Function (anti-symmetric)	Even Function (symmetric)	who knows
No symmetry (neither)	who knows	who knows	who knows

Notice that the Hermite polynomials in Figure 5.7.1 oscillate from even to odd. We can take advantage of that aspect in our calculation of Harmonic Oscillator wavefunctions. Hermite Polynomial is an even or odd function depends on its degree *[Math Processing Error]*. Based on

[Math Processing Error]

- *[Math Processing Error]* is an even function, when *[Math Processing Error]* is even.
- *[Math Processing Error]* is an odd function, when *[Math Processing Error]* is odd.

Integration over Symmetric Functions

You often consider integrals of the form

[Math Processing Error]

If *[Math Processing Error]* is odd or even, then sometimes you can make solving this integral easier. For example, we can rewrite that integral in the following way:

[Math Processing Error]

For an even function, we have *[Math Processing Error]* and Equation *[Math Processing Error]* can be simplified

[Math Processing Error]

For an odd function, we have *[Math Processing Error]* and Equation *[Math Processing Error]* can be simplified

[Math Processing Error]

That's what it means to simplify the integration: the integral of an odd or even function over the interval *[Math Processing Error]* can be put into a nicer form (and sometimes we can see that it vanishes without ever computing an integral).

Example 5.7.1

Technically, evaluating the orthogonality of Hermite polynomials requires integrating over the *[Math Processing Error]* weight function (Equations *[Math Processing Error]* and *[Math Processing Error]*).

Solution

For the Hermite polynomials *[Math Processing Error]*, the relevant inner product (using Dirac Notation)

[Math Processing Error]

While the *[Math Processing Error]* product is indeed an odd function (Table 5.7.1), while *[Math Processing Error]* is even. Their product is odd, and thus *[Math Processing Error]* certainly ought to be zero.

Symmetry is an important aspect of quantum mechanics and mathematics, especially in calculating integrals. Using this symmetry, integrals can be identified to be equal to zero without explicitly solving them. For example, the integral of an odd integrand over all possible values will **always** be zero irrespective of the exact nature of the function:

[Math Processing Error]

This simplifies calculations greatly as demonstrated in the following chapters.

Hermite Polynomials are Orthogonal

Hermite polynomials *[Math Processing Error]* are *n*th-degree polynomials for $n = 0, 1, 2, 3$ and form an orthogonal set of functions for the weight function *[Math Processing Error]*. The exact relation is:

[Math Processing Error]

if *[Math Processing Error]* and

[Math Processing Error]

if *[Math Processing Error]*.

This will not be proved, but can the demonstrated using any of the Hermite polynomials listed in the previous section. The orthogonality property becomes important when solving the Harmonic oscillator problems. Note that the integral of Equation *[Math Processing Error]* is important for normalizing the quantum harmonic oscillator wavefunctions discussed in last Section.

Example 5.7.2 : Hermite Polynomials are Orthogonal

Demonstrate that *[Math Processing Error]* and *[Math Processing Error]* are orthogonal.

Solution

We need to confirm

[Math Processing Error]

or when substituted

[Math Processing Error]

because it says I need to show it's orthogonal on *[Math Processing Error]* or we can just evaluate it on a finite interval *[Math Processing Error]*, where *[Math Processing Error]* is a constant.

[Math Processing Error]

Concluding

Hermite polynomials are a component in the harmonic oscillator wavefunction that dictates the symmetry of the wavefunctions. If your integration interval is symmetric around 0, then the integral over *any* integrable odd function is zero, no exception. Therefore as soon as you've found that your integrand is odd and your integration interval is symmetric, you're done. Also, for general

functions, if you can easily split them into even and odd parts, you only have to consider the integral over the even part for symmetric integration intervals.

Another important property is that the product of two even or of two odd functions is even, and the product of an even and an odd function is odd. For example, if ff is even, *[Math Processing Error]* is odd, and therefore the integral over it is zero (provided it is well defined).

3.2.7: Hermite Polynomials are either Even or Odd Functions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.7: Hermite Polynomials are either Even or Odd Functions** by Delmar Larsen is licensed CC BY-SA 4.0.

3.2.8: The Energy Levels of a Rigid Rotor

Learning Objectives

- Compare the classical and quantum rigid rotor in three dimensions
- Demonstrate how to use the Separation of Variable technique to solve the 3D rigid rotor Schrödinger Equation
- Identify and interpret the two quantum numbers for a 3D quantum rigid rotor including the range of allowed values
- Describe the wavefunctions of the 3D quantum rigid rotor in terms of nodes, average displacements and most probable displacements
- Describe the energies of the 3D quantum rigid rotor in terms of values and degeneracies

Rigid rotor means when the distance between particles do not change as they rotate. A rigid rotor only approximates a rotating diatomic molecular if vibration is ignored.

The Classical Rigid Rotor in 3D

The **rigid rotor** is a mechanical model that is used to explain rotating systems. The linear rigid rotor model consists of two point masses located at fixed distances from their center of mass. The fixed distance between the two masses and the values of the masses are the only characteristics of the rigid model. However, for many actual diatomics this model is too restrictive since distances are usually not completely fixed and corrections on the rigid model can be made to compensate for small variations in the distance. Even in such a case the rigid rotor model is a useful model system to master.

For a rigid rotor, the total energy is the sum of kinetic (T) and potential (V) energies

$$E_{tot} = T + V \tag{3.2.8.1}$$

The potential energy, V, is set to 0 because the distance between particles does not change within the rigid rotor approximation. However, In reality, $V \neq 0$ because even though the average distance between particles does not change, the particles still vibrate. The rigid rotor approximation greatly simplifys our discussion.

Since $V = 0$ then $E_{tot} = T$ and we can also say that:

$$T = \frac{1}{2}\sum m_i v_i^2 \tag{3.2.8.2}$$

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

$$\omega = \frac{v}{r} \tag{3.2.8.3}$$

where ω is the **angular velocity**, we can say that:

$$v_i = \omega X r_i \tag{3.2.8.4}$$

Thus we can rewrite Equation 3.2.8.2as:

$$T = \frac{1}{2}\sum m_i v_i \left(\omega X r_i\right) \tag{3.2.8.5}$$

Since ω is a scalar constant, we can rewrite Equation 3.2.8.5as:

$$T = \frac{\omega}{2}\sum m_i \left(v_i X r_i\right) = \frac{\omega}{2}\sum l_i = \omega\frac{L}{2} \tag{3.2.8.6}$$

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,

$$L = I\omega \tag{3.2.8.7}$$

where I is the moment of inertia of the rigid body relative to the axis of rotation. We can rewrite Equation 3.2.8.2as

$$T = \omega\frac{I\omega}{2} = \frac{1}{2}I\omega^2 \tag{3.2.8.8}$$

Equation 3.2.8.8 shows that the energy of the rigid rotor scales with increasing angular frequency (i.e., the faster is rotates) and with increasing moment of inertia (i.e, the inertial resistance to rotation). Also, as expected, the classical rotational energy is not quantized (i.e., all possible rotational frequencies are possible).

The Quantum Rigid Rotor in 3D

It is convenient to discuss rotation with in the spherical coordinate system rather than the Cartesian system (Figure 5.8.1).

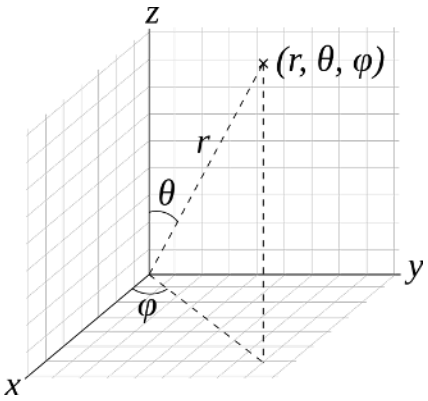


Figure 5.8.1 : The spherical coordinate system in terms of the Cartesian system. (Public Domain; Andeggs via Wikipedia).

To solve the Schrödinger equation for the rigid rotor, we will separate the variables and form single-variable equations that can be solved independently. Only two variables θ and φ are required in the rigid rotor model because the bond length, r, is taken to be the constant r_0. We first write the rigid rotor wavefunctions as the product of a theta-function depending only on θ and a phi-function depending only on φ

$$|\psi(\theta,\varphi)\rangle = |\Theta(\theta)\Phi(\varphi)\rangle \tag{3.2.8.9}$$

We then substitute the product wavefunction and the Hamiltonian written in spherical coordinates into the Schrödinger Equation 3.2.8.10

$$\hat{H}|\Theta(\theta)\Phi(\varphi)\rangle = E|\Theta(\theta)\Phi(\varphi)\rangle \tag{3.2.8.10}$$

to obtain

$$-\frac{\hbar^2}{2\mu r_0^2}\left[\frac{\partial}{\partial r_0}r_0^2\frac{\partial}{\partial r_0}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\Theta(\theta)\Phi(\varphi)\rangle = E|\Theta(\theta)\Phi(\varphi)\rangle \tag{3.2.8.11}$$

Since $r = r_0$ is constant for the **rigid rotor** and does not appear as a variable in the functions, the partial derivatives with respect to r are zero; i.e. the functions do not change with respect to r. We also can substitute the symbol I for the moment of inertia, μr_0^2 in the denominator of the left hand side of Equation 3.2.8.11, to give

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\Theta(\theta)\Phi(\varphi)\rangle = E|\Theta(\theta)\Phi(\varphi)\rangle \tag{3.2.8.12}$$

To begin the process of the Separating of Variables technique, multiply each side of Equation 3.2.8.12by $\frac{2I}{\hbar^2}$ and $\frac{-\sin^2\theta}{\Theta(\theta)\Phi(\varphi)}$ to give

$$\frac{1}{\Theta(\theta)\psi(\varphi)}\left[\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{\partial^2}{\partial\varphi^2}\right]\Theta(\theta)\Phi(\varphi) = \frac{-2IE\sin^2\theta}{\hbar^2} \tag{3.2.8.13}$$

Simplify the appearance of the right-hand side of Equation 3.2.8.13by defining a parameter λ:

$$\lambda = \frac{2IE}{\hbar^2}. \tag{3.2.8.14}$$

Note that this λ has no connection to a wavelength; it is merely being used as an algebraic symbol for the combination of constants shown in Equation 3.2.8.14

Inserting λ, evaluating partial derivatives, and rearranging Equation 3.2.8.13produces

$$\frac{1}{\Theta(\theta)}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\left(\lambda\sin^2\theta\right)\Theta(\theta)\right]=-\frac{1}{\Phi(\varphi)}\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi) \tag{3.2.8.15}$$

? Exercise 5.8.1

Carry out the steps leading from Equation 3.2.8.13to Equation 3.2.8.15. Keep in mind that, if y is not a function of x,

$$\frac{dy}{dx}=y\frac{d}{dx}$$

Equation 3.2.8.15 says that the function on the left, depending only on the variable θ, always equals the function on the right, depending only on the variable φ, for all values of θ and φ. The only way two different functions of independent variables can be equal for all values of the variables is if both functions are equal to a constant (review separation of variables). We call this constant m_J^2 because soon we will need the square root of it. The two differential equations to solve are the θ-equation

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)\Theta(\theta)+\left(\lambda\sin^2\theta-m_J^2\right)\Theta(\theta)=0 \tag{3.2.8.16}$$

and the φ-equation

$$\frac{d^2}{d\varphi^2}\Phi(\varphi)+m_J^2\Phi(\varphi)=0 \tag{3.2.8.17}$$

The partial derivatives have been replaced by total derivatives because only a single variable is involved in each equation.

> *Often m_J is referred to as just m for convenience.*

? Exercise 5.8.2

Show how Equations 3.2.8.16and 3.2.8.17are obtained from Equation 3.2.8.15.

Solving the φ Equation

The φ-equation is similar to the Schrödinger Equation for the free particle. Since we already solved this previously, we immediately write the solutions:

$$\Phi_m(\varphi)=Ne^{\pm im_J\varphi} \tag{3.2.8.18}$$

where we introduce the number m to track how many wavelengths of the wavefunction occur around one rotation (similar to the wavelength description of the Bohr atom).

? Exercise 5.8.3

Substitute Equation 3.2.8.18into Equation 3.2.8.17to show that it is a solution to that differential equation.

Answer

Substitute

$$\Phi_m(\varphi)=\mathrm{N}e^{\pm\mathrm{i}m_J\varphi}$$

into

$$\frac{d^2}{d\varphi^2}\Phi(\varphi)+m_J^2\Phi(\varphi)=0$$

$$\frac{d^2}{d\varphi^2}\Phi_{\mathrm{m}}(\varphi)+m_J^2\Phi_{\mathrm{m}}(\varphi)=\frac{d}{d\varphi}\left(\mathrm{N}\left(\pm\mathrm{i}m_J\right)e^{\pm\mathrm{i}m_J\varphi}\right)+m_J^2\Phi_{\mathrm{m}}(\varphi)$$
$$=\mathrm{N}(\pm\mathrm{i}m_J)^2e^{\pm im_J\varphi}\Big)+m_J^2\left(\mathrm{N}e^{\pm\mathrm{i}m_J\varphi}\right)$$
$$=-\mathrm{N}m_J^2e^{\pm im_J\varphi}+\mathrm{N}m_J^2e^{\pm im_J\varphi}=0$$

Thus

$$\Phi_m(\varphi)=Ne^{\pm im_J\varphi}$$

is a solution to the differential equations.

The normalization condition, Equation 3.2.8.19is used to find a value for N that satisfies Equation 3.2.8.18

$$\int_0^{2\pi}\Phi^*(\varphi)\Phi(\varphi)d\varphi=1 \tag{3.2.8.19}$$

The range of the integral is only from 0 to 2π because the angle φ specifies the position of the internuclear axis relative to the x-axis of the coordinate system and angles greater than 2π do not specify additional new positions.

Exercise 5.8.4

Use the normalization condition in Equation 3.2.8.19to demonstrate that $N=1/\sqrt{2\pi}$.

Answer

We need to evaluate Equation 3.2.8.19with $\psi(\varphi)=Ne^{\pm imJ\varphi}$

$$\psi^*(\varphi)\psi(\varphi)=Ne^{+imJ\varphi}\,Ne^{-imJ\varphi}$$
$$=N^2$$
$$1=\int_0^{2\pi}N^*Nd\varphi=1$$
$$N^2(2\pi)=1$$
$$N=\sqrt{1/2\pi}$$

Values for m are found by using a **cyclic boundary condition**. The cyclic boundary condition means that since φ and $\varphi+2\varphi$ refer to the same point in three-dimensional space, $\Phi(\varphi)$ must equal $\Phi(\varphi+2\pi)$, i.e.

$$e^{im_J\varphi}=e^{im_J(\varphi+2\pi)} \tag{3.2.8.20}$$
$$=e^{im_J\varphi}e^{im_J2\pi} \tag{3.2.8.21}$$

For the equality in Equation 3.2.8.21to hold, $e^{im_J2\pi}$ must equal 1, which is true only when

$$m_J=\cdots,-3,-2,-1,0,1,2,3,\cdots \tag{3.2.8.22}$$

In other words m_J can equal **any positive or negative integer or zero.**

Exercise 5.8.5 : Cyclic Boundary Conditions

Use Euler's Formula to show that $e^{im_J2\pi}$ equals 1 for m_J equal to zero or any positive or negative integer.

Thus, the Φ function is

$$\Phi_{m_J}(\varphi)=\sqrt{\frac{1}{2\pi}}e^{\pm im_J\varphi}$$

with

$$m_J = 0, \pm 1, \pm 2, \cdots$$

Solving the $\Theta(\theta)$ Equation

Finding the $\Theta(\theta)$ functions that are solutions to the θ-equation (Equation 3.2.8.16) is a more complicated process. Solutions are found to be a set of power series called *Associated Legendre Functions* (Table M2), which are power series of trigonometric functions, i.e., products and powers of sine and cosine functions. The $\Theta(\theta)$ functions, along with their normalization constants, are shown in the third column of Table 5.8.1 .

Table 5.8.1 : Spherical Harmonic Wavefunctions

m_J	J	$\Theta_J^{m_J}(\theta)$	$\Phi(\varphi)$	$Y_J^{m_J}(\theta,\varphi)$
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{4\pi}}$
0	1	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{3}{4\pi}}\cos\theta$
1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\varphi}$
-1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi}$
0	2	$\sqrt{\frac{5}{8}}(3\cos^2\theta-1)$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$
1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\varphi}$
-1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\varphi}$
2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\varphi}$
-2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\varphi}$

The solution to the θ-equation requires that λ in Equation 3.2.8.15be given by

$$\lambda = J(J+1) \tag{3.2.8.23}$$

where

$$J \geq |m_J| \tag{3.2.8.24}$$

J can be 0 or any positive integer greater than or equal to m_J. Each pair of values for the quantum numbers, J and m_J, identifies a rotational state with a wavefunction (Equation 3.2.8.9) and energy (below). Equation 3.2.8.24means that J controls the allowed values of m_J.

> *Each pair of values for the quantum numbers, J and m_J, identifies a rotational state and hence a specific wavefunction with associated energy.*

The combination of Equations 3.2.8.14and 3.2.8.23reveals that the energy of this system is quantized.

$$E = \frac{\hbar^2\lambda}{2I} = J(J+1)\frac{\hbar^2}{2I} \tag{3.2.8.25}$$

Using Equation 3.2.8.25, you can construct a rotational energy level diagram (Figure 5.8.2). For simplicity, use energy units of $\frac{\hbar^2}{2I}$.

- $J = 0$: The lowest energy state has $J = 0$ and $m_J = 0$. This state has an energy $E_0 = 0$. There is only **one state** with this energy, i.e. one set of quantum numbers, one wavefunction, and one set of properties for the molecule.
- $J = 1$: The next energy level is $J = 1$ with energy $\frac{2\hbar^2}{2I}$. There are **three states** with this energy because m_J can equal +1, 0, or -1. These different states correspond to different orientations of the rotating molecule in space. States with the same energy are said to be degenerate. The degeneracy of an energy level is the number of states with that energy. The degeneracy of the $J = 1$ energy level is 3 because there are three states with the energy $\frac{2\hbar^2}{2I}$.
- $J = 2$: The next energy level is for $J = 2$. The energy is $\frac{6\hbar^2}{2I}$, and there are **five states** with this energy corresponding to $m_J = +2,\ +1,\ 0,\ -1,\ -2$. The energy level degeneracy is five. Note that the spacing between energy levels increases as J increases. Also note that the degeneracy increases. The degeneracy is always $2J+1$ because m_J ranges from $+J$ to $-J$ in integer steps, including 0.

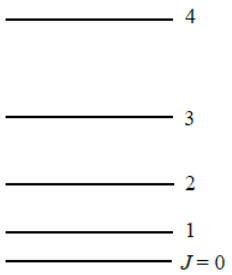


Figure 5.8.2 : Energy spacing for a rigid rotor (in 3D). Notice the energy depends only on J and not depend on m_J. That is, the energy of the rotor is not affected by its orientation.

> *Each allowed energy of rigid rotor is $(2J+1)$-fold degenerate. Hence, there exist $(2J+1)$ different wavefunctions with that energy.*

Exercise 5.8.6

Compute the energy levels for a rotating molecule for $J = 0$ to $J = 5$ using units of $\frac{\hbar^2}{2I}$.

Answer

This rotating molecule can be assumed to be a rigid rotor molecule. From solving the Schrödinger equation for a rigid rotor we have the relationship for energies of each rotational eigenstate (Equation 3.2.8.25):

$$E = J(J+1)(\hbar^2/2I)$$

Using this equation, we can plug in the different values of the J quantum number so that

For J=0, $E = (0)(1)(\hbar^2/2I) = 0$ For J=1, $E = (1)(2)(\hbar^2/2I) = 2(\hbar^2/2I)$

This shows that as J increases, the energy levels get farther apart (Figure 5.8.2).

- For J=2, $E = (2)(3)(\hbar^2/2I) = 6(\hbar^2/2I)$
- For J=3, $E = (3)(4)(\hbar^2/2I) = 12(\hbar^2/2I)$
- For J=4, $E = (4)(5)(\hbar^2/2I) = 20(\hbar^2/2I)$
- For J=5, $E = (5)(6)(\hbar^2/2I) = 30(\hbar^2/2I)$

Exercise 5.8.7

For $J = 0$ to $J = 5$, identify the degeneracy of each energy level and the values of the m_J quantum number that go with each value of the J quantum number. Construct a rotational energy level diagram including $J = 0$ through $J = 5$. Label each level with the appropriate values for the quantum numbers J and m_J. Describe how the spacing between levels varies with increasing J.

Answer

This rotating molecule can be assumed to be a rigid rotor molecule. From solving the Schrödinger equation for a rigid rotor, we have:

$$\lambda = 2IE/\hbar^2$$

Where λ is an arbitrary parameter not related to wavelength. Additionally, λ is assigned a quantum relation so that

$$\lambda = J(J+1)$$

Thus, combining the two equations and solving for E yields

$$E = J(J+1)(\hbar^2/2I)$$

Using this equation, we can plug in the different values of J so that

- For J=0, $E = (0)(1)(\hbar^2/2I) = 0$
- For J=1, $E = (1)(2)(\hbar^2/2I) = 2(\hbar^2/2I)$
- For J=2, $E = (2)(3)(\hbar^2/2I) = 6(\hbar^2/2I)$
- For J=3, $E = (3)(4)(\hbar^2/2I) = 12(\hbar^2/2I)$
- For J=4, $E = (4)(5)(\hbar^2/2I) = 20(\hbar^2/2I)$
- For J=5, $E = (5)(6)(\hbar^2/2I) = 30(\hbar^2/2I)$

This shows that as J increases, the energy levels get closer and closer together.

Interpretation of Quantum Numbers for a Rigid Rotor

The m_J quantum number reflects the component of the angular momentum along the z direction (and hence is sometimes called the azimuthal quantum number). For a fixed value of J, the different values of m_J reflect the different **directions** the angular momentum vector could be pointing – for large, positive m_J the angular momentum is mostly along +z; if m_J is zero the angular momentum is orthogonal to z. Physically, the energy of the rotation does not depend on the direction, which is reflected in the fact that the energy depends only on J (Equation 3.2.8.25), which measures the length of the vector, not its direction given mb m_J.

Example 5.8.7 : Molecular Oxygen

Calculate $J = 0$ to $J = 1$ rotational transition of the O_2 molecule with a bond length of 121 pm.

Solution

$$E = \frac{\hbar^2}{I} = \frac{\hbar^2}{\mu r^2}$$

$$\mu_{O2} = \frac{m_O m_O}{m_O + m_O} = \frac{(15.9994)(15.9994)}{15.9994 + 15.9994} = 7.9997$$

convert from atomic units to kilogram using the conversion: 1 au = 1.66 x 10^{-27} kg. Plug and chug.

$$E = 5.71 \times 10^{-27}\ Joules$$

Spherical Harmonics

A wavefunction that is a solution to the rigid rotor Schrödinger Equation (Equation 3.2.8.9) can be written as a single function $Y(\theta, \varphi)$, which is called a spherical harmonic function.

$$Y_J^{m_J}(\theta, \varphi) = \Theta_J^{|m_J|}(\theta)\Phi_{m_J}(\varphi) \tag{3.2.8.26}$$

The spherical harmonic wavefunction is labeled with m_J and J because its functional form depends on both of these quantum numbers. These functions are tabulated above for $J = 0$ through $J = 2$ and for $J = 3$ in the Spherical Harmonics Table (M4)

Polar plots of some of the θ-functions are shown in Figure 5.8.3 .

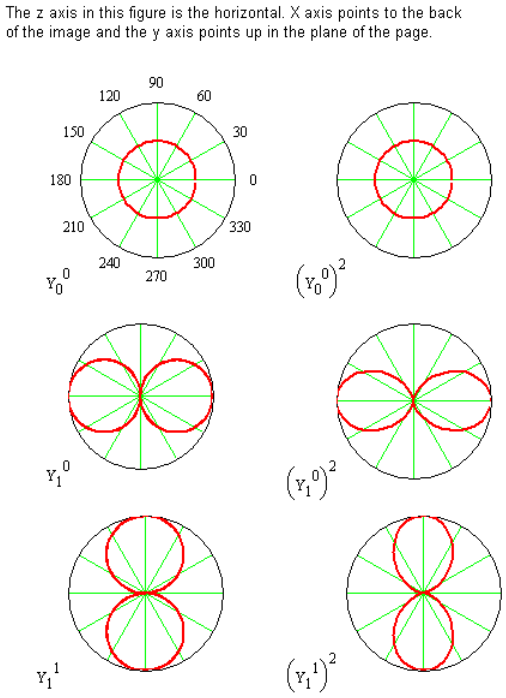


Figure 5.8.3 : Polar plots in which the distance from the center gives the value of the function Y for the indicated angle θ.

The two-dimensional space for a rigid rotor is defined as the surface of a sphere of radius r_0, as shown in Figure 5.8.2 .

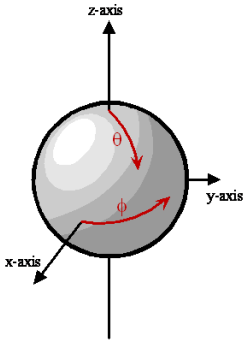


Figure 5.8.4 : Space for a rigid rotor is restricted to the surface of a sphere of radius r_0. The only degrees of freedom are motions along θ or φ on the surface of the sphere.

The probability of finding the internuclear axis at specific coordinates θ_0 and φ_0 within an infinitesimal area ds on this curved surface is given by

$$Pr\left[\theta_0, \varphi_0\right] = Y_J^{m_{J*}}(\theta_0, \varphi_0) Y_J^{m_J}(\theta_0, \varphi_0) ds \tag{3.2.8.27}$$

where the area element ds is centered at θ_0 and φ_0.

Within the Copenhagen interpretation of wavefunctions, the absolute square (or modulus squared) of the rigid rotor wavefunction $Y_J^{m_{J*}}(\theta, \varphi) Y_J^{m_J}(\theta, \varphi)$ gives the probability density for finding the internuclear axis oriented at θ to the z-axis and φ to the x-axis. In spherical coordinates the area element used for integrating θ and φ is

$$ds = \sin\theta \, d\theta \, d\varphi \tag{3.2.8.28}$$

? Exercise 5.8.8

Use calculus to evaluate the probability of finding the internuclear axis of a molecule described by the $J = 1$, $m_J = 0$ wavefunction somewhere in the region defined by a range in θ of 0° to 45°, and a range in of 0° to 90°. Note that a double

integral will be needed. Sketch this region as a shaded area on Figure 5.8.1 .

Consider the significance of the probability density function by examining the $J = 1$, $m_J = 0$ wavefunction. The Spherical Harmonic for this case is

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta \tag{3.2.8.29}$$

The polar plot of $(Y_1^0)^2$ is shown in Figure 5.8.1 . For $J = 1$ and $m_J = 0$, the probability of finding the internuclear axis is independent of the angle φ from the x-axis, and greatest for finding the internuclear axis along the z-axis, but there also is a probability for finding it at other values of θ as well. So, although the internuclear axis is not always aligned with the z-axis, the probability is highest for this alignment. Also, since the probability is independent of the angle φ, the internuclear axis can be found in any plane containing the z-axis with equal probability.

The $J = 1$, $m_J = 0$ function is 0 when θ = 90°. Therefore, the entire xy-plane is a **node**. This fact means the probability of finding the internuclear axis in this particular horizontal plane is 0 in contradiction to our classical picture of a rotating molecule. In the classical picture, a molecule rotating in a plane perpendicular to the xy-plane must have the internuclear axis lie in the xy-plane twice every revolution, but the quantum mechanical description says that the probability of being in the xy-plane is zero. This conclusion means that molecules are not rotating in the classical sense, but they still have some, but not all, of the properties associated with classical rotation. The properties they retain are associated with angular momentum.

? Exercise 5.8.9

For each state with $J = 0$ and $J = 1$, use the function form of the Y spherical harmonics and Figure 5.8.1 to determine the most probable orientation of the internuclear axis in a diatomic molecule, i.e., the most probable values for θ and θ.

? Exercise 5.8.10

Write a paragraph describing the information about a rotating molecule that is provided in the polar plot of $Pr[\theta, \theta]$ for the $J = 1$, $m_J = \pm 1$ state in Figure 5.8.1 . Compare this information to the classical picture of a rotating object.

Summary

There are two quantum numbers that describe the quantum behavior of a rigid rotor in three-deminesions: J is the total angular momentum quantum number and m_J is the z-component of the angular momentum. The spherical harmonics called $Y_J^{m_J}$ are functions whose probability $|Y_J^{m_J}|^2$ has the well known shapes of the s, p and d orbitals etc learned in general chemistry.

References

1. Anderson, J.M. Introduction to Quantum Chemistry, 1969, W.A. Benjamin, Inc, pg.91-100.
2. Atkins, Peter and de Paula, Julio. Physical Chemistry for the Life Sciences. New York: W.H. Freeman and Company. p. 515.

Contributors and Attributions

- Ian Huh
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Mark Tuckerman (New York University)
- MIT OpenCourseWare (Robert Guy Griffin and Troy Van Voorhis)

3.2.8: The Energy Levels of a Rigid Rotor is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.8: The Energy Levels of a Rigid Rotor** is licensed CC BY-NC-SA 4.0.

3.2.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule

Learning Objectives

- Demonstrate how to use the 3D regid rotor to describe a rotating diatomic molecules
- Demonstate how microwave spectroscopy can get used to characterize rotating diatomic molecules
- Interprete a simple microwave spectrum for a diatomic molecule

To develop a description of the rotational states, we will consider the molecule to be a rigid object, i.e. the bond lengths are fixed and the molecule cannot vibrate. This model for rotation is called the rigid-rotor model. It is a good approximation (even though a molecule vibrates as it rotates, and the bonds are elastic rather than rigid) because the amplitude of the vibration is small compared to the bond length.

The rotation of a rigid object in space is very simple to visualize. Pick up any object and rotate it. There are orthogonal rotations about each of the three Cartesian coordinate axes just as there are orthogonal translations in each of the directions in three-dimensional space (Figures 5.9.1 and 5.9.2). These rotations are said to be *orthogonal* because one can not describe a rotation about one axis in terms of rotations about the other axes just as one can not describe a translation along the x-axis in terms of translations along the y- and z-axes. For a linear molecule, the motion around the interatomic axis (x-axis) is not considered a rotation.

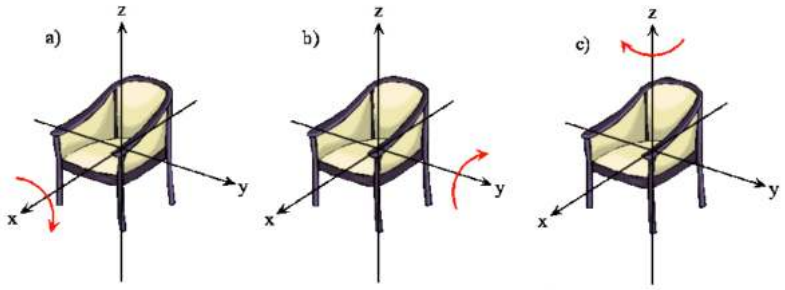


Figure 5.9.1 : Cartesian rotations of a chair. Rotations about the (a) x axis, (b) y axis, and (c) z axis.

In this section we examine the rotational states for a diatomic molecule by comparing the classical interpretation of the angular momentum vector with the probabilistic interpretation of the angular momentum wavefunctions. We want to answer the following types of questions. How do we describe the orientation of a rotating diatomic molecule in space? Is the molecule actually rotating? What properties of the molecule can be physically observed? In what ways does the quantum mechanical description of a rotating molecule differ from the classical image of a rotating molecule?

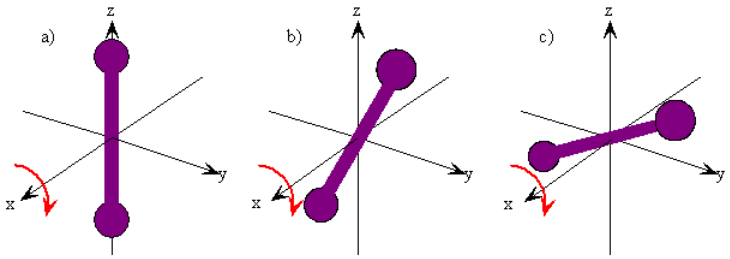


Figure 5.9.2 : Rotation of a diatomic molecule about the x axis.

Introduction to Microwave Spectroscopy

The permanent electric dipole moments of polar molecules can couple to the electric field of electromagnetic radiation. This coupling induces transitions between the rotational states of the molecules. The energies that are associated with these transitions are detected in the far infrared and microwave regions of the spectrum. For example, the microwave spectrum for carbon monoxide spans a frequency range of 100 to 1200 GHz, which corresponds to 3 - 40 cm^{-1}.

The selection rules for the rotational transitions are derived from the transition moment integral by using the spherical harmonic functions and the appropriate dipole moment operator, $\hat{\mu}$.

$$\mu_T = \int Y_{J_f}^{m_f *} \hat{\mu} Y_{J_i}^{m_i} \sin\theta \, d\theta \, d\varphi \tag{3.2.9.1}$$

or in braket notation

$$\mu_T = \langle Y_{J_f}^{m_f} | \hat{\mu} | Y_{J_i}^{m_i} \rangle \tag{3.2.9.2}$$

Evaluating the transition moment integral involves a bit of mathematical effort. This evaluation reveals that the transition moment depends on the square of the dipole moment of the molecule, μ^2 and the rotational quantum number, J, of the initial state in the transition,

$$\mu_T = \mu^2 \frac{J+1}{2J+1} \tag{3.2.9.3}$$

and that the selection rules for rotational transitions are

$$\Delta J = \pm 1 \tag{3.2.9.4}$$

and

$$\Delta m_J = 0, \pm 1 \tag{3.2.9.5}$$

A photon is absorbed for $\Delta J = +1$ and emitted for $\Delta J = -1$.

? Exercise 5.9.1

Explain why your microwave oven heats water, but not air. Hint: draw and compare Lewis structures for components of air and for water.

The energies of the Jth rotational levels are given by

$$E_J = J(J+1)\frac{\hbar^2}{2I} \tag{3.2.9.6}$$

with each Jth energy level having a degeneracy of $2J+1$ due to the different possible m_J values.

Microwave Transition Energies

The transition energies for absorption of radiation are given by

$$E_{photon} = \Delta E \tag{3.2.9.7}$$
$$= E_f - E_i \tag{3.2.9.8}$$
$$= h\nu \tag{3.2.9.9}$$
$$= hc\bar{\nu} \tag{3.2.9.10}$$

Substituting the relationship for energy (Equation 3.2.9.6) into Equation 3.2.9.8results in

$$E_{photon} = E_f - E_i \tag{3.2.9.11}$$
$$= J_f(J_f+1)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I} \tag{3.2.9.12}$$

with J_i and J_f representing the rotational quantum numbers of the initial (lower) and final (upper) levels involved in the absorption transition.

Since microwave spectroscopists use frequency units and infrared spectroscopists use wavenumber units when describing rotational spectra and energy levels, both ν and $\bar{\nu}$ are important to calculate. When we add in the constraints imposed by the selection rules to identify possible transitions, J_f in Equation 3.2.9.12can be replaced by $J_i + 1$, since the selection rule requires $J_f - J_i = 1$ for the absorption of a photon (Equation 3.2.9.4). The equation for absorption transitions (Equation 3.2.9.12) then can be written in terms of the only the quantum number J_i of the initial state.

$$E_{photon} = h\nu \tag{3.2.9.13}$$

$$= hc\bar{\nu} \tag{3.2.9.14}$$

$$= 2(J_i + 1)\frac{\hbar^2}{2I} \tag{3.2.9.15}$$

Equation 3.2.9.15 can be rewritten as

$$E_{photon} = 2B(J_i + 1)$$

where B is the **rotational constant** for the molecule and is defined in terms of the *energy* of the absorbed photon

$$B = \frac{\hbar^2}{2I} \tag{3.2.9.16}$$

Often spectroscopists want to express the rotational constant in terms of *frequency* of the absorbed photon and do so by dividing Equation 3.2.9.16 by h

$$B(\text{in freq}) = \frac{B}{h} \tag{3.2.9.17}$$

$$= \frac{h}{8\pi^2\mu r_0^2} \tag{3.2.9.18}$$

More often, spectroscopists want to express the rotational constant in terms of *wavenumbers* ($\bar{\nu}$) of the absorbed photon by dividing Equation 3.2.9.16 by hc,

$$\tilde{B} = \frac{B}{hc} = \frac{h}{8\pi^2 c\mu r_0^2} \tag{3.2.9.19}$$

The rotational constant depends on the distance (R) and the masses of the atoms (via the reduced mass) of the nuclei in the diatomic molecule.

? Exercise 5.9.2

Construct a rotational energy level diagram for $J = 0$, 1, and 2 and add arrows to show all the allowed transitions between states that cause electromagnetic radiation to be absorbed or emitted.

? Exercise 5.9.3

Complete the steps going from Equation 3.2.9.12 to Equation 3.2.9.16 and identify the units of B at the end.

Answer

$$\begin{aligned}
\Delta E_{photon} &= E_f - Ei \\
E_{r.rotor} &= J(J+1)\frac{\hbar^2}{2I} \\
E_{photon} = h_\nu = hc\tilde{\nu} &= J_f(J_f+1)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I} \\
J_f - J_i &= 1 \\
J_f &= 1 + J_i \\
E_{photon} = h_\nu = hc\tilde{\nu} &= (1+J_i)(2+J_i)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I} \\
&= \frac{\hbar^2}{2I}[2+3J_i+J_i^2-J_i^2-J_i] \\
&= \frac{\hbar^2}{2I}2(J_i+1) \\
&= 2B(J_i+1)
\end{aligned}$$

Now we do a standard dimensional analysis

$$B = \frac{\hbar^2}{2I} \equiv \left[\frac{kgm^2}{s^2}\right] = [J]$$

$$\frac{B}{h} = B(infreq.) = \frac{h}{8\pi^2\mu r_o^2} \equiv \left[\frac{1}{s}\right]$$

$$\frac{B}{hc} = \tilde{B} = \frac{h}{8\pi^2\mu c r_o^2} \equiv \left[\frac{s}{m}\right]$$

? Exercise 5.9.4

Infrared spectroscopists use units of wavenumbers. Rewrite the steps going from Equation 3.2.9.12 to Equation 3.2.9.16 to obtain expressions for $h\nu$ and B in units of wavenumbers. Note that to convert B in Hz to B in cm^{-1}, you simply divide the former by c.

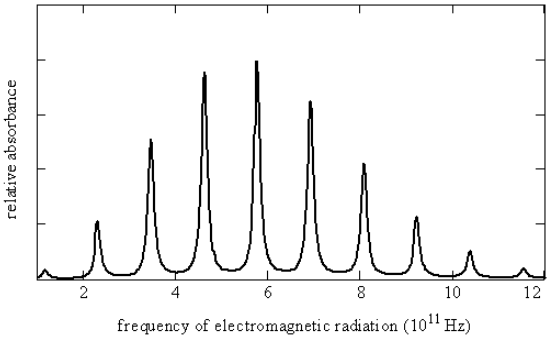


Figure 5.9.3: The rotation spectrum of $^{12}C^{16}O$ at 40 K. The peaks are tabulated in Table 5.9.1.

Figure 5.9.3 shows the rotational spectrum as a series of nearly equally spaced lines. The line positions ν_J, line spacings, and the maximum absorption coefficients (γ_{max}, the absorption coefficients associated with the specified line position) for each line in this spectrum are given here in Table 5.9.1.

Table 5.9.1 : Rotational Transitions in $^{12}C^{16}O$ at 40 K

J	ν_J (MHz)	Spacing from previous line (MHz)	γ_{max}
$0 \rightarrow 1$	115,271.21	0	0.0082

J	ν_J (MHz)	Spacing from previous line (MHz)	γ_{max}
$1 \rightarrow 2$	230,538.01	115,266.80	0.0533
$2 \rightarrow 3$	345,795.99	115,257.99	0.1278
$3 \rightarrow 4$	461,040.76	115,244.77	0.1878
$4 \rightarrow 5$	576,267.91	115,227.15	0.1983
$6 \rightarrow 6$	691,473.03	115,205.12	0.1618
$6 \rightarrow 7$	806,651.78	115,178.68	0.1064
$7 \rightarrow 8$	921,799.55	115,147.84	0.0576
$8 \rightarrow 9$	1,036,912.14	115,112.59	0.0262
$9 \rightarrow 10$	1,151,985.08	115,072.94	0.0103

Let's try to reproduce Figure 5.9.3 from the data in Table 5.9.1 by using the quantum theory that we have developed so far. Equation 3.2.9.19predicts a pattern of exactly equally spaced lines. The lowest energy transition is between $J_i = 0$ and $J_f = 1$ so the first line in the spectrum appears at a frequency of $2B$. The next transition is from $J_i = 1$ to $J_f = 2$ so the second line appears at $4B$. The spacing of these two lines is $2B$. In fact the spacing of all the lines is $2B$, which is consistent with the experimental data in Table 5.9.1 showing that the lines are very nearly equally spaced. The difference between the first spacing and the last spacing is less than 0.2%.

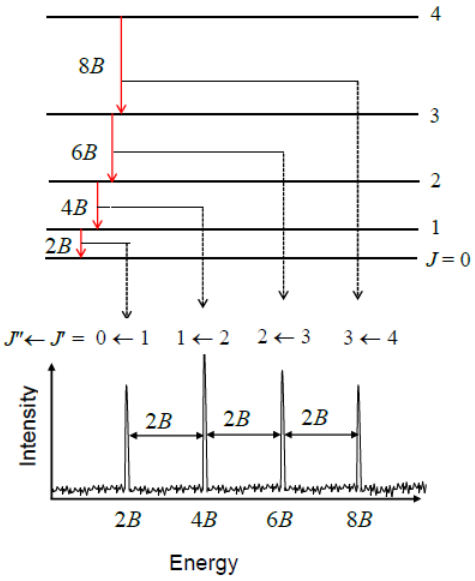


Figure 5.9.4 : Energy levels and line positions calculated in the rigid rotor approximation. (CC BY-SA 3.0; Nrrw via Wikipedia)

? Exercise 5.9.5

Use Equation 3.2.9.19to prove that the spacing of any two lines in a rotational spectrum is $2B$, i.e. derive:

$$\nu_{J_i+1} - \nu_{J_i} = 2B$$

Answer

To prove the relationship, evaluate the LHS. First, define the terms:

$$\nu_{J_i} = 2B(J_i + 1), \nu_{J_i+1} = 2B((J_i + 1) + 1)$$

Substitute into the equation and evaluate:

$$2B((J_i+1)+1)-2B(J_i+1)=2B$$

$$2B(J_i+1)+2B-2B(J_i+1)=2B$$

$$2B=2B$$

LHS equals RHS.Therefore, the spacing between any two lines is equal to $2B$.

Example 5.9.1 : Rotation of Sodium Hydride

The molecule NaH undergoes a rotational transition from $J=0$ to $J=1$ when it absorbs a photon of frequency $2.94\times10^{11}\ Hz$. What is the equilibrium bond length of the molecule?

Solution

We use $J=0$ in the formula for the transition frequency

$$\nu=2B=\frac{\hbar}{2\pi I}=\frac{\hbar}{2\pi\mu R_e^2}$$

Solving for R_e gives

$$R_e=\sqrt{\frac{\hbar}{2\pi\mu\nu}}$$

The reduced mass is given by

$$\begin{aligned}\mu&=\frac{m_{Na}m_H}{m_{Na}+m_H}\\&=\frac{(22.989)(1.0078)}{22.989+1.0078}\\&=0.9655\end{aligned}$$

which is in atomic mass units or relative units. To convert to kilograms, we need the conversion factor $1\ au=1.66\times10^{-27}\ kg$. Multiplying this by 0.9655gives a reduced mass of $1.603\times10^{-27}\ kg$. Substituting in for R_e gives

$$\begin{aligned}R_e&=\sqrt{\frac{(1.055\times10^{-34}\ J\cdot s)}{2\pi(1.603\times10^{-27}\ kg)(2.94\times10^{11}\ Hz)}}\\&=1.899\times10^{-10}\ m\\&=1.89\ \mathring{A}\end{aligned}$$

Example 5.9.6

Use the frequency of the $J=0$ to $J=1$ transition observed for carbon monoxide to determine a bond length for $^{12}C^{16}O$.

Solution

- J=0: $v_0=115271.21$ MHz
- J=1: $v_1=230538.01$ MHz

$$\begin{aligned}\Delta v&=230538.01\text{ MHz}-115271.21\text{ MHz}\\&=115266.8\text{ MHz}\\&=1.153\times10^{11}\text{ Hz}\\&=\frac{\hbar}{2\pi\mu R_e^2}\end{aligned}$$

The reduced mass is

$$\begin{aligned}\mu &= \frac{m_C m_O}{m_C + m_O} \\ &= \frac{12.01 \times 16.00}{12.01 + 16.00} \\ &= 6.86 \text{ amu}\end{aligned}$$

Convert to kg

$$6.86 amu \left(\frac{1.661 \times 10^{-27} \text{ kg}}{12 \text{ amu}} \right) = 1.139 \times 10^{-26} \text{ kg}$$

$$\begin{aligned}R_e &= \sqrt{\frac{\hbar}{2\pi\mu\Delta v}} \\ &= \sqrt{\frac{1.055 \times 10^{-34}\ J \cdot s}{2\pi \cdot 1.139 \times 10^{-26} \text{ kg} \cdot 1.153 \times 10^{11} \text{ Hz}}} \\ &= 1.131 \times 10^{-10} \text{m} \\ &= 1.131\ \mathring{A}\end{aligned}$$

Advanced: Non-Rigid Rotors

Centrifugal stretching of the bond as J increases causes the decrease in the spacing between the lines in an observed spectrum (Table 5.9.1). This decrease shows that the molecule is not really a rigid rotor. As the rotational angular momentum increases with increasing J, the bond stretches. This stretching increases the moment of inertia and decreases the rotational constant (Figure 5.9.5).



Figure 5.9.5 : Two atoms connected by a vibrating bond. There is a rotation around the common center of mass, and oscillation in bond distance. (CC SA-BY 3.0; www.cleonis.nl).

The effect of centrifugal stretching is smallest at low J values, so a good estimate for B can be obtained from the $J = 0$ to $J = 1$ transition. From B, a value for the bond length of the molecule can be obtained since the moment of inertia that appears in the definition of B (Equation 3.2.9.16) is the reduced mass times the bond length squared. When the centrifugal stretching is taken into account quantitatively, the development of which is beyond the scope of the discussion here, a very accurate and precise value for B can be obtained from the observed transition frequencies because of their high precision. Rotational transition frequencies are routinely reported to 8 and 9 significant figures.

As we have just seen, quantum theory successfully predicts the line spacing in a rotational spectrum. An additional feature of the spectrum is the line intensities. The lines in a rotational spectrum do not all have the same intensity, as can be seen in Figure 5.9.3 and Table 5.9.1. This is related to the populations of the initial and final states. This aspect of spectroscopy will be discussed in more detail in the following chapters

3.2.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

3.2.E: The Harmonic Oscillator and the Rigid Rotor (Exercises)

3.2.E: The Harmonic Oscillator and the Rigid Rotor (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

4: Partition Functions of Model Systems



In che typically co a collection However, if are reasonably far apart as in the case of a dilute gas, we can approximately treat the system as an ideal gas system and ignore the intermolecular forces. The present chapter deals with systems in which intermolecular interactions are ignored. In ensemble theory, we are concerned with the ensemble probability density, i.e., the fraction of members of the ensemble possessing certain characteristics such as a total energy E, volume V, number of particles N or a given chemical potential μ and so on. The molecular partition function enables us to calculate the probability of finding a collection of molecules with a given energy in a system. The equivalence of the ensemble approach and a molecular approach may be easily realized if we treat part of the molecular system to be in equilibrium with the rest of it and consider the probability distribution of molecules in this subsystem (which is actually quite large compared to systems containing a small number of molecules of the order of tens or hundreds).

4.1: Translational Partition Functions of Monotonic Gases
4.2: Most Atoms are in the Ground Electronic State
4.3: The Energy of a Diatomic Molecule Can Be Approximated as a Sum of Separate Terms
4.4: Most Molecules are in the Ground Vibrational State
4.5: Most Molecules are Rotationally Excited at Ordinary Temperatures
4.6: Rotational Partition Functions of Diatomic Gases
4.7: Vibrational Partition Functions of Polyatomic Molecules
4.8: Rotational Partition Functions of Polyatomic Molecules
4.9: Molar Heat Capacities
4.E: Partition Functions and Ideal Gases (Exercises)
4.10: Ortho and Para Hydrogen
4.11: The Equipartition Principle
Symmetry and Group Theory

4: Partition Functions of Model Systems is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.1: 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:

$$q_{\text{trans}} = q_x q_y q_z \tag{4.1.1}$$

$$= \sum_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \sum_{n_y=1}^{\infty} e^{-\epsilon_y/kT} \sum_{n_z=1}^{\infty} e^{-\epsilon_z/kT} \tag{4.1.2}$$

Since the levels are very closely spaced (continuous), we can replace each sum in Equation 4.1.2 with an integral. For example:

$$q_x = \sum_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \tag{4.1.3}$$

$$\approx \int_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \tag{4.1.4}$$

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 4.1.4:

$$q_x = \int_1^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2kT}} \approx \int_0^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2kT}}$$

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 4.1.1) and using V as the volume of the box L^3, we arrive at:

$$q_{\text{trans}} = \left(\frac{\sqrt{2\pi 8mkT}}{h}\right)^{3/2} V = \frac{V}{\Lambda^3} \tag{4.1.5}$$

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 4.1.5

$$q_{\text{trans}} = \frac{V}{\Lambda^3} = \frac{1000 \times 10^{-6} m^3}{(6.326 \times 10^{-12}\ m)^3} = 3.95 \times 10^{30}$$

This means that 3.95×10^{30} quantum states are thermally accessible to the molecular system

Contributors and Attributions

- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf

4.1: Translational Partition Functions of Monotonic Gases is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.1: Translational Partition Functions of Monotonic Gases** is licensed CC BY-NC-SA 4.0.

4.2: Most Atoms are in the Ground Electronic State

Writing the electronic energies as $E_1, E_2, E_3, \ldots$ with corresponding degeneracies $g_1, g_2, g_3, \ldots$. The electronic partition function is then given by the following summation:

$$q_{el}(T) = g_1 e^{-E_1/kT} + g_2 e^{-E_2/kT} + g_3 e^{-E_3/kT} + \ldots \tag{4.2.1}$$

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 4.2.1) can be approximated as:

$$q_{elec}(T) = g_1 + g_2 e^{-E_2/kT} + g_3 e^{-E_3/kT} + \ldots \tag{4.2.2}$$

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

$$q_{el} = e_0 + e^{-5eV/kT} + \ldots$$

At 300 K, T = 0.02\; eV and

$$q_{el} = 1 + e^{-200} + \ldots$$
$$\approx 1.0$$

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.

Contributors and Attributions

- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf

4.2: Most Atoms are in the Ground Electronic State is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.2: Most Atoms are in the Ground Electronic State** is licensed CC BY-NC-SA 4.0.

4.3: The Energy of a Diatomic 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.

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

4.3: The Energy of a Diatomic Molecule Can Be Approximated as a Sum of Separate Terms is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.3: The Energy of a Diatomic/Polyatomic Molecule Can Be Approximated as a Sum of Separate Terms** is licensed CC BY-NC-SA 4.0.

4.4: 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:

$$\begin{aligned} q_{\text{vib}} &= \sum_{v=0}^{\infty} e^{-(v+1/2)h\nu/kT} \\ &= e^{-h\nu/2kT}\left(1+e^{-h\nu/2kT}+e^{-2h\nu/2kT}+\ldots\right) \end{aligned}$$

or rewritten as:

$$q_{\text{vib}} = e^{-h\nu/2kT}\left(1+x+x^2+x^3+\ldots\right) \tag{4.4.1}$$

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 4.4.1 can be rewritten as:

$$q_{\text{vib}} = e^{-h\nu/2kT}\left(\frac{1}{1-x}\right)$$

or:

$$q_{\text{vib}} = \frac{e^{-h\nu/2kT}}{1-e^{-h\nu/kT}} \tag{4.4.2}$$

If the zero of energy scale is at $h\nu/2kT$, then Equation 4.4.2 can be rewritten as:

$$q_{\text{vib}} \approx \frac{1}{1-e^{-h\nu/kT}} \tag{4.4.3}$$

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 18.4.1 : 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)
$\boldsymbol{H_2}$	1	0.7474	4400	6332	60.9	87.6	5.749	103.2
$\boldsymbol{D_2}$	1	0.7415	3118	4487	30.45	43.8	5.77	104.6
$\boldsymbol{N_2}$	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

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)
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.

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:

$$\frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta} \tag{4.4.4}$$

$$= \frac{-1}{kT^2}\frac{\partial}{\partial \beta} \tag{4.4.5}$$

$$= \left(-k\beta^2\right)\left(\frac{\partial}{\partial \beta}\right) \tag{4.4.6}$$

Therefore:

$$\bar{C}_V = \left(-k\beta^2\right)\left(\frac{\partial \varepsilon_{vib}}{\partial \beta}\right)$$

and when the vibrational partition function (Equation 4.4.3) is introduced:

$$q_{\text{vib}} = -k\beta^2 \frac{\left[(1-e^{-hc\nu/kT})(-hc\tilde{\nu}) - e^{-hc\nu/kT}(+hc\tilde{\nu})\right] e^{-hc\nu/kT}}{(1-e^{-hc\nu/kT})^2} h\nu\tilde{\nu} \tag{4.4.7}$$

$$= k\left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{\left(1-e^{-\Theta_{\text{vib}}/T}\right)^2} \tag{4.4.8}$$

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 .

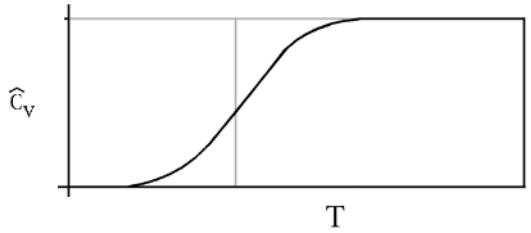


Figure 18.4.1 : Vibrational heat capacity of a diatomic

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.

Vibrational Populations

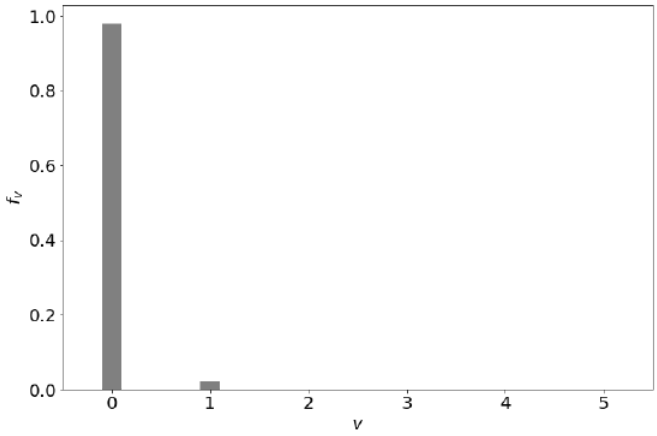
We can calculate the fraction of molecules in each vibrational state. The fraction of molecules in the vth vibrational state is given by:

$$f_v = \frac{e^{-h\nu(v+\frac{1}{2})/kT}}{q_{\text{vib}}}$$

Substituting in Equation 4.4.2, we get:

$$\begin{aligned} f_v &= \left(1-e^{-h\nu/kT}\right) e^{-h\nu v/kT} \\ &= \left(1-e^{-\Theta_{\text{vib}}/T}\right) e^{-\Theta_{\text{vib}} v/T} \end{aligned}$$

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.

Contributors and Attributions

- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf

4.4: Most Molecules are in the Ground Vibrational State is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.4: Most Molecules are in the Ground Vibrational State** is licensed CC BY-NC-SA 4.0.

4.5: 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 $q_{\text{rot}}(T)$ 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 $T >> \Theta_{\text{rot}}$.

? 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 He and 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 $T = 300\,\text{K}$, 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

$$C_v = C_v^{trans} = \frac{3}{2}nR$$

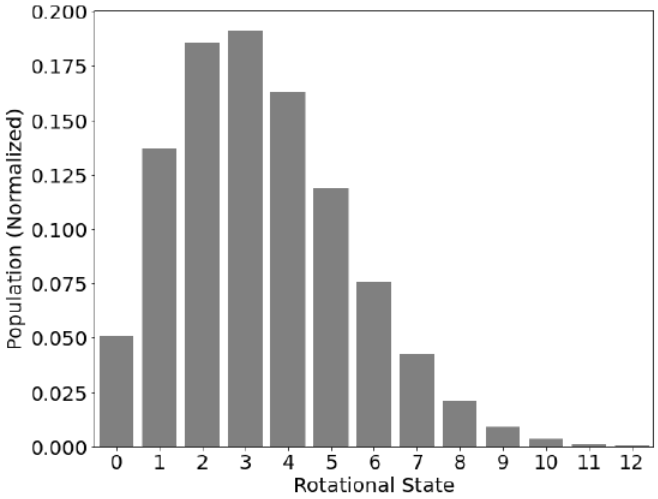
- diatomic

$$C_v = C_v^{trans} + C_v^{rot} \tag{4.5.1}$$

$$= \frac{3}{2}nR + nR \tag{4.5.2}$$

$$= \frac{5}{2}nR \tag{4.5.3}$$

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.

4.5: Most Molecules are Rotationally Excited at Ordinary Temperatures is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.5: Most Molecules are Rotationally Excited at Ordinary Temperatures** is licensed CC BY-NC-SA 4.0.

4.6: Rotational Partition Functions of Diatomic Gases

The rotational energy levels of a **diatomic molecule** are given by:

$$E_{\text{rot}}(J) = \tilde{B}J(J+1) \tag{4.6.1}$$

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:

$$\Theta_{\text{rot}} = \frac{r^2}{8\pi^2 Ik} \tag{4.6.2}$$

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 4.6.3, we can do an explicit summation:

$$q_{\text{rot}} = \sum_{j=0} (2J+1)e^{-E_J/kT} \tag{4.6.3}$$

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 4.6.1 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 $dx = (2J+1)dJ$:

$$q_{\text{rot}} = \frac{kT}{\tilde{B}} \tag{4.6.4}$$

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:

$$q_{\text{rot}} = \frac{kT}{\tilde{B}\sigma} \tag{4.6.5}$$

or commonly expressed in terms of Θ_{rot}:

$$q_{\text{rot}} = \frac{T}{\Theta_{\text{rot}}\sigma} \tag{4.6.6}$$

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 4.6.5,

$$\begin{aligned} q_{\text{rot}} &= \frac{kT}{\tilde{B}\sigma} \\ &= \frac{209.7\ cm^{-1}}{(2)(60.864\ cm^{-1})} \\ &= 1.723 \end{aligned}$$

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

4.6: Rotational Partition Functions of Diatomic Gases is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.6: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number** is licensed CC BY-NC-SA 4.0.

4.7: Vibrational Partition Functions of Polyatomic Molecules

As with diatomic molecules, the energies of polyatomic molecules can be approximated by the sum of its individual degrees of freedom. Therefore, we can write the partition function as:

$$Q(N,V,T) = \frac{[q(V,T)]^2}{N!}$$

We can write the polyatomic analog to diatomic molecules:

$$Q(N,V,T) = \frac{(q_{\text{trans}}q_{\text{rot}}q_{\text{vib}}q_{\text{elec}})^N}{N!}$$

When derived for diatomic molecules, we assumed the rigid rotor model for rotations and the harmonic oscillator for vibrations. This allowed us to separate the rotational motion from the vibrational motion of the molecule. Polyatomic molecules are a bit more complicated, but we will still make use of these approximations.

The number of translational states available to any given molecule is far greater than the number of molecules in the system. q_{trans} is given by:

$$q_{\text{trans}} = \left[\frac{2\pi MkT}{h^2}\right]^{3/2} V$$

where M is the mass of the particle. Moving to the electronic partition function:

$$q_{\text{elec}} = \sum_i g_i e^{-E_i/kT}$$

where E_i is the energy of the electronic state i and {g_i} is its degeneracy. Electronic states are typically spaced far apart from each other. The probability of the system being in any state but the ground state is extremely small. We can therefore simplify the electronic partition function to include only the ground electronic state:

$$q_{\text{elec}} = g_{e1}e^{D_e/kT}$$

where $-D_e$ is the energy of the ground electronic state. To complete the polyatomic partition function, we still need q_{vib} and q_{rot}. We will finish this section with q_{vib} and talk about q_{rot} in the next.

The vibrational motion of diatomic molecules can be expressed as a set of independent harmonic oscillators. For polyatomic molecules, the independent vibrational motions are referred to as normal modes of vibration. The vibrational energy is then the sum of the energies for each normal mode:

$$E_{\text{vib}} = \sum_i^{\alpha} \left(v_i + \frac{1}{2}\right) h\nu$$

where ν_i is the vibrational frequency for the ith normal mode and α is the number of vibration degrees of freedom. A linear molecule has $3n-5$ vibrational degrees of freedom and a nonlinear molecule has $3n-6$ vibrational degrees of freedom. Because the normal modes are independent of each other, we can take out results from previous sections:

$$q_{\text{vib}} = \prod_i^{\alpha} \frac{e^{-\theta_{\text{vib},i}/2T}}{1-e^{-\theta_{\text{vib},i}/T}}$$

$$E_{\text{vib}} = Nk\sum_i^{\alpha}\left(\frac{\theta_{\text{vib},i}}{2} + \theta_{\text{vib},i}\frac{e^{-\theta_{\text{vib},i}/T}}{1-e^{-\theta_{\text{vib},i}/T}}\right)$$

$$C_{V,\text{vib}} = Nk\sum_i^{\alpha}\left(\left(\frac{\theta_{\text{vib},i}}{2}\right)^2 + \frac{e^{-\theta_{\text{vib},i}/T}}{(1-e^{-\theta_{\text{vib},i}/T})^2}\right)$$

where $\theta_{\text{vib},i}$ is the characteristic vibrational temperature defined by:

$$\theta_{\text{vib},i} = \frac{h\nu_i}{k}$$

Vibrational Entropy

There is a great deal of utility for thermodynamic functions calculated from the vibrational normal modes of a molecule. The vibrational energy and entropy depend on the shape a multidimensional potential energy surface. If one performs a conformational search of macromolecule it is one obtains energies and structures but little direct information concerning the shape of the potential energy surface for each conformation. The vibrational entropy gives a means determining whether there are significant entropic differences in the structures and therefore whether certain conformations will be favored based on the entropy.

However, it is possible to take appropriate linear combinations of the coordinates so that the cross terms are eliminated and the classical Hamiltonian as well as the operator corresponding to it contains no cross terms and in terms of the new coordinates, the Hamiltonian can be written as,

$$H = \sum_{i=1}^{f} \frac{h^2}{2\mu_i} \frac{\partial}{\partial q_i^2} + \sum_{i=1}^{f} \frac{k_i}{2} q_i^2 \tag{4.7.1}$$

Here, the degrees of freedom f is $3N-5$ for a linear molecule and $3N-6$ for a nonlinear molecule. Here, k_i is the force constant and μ_i is the reduced mass for that particular vibrational mode which is referred to as a **normal mode**.

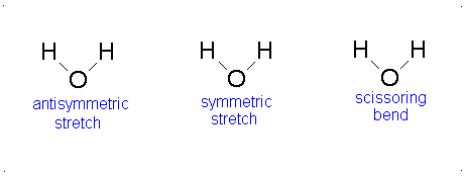


Figure 18.7.1 : The three vibrational modes of water, the symmetric stretch (3656.7 cm^{-1}, 5160 K), the asymmetric stretch (3755.8 cm^{-1} , 5360 K) and the bending mode (1594.8 cm^{-1} ,2290 K) are shown. The vibrational frequencies and the characteristic temperature for each mode are shown in parenthesis. Although not shown in the animation, the oxygen atom also moves with each of these normal modes.

The Equation 4.7.1 represents f linearly independent harmonic oscillators and the total energy for such a system is

$$\epsilon_{vib} = \sum_{i=1}^{f} \left(v_i + \frac{1}{2} \right) h\nu_i$$

The vibrational frequencies are given by

$$\nu_i = \frac{1}{2\pi} \sqrt{\frac{k_i}{\mu_i}}$$

The vibrational partition function is given by the product of f vibrational functions for each frequency.

$$q_{vib} = \prod_{i=1}^{f} \frac{e^{-\Theta_{vib,i}/2T}}{1 - e^{-\Theta_{vib,i}/T}} \tag{4.7.2}$$

with

$$\Theta_{vib,i} = \frac{h\nu_i}{k_B}$$

As with the previous discussion regarding simple diatomics, $\Theta_{vib,i}$ is called the **characteristic vibrational temperature**. The molar energies and the heat capacities are given by

$$\langle E_{vib} \rangle = Nk \sum_{i=1}^{f} \left[\frac{\Theta_{vib,i}}{2} + \frac{\Theta_{vib,i} e^{-\Theta_{vib,i}/T}}{1 - e^{-\Theta_{vib,i}/T}} \right]$$

and

$$\bar{C}_V = Nk_B \sum_{i=1}^{f} \left(\frac{\Theta_{vib,i}}{T} \right)^2 \frac{e^{-\Theta_{vib,i}/T}}{\left(1 - e^{-\Theta_{vib,i}/T}\right)^2}$$

Example

The three characteristic vibrational temperatures for NO_2 are 1900 K, 1980 K and 2330 K. Calculate the vibrational partition function at 300 K.

Solution

The vibrational partition is (Equation 4.7.2)

$$q_{vib} = \prod_{i=1}^{f} \frac{e^{-\Theta_{vib,i}/2T}}{1 - e^{-\Theta_{vib,i}/T}}$$

If we calculate q_{vib} by taking the zero point energies as the reference points with respect to which the other energies are measured

$$q_{vib} = \prod_{i=1}^{f} \frac{1}{1 - e^{-\Theta_{vib,i}/T}} = \left(\frac{1}{1 - e^{-1900/300}}\right)\left(\frac{1}{1 - e^{-1980/300}}\right)\left(\frac{1}{1 - e^{-2330/300}}\right)$$

$$= (1.0018)(1.0014)(1.0004) = 1.0035$$

The implication is that very few vibrational states of NO_2 (other than the ground vibrational state) are accessible at 300 K. This is standard of the vibrations of most molecules.

Contributors and Attributions

- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf

4.7: Vibrational Partition Functions of Polyatomic Molecules is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.7: Vibrational Partition Functions of Polyatomic Molecules Include the Partition Function for Each Normal Coordinate** is licensed CC BY-NC-SA 4.0.

4.8: Rotational Partition Functions of Polyatomic Molecules

For a polyatomic molecule containing N atoms, the total number of degrees of freedom is $3N$. Out of these, three degrees of freedom are taken up for the translational motion of the molecule as a whole. For nonlinear molecules, there are three rotational degrees of freedom and the $3N-6$ vibrational degrees. For linear molecules, the rotational motion along the molecular axis is quantum mechanically not meaningful as the rotated configuration is indistinguishable from the original configuration. Therefore, linear molecules have two rotational degrees of freedom and $3N-5$ vibrational degrees of freedom.

To investigate the rotational motion, we need to fix the center of mass of the molecule and calculate the three principal moments of inertia I_A, I_B, and I_C of the ellipsoid of inertia. The center of mass is defined as the point for which the following identities hold:

$$\sum_i m_i x_i = \sum_i m_i y_i = \sum_i m_i z_i$$

The inertia products are defined by:

$$I_{xx} = \sum_i m_i \left(y_i^2 + z_i^2\right)$$

$$I_{xy} = \sum_i m_i \left(x_i y_i\right)$$

The other components I_{yy}, I_{xz},.. are defined analogously. To find the direction cosines $\alpha_i, \beta_o, \gamma_i$ of the three principle moments of inertia, we need to solve the following matrix equations:

$$\alpha(I_{xx} - \eta) - \beta I_{xy} - \gamma I_{xz} = 0$$

$$\alpha I_{xy} - \beta(I_{yy} - \eta) - \gamma I_{yz} = 0$$

$$-\alpha I_{xz} - \beta I_{yz} + \gamma(I_{zz} - \eta) = 0$$

If the off diagonal terms I_{xy} are zero in the above equations, then the x, y, z axis will be the principal axis. The energy of a rotor with the three moments of inertia I_A, I_B. and I_C is given by:

$$\begin{aligned}\epsilon &= \frac{1}{2} I_A \omega_A^2 + \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2 \\ &= \frac{L_A^2}{2I_A} + \frac{L_B^2}{2I_B} + \frac{L_C^2}{2I_C}\end{aligned}$$

Each of the rotational degrees of freedom will have a characteristic rotational temperature in terms of the moment of inertia:

$$\Theta_{rot,i} = \frac{hbar^2}{2I_i k} \qquad i = A, B, C$$

There are many different shapes of molecules and these shapes affect the rotational behavior of the molecules. Molecules are therefore classified according to symmetry into different groups called tops. The three different tops are:

$$\begin{aligned}&\text{Spherical top} && \Theta_{rot,A} = \Theta_{rot,B} = \Theta_{rot,C} \\ &\text{Symmetric top} && \Theta_{rot,A} = \Theta_{rot,B} \neq \Theta_{rot,C} \\ &\text{Asymmetric top} && \Theta_{rot,A} \neq \Theta_{rot,B} \neq \Theta_{rot,C}\end{aligned}$$

Spherical Tops

The spherical top can be solved exactly to give:

$$E_J = \frac{J(J+1)\hbar^2}{2I}$$

$$g_J = (2J+1^2) \qquad J = 0, 1, 2, \ldots$$

The rotational partition function is:

$$q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1)^2 e^{\hbar^2 J(J+1)/2IkT}$$
$$= \sum_{J=0}^{\infty} (2J+1)^2 e^{\Theta_{\text{rot}} J(J+1)/T}$$

For almost all spherical top molecules:

$$\Theta_{\text{rot}} \gg T$$

Therefore, we can convert the sum to an integral:

$$q_{\text{rot}} = \frac{1}{\sigma} \int_0^{\infty} (2J+1)^2 e^{\Theta_{\text{rot}} J(J+1)/T}$$

where we have now included the symmetry term, σ. Solving for this integral, we get:

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma} \left(\frac{T}{q_{\text{rot}}} \right)^{3/2}$$

Symmetric Tops

Here, ω_A, ω_B, and ω_C are the three angular speeds and L_A, L_B, and L_C are the three angular momenta. For a symmetric top molecule such as ammonia, or chloromethane, two components of the moments of inertia are equal, i.e., $I_B = I_C$. The rotational energy levels of such a molecule are specified by two quantum numbers J and K. The total angular momentum is determined by J and the component of this angular momentum along the unique molecular axis is determined by K. The energy levels are given by:

$$\epsilon_{J,K} = \tilde{B} J(J+1) + (\tilde{A} - \tilde{B}) K^2$$

with rotational constants in units of wavenumbers:

$$\tilde{B} = \frac{h}{8\pi^2 c I_B}$$

and:

$$\tilde{A} = \frac{h}{8\pi^2 c I_A}$$

where

- J takes on values $0, 1, 2, \ldots . \infty$and
- $K = -J, -J+1, -J+2, \ldots 0, 1, 2, \ldots J$.

The rotational partition function is given by:

$$q_{rot} = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1) e^{-\tilde{B} J(J+1)/kT} \sum_{K=-J}^{J} (2J+1) e^{\tilde{A}-\tilde{B}) K^2/kT}$$

This can be converted to an integral and the result is:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi I_B kT}{h^2} \right) \left(\frac{8\pi I_A kT}{h^2} \right)^{1/2}$$

Asymmetric Tops

For asymmetric tops, the expressions for rotational energies are more complex and the conversions to integrations are not easy. One can actually calculate the sum of terms using a computer. An intuitive answer can be obtained by integrating over the angular momenta L_A, L_B and L_C as:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{H(p,q)/kT} \, dL_A \, dL_B \, dL_C = \sqrt{2\pi I_A kT} \sqrt{2\pi I_B kT} \sqrt{2\pi I_C kT}$$

And then multiplying by a factor of $8\pi^2/\sigma h^3$, we get the rotational partition function. The factor of $8\pi^2$ accounts for the angular integration. For any axis chosen in a molecule, a complete rotation contributes a factor of 2π. Integration over all possible orientations of this axis contribute another factor of 4π. The factor of h^3 is for the conversion from the classical phase space to the quantum mechanical phase space.

Symmetry Number

As discussed previously, the **symmetry number** σ corrects for overcounting of rotational configurations. If the molecule has no center of symmetry (e.g. HCN) $\sigma = 1$ whereas if the molecule has a center of symmetry (e.g. CO_2) then $\sigma = 2$.

The final result is:

$$q_{rot} = \frac{\pi^2}{\sigma}\sqrt{\frac{8\pi I_A kT}{h^2}}\sqrt{\frac{8\pi I_B kT}{h^2}}\sqrt{\frac{8\pi I_C kT}{h^2}} \tag{4.8.1}$$

Classical Derivation (Optional)

We can explicitly obtain the classical rotational partition function of an asymmetric top by writing the classical expression for the rotational energy in terms of the Euler angles. The orientation of a rigid rotor can be specified by there Euler angles θ, φ, and ψ with the ranges of angles 0 to π, 0 to 2π and 0 to 2π respectively. The rotational Hamiltonian for the kinetic energy can be written in terms of the angles and their conjugate momenta (p_θ, p_ϕ, p_ψ)

$$H = \frac{\sin^2\psi}{2I_A}\left(p_\theta - \frac{\cos\psi}{\sin\theta\sin\psi}(p_\phi - \cos\theta p_\psi)\right)^2$$
$$+\frac{\cos^2\psi}{2I_B}\left(p_\theta - \frac{\sin\psi}{\cos\theta\cos\psi}(p_\phi - \cos\theta p_\psi)\right)^2 + \frac{1}{2I_C}p_\psi^2$$

The classical rotational partition function is given by

$$q_{rot} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}\frac{1}{h^3}e^{-H(p,q)/kT}dp_\theta\, dp_\phi\, dp_\psi\, d\theta\, d\phi\, d\psi$$

The integrations can be simplified by rewriting $H(p,q)/kT$ as

$$\frac{H}{kT} = \frac{1}{2I_A kT}\left(\frac{\sin^2\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)\left(p_\theta + \left(\frac{1}{I_B} - \frac{1}{I_A}\right)\frac{\sin\psi\cos\psi}{\sin\theta\left(\frac{\sin^\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)}(p_\phi - \cos\theta p_\psi)\right)^2$$
$$+\frac{1}{2kTI_A I_B\sin^2\theta}\left(\frac{1}{\sin\theta\left(\frac{\sin^\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)}(p_\phi - \cos\theta p_\psi)\right)^2 + \frac{1}{2KTI_c}p_\psi^2$$

Using the following integral,

$$\int_{-\infty}^{\infty}e^{-a(x+b)^2}dx = \int_{-\infty}^{\infty}e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$$

Integration over p_θ gives using the above expression

$$\sqrt{2\pi kT}\left(\frac{\sin^2\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)^{-1/2} \tag{4.8.2}$$

Integration over p_φ gives the factor,

$$\sqrt{2\pi kTI_AI_B}\sin\theta\left(\frac{\sin^2\psi}{I_A}+\frac{\cos^2\psi}{I_B}\right)^{1/2}$$

This cancels partly the second square root in Equation 4.8.2. Integration over p_ψ gives the factor

$$\sqrt{2\pi kTI_c}$$

Integration over θ, φ and ψ gives a factor of $8\pi^2$.

$$\int_0^\pi \sin\theta\, d\theta = 2$$

$$\int_0^{2\pi} d\phi = 2\pi$$

$$\int_0^{2\pi} d\psi = 2\pi$$

Combining all the integrals, we finally get Equation 4.8.1 after reintroduced the symmetry number σ as before with diatomic molecular rotation.

We can simplify calculations by defining **characteristic rotational temperatures** for each axis of rotational:

$$\Theta_A = \frac{h^2}{8\pi^2 I_A k}$$

$$\Theta_B = \frac{h^2}{8\pi^2 I_B k}$$

$$\Theta_C = \frac{h^2}{8\pi^2 I_C k}$$

The polyatomic rotational partition function expressed in Equation 4.8.1 can then be re-expressed as:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}} \tag{4.8.3}$$

or alternatively:

$$\ln q_{rot} = \frac{1}{2}\ln\frac{\pi T}{\Theta_A\Theta_B\Theta_C\sigma^2}$$

Example: Nitrogen Dioxide

The three characteristic rotational temperatures for NO_2 are $111.5\ K$, $0.624\ K$ and $0.590\ K$. Calculate the rotational partition function at 300 K.

Solution

The rotational temperature is given by Equation 4.8.3:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}}$$

The rotational partition function becomes,

$$q_{rot} = \frac{1.772}{2}\sqrt{\frac{300\ K}{(11.5\ K)(0.624\ K)(22.55\ K)}} = 2242.4$$

Thermodynamics Properties

The molar thermodynamic functions can be readily calculated including average rotation energy and molar heat capacity:

$$E_{rot} = \frac{3}{2}RT$$

and:

$$\bar{C_V} = \frac{3}{2}R$$

Improvements over the classical approximation for the rotational partition function derived above have been obtained. One of the improved versions (with no derivation) is:

$$q_{rot} = q^0_{rot}\left[1 + \frac{h^2}{96\pi^2 kT}\left(\frac{2}{I_A} + \frac{2}{I_C} + \frac{2}{I_C} + \frac{I_C}{I_B I_B} - \frac{I_A}{I_B I_C} - \frac{I_B}{I_A I_C}\right)\right]$$

where q^0_{rot} is the classical approximation in Equation 4.8.1.

Comparing this result with the vibrational partition function calculation before ($q_{vib} = 1.0035$), give the implication that while multiple rotational states are accessible at room temperature, very few vibrational states (other than the ground vibrational state) are accessible.

Contributors and Attributions

- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf

4.8: Rotational Partition Functions of Polyatomic Molecules is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.8: Rotational Partition Functions of Polyatomic Molecules Depend on the Sphar of the Molecule** is licensed CC BY-NC-SA 4.0.

4.9: Molar Heat Capacities

Learning Objectives

- **Goal**: Specific heat capacity data for a wide range of elements are used to assess the accuracy and limitations of the Dulong-Petit Law.
- **Prerequisites**: An introductory knowledge of statistical thermodynamics including the derivation of the vibrational (harmonic oscillator) contributions to the heat capacity are recommended.
- **Resources you will need**: This exercise should be carried out within a data analysis software environment which is capable of graphing and generating a best-fit line for an x-y data set.

The heat capacity (C) of a substance is a measure of how much heat is required to raise the temperature of that substance by one degree Kelvin. For a simple molecular gas, the molecules can simultaneously store kinetic energy in the translational, vibrational, and rotational motions associated with the individual molecules. In this case, the heat capacity of the substance can be broken down into translational, vibrational, and rotational contributions;

$$C = C_{trans} + C_{vib} + C_{rot} \tag{4.9.1}$$

Monoatomic crystalline solids represent a much simpler case. Einstein proposed a simple model for such substances whereby the atoms only have vibrational energy (each atom can vibrate in three perpendicular directions around its lattice position). Specifically, the 'Einstein Solid Model' assumes that the atoms act like three-dimensional harmonic oscillators (with the vibrational motion of each atom in each perpendicular dimension entirely independent). Statistical mechanics provides a relatively simple expression for the constant volume molar heat capacity ($C_{V,m}$) of a one-dimensional harmonic oscillator

$$C_{V,m}^{1-D} = R\left(\frac{\Theta_v}{T}\right)^2\left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2 \tag{4.9.2}$$

where R is the universal gas constant, T is absolute temperature, and Θ_v is called the 'characteristic vibrational temperature' of the oscillator and depends on the vibrational frequency (ν) according to

$$\Theta_v = \frac{hv}{k} \tag{4.9.3}$$

with h representing Plank's constant and k representing Boltzmann's constant.

Since the vibrations in each dimension are assumed to be independent, the expression for the constant volume molar heat capacity of a 'three-dimensional' Einstein Solid is obtained by simply multiplying Equation 4.9.2 by three;

$$C_{V,m}^{3-D} = 3R\left(\frac{\Theta_v}{T}\right)^2\left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2 \tag{4.9.4}$$

The temperature variation of the heat capacity of most metallic solids is well described by Equation 4.9.4. Furthermore, plots of Equation 4.9.4 as a function of temperature for metals with widely varying vibrational frequencies reveal that the heat capacity always approaches the same asymptotic limit of $3R$ at high temperatures. Stated another way, at high temperatures

$$\lim_{T\to\infty}\left[\left(\frac{\Theta_v}{T}\right)^2\left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2\right] = 1 \tag{4.9.5}$$

and Equation 4.9.4 reduces to

$$\lim_{T\to\infty}\left[C_{V,m}^{3D}\right] = 3R \tag{4.9.6}$$

(You will be asked to verify this result in the exercise below). According to Equation 4.9.6, the molar heat capacities of metallic solids should approach 24.9 J/(K mol) at high temperatures, regardless of the identity of the metal.

The vibrational frequencies of most metallic solids are usually small enough so that Θ_v lies considerably below room temperature ($\Theta_v \ll 298\ K$). For these substances, the limits implied by Equations 4.9.5 and 4.9.6 are well approximated even at room temperature, leading to the result that $C_{v,m} = 24.9\ J/(K\cdot mol)$ for most metals at room temperature.

In the early 1800s, two French scientists by the names of Pierre Louis Dulong and Alexis Therese Petit empirically discovered the same remarkable result. The Dulong-Petit Law is normally expressed in terms of the specific heat capacity (C_s) and the molar mass (M) of the metal

$$C_s M = C_{V,m} \approx 25 (J\,K^{-1}\,mol^{-1}) \tag{4.9.7}$$

where C_s represents how much heat is required to raise the temperature of 'one gram' of that substance by one degree Kelvin. Dulong and Petit, as well as other scientists of their time, used this famous relationship as a means of establishing more accurate values for the atomic weight of metallic elements (by instead measuring the specific heat capacity of the element and using the Dulong-Petit relationship, which is a relatively simple method of establishing weights in comparison to the more disputable gravimetric methods that were being used at the time to establish the equivalent weights of elements).

In the exercise below, you will look up the specific heat capacities of a number of elements that exist as simple monoatomic solids at room temperature and assess the accuracy of the Dulong-Petit law.

Experimental Data

Consult the CRC Handbook of Chemistry and Physics (CRC Press: Boca Raton, FL) and compile a table of specific heat capacities for a large number of elements that are known to exist as monoatomic solids at room temperature. Also look up and record the molar mass of these elements. The elements that you consider should be restricted to those appearing in groups 1-14 of the periodic table. Make sure you generate a fairly large list which includes a number of elements that are normally considered as metallic in character (such as copper, iron, sodium, lithium, gold, platinum, barium, and aluminum), but also some non-metallic elements that are nonetheless monoatomic isotropic solids (such as carbon-diamond, beryllium, boron, and silicon). Heat capacities that are usually reported in the literature are not actual constant volume heat capacities (C_v), but are instead constant pressure heat capacities (C_p). Fortunately, C_p and C_v are essentially equal for simple solids (within the level of precision that we consider in this exercise), and you can assume that the values from the CRC Handbook represent C_s.

Exercises

1. Enter the element name, the specific heat capacity, and the molar mass of each element in a spreadsheet. Calculate the product of specific heat and molar mass for each element and calculate how much this product differs from the Dulong-Petit prediction (express your result as a percent difference relative to $3R$).
2. Assess the generality of the Dulong-Petit law in an alternate way by generating a plot of specific heat as a function of reciprocal Molar Mass (C_s versus $1/M$), which should be linear with a slope equal to 3R if the data behave according to Equation 4.9.7.
3. Inspect your results from 1 and 2 above and identify any elements that significantly deviate from the Dulong-Petit law. When they occur, do deviations tend to be smaller or larger than 3R? Does the degree of deviation from the Dulong-Petit law seem to correlate with periodic trends in metallic (or covalent) bonding for these elements? Do deviations tend to occur more readily for elements of smaller or higher atomic weight? Explain how the type of bonding and the magnitude of the atomic weight can lead to deviations from the arguments made in Equations 4.9.5-4.9.7 above.
4. Use the plotting method that you employed in step 2 above as a means of determining a value for the universal gas constant (R) - but make sure you throw-out any specific heat data for elements that you suspect do not fall within the limit $\Theta_v \ll 298\,K$. Calculate the percent error in the value of R that you determine.
5. Verify that the limit expressed in Equation 4.9.5 above is true (HINT: expand each of the exponential terms in a power series and note that higher-order terms are negligible in the limit $T \gg \Theta_v$).

4.9: Molar Heat Capacities is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Specific Heat Capacities and the Dulong-Petit Law** by Tandy Grubbs is licensed CC BY-NC-SA 4.0.

4.E: Partition Functions and Ideal Gases (Exercises)

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

These are homework exercises to accompany Chapter 18 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

1) If the nucleus has a spin of s_n, then its spin degeneracy $g_n = 2s_n + 1$. The diatomic molecule formed from such a nucleus will have g n 2 spin functions which have to be combined to form symmetric and antisymmetric functions. Carry out an analysis similar to that of H 2 for D 2 where the deuterium nucleus has a spin of 1.

2) Derive the thermodynamic functions from the polyatomic rotational partition function. 3) Carry out the integration for the rotational partition function of the symmetric top.

4) Calculate the total partition function and the thermodynamic functions of water at 1000K. The three moments of inertia of water are 1.02, 1.91 and 2.92 in 10 - 47 kg m 2 . The symmetry number is 2. The vibrational data in given in Fig. 3.5. Assume a non-degenerate electronic ground state.

5) Verify that the symmetry numbers for methane, benzene and SF 6 are 12, 12 and 24 respectively.

6) The ground state of Na is a doublet (two states with the same energy). Assuming this to be the zero of energy and assuming that the next energy level to be 2 eV higher than the ground state, calculate q el .

7) The bond length r_{eq} of O_2 is 1.2 Å. The moment of inertia I is $mr_{eq}^2/2$ where m of O is $16X1.66times10^{-27}$ kg Calculate $\tilde{B}$ and the rotational partition function of O_2 at 300 K.

8) The vibrational frequency ν of ICl is 384 cm -1 . What is its vibrational partition function at 300 K? What is the fraction of molecules in the ground state (n = 0) and the first excited state n = 1? 9) Calculate the translational partition function of N 2 at 300 K. For volume, use the molar volume at 300 K.

10) An isotope exchange reaction between isotopes of bromine is 79 79 81 81 79 81 2 Br Br Br Br Br Br +

The fundamental vibrational frequency of 79 81 Br Br 323.33 cm -1 . All the molecules can be assumed to have the same bond length and have a singlet ground electronic state. Calculate the equilibrium constant at 300K and 1000K.

11) For the reaction I 2 ↔ 2I, calculate the equilibrium constant at 1000K. The relevant data are as follows. The ground electronic state of I is 2 3/ 2 P whose degeneracy is 4. The rotational and vibrational frequencies of I 2 are 0.0373 cm -1 and 214.36 cm -1 respectively. The dissociation energy of I 2 is 1.5422 eV.

12) The representative molecular data for a few molecules is given in table 3.1. Using the relevant data, calculate the equilibrium constant for the reaction H 2 + Cl 2 I HCl at 1000K. What is the value of the equilibrium constant as T → ∞?

13) Eq. (3.50) is related to the Giauque function. Estimate the total molar Giauque function for molecules that behave as harmonic oscillators-rigid rotors.

14) The energy of a molecule in the rigid rotor – harmonic oscillator approximation is E vib, rot is (n +1/2) hν + B J (J+1) Real molecules deviate from this behaviour due to the existence of anharmonicity (anharmonicity constant x e), centrifugal distortion (centrifugal distortion constant D) and the interaction between vibration and rotation (α is the coupling constant between the vibrational and rotational modes). The expression for the energy when these affects are included is 2 2 2 1 1 1 2 2 2 , ( ) (1) ( ) (1) ( ) (1) vib rot e E n h BJ J x n h DJ J n J J ν ν α = + + + − + + + − + + Here, the third term is due to anharmonicity, the fourth term is due to centrifugal distortion and the last term is due to the interaction between vibration and rotation. Calculate the q vib, rot which includes the effects of these distortions.

Q18.4

Using the data in Table 8.6, calculate the fraction of sodium atoms in the first excited state at temperatures 300 K, 1000 K, and 2000 K.

S18.4

Using Equation 18.10, we can calculate the fraction of sodium atoms in the first excited state, with $g_{e1} = 2, g_{e2} = 2, g_{e3} = 4, g_{e4} = 2$:

$$f_2 = \frac{2e^{-\beta\epsilon_{e2}}}{2 + 2e^{-\beta\epsilon_{e2}} + 4e^{-\beta\epsilon_{e3}} + 2e^{-\beta\epsilon_{e4}} + \ldots} \tag{4.E.1}$$

Using the data in Table 8.6, the numerator of this fraction becomes

$$2exp[-\frac{16956.183cm^{-1}}{(0.6950cm^{-1}K^{-1})T}] \tag{4.E.2}$$

and the denominator becomes

$$2 + 2exp[-\frac{16956.183cm^{-1}}{(0.6950cm^{-1}K^{-1})T}] + 4exp[-\frac{16973.379cm^{-1}}{(0.6950cm^{-1}K^{-1})T}] + 2exp[-\frac{25739.86cm^{-1}}{(0.6950cm^{-1}K^{-1})T}] + \ldots$$

Using these values, we can find the values of f_2 at the different temperatures.

$$f_2(T = 300K) = 4.8x10^{-36}$$

$$f_2(T = 1000K) = 2.5x10^{-11}$$

$$f_2(T = 2000K) = 5.0x10^{-6}$$

Q18.5

Using the data in the table, calculate the fraction of hydrogen atoms in the first excited state at 400 K, 1800 K, and 2100 K.

Electronic Configuration	Term Symbol	Degeneracy $g_e = 2J + 1$	energy/cm^{-1}
$1s$	$^2S_{1/2}$	2	0
$2p$	$^2P_{1/2}$	2	82 258.907
$2s$	$^2S_{1/2}$	2	82 258.942
$2p$	$^2P_{3/2}$	4	82 259.272

S18.5

Use the equation:

$$f_2 = \frac{g_{e2}e^{-\beta\varepsilon_{e2}}}{g_{e1} + g_{e2}e^{-\beta\varepsilon_{e2}} + g_{e3}e^{-\beta\varepsilon_{e3}} + \cdots} \tag{4.E.3}$$

and

$$\beta \approx \frac{1}{T\ 0.6950\ cm^{-1}K^{-1}} \tag{4.E.4}$$

to get:

$$f_2 = \frac{2e^{-\frac{82\ 258.907\ cm}{T\ 0.6950\ cm^{-1}K^{-1}}}}{2 + 2e^{-\frac{82\ 258.907\ cm}{T\ 0.6950\ cm^{-1}K^{-1}}} + 2e^{-\frac{82\ 258.942\ cm}{T\ 0.6950\ cm^{-1}K^{-1}}} + 4e^{-\frac{82\ 259.272\ cm}{T\ 0.6950\ cm^{-1}K^{-1}}}} \tag{4.E.5}$$

$$f_2(400\ K) = 0.2498$$

$$f_2(900\ K) = 0.2499$$

$$f_2(2100\ K) = 0.2500$$

4.E: Partition Functions and Ideal Gases (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.10: Ortho and Para Hydrogen

The molecules of hydrogen can exist in two forms depending on the spins on the two hydrogen nuclei. If both the nuclear spins are parallel, the molecule is called ortho and if the spins are antiparallel, it is referred to as para (in disubstituted benzene, **para** refers to the two groups at two opposite ends, while in **ortho**, they are adjacent or "parallel" to each other). The spin on the hydrogen nucleus has a magnitude of ½$\hbar$. The presence of nuclear spins leads to very interesting consequences for the populations of the rotational states and on a macroscopic scale, has consequences on measured entropies and heat capacities as well. The total partition function of H_2 can be written as:

$$q_{tot} = q_{elec} q_{vib} q_{rot} q_{trans} q_{nuc}$$

where, the subscripts refer to the respective motions. After "half" a rotation, the nuclei are superimposed on each other. Since a proton is a spin half nucleus, the total wave function must be antisymmetic with respect to the exchange of the particles. i.e.:

$$\psi(1,2) = -\psi(2,1)$$

The translational motion refers to the motion of the molecular center of mass and has no influence on the symmetry of the nuclear wave function. Vibrational motion depends on the magnitude of the internuclear distance and has no effect on the particle exchange. The electronic motion also has no effect on the symmetry properties of the nuclear wave function. Therefore, the product of the nuclear spin and rotational wave functions must be antisymmetric with respect to the particle exchange. For the nuclear spin functions, there are four combinations. One combination is a singlet:

$$|\psi_{\nu,s}\rangle = \alpha(1)\beta(2) - \alpha(2)\beta(1)$$

And the other three combinations are the three states of a triplet:

$$\begin{aligned} |\psi_{\nu,s}\rangle &= \alpha(1)\alpha(2) \\ |\psi_{\nu,s}\rangle &= \alpha(1)\beta(2) + \alpha(2)\beta(1) \\ |\psi_{\nu,s}\rangle &= \beta(1)\beta(2) \end{aligned}$$

The rotational wavefunctions (ψ_r) are given in terms of the associated Legendre polynomials $P_l^{|m|}(x)$ where $x = \cos\theta$:

$$|\psi_r\rangle = e^{im\phi} P_l^{|m|}(\cos\theta) \tag{4.10.1}$$

with:

$$P_l^{(m)}(x) = \left(1 - x^2\right)^{|m/2} \frac{d^{|m|} P_l(x)}{dx^{m|}} \tag{4.10.2}$$

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l \left(x^2 - 1\right)^l}{dx^l} \tag{4.10.3}$$

When the nuclei are interchanged, θ becomes $\pi - \theta$ and φ is changed to $\varphi + \pi$. The polynomials change as:

$$P_l(-x) = (-1)' P_l(x); \quad P_l^{|m|}(-x) = (-1)^{l-|m|||} P_l^{|m|}(x) \tag{4.10.4}$$

The exponential function changes as:

$$e^{im(\phi+\pi)} = e^{im\pi} e^{im\varphi} = (-1)^{|m|} e^{im\varphi} \tag{4.10.5}$$

Therefore, the rotational wave function changes as:

$$P_l(-x) = (-1)^l P_l(x) \tag{4.10.6}$$

$$P_l^{|m|}(-x) = (-1)^{l-|m|} P_l^{|m|}(x) \tag{4.10.7}$$

- $|\psi_r\rangle$ is symmetrical for even J, and
- $|\psi_r\rangle$ is antisymmetrical for odd J

Combining the nuclear spin and the rotational parts, we see that, the product ψ_r, ψ_m must be antisymmetrical (with respect to the exchange of nuclei) for half integral nuclear spins and symmetrical for integral spins. To accomplish this, the singlet nuclear states

(para) must be combined with the even rotational functions and the triplet nuclear states must be combined with the odd rotational states. The rotational partition functions for ortho and para hydrogens are, thus:

$$q_{\text{ortho}} = q_{\nu,t} q_{r,\text{odd}} = 3 \sum_{J=1,3,5,\ldots} (2J+1) e^{-J(J+1)\Theta_R/T} \tag{4.10.8}$$

and:

$$q_{\text{para}} = q_{\backslash \text{nu,s}}\, q_{r,\text{even}} = 1 \sum_{J=0,2,4,\ldots} (2J+1) e^{-J(J+1)\Theta_R/T} \tag{4.10.9}$$

where Θ_R is the rotational temperature defined previously. The total partition function consisting both ortho and para hydrogens is given by:

$$q_{\text{rot},nu} = 1 \sum_{j=0.2.4} (2J+1) e^{-J(J+1)\Theta_k/T} + 3 \sum_{j=1,3,5,n} (2J+1) e^{-J(J+1)\Theta_R/T} \tag{4.10.10}$$

The ratio of ortho to para hydrogens at thermal equilibrium is given by:

$$\frac{N_o}{N_p} = \frac{3 \sum_{j=1,2,3\ldots} (2J+1) e^{-J(J+1)\Theta_R/T}}{\sum_{j=0} 2(2J+1) e^{-J(J+1)\Theta_R/T}} \tag{4.10.11}$$

At high temperature, the two summations become equal and therefore, the high temperature limit of N_o/N_p is 3. At low temperature, the ratio becomes:

$$\frac{N_o}{N_p} = \frac{3\left(3e^{-2\Theta_k/T} + \ldots\ldots\right)}{1\left(1 + 5e^{-5\Theta_n/T} + \ldots\right)} \to 0, \text{ as } T \to 0 \tag{4.10.12}$$

A good experimental verification of the above analysis is a comparison between the calculated rotational heat capacities at constant volume (C_V) rot, nu (calculated from:

$$C_V = \frac{\partial \langle E \rangle}{\partial T}$$

where:

$$\langle E \rangle = \frac{\partial \ln q_{\text{rot},\nu}}{\partial \beta}$$

The heat capacities are shown as a function of temperature in Figure 18.10.1 .

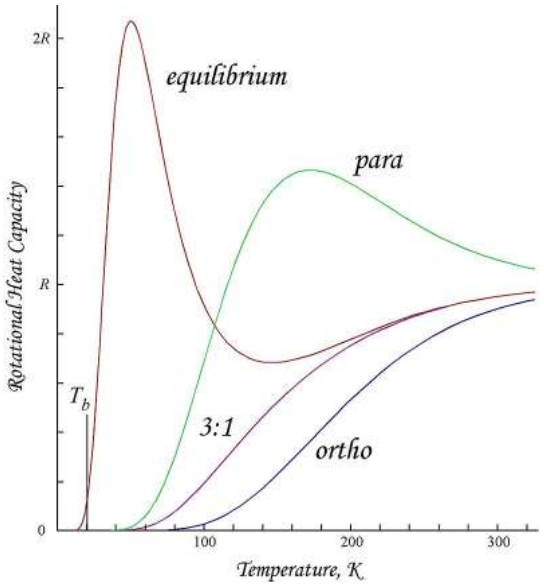


Figure 18.10.1 : The heat capacities of o- and p- hydrogens as a function of temperature. The curve marked Exp depicts the experimental data, the curve eq represents the data for an equilibrated mixture of o- and p- at a given temperature and the curves o- and p-represent the heat capacities of pure o- and pure p- hydrogens. (CC-SA-BY 3.0; Gadolinist).

The purple curve marked 3:1 gives the experimental data, the curve eq represents the data for an equilibrated mixture of o- and p- at a given temperature. The curves o- and p- represent the heat capacities of pure o- and pure p- hydrogens calculated from the o- and p- partition functions given by Equations 4.10.8 and 4.10.9 respectively. Initially it was a puzzle as to why the experimental data differs from the calculated values. In fact, the experimental data seemed to agree very well with the following equation:

$$(C_V)_{\mathrm{rot},\nu} = \frac{3}{4}(C_V)_{\mathrm{rot},\nu}(\mathrm{ortho}) + \frac{1}{4}(C_V)_{\mathrm{rot},\nu}(\mathrm{para}) \tag{4.10.13}$$

The reason for this is that, when $\mathrm{H_2}$ is cooled down from a higher temperature, the ortho:para ratio continues to remain 0.75 / 0.25 (the high temperature value) because the $\mathrm{ortho} \rightarrow \mathrm{para}$ interconversion rate is very very small and we do not reach the equilibrium composition unless a catalyst such as activated charcoal is added to the gas mixture. Equation 4.10.13 corresponds to a “frozen high temperature mixture” of ortho:para hydrogens. In the presence of the catalyst, the experiments also give the curve labeled as eq in the graph. This in indeed a very nice case where the experiments support not only the methods of statistical thermodynamics but also of the antisymmetry principle for bosons and fermions. If we consider the case of $^{16}\mathrm{O}_2$, where the nuclear spins are zero, the rotational wave function has to be symmetric as only symmetric wave functions are permitted for bosons. Thus, only even rotational states contribute to the partition function:

$$q_{\mathrm{rot},V}(^{16}\mathrm{O}_2) = \sum_{J=0,2,4,\ldots} (2J+1)e^{-J(J+1)\theta_R/T}$$

Contributors and Attributions

- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf

4.10: Ortho and Para Hydrogen is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.10: Ortho and Para Hydrogen** is licensed CC BY-NC-SA 4.0.

4.11: The Equipartition Principle

The equipartition theorem, also known as the law of equipartition, equipartition of energy or simply equipartition, states that every degree of freedom that appears only quadratically in the total energy has an average energy of ½k_BT in thermal equilibrium and contributes ½k_B to the system's heat capacity. Here, k_B is the Boltzmann constant, and T is the temperature in Kelvin. The law of equipartition of energy states that each quadratic term in the classical expression for the energy contributes ½kBT to the average energy. For instance, the motion of an atom has three degrees of freedom (number of ways of absorbing energy), corresponding to the x, y and z components of its momentum. Since these momenta appear quadratically in the kinetic energy, every atom has an average kinetic energy of $3/2k_BT$ in thermal equilibrium. The number of degrees of freedom of a polyatomic gas molecule is $3N$ where N is the number of atoms in the molecule. This is equal to number of coordinates for the system; e.g. for two atoms you would have x, y, z for each atom.

Translations

The translational contribution to the average energy is derived in terms of the derivative of the translational partition:

$$\langle E_{trans} \rangle = -\frac{1}{q_{trans}} \frac{\partial q_{trans}}{\partial \beta} \tag{4.11.1}$$

Introducing the translational partition function derived earlier, Equation 4.11.1 becomes

$$= -\frac{\Lambda^3}{V} \frac{\partial}{\partial \beta} \frac{V}{\Lambda^3} = -\frac{3}{\Lambda} \frac{\partial \Lambda}{\partial \beta} = \frac{3}{2} k_B T$$

Thus, the three translational degrees of freedom in three dimensions satisfy the equipartition theorem with each translational degree providing ½k_BT of energy.

Rotations

Consider the molecular partition functions. The average rotational energy to the average energy is derived in terms of the derivative of the translational partition:

$$\langle E_{rot} \rangle = -\frac{1}{q_{rot}} \frac{\partial q_{rot}}{\partial \beta} \tag{4.11.2}$$

which when you introduce the rotational partition function, Equation 4.11.2 becomes

$$\langle E_{rot} \rangle = -\sigma \beta \tilde{B} \frac{1}{\sigma \tilde{B}} \frac{\partial}{\partial \beta} \frac{1}{\beta} = \frac{1}{\beta} = k_B T$$

The classical expression for the rotational energy of a diatomic molecule is

$$E_{rot}^{(classical)} = \frac{1}{2} I(\omega_x^2 + \omega_y^2)$$

where I is the moment of inertia and ω_x and ω_y are the angular velocities in the x and y directions. The rotation along the molecular axis (the z axis here) has no meaning in quantum mechanics because the rotations along the molecular axis lead to configurations which are indistinguishable from the original configuration. The two rotational degrees of freedom have thus given a value of kT with with each rotational degree providing ½k_BT of energy.

Vibrations

Consider vibrational motions. The average vibrational energy to the average energy is derived in terms of the derivative of the translational partition:

$$\langle E_{vib} \rangle = -\frac{1}{q_{vib}} \frac{\partial q_{vib}}{\partial \beta} \tag{4.11.3}$$

which when you introduce the partition function for vibration, Equation 4.11.3 becomes

$$\langle E_{vib} \rangle = \frac{-1}{q_{vib}} \left(-hc\tilde{\nu} \frac{e^{-hc\tilde{\nu}/k_BT}}{(1-e^{-hc\tilde{\nu}/k_BT})^2} \right) = hc\tilde{\nu} \frac{e^{-hc\tilde{\nu}/k_BT}}{\left(1-e^{-hc\tilde{\nu}/k_BT}\right)} \tag{4.11.4}$$

This can be simplified by dividing both numerator and denominator of Equation 4.11.4 by $e^{-hc\tilde{\nu}/k_BT}$

$$\langle E_{vib} \rangle = hc\tilde{\nu} \left(\frac{1}{e^{hc\tilde{\nu}/k_BT}-1} \right) \tag{4.11.5}$$

Equation 4.11.5 is applicable at all temperatures, but if $hc\tilde{\nu}/k_BT \ll 1$ (i.e., the high temperature limit), then the exponential in the denominator can be expanded

$$e^{hc\tilde{\nu}/k_BT} - 1 \approx 1 + hc\tilde{\nu}/k_BT - 1 = hc\tilde{\nu}/k_BT \tag{4.11.6}$$

and Equation 4.11.5 becomes

$$\langle E_{vib} \rangle \approx \cancel{hc\tilde{\nu}} \left(\frac{1}{\cancel{hc\tilde{\nu}}/k_BT} \right)$$

$$\langle E_{vib} \rangle \approx k_BT \tag{4.11.7}$$

with each vibrational degree providing k_BT of energy (since there ar two quadratic terms in the Hamiltonian for a harmonic oscillator (kinetics energy and potential energy).

Compare Equation 4.11.7 with the classical expression for the vibrational energy

$$E_{vib}^{(classical)} = ½kx^2 + ½\mu v_x^2$$

At high temperature the equipartition theorem is valid, but at low temperature, the expansion in Equation 4.11.6 fails (or more terms are required). In this case, only a few vibrational states are occupied and the equipartition principle is not typically applicable.

Heat Capacity

Heat capacity at constant volume C_v, is defined as

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v$$

The equipartition theorem requires that each degree of freedom that appears only quadratically in the total energy has an average energy of ½k_BT in thermal equilibrium and, thus, contributes ½kB to the system's heat capacity. Thus the three translational degrees of freedom each contribute ½R to (3/2 R). The contribution of rotational kinetic energy will be R for the linear, and 3/2R for the nonlinear molecules. For the vibration, an oscillator has quadratic kinetic and potential terms, making the contribution of each vibrational mode R. However, k_BT has to be much greater than the spacing between the quantum energy levels. If this is not satisfied, the heat capacity will be reduced and which drop to zero at low temperatures. The corresponding degree of freedom is said to be **frozen out**; this is the situation for the vibrational degrees of freedom at room temperature and that is why the usual assumption is that they will not contribute.

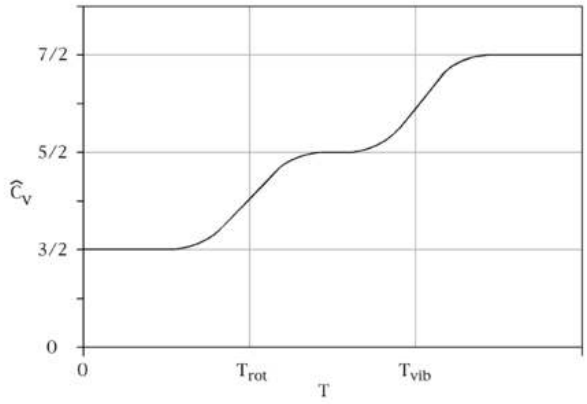


Figure 18.11.1 : Idealized plot of the molar specific heat of a diatomic gas against temperature. It agrees with the value (7/2)R predicted by equipartition at high temperatures (where R is the gas constant), but decreases to (5/2)R and then (3/2)R at lower temperatures, as the vibrational and rotational modes of motion are "frozen out". The failure of the equipartition theorem led to a paradox that was only resolved by quantum mechanics. For most molecules, the transitional temperature T_{rot} is much less than room temperature, whereas T_{vib} can be ten times larger or more. A typical example is carbon monoxide, CO, for which $T_{rot} \approx 2.8$ K and $T_{vib} \approx 3103$ K. For molecules with very large or weakly bound atoms, T_{vib} can be close to room temperature (about 300 K); for example, $T_{vib} \approx 308$ K for iodine gas, I_2. (Public domain; PD-Self)

22✔ Example: CO vs. NO

For comparing the molar heat capacities of nitrogen dioxide and carbon dioxide at constant volume (at room temperature), let us use the law of equipartition and assume the vibrations to be frozen out at room temperature. The predicted molar for the linear CO_2 (with three translational and two rotational degrees of freedom) is $5/2R\,20.8\,JK^{-1}mo'^{-1}$).

The estimated molar for NO_2 (a bent molecule, with three translational and three rotational degrees of freedom) is $3R\,(25.0\,JK^{-1}mol^{-1}$). These estimations are close to the experimental values:

- 30.1 JK^{-1} mol^{-1} for CO_2
- 29.5 JK^{-1} mol^{-1} for NO_2

Especially for CO_2, the deviation is significant. This suggests that, although not all vibrational degrees of freedom are available, they cannot be totally ignored. The bigger deviation in the prediction of molar heat capacities is probably due to the existence of the lower frequency-bending vibration in carbon dioxide.

References

1. Thermodynamics and Statistical Mechanics, Greiner W., Neise, Stocker, Springer, 2001
2. Physical Chemistry, 5th ed., Atkins P., W. H. Freeman and Company, 1994.

Contributors and Attributions

- Zane Sterkewolf (UC Davis)
- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf
- Sudarson S Sinha (Tel Aviv University)

4.11: The Equipartition Principle is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.11: The Equipartition Principle** is licensed CC BY-NC-SA 4.0.

Symmetry and Group Theory



Symmetry and Group Theory is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

5: Energy and Enthalpy



5.1: First Law of Thermodynamics (Summary)
5.2: Prelude to Thermodynamics
5.3: Work and Heat
5.4: Reversible and Irreversible Pathways
5.5: The Joule Experiment
5.6: Calorimetry
5.7: Reaction Enthalpies
5.8: Lattice Energy and the Born-Haber Cycle
5.E: First Law of Thermodynamics (Exercises)

Thumbnail: A thermite reaction using iron(III) oxide. The sparks flying outwards are globules of molten iron trailing smoke in their wake. Image used with permission (CC SA-BY 3.0; Nikthestunned)

5: Energy and Enthalpy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

5.1: First Law of Thermodynamics (Summary)

Learning Objectives

After mastering the material covered in this chapter, one will be able to:

1. Define the internal energy of a system as a measure of its capacity to do work on its surroundings.
2. Define work and heat and relate them to changes in the internal energy of a system.
3. Explain the difference between path dependent variables and path independent variables.
4. Define enthalpy in terms of internal energy, pressure, and volume.
5. Calculate First Law quantities such as q, w, ΔU and ΔH, for an ideal gas undergoing changes in temperature, pressure, and/or volume along isothermal, isobaric, isochoric, or adiabatic pathways.
6. Perform calculations using data collected using calorimetry (at either constant pressure or constant volume).
7. Write a formation reaction (the reaction for which the standard enthalpy of formation is defined) for any compound.
8. Use enthalpies of formation to calculate reaction enthalpies.
9. Estimate reaction enthalpies from average bond dissociation enthalpies.
10. Define and utilize enthalpies for phase changes such as ΔH_{fus}, ΔH_{sub}, and ΔH_{vap} to calculate the heat energy transferred in the corresponding phase change processes.
11. Define important thermodynamic functions such as ionization energy, electron affinity, bond dissociation energy, and lattice energy. Construct a Born-Haber cycle diagram using these values to describe the formation of an ionic crystalline compound.

Vocabulary and Concepts

- adiabatic
- Bomb calorimetry
- bond dissociation energy
- Born-Haber cycle
- calorimetry
- combustion reactions
- constant pressure heat capacity
- constant volume
- constant volume heat capacity
- electron affinity
- endothermic
- enthalpy
- enthalpy of combustion
- exothermic
- First Law of Thermodynamics
- heat
- heat capacity
- Hess' Law
- internal energy
- ionization potential
- isothermal
- maximum work
- Reaction enthalpies
- reversible
- reversibly
- specific heat
- standard enthalpy of formation
- standard formation reaction
- state variables
- work
- work of expansion

References

1. Balcan, M., Arzik, S., & Altunata, T. (1996). The determination of the heats of combustion and the resonance energies of some substituted naphthalenes. *Thermichimica Acta, 278*, 49-56.
2. Einstein, A. (1979). *Autobiographical Notes. A Centennial Edition.* Open Court Publishing Company.
3. Encyclopedia.com. (2008). *James Prescott Joule*. Retrieved March 30, 2016, from Complete Dictionary of Scientific Biography: http://www.encyclopedia.com/doc/1G2-2830902225.html

Contributors

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)

This page titled 5.1: First Law of Thermodynamics (Summary) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **3.S: First Law of Thermodynamics (Summary)** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

5.2: Prelude to Thermodynamics

Albert Einstein, a noted physicist, said of thermodynamics (Einstein, 1979)

> *"A law is more impressive the greater the simplicity of its premises, the more different are the kinds of things it relates, and the more extended its range of applicability. (..) It is the only physical theory of universal content, which I am convinced, that within the framework of applicability of its basic concepts will never be overthrown."*

Thermodynamics is the study of how energy flows into and out of systems and how it flows through the universe. People have been studying thermodynamics for a very long time and have developed the field a great deal, including the incorporation of high-level mathematics into the process. Many of the relationships may look cumbersome or complicated, but they are always describing the same basic thing: the flow of energy through the universe.

Energy, of course, can be used to do many useful things, such as allow us to drive our cars, use electronic devices, heat our homes, and cook our food. Chemistry is important as well since many of the processes in which we generate energy depend on chemical reactions (such as the combustion of hydrocarbons to generate heat or electron transfer reactions to generate electron flow.) The previous chapter investigated gases which are convenient systems to use to frame many discussions of thermodynamics since they can be modeled using specific equations of state such as the ideal gas law or the van der Waals law. These relationships depend on an important class of variables known as **state variables**.

State variables are those variables which depend only upon the current conditions affecting a system. Pressure, temperature and molar volume are examples of state variables. A number of variables required to describe the flow of energy in a system do depend on the pathway a system follows to come into its current state.

To illustrate the difference, consider climbing a mountain. You may choose to walk straight up the side of the mountain, or you may choose to circle the mountain several times in order to get to the top. These two pathways will differ in terms of how far you actually walk (a path-dependent variable) to attain the same change in altitude (an example of a state variable.)

This page titled 5.2: Prelude to Thermodynamics is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **3.1: Prelude to Thermodynamics** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

5.3: Work and Heat

One of the pioneers in the field of modern thermodynamics was James P. Joule (1818 - 1889). Among the experiments Joule carried out, was an attempt to measure the effect on the temperature of a sample of water that was caused by doing work on the water. Using a clever apparatus to perform work on water by using a falling weight to turn paddles within an insulated canister filled with water, Joule was able to measure a temperature increase in the water.

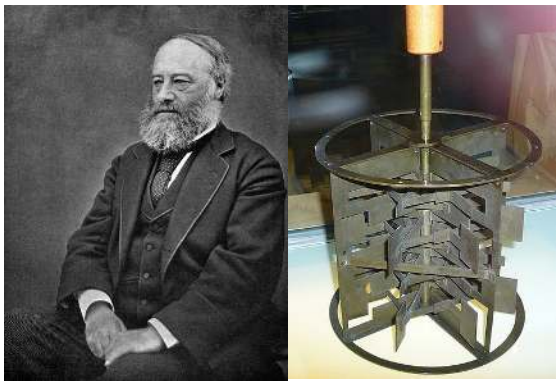


Figure 5.3.1: (left) James Prescott Joule (1818 - 1889) (right) Joule's apparatus for measuring the work equivalent of heat. (CC BY-SA 3.0; Dr. Mirko Junge)

Thus, Joule was able to show that work and heat can have the same effect on matter – a change in temperature! It would then be reasonable to conclude that heating, as well as doing work on a system will increase its energy content, and thus it's ability to perform work in the surroundings. This leads to an important construct of the **First Law of Thermodynamics**:

> *The capacity of a system to do work is increased by heating the system or doing work on it.*

The **internal energy** (U) of a system is a measure of its capacity to supply energy that can do work within the surroundings, making U the ideal variable to keep track of the flow of heat and work energy into and out of a system. Changes in the internal energy of a system (ΔU) can be calculated by

$$\Delta U = U_f - U_i \tag{5.3.1}$$

where the subscripts i and f indicate initial and final states of the system. U as it turns out, is a state variable. In other words, the amount of energy available in a system to be supplied to the surroundings is independent on how that energy came to be available. That's important because the manner in which energy is transferred is path dependent.

There are two main methods energy can be transferred to or from a system. These are suggested in the previous statement of the first law of thermodynamics. Mathematically, we can restate the first law as

$$\Delta U = q + w$$

or

$$dU = dq + dw$$

where q is defined as the amount of energy that flows into a system in the form of **heat** and w is the amount of energy lost due to the system doing **work** on the surroundings.

Heat

Heat is the kind of energy that in the absence of other changes would have the effect of changing the temperature of the system. A process in which heat flows into a system is **endothermic** from the standpoint of the system ($q_{system} > 0$, $q_{surroundings} < 0$). Likewise, a process in which heat flows out of the system (into the surroundings) is called **exothermic** ($q_{system} < 0$, $q_{surroundings} > 0$). In the absence of any energy flow in the form or work, the flow of heat into or out of a system can be measured by a change in temperature. In cases where it is difficult to measure temperature changes of the system directly, the amount of heat

energy transferred in a process can be measured using a change in temperature of the soundings. (This concept will be used later in the discussion of calorimetry).

An infinitesimal amount of heat flow into or out of a system can be related to a change in temperature by

$$dq = C\,dT$$

where C is the **heat capacity** and has the definition

$$C = \frac{dq}{\partial T}$$

Heat capacities generally have units of (J mol^{-1} K^{-1}) and magnitudes equal to the number of J needed to raise the temperature of 1 mol of substance by 1 K. Similar to a heat capacity is a **specific heat** which is defined per unit mass rather than per mol. The specific heat of water, for example, has a value of 4.184 J g^{-1} K^{-1} (at constant pressure – a pathway distinction that will be discussed later.)

Example 5.3.1: Heat required to Raise Temperature

How much energy is needed to raise the temperature of 5.0 g of water from 21.0 °C to 25.0 °C?

Solution

$$\begin{aligned} q &= mC\Delta T \\ &= (5.0\ \cancel{g})(4.184\frac{J}{\cancel{g}\ ^{\circ}\cancel{C}})(25.0\ ^{\circ}\cancel{C} - 21.0\ ^{\circ}\cancel{C}) \\ &= 84\,J \end{aligned}$$

What is a partial derivative?

A partial derivative, like a total derivative, is a slope. It gives a magnitude as to how quickly a function changes value when one of the dependent variables changes. Mathematically, a partial derivative is defined for a function $f(x_1, x_2, \ldots x_n)$ by

$$\left(\frac{\partial f}{\partial x_i}\right)_{x_j \neq i} = \lim_{\Delta_i \to 0}\left(\frac{f(x_1 + \Delta x_1, x_2 + \Delta x_2, \ldots, x_i + \Delta x_i, \ldots x_n + \Delta x_n) - f(x_1, x_2, \ldots x_i, \ldots x_n)}{\Delta x_i}\right)$$

Because it measures how much a function changes for a change in a given dependent variable, infinitesimal changes in the in the function can be described by

$$df = \sum_i \left(\frac{\partial f}{\partial x_i}\right)_{x_j \neq i}$$

So that each contribution to the total change in the function f can be considered separately.

For simplicity, consider an ideal gas. The pressure can be calculated for the gas using the ideal gas law. In this expression, pressure is a function of temperature and molar volume.

$$p(V,T) = \frac{RT}{V}$$

The partial derivatives of p can be expressed in terms of T and V as well.

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2} \tag{5.3.2}$$

and

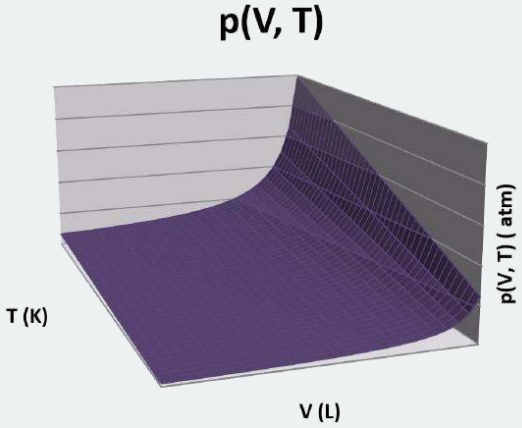
$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} \tag{5.3.3}$$

So that the change in pressure can be expressed

$$dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT \tag{5.3.4}$$

or by substituting Equations 5.3.2 and 5.3.3

$$dp = \left(-\frac{RT}{V^2}\right) dV + \left(\frac{R}{V}\right) dT$$



Macroscopic changes can be expressed by integrating the individual pieces of Equation 5.3.4 over appropriate intervals.

$$\Delta p = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial V}\right)_T dV + \int_{T_1}^{T_2} \left(\frac{\partial p}{\partial T}\right)_V dT$$

This can be thought of as two consecutive changes. The first is an **isothermal** (constant temperature) expansion from V_1 to V_2 at T_1 and the second is an **isochoric** (constant volume) temperature change from T_1 to T_2 at V_2. For example, suppose one needs to calculate the change in pressure for an ideal gas expanding from 1.0 L/mol at 200 K to 3.0 L/mol at 400 K. The set up might look as follows.

$$\Delta p = \underbrace{\int_{V_1}^{V_2} \left(-\frac{RT}{V^2}\right) dV}_{\text{isothermal expansion}} + \underbrace{\int_{T_1}^{T_2} \left(\frac{R}{V}\right) dT}_{\text{isochoric heating}}$$

or

$$\begin{aligned}
\Delta p &= \int_{1.0\ L/mol}^{3.0\ L/mol} \left(-\frac{R(400\ K)}{V^2}\right) dV + \int_{200\ K}^{400,\ K} \left(\frac{R}{1.0\ L/mol}\right) dT \\
&= \left[\frac{R(200\ K)}{V}\right]_{1.0\ L/mol}^{3.0\ L/mol} + \left[\frac{RT}{3.0\ L/mol}\right]_{200\ K}^{400\ K} \\
&= R\left[\left(\frac{200\ K}{3.0\ L/mol} - \frac{200\ K}{1.0\ L/mol}\right) + \left(\frac{400\ K}{3.0\ L/mol} - \frac{200\ K}{3.0\ L/mol}\right)\right] \\
&= -5.47\ atm
\end{aligned}$$

Alternatively, one could calculate the change as an isochoric temperature change from T_1 to T_2 at V_1 followed by an isothermal expansion from V_1 to V_2 at T_2:

$$\Delta p = \int_{T_1}^{T_2} \left(\frac{R}{V}\right) dT + \int_{V_1}^{V_2} \left(-\frac{RT}{V^2}\right) dV$$

or

$$\Delta p = \int_{200\ K}^{400,\ K} \left(\frac{R}{1.0\ L/mol}\right) dT + \int_{1.0\ L/mol}^{3.0\ L/mol} \left(-\frac{R(400\ K)}{V^2}\right) dV$$

$$= \left[\frac{RT}{1.0\ L/mol}\right]_{200\ K}^{400\ K} + \left[\frac{R(400\ K)}{V}\right]_{1.0\ L/mol}^{3.0\ L/mol}$$

$$= R\left[\left(\frac{400\ K}{1.0\ L/mol} - \frac{200\ K}{1.0\ L/mol}\right) + \left(\frac{400\ K}{3.0\ L/mol} - \frac{400\ K}{1.0\ L/mol}\right)\right]$$

$$= -5.47\ atm$$

This results demonstrates an important property of pressure in that pressure is a state variable, and so the calculation of changes in pressure do not depend on the pathway!

Work

Work can take several forms, such as expansion against a resisting pressure, extending length against a resisting tension (like stretching a rubber band), stretching a surface against a surface tension (like stretching a balloon as it inflates) or pushing electrons through a circuit against a resistance. The key to defining the work that flows in a process is to start with an infinitesimal amount of work defined by what is changing in the system.

Table 3.1.1: Changes to the System

Type of work	Displacement	Resistance	dw
Expansion	dV (volume)	-p_{ext} (pressure)	-p_{ext}dV
Electrical	dQ (charge)	W (resistence)	-W dQ
Extension	dL (length)	-t (tension)	t dL
Stretching	dA	-s (surf. tens.)	sdA

The pattern followed is always an infinitesimal displacement multiplied by a resisting force. The total work can then be determined by integrating along the pathway the change follows.

Example 5.3.2: Work from a Gas Expansion

What is the work done by 1.00 mol an ideal gas expanding from a volume of 22.4 L to a volume of 44.8 L against a constant external pressure of 0.500 atm?

Solution

$$dw = -p_{ext}\, dV$$

since the pressure is constant, we can integrate easily to get total work

$$w = -p_{exp} \int_{V_1}^{V_2} dV$$

$$= -p_{exp}(V_2 - V_1)$$

$$= -(0.500\ am)(44.8\ L - 22.4\ L)\left(\frac{8.314\ J}{0.08206\ atm\ L}\right)$$

$$= -1130\ J = -1.14\ kJ$$

Note: The ratio of gas law constants can be used to convert between atm·L and J quite conveniently!

This page titled 5.3: Work and Heat is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **3.2: Work and Heat** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

5.4: Reversible and Irreversible Pathways

The most common example of work in the systems discussed in this book is the work of expansion. It is also convenient to use the work of expansion to exemplify the difference between work that is done reversibly and that which is done irreversibly. The example of expansion against a constant external pressure is an example of an irreversible pathway. It does not mean that the gas cannot be re-compressed. It does, however, mean that there is a definite direction of spontaneous change at all points along the expansion.

Imagine instead a case where the expansion has no spontaneous direction of change as there is no net force push the gas to seek a larger or smaller volume. The only way this is possible is if the pressure of the expanding gas is the same as the external pressure resisting the expansion at all points along the expansion. With no net force pushing the change in one direction or the other, the change is said to be **reversible** or to occur **reversibly**. The work of a reversible expansion of an ideal gas is fairly easy to calculate.



If the gas expands reversibly, the external pressure (p_{ext}) can be replaced by a single value (p) which represents both the pressure of the gas and the external pressure.

$$dw = -pdV$$

or

$$w = -\int pdV$$

But now that the external pressure is not constant, p cannot be extracted from the integral. Fortunately, however, there is a simple relationship that tells us how p changes with changing V – **the equation of state**! If the gas is assumed to be an ideal gas

$$w = -\int pdV - \int \left(\frac{nRT}{V}\right) dV$$

And if the temperature is held constant (so that the expansion follows an **isothermal** pathway) the nRT term can be extracted from the integral.

$$w = -nRT\int_{V_1}^{V_2} \frac{dV}{V} = -nRT\ln\left(\frac{V_2}{V_1}\right) \tag{5.4.1}$$

Equation 5.4.1 is derived for ideal gases only; a van der Waal gas would result in a different version.

Example 5.4.1: Gas Expansion

What is the work done by 1.00 mol an ideal gas expanding reversibly from a volume of 22.4 L to a volume of 44.8 L at a constant temperature of 273 K?

Solution

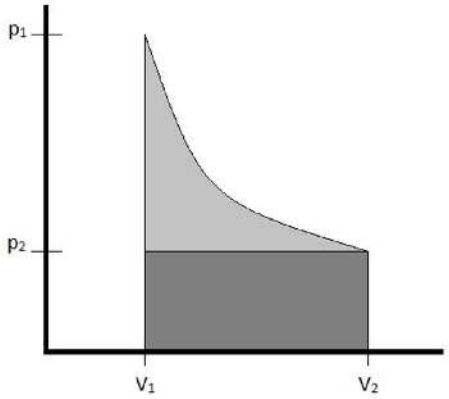
Using Equation 5.4.1 to calculate this

$$w = -(1.00\ \cancel{mol})\left(8.314\ \frac{J}{\cancel{mol}\ \cancel{K}}\right)(273\ \cancel{K})\ln\left(\frac{44.8\ L}{22.4\ L}\right)$$

$$= -1570\ J = 1.57\ kJ$$

Note: A reversible expansion will **always** require more work than an irreversible expansion (such as an expansion against a constant external pressure) when the final states of the two expansions are the same!

The work of expansion can be depicted graphically as the area under the p-V curve depicting the expansion. Comparing examples 5.4.1 and 3.1.2, for which the initial and final volumes were the same, and the constant external pressure of the irreversible expansion was the same as the final pressure of the reversible expansion, such a graph looks as follows.



The work is depicted as the shaded portion of the graph. It is clear to see that the reversible expansion (the work for which is shaded in both light and dark gray) exceeds that of the irreversible expansion (shaded in dark gray only) due to the changing pressure of the reversible expansion. In general, it will always be the case that the work generated by a reversible pathway connecting initial and final states will be the maximum work possible for the expansion.

It should be noted (although it will be proven in a later chapter) that ΔU for an isothermal reversible process involving only p-V work is 0 for an ideal gas. This is true because the internal energy, U, is a measure of a system's capacity to convert energy into work. In order to do this, the system must somehow store that energy. The only mode in which an ideal gas can store this energy is in the translational kinetic energy of the molecules (otherwise, molecular collisions would not need to be elastic, which as you recall, was a postulate of the kinetic molecular theory!) And since the average kinetic energy is a function only of the temperature, it (and therefore U) can only change if there is a change in temperature. Hence, for any isothermal process for an ideal gas, $\Delta U = 0$. And, perhaps just as usefully, for an isothermal process involving an ideal gas, $q = -w$, as any energy that is expended by doing work must be replaced with heat, lest the system temperature drop.

Constant Volume Pathways

One common pathway which processes can follow is that of constant volume. This will happen if the volume of a sample is constrained by a great enough force that it simply cannot change. It is not uncommon to encounter such conditions with gases (since they are highly compressible anyhow) and also in geological formations, where the tremendous weight of a large mountain may force any processes occurring under it to happen at constant volume.

If reversible changes in which the only work that can be done is that of expansion (so-called p-V work) are considered, the following important result is obtained:

$$dU = dq + dw = dq - pdV$$

However, $dV = 0$ since the volume is constant! As such, dU can be expressed only in terms of the heat that flows into or out of the system at constant volume

$$dU = dq_v$$

Recall that dq can be found by

$$dq = \frac{dq}{\partial T} dT = C\, dt \tag{5.4.2}$$

This suggests an important definition for the **constant volume heat capacity** (C_V) which is

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V$$

When Equation 5.4.2 is integrated the

$$q = \int_{T_1}^{T_2} nC_V dt \tag{5.4.3}$$

Example 5.4.2: Isochoric Pathway

Consider 1.00 mol of an ideal gas with $C_V = 3/2R$ that undergoes a temperature change from 125 K to 255 K at a constant volume of 10.0 L. Calculate ΔU, q, and w for this change.

Solution

Since this is a constant volume process

$$w = 0$$

Equation 5.4.3 is applicable for an isochoric process,

$$q = \int_{T_1}^{T_2} nC_V dt$$

Assuming C_V is independent of temperature:

$$\begin{aligned} q &= nC_V \int_{T_1}^{T_2} dt \\ &= nC_V(T_2 - T_1) \\ &= (1.00\,mol)\left(\frac{3}{2}8.314\,\frac{J}{mol\,K}\right)(255\,K - 125\,K) \\ &= 1620\,J = 1.62\,kJ \end{aligned}$$

Since this a constant volume pathway,

$$\begin{aligned} \Delta U &= q + \cancel{w} \\ &= 1.62\,kJ \end{aligned}$$

Constant Pressure Pathways

Most laboratory-based chemistry occurs at constant pressure. Specifically, it is exposed to the constant air pressure of the laboratory, glove box, or other container in which reactions are taking place. For constant pressure changes, it is convenient to define a new thermodynamic quantity called **enthalpy**.

$$H \equiv U + pV$$

or

$$\begin{aligned} dH &\equiv dU + d(pV) \\ &= dU + pdV + Vdp \end{aligned}$$

For reversible changes at constant pressure ($dp = 0$) for which only p-V work is done

$$dH = dq + dw + pdV + Vdp \tag{5.4.4}$$

$$= dq - \cancel{pdV} + \cancel{pdV} + \cancel{Vdp}^{\,0} \tag{5.4.5}$$

$$= dq \tag{5.4.6}$$

And just as in the case of constant volume changes, this implies an important definition for the **constant pressure heat capacity**

$$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p$$

Example 5.4.3: Isobaric Gas Expansion

Consider 1.00 mol of an ideal gas with $C_p = 5/2R$ that changes temperature change from 125 K to 255 K at a constant pressure of 10.0 atm. Calculate ΔU, ΔH, q, and w for this change.

Solution

$$q = \int_{T_1}^{T_2} nC_p dT$$

assuming C_p is independent of temperature:

$$\begin{aligned} q &= nC_p \int_{T_1}^{T_2} dT \\ &= nC_p(T_2 - T_1) \\ &= (1.00\,mol)\left(\frac{5}{2}8.314\frac{J}{mol\,K}\right)(255\,K - 125\,K) = 2700\,J = 1.62\,kJ \end{aligned}$$

So via Equation 5.4.6 (specifically the integrated version of it using differences instead of differentials)

$$\Delta H = q = 1.62\,kJ$$

$$\begin{aligned} \Delta U &= \Delta H - \Delta(pV) \\ &= \Delta H - nR\Delta T \\ &= 2700\,J - (1.00\,mol)\left(8.314\,\frac{J}{mol\,K}\right)(255\,K - 125\,K) \\ &= 1620\,J = 1.62\,kJ \end{aligned}$$

Now that ΔU and q are determined, then work can be calculated

$$\begin{aligned} w &= \Delta U - q \\ &= 1.62\,kJ - 2.70\,kJ = -1.08\,kJ \end{aligned}$$

It makes sense that w is negative since this process is an gas expansion.

Example 5.4.4: Isothermal Gas Expansion

Calculate q, w, ΔU, and ΔH for 1.00 mol of an ideal gas expanding reversibly and isothermally at 273 K from a volume of 22.4 L and a pressure of 1.00 atm to a volume of 44.8 L and a pressure of 0.500 atm.

Solution

Since this is an isothermal expansion, Equation 5.4.1 is applicable

$$\begin{aligned} w &= -nRT\ln\frac{V_2}{V_1} \\ &= (1.00\,mol)\left(8.314\,\frac{J}{mol\,K}\right)(255\,K)\ln\left(\frac{44.8\,L}{22.4\,L}\right) \\ &= 1572\,J = 1.57\,kJ \end{aligned}$$

$$\begin{aligned} \Delta U &= q + w \\ &= q + 1.57\,KJ \\ &= 0 \end{aligned}$$

$$q = -1.57\,kJ$$

Since this is an isothermal expansion

$$\Delta H = \Delta U + \Delta(pV) = 0 + 0$$

where $\Delta(pV) = 0$ due to Boyle's Law!

Adiabatic Pathways

An **adiabatic** pathway is defined as one in which no heat is transferred ($q = 0$). Under these circumstances, if an ideal gas expands, it is doing work ($w < 0$) against the surroundings (provided the external pressure is not zero!) and as such the internal energy must drop ($\Delta U < 0$). And since ΔU is negative, there must also be a decrease in the temperature ($\Delta T < 0$). How big will the decrease in temperature be and on what will it depend? The key to answering these questions comes in the solution to how we calculate the work done.

If the adiabatic expansion is reversible and done on an ideal gas,

$$dw = -pdV$$

and

$$dw = nC_v dT \tag{5.4.7}$$

Equating these two terms yields

$$-pdV = nC_v dT$$

Using the ideal gas law for an expression for p ($p = nRT/V$)

$$-\frac{nRT}{V}dV = nC_v dT$$

And rearranging to gather the temperature terms on the right and volume terms on the left yields

$$\frac{dV}{V} = -\frac{C_V}{R}\frac{dT}{T}$$

This expression can be integrated on the left between V_1 and V_2 and on the right between T_1 and T_2. Assuming that C_v/nR is independent of temperature over the range of integration, it can be pulled from the integrand in the term on the right.

$$\int_{V_1}^{V_2} \frac{dV}{V} = -\frac{C_V}{R}\int_{T_1}^{T_2} \frac{dT}{T}$$

The result is

$$\ln\left(\frac{V_2}{V_1}\right) = -\frac{C_V}{R}\ln\left(\frac{T_2}{T_1}\right)$$

or

$$\left(\frac{V_2}{V_1}\right) = \left(\frac{T_2}{T_1}\right)^{-\frac{C_V}{R}}$$

or

$$V_1 T_1^{\frac{C_V}{R}} = V_2 T_2^{\frac{C_V}{R}}$$

or

$$T_1\left(\frac{V_1}{V_2}\right)^{-\frac{R}{C_V}} = T_2 \tag{5.4.8}$$

Once ΔT is known, it is easy to calculate w, ΔU and ΔH.

Example 5.4.5:

1.00 mol of an ideal gas (C_V = 3/2 R) initially occupies 22.4 L at 273 K. The gas expands adiabatically and reversibly to a final volume of 44.8 L. Calculate ΔT, q, w, ΔU, and ΔH for the expansion.

Solution

Since the pathway is adiabatic:

$$q = 0$$

Using Equation 5.4.8

$$\begin{aligned} T_2 &= T_1 \left(\frac{V_1}{V_2} \right)^{-\frac{R}{C_V}} \\ &= (273\ K) \left(\frac{22.4\ L}{44.8\ L} \right)^{2/3} \\ &= 172\ K \end{aligned}$$

So

$$\Delta T = 172\ K - 273\ K = -101\ K$$

For calculating work, we integrate Equation 5.4.7 to get

$$\begin{aligned} w &= \Delta U = nC_v \Delta T \\ &= (1.00\ mol) \left(\frac{3}{2} 8.314\ \frac{J}{mol\ K} \right) (-101\ K) \\ &= 1.260\ kJ \\ \Delta H &= \Delta U + nR\Delta T \\ &= -1260\ J + (1.00\ mol) \left(\frac{3}{2} 8.314\ \frac{J}{mol\ K} \right) (-101\ K) \\ &= -2100\ J \end{aligned}$$

The following table shows recipes for calculating q, w, ΔU, and ΔH for an ideal gas undergoing a reversible change along the specified pathway.

Table 3.2.1: Thermodynamics Properties for a Reversible Expansion or Compression

Pathway	q	w	ΔU	ΔH
Isothermal	$nRT\ln(V_2/V_1)$	$-nRT\ln(V_2/V_1)$	0	0
Isochoric	$C_V \Delta T$	0	$C_V \Delta T$	$C_V \Delta T + V\Delta p$
Isobaric	$C_p \Delta T$	$-p\Delta V$	$C_p \Delta T - p\Delta V$	$C_p \Delta T$
adiabatic	0	$C_V \Delta T$	$C_V \Delta T$	$C_p \Delta T$

This page titled 5.4: Reversible and Irreversible Pathways is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **3.3: Reversible and Irreversible Pathways** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

5.5: The Joule Experiment

Going back to the expression for changes in internal energy that stems from assuming that U is a function of V and T (or $U(V,T)$ for short)

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

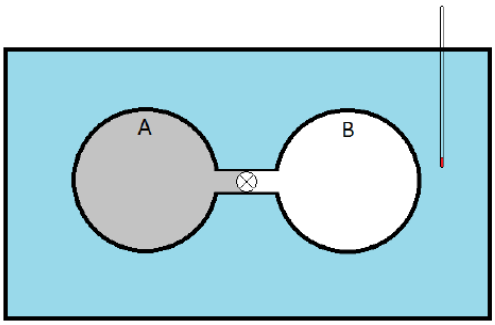
one quickly recognizes one of the terms as the constant volume heat capacity, C_V. And so the expression can be re-written

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + C_V dT$$

But what about the first term? The partial derivative is a coefficient called the "internal pressure", and given the symbol π_T.

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$

James Prescott Joule (1818-1889) recognized that π_T should have units of pressure (Energy/volume = pressure) and designed an experiment to measure it.



He immersed two copper spheres, A and B, connected by a stopcock. Sphere A is filled with a sample of gas while sphere B was evacuated. The idea was that when the stopcock was opened, the gas in sphere A would expand ($\Delta V > 0$) against the vacuum in sphere B (doing no work since $p_{ext} = 0$. The change in the internal energy could be expressed

$$dU = \pi_T dV + C_V dT$$

But also, from the first law of thermodynamics

$$dU = dq + dw$$

Equating the two

$$\pi_T dV + C_V dT = dq + dw$$

and since $dw = 0$

$$\pi_T dV + C_V dT = dq$$

Joule concluded that $dq = 0$ (and $dT = 0$ as well) since he did not observe a temperature change in the water bath which could only have been caused by the metal spheres either absorbing or emitting heat. And because $dV > 0$ for the gas that underwent the expansion into an open space, π_T must also be zero! In truth, the gas did undergo a temperature change, but it was too small to be detected within his experimental precision. Later, we (once we develop the *Maxwell Relations*) will show that

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{5.5.1}$$

Application to an Ideal Gas

For an ideal gas $p = RT/V$, so it is easy to show that

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} \tag{5.5.2}$$

so combining Equations 5.5.1 and 5.5.2 together to get

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V} - p \tag{5.5.3}$$

And since also becuase $p = RT/V$, then Equation 5.5.3 simplifies to

$$\left(\frac{\partial U}{\partial V}\right)_T = p - p = 0$$

So while Joule's observation was consistent with limiting ideal behavior, his result was really an artifact of his experimental uncertainty masking what actually happened.

Appliation to a van der Waals Gas

For a van der Waals gas,

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \tag{5.5.4}$$

so

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b} \tag{5.5.5}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{R}{V-b} - p \tag{5.5.6}$$

Substitution of the expression for p (Equation 5.5.4) into this Equation 5.5.6

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

In general, it can be shown that

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

And so the internal pressure can be expressed entirely in terms of measurable properties

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\alpha}{\kappa_T} - p$$

and need not apply to only gases (real or ideal)!

This page titled 5.5: The Joule Experiment is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

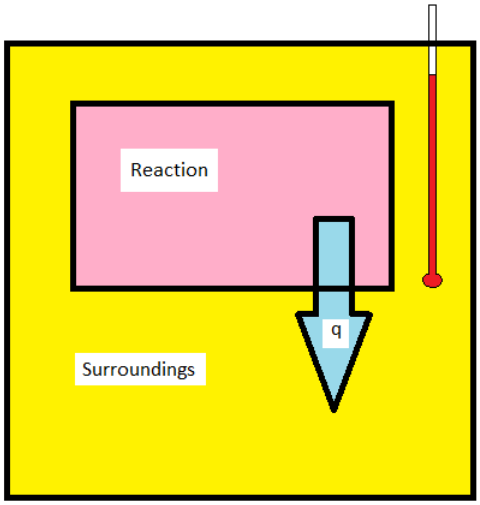
- **4.4: The Joule Experiment** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

5.6: Calorimetry

As chemists, we are concerned with chemical changes and reactions. The thermodynamics of chemical reactions can be very important in terms of controlling the production of desired products and preventing safety hazards such as explosions. As such, measuring and understanding the thermochemistry of chemical reactions is not only useful, but essential!

Calorimetry

The techniques of **calorimetry** can be used to measure q for a chemical reaction directly. The enthalpy change for a chemical reaction is of significant interest to chemists. An exothermic reaction will release heat ($q_{reaction} < 0$, $q_{surroundings} > 0$) causing the temperature of the surrounding to increase. Conversely, an endothermic reaction ($q_{reaction} > 0$, $q_{surroundings} < 0$) will draw heat from the surroundings, causing the temperature of the surrounding to drop. Measuring the temperature change in the surroundings allows for the determination of how much heat was released or absorbed in the reaction.



Bomb Calorimetry

Bomb calorimetry is used predominantly to measure the heat evolved in combustion reactions, but can be used for a wide variety of reactions. A typical bomb calorimetry set up is shown here. The reaction is contained in a heavy metallic container (the bomb) forcing the reaction to occur at constant volume. As such, the heat evolved (or absorbed) by the reaction is equal to the change in internal energy (DU_{rxn}). The bomb is then submerged in a reproducible quantity of water, the temperature of which is monitored with a high-precision thermometer.

For combustion reactions, the bomb will be loaded with a small sample of the compound to be combusted, and then the bomb is filled with a high pressure (typically about 10 atm) of O_2. The reaction is initiated by supplying heat using a short piece of resistive wire carrying an electrical current.

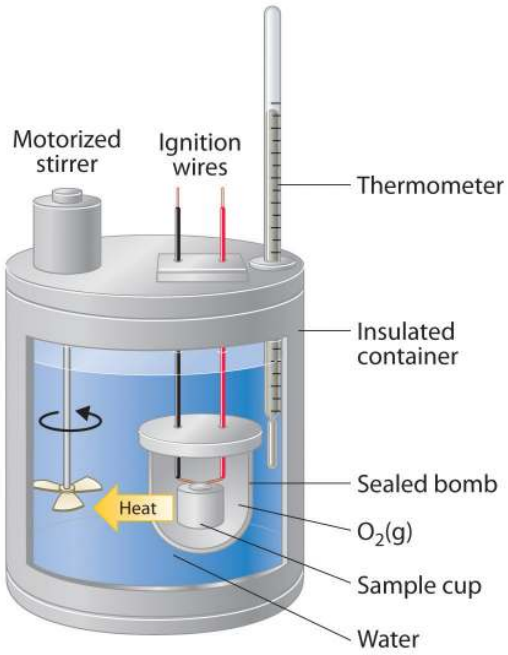


Figure 5.6.1: A Bomb Calorimeter. After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction. (CC BY-SA-NC; Anonymous by request).

The calorimeter must be calibrated by carrying out a reaction for which ΔU_{rxn} is well known, so that the resulting temperature change can be related to the amount of heat released or absorbed. A commonly used reaction is the combustion of benzoic acid. This makes a good choice since benzoic acid reacts reliably and reproducibly under normal bomb calorimetry conditions. The "water equivalent" of the calorimeter can then be calculated from the temperature change using the following relationship:

$$W = \frac{n\Delta U_c + e_{wrire} + e_{other}}{\Delta T}$$

where n is the number of moles of benzoic acid used, ΔU_c is the internal energy of combustion for benzoic acid (3225.7 kJ mol^{-1} at 25 ^oC), e_{wire} accounts for the energy released in the combustion of the fuse wire, e_{other} account for any other corrections (such as heat released due to the combustion of residual nitrogen in the bomb), and DT is the measured temperature change in the surrounding water bath.

Once the "water equivalent" is determined for a calorimeter, the temperature change can be used to find ΔU_c for an unknown compound from the temperature change created upon combustion of a known quantity of the substance.

$$\Delta U_c = \frac{W\Delta T - e_{wire} - e_{other}}{n_{sample}}$$

The experiment above is known as "isothermal bomb calorimetry" as the entire assembly sits in a constant temperature laboratory. Another approach is to employ "adiabatic bomb calorimetry" in which the assembly sits inside of a water jacket, the temperature of which is controlled to match the temperature of the water inside the insulated container. By matching this temperature, there is no thermal gradient, and thus no heat leaks into or out of the assembly during an experiment (and hence the experiment is effectively "adiabatic").

Finding ΔU_c

The **enthalpy of combustion** can be calculated from the internal energy change if the balanced chemical reaction is known. Recall from the definition of enthalpy

$$\Delta H = \Delta U + \Delta(pV)$$

and if the gas-phase reactants and products can be treated as ideal gases ($pV = nRT$)

$$\Delta H = \Delta U + RT\Delta n_{gas}$$

at constant temperature. For the combustion of benzoic acid at 25 °C

$$\mathrm{C_6H_5COOH(s) + \tfrac{15}{2}O_2(g) \longrightarrow 7\,CO_2(g) + 3\,H_2O(l)}$$

it can be seen that Δn_{gas} is -0.5 mol of gas for every mole of benzoic acid reacted.

Example 5.6.1: Combustion of Naphthalene

A student burned a 0.7842 g sample of benzoic acid ($\mathrm{C_7H_6O_2}$) in a bomb calorimeter initially at 25.0 °C and saw a temperature increase of 2.02 °C. She then burned a 0.5348 g sample of naphthalene ($\mathrm{C_{10}H_8}$) (again from an initial temperature of 25 °C) and saw a temperature increase of 2.24 °C. From this data, calculate ΔH_c for naphthalene (assuming e_{wire} and e_{other} are unimportant.)

Solution

First, the water equivalent:

$$W = \frac{\left[(0.7841\ g)\left(\frac{1\ mol}{122.124\ g}\right)\right](3225.7\ kJ/mol)}{2.02\ ^\circ C} = 10.254\ kJ/^\circ C$$

Then ΔU_c for the sample:

$$\Delta U_c = \frac{(10.254\ kJ/^\circ C)(2.24\ ^\circ C)}{(0.5308\ g)\left(\frac{1\ mol}{128.174\ g}\right)} = 5546.4\ kJ/^\circ C$$

ΔH_c is then given by

$$\Delta H_c = \Delta U_c + RT\Delta n_{gas}$$

The reaction for the combustion of naphthalene at 25 °C is:

$$\mathrm{C_{10}H_8(s) + 12\,O_2(g) \longrightarrow 10\,CO_2(g) + 4\,H_2O(l)}$$

with $\Delta n_{gas} = -2$.

So

$$\Delta H_c = 5546.4\ kJ/mol + \left(\frac{8.314}{1000} kJ/(mol\ K)\right)(298\ L)(-2) = 5541\ kJ/mol$$

The literature value (Balcan, Arzik, & Altunata, 1996) is 5150.09 kJ/mol. So that's not too far off!

This page titled 5.6: Calorimetry is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **3.4: Calorimetry** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

5.7: Reaction Enthalpies

Reaction enthalpies are important, but difficult to tabulate. However, because enthalpy is a state function, it is possible to use **Hess' Law** to simplify the tabulation of reaction enthalpies. Hess' Law is based on the addition of reactions. By knowing the reaction enthalpy for constituent reactions, the enthalpy of a reaction that can be expressed as the sum of the constituent reactions can be calculated. The key lies in the canceling of reactants and products that °Ccur in the "data" reactions but not in the "target reaction.

Example 5.7.1:

Find ΔH_{rxn} for the reaction

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

Given

$$C(gr) + ½O_2(g) \rightarrow CO(g)$$

with $\Delta H_1 = -110.53\ kJ$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_2 = -393.51\ kJ$

Solution

The target reaction can be generated from the data reactions.

$$2\times [CO(g) \rightarrow C(gr) + O_2(g)]$$

plus

$$2\times [C(gr) + 2O_2(g) \rightarrow 2CO_2(g)]$$

equals

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

so

$$2\times\Delta H_1 = -787.02\ kJ$$

$$2\times\Delta H_2 = 221.06\ kJ$$

$$2\times\Delta H_1 + 2\times\Delta H_2 = -565.96\ kJ$$

Standard Enthalpy of Formation

One of the difficulties with many thermodynamic state variables (such as enthalpy) is that while it is possible to measure changes, it is impossible to measure an absolute value of the variable itself. In these cases, it is necessary to define a zero to the scale defining the variable. For enthalpy, the definition of a zero is that the standard enthalpy of formation of a pure element in its standard state is zero. All other enthalpy changes are defined relative to this standard. Thus it is essential to very carefully define a standard state.

Definition: the Standard State

The standard state of a substance is the most stable form of that substance at 1 atmosphere pressure and the specified temperature.

Using this definition, a convenient reaction for which enthalpies can be measured and tabulated is the **standard formation reaction**. This is a reaction which forms one mole of the substance of interest in its standard state from elements in their standard states. The enthalpy of a standard formation reaction is the **standard enthalpy of formation** (ΔH_{f°). Some examples are

- $NaCl(s)$:

$$Na(s) + ½Cl_2(g) \rightarrow NaCl(s)$$

with $\Delta H_f^o = -411.2\, kJ/mol$

- $C_3H_8(g)$:

$$3C(gr) + 4H_2(g) \rightarrow C_3H_8(g)$$

with $\Delta H_f^o = -103.8\, kJ/mol$

It is important to note that the standard state of a substance is **temperature dependent**. For example, the standard state of water at -10 °C is solid, whereas the standard state at room temperature is liquid. Once these values are tabulated, calculating reaction enthalpies becomes a snap. Consider the heat combustion (ΔH_c) of methane (at 25 °C) as an example.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

The reaction can expressed as a sum of a combination of the following standard formation reactions.

$$C(gr) + 2H_2(g) \rightarrow CH_4(g)$$

with $\Delta H_f^o = -74.6\, kJ/mol$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_f^o = -393.5\, kJ/mol$

$$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$$

with $\Delta H_f^o = -285.8\, kJ/mol$

The target reaction can be generated from the following combination of reactions

$$-1 \times [C(gr) + 2H_2(g) \rightarrow CH_4(g)]$$

$$CH_4(g) \rightarrow C(gr) + 2H_2(g)$$

with $\Delta H_f^o = -1 \times [-74.6\, kJ/mol] = 74.6\, kJ/mol$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_f^o = -393.5\, kJ/mol$

$$2 \times [H_2(g) + ½O_2(g) \rightarrow H_2O(l)]$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

with $\Delta H_f^o = 2 \times [-285.8\, kJ/mol] = -571.6\, kJ/mol$

$$CH_4(g) + 2O_2(g) \rightarrow CO2_(g) + 2H_2O(l)$$

with $\Delta H_c^o = -890.5\, kJ/mol$

Alternately, the reaction enthalpy could be calculated from the following relationship

$$\Delta H_{rxn} = \sum_{products} \nu \cdot \Delta H_f^o - \sum_{reactants} \nu \cdot \Delta H_f^o$$

where ν is the stoichiometric coefficient of a species in the balanced chemical reaction. For the combustion of methane, this calculation is

$$\begin{aligned} \Delta_{rxn} &= (1\, mol)\left(\Delta H_f^o(CO_2)\right) + (2\, mol)\left(\Delta H_f^o(H_2O)\right) - (1\, mol)\left(\Delta H_f^o(CH_4)\right) && (5.7.1) \\ &= (1\, mol)(-393.5\, kJ/mol) + (2\, mol)\,(-285.8\, kJ/mol) - (1\, mol)\,(-74.6\, kJ/mol) && (5.7.2) \\ &= -890.5\, kJ/mol && (5.7.3) \end{aligned}$$

A note about units is in order. Note that reaction enthalpies have units of kJ, whereas enthalpies of formation have units of kJ/mol. The reason for the difference is that enthalpies of formation (or for that matter enthalpies of combustion, sublimation, vaporization, fusion, etc.) refer to specific substances and/or specific processes involving those substances. As such, the total enthalpy change is scaled by the amount of substance used. General reactions, on the other hand, have to be interpreted in a very specific way. When examining a reaction like the combustion of methane

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

with $\Delta H_{rxn} = -890.5\, kJ$. The correct interpretation is that the reaction of one mole of CH_4(g) with two moles of O_2(g) to form one mole of CO_2(g) and two moles of H_2O(l) releases 890.5 kJ at 25 °C.

Ionization Reactions

Ionized species appear throughout chemistry. The energy changes involved in the formation of ions can be measured and tabulated for several substances. In the case of the formation of positive ions, the enthalpy change to remove a single electron at 0 K is defined as the **ionization potential**.

$$M(g) \rightarrow M^+(g) + e^-$$

with $\Delta H(0K) \equiv 1^{st}\ \text{ionization potential (IP)}$

The removal of subsequent electrons requires energies called the 2nd Ionization potential, 3rd ionization potential, and so on.

$$M^+(g) \rightarrow M^{2+}(g) + e^-$$

with $\Delta H(0K) \equiv 2^{nd} IP$

$$M^{2+}(g) \rightarrow M^{3+}(g) + e^-$$

with $\Delta H(0K) \equiv 3^{rd} IP$

An atom can have as many ionization potentials as it has electrons, although since very highly charged ions are rare, only the first few are important for most atoms.

Similarly, the **electron affinity** can be defined for the formation of negative ions. In this case, the first electron affinity is defined by

$$X(g) + e^- \rightarrow X^-(g)$$

with $-\Delta H(0K) \equiv 1^{st}\ \text{electron affinity (EA)}$

The minus sign is included in the definition in order to make electron affinities mostly positive. Some atoms (such as noble gases) will have negative electron affinities since the formation of a negative ion is very unfavorable for these species. Just as in the case of ionization potentials, an atom can have several electron affinities.

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

with $-\Delta H(0K) \equiv 2^{nd} EA$.

$$X^{2-}(g) + e^- \rightarrow X^{3-}(g)$$

with $-\Delta H(0K) \equiv 3^{rd} EA$.

Average Bond Enthalpies

In the absence of standard formation enthalpies, reaction enthalpies can be estimated using average bond enthalpies. This method is not perfect, but it can be used to get ball-park estimates when more detailed data is not available. A **bond dissociation energy** D is defined by

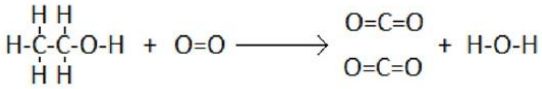
$$XY(g) \rightarrow X(g) + Y(g)$$

with $\Delta H \equiv D(X-Y)$

In this process, one adds energy to the reaction to break bonds, and extracts energy for the bonds that are formed.

$$\Delta H_{rxn} = \sum(\text{bonds broken}) - \sum(\text{bonds formed})$$

As an example, consider the combustion of ethanol:



In this reaction, five C-H bonds, one C-C bond, and one C-O bond, and one O=O bond must be broken. Also, four C=O bonds, and one O-H bond are formed.

Bond	Average Bond Energy (kJ/mol)
C-H	413
C-C	348
C-O	358
O=O	495
C=O	799
O-H	463

The reaction enthalpy is then given by

$$\begin{aligned} \Delta H_c &= 5(413\ kJ/mol) + 1(348\ kJ/mol) + 1(358\ kJ/mol) \\ &\quad + 1(495\ kJ/mol) - 4(799\ kJ/mol) - 2(463\ kJ/mol) \\ &= -856\ kJ/mol \end{aligned} \tag{5.7.4}$$

Because the bond energies are defined for gas-phase reactants and products, this method does not account for the enthalpy change of condensation to form liquids or solids, and so the result may be off systematically due to these differences. Also, since the bond enthalpies are averaged over a large number of molecules containing the particular type of bond, the results may deviate due to the variance in the actual bond enthalpy in the specific molecule under consideration. Typically, reaction enthalpies derived by this method are only reliable to within ± 5-10%.

This page titled 5.7: Reaction Enthalpies is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **3.6: Reaction Enthalpies** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

5.8: Lattice Energy and the Born-Haber Cycle

An important enthalpy change is the Lattice Energy, which is the energy required to take one mole of a crystalline solid to ions in the gas phase. For $\mathrm{NaCl(s)}$, the lattice energy is defined as the enthalpy of the reaction

$$\mathrm{NaCl(s) \rightarrow Na^+(g) + Cl^-(g)}$$

with ΔH called the lattice energy (ΔH_{Lat}).

The Born-Haber Cycle

A very handy construct in thermodynamics is that of the thermodynamic cycle. This can be represented graphically to help to visualize how all of the pieces of the cycle add together. A very good example of this is the **Born-Haber cycle**, describing the formation of an ionic solid.

Two pathways can be envisioned for the formation. Added together, the two pathways form a cycle. In one pathway, the ionic solid if formed directly from elements in their standard states.

$$\mathrm{Na(s) + \tfrac{1}{2}Cl_2 \rightarrow NaCl(s)}$$

with $\Delta H_f(NaCl)$.

The other pathway involves a series of steps that take the elements from neutral species in their standard states to ions in the gas phase.

$$Na(s) \rightarrow Na(g)$$

with $\Delta H_{sub}(Na)$

$$Na(g) \rightarrow Na^+(g) + e^-$$

with $1^{st}\ IP(Na)$

$$½Cl_2(g) \rightarrow Cl(g)$$

with $½D(Cl-Cl)$

$$Cl(g) + e^- \rightarrow Cl^-(g)$$

with $1^{st} EA(Cl)$

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$$

with $\Delta H_{Lat}(NaCl)$

It should be clear that when added (after proper manipulation if needed), the second set of reactions yield the first reaction. Because of this, the total enthalpy changes must all add.

$$\Delta H_{sub}(Na) + 1^{st} IP(Na) + ½D(Cl-Cl) + 1^{st} EA(Cl) + \Delta H_{lat}(NaCl) = \Delta H_f(NaCl)$$

This can be depicted graphically, the advantage being that arrows can be used to indicate endothermic or exothermic changes. An example of the Born-Haber Cycle for NaCl is shown below.

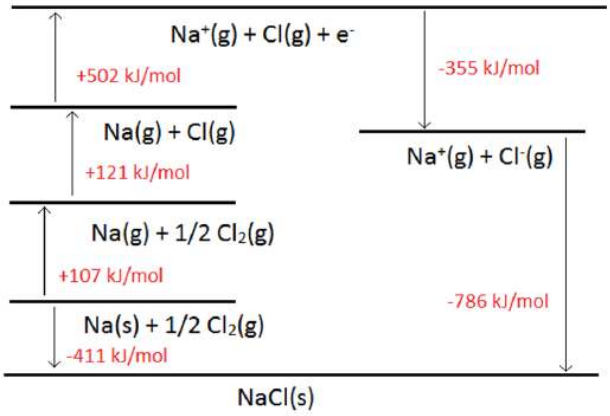


Figure 3.6.1: the Born-Haber Cycle for NaCl.

In many applications, all but one leg of the cycle is known, and the job is to determine the magnitude of the missing leg.

Exercise 5.8.1: Potassium Bromide

Find ΔH_f for KBr given the following data.

$$\mathrm{K(s) \rightarrow K(g)}$$

with $\Delta H_{sub} = 89\ kJ/mol$

$$\mathrm{Br_2(l) \rightarrow Br_2(g)}$$

with $\Delta H_{vap} = 31\ kJ/mol$

$$\mathrm{Br_2(g) \rightarrow 2\,Br(g)}$$

with $D(Br - Br) = 193\ kJ/mol$

$$\mathrm{K(g) \rightarrow K^+(g) + e^-}$$

with $1^{st} IP(K) = 419 kJ/mol$

$$\mathrm{Br(g) + e^- \rightarrow Br{-}(g)}$$

with $1^{st} EA(Br) = 194 kJ/mol$

$$\mathrm{K^+(g) + Br{-}(g) \rightarrow KBr(s)}$$

with $\Delta H_{Lat} = 672 kJ/mol$

Answer

$\Delta H_f = -246\ kJ/mol$

Note: This cycle required the extra leg of the vaporization of Br_2. Many cycles involve ions with greater than unit charge and may require extra ionization steps as well!

This page titled 5.8: Lattice Energy and the Born-Haber Cycle is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **3.7: Lattice Energy and the Born-Haber Cycle** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

5.E: First Law of Thermodynamics (Exercises)

This page titled 5.E: First Law of Thermodynamics (Exercises) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

CHAPTER OVERVIEW

6: Entropy, Part I



6.1: o the Secon
6.2: Heat Engines and the Carnot Cycle
6.3: Entropy
6.4: Calculating Entropy Changes
6.5: Comparing the System and the Surroundings
6.6: Entropy and Disorder
6.7: The Third Law of Thermodynamics
6.8: Adiabatic Compressibility
6.E: The Second Law (Exercises)
6.S: The Second Law (Summary)

6: Entropy, Part I is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

6.1: Introduction to the Second Law

Rudolph Clausius is kind enough in his 1879 work "The Mechanical Theory of Heat" (Clausius, 1879) to indicate where we have been in our discussion of thermodynamics, as well as where we are going.

> "The fundamental laws of the universe which correspond to the two fundamental theorems of the mechanical theory of heat:
> 1. The energy of the universe is constant.
> 2. The entropy of the universe tends to a maximum."
> — Rudolf Clausius, The Mechanical Theory Of Heat

The **second law of thermodynamics**, which introduces us to the topic of entropy, is amazing in how it constrains what we can experience and what we can do in the universe. As Sean M. Carroll, a CalTech Theoretical physicist, suggests in a 2010 interview with Wired Magazine (Biba, 2010),

> *I'm trying to understand how time works. And that's a huge question that has lots of different aspects to it. A lot of them go back to Einstein and spacetime and how we measure time using clocks. But the particular aspect of time that I'm interested in is the arrow of time: the fact that the past is different from the future. We remember the past but we don't remember the future. There are irreversible processes. There are things that happen, like you turn an egg into an omelet, but you can't turn an omelet into an egg.*

We, as observers of nature, are time travelers. And the constraints on what we can observe as we move through time step from the **second law of thermodynamics**. But more than just understanding what the second law says, we are interested in what sorts of processes are possible. And even more to the point, what sorts of processes are **spontaneous**.

A spontaneous process is one that will occur without external forces pushing it. A process can be spontaneous even if it happens very slowly. Unfortunately, Thermodynamics is silent on the topic of how fast processes will occur, but is provides us with a powerful toolbox for predicting which processes will be spontaneous. But in order to make these predictions, a new thermodynamic law and variable is needed since the first law (which defined ΔU and ΔH) is insufficient.

Consider the following processes:

$$NaOH(s) \rightarrow Na^{+}(aq) + OH^{-}(aq)$$

with $\Delta H < 0$

$$NaHCO_3(s) \rightarrow Na + (aq) + HCO_3^{-}(aq)$$

with $\Delta H > 0$

Both reactions will occur spontaneously, but one is exothermic and the other endothermic. So while it is intuitive to think that an exothermic process will be spontaneous, there is clearly more to the picture than simply the release of energy as heat when it comes to making a process spontaneous. The Carnot cycle because a useful thought experiment to explore to help to answer the question of why a process is spontaneous.

Contributors

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)

This page titled 6.1: Introduction to the Second Law is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

6.2: Heat Engines and the Carnot Cycle

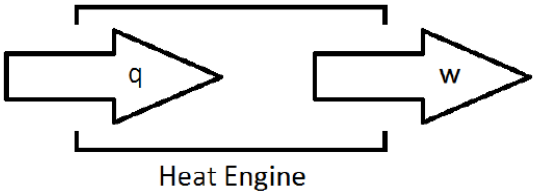
Heat Engines

Sadi Carnot (1796 – 1832) (Mendoza, 2016), a French physicist and engineer was very interested in the improvement of steam engines to perform the tasks needed by modern society.



Figure 6.2.1: Sadi Carnot (1796 - 1832)

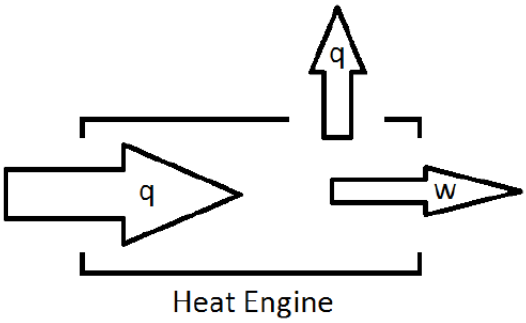
To simplify his analysis of the inner workings of an engine, Carnot devised a useful construct for examining what affect engine efficiency. His construct is the **heat engine**. The idea behind a heat engine is that it will take energy in the form of heat, and transform it into an equivalent amount of work.



Unfortunately, such a device is impractical. As it turns out, nature prevents the complete conversion of energy into work with perfect efficiency. This leads to an important statement of the **Second Law of Thermodynamics**.

> *It is impossible to convert heat into an equivalent amount of work without some other changes occurring in the universe.*

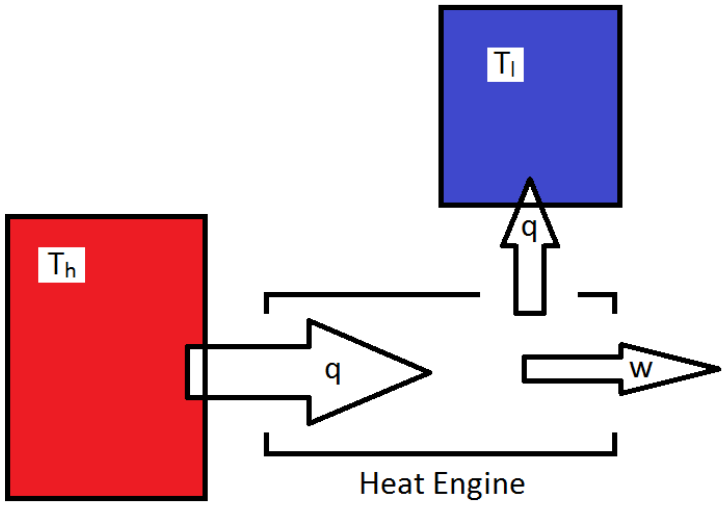
As such, a more reasonable picture of the heat engine is one which will allow for losses of energy to the surroundings.



The fraction of energy supplied to the engine that can be converted to work defines the efficiency of the engine.

The Carnot Cycle

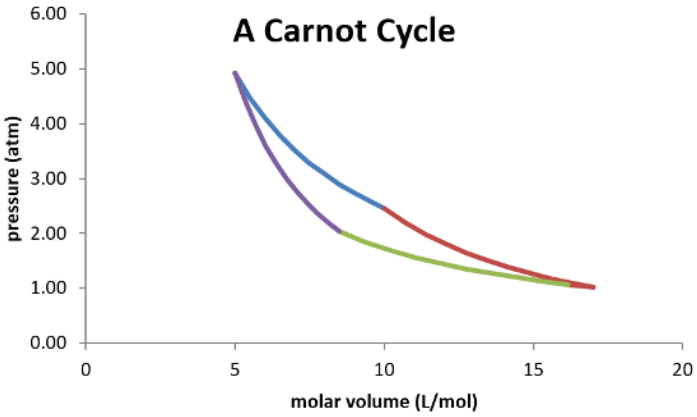
The Carnot cycle is a theoretical cyclic heat engine that can used to examine what is possible for an engine for which the job is convert heat into work. For simplicity, all energy provided to the engine occurs isothermally (and reversibly) at a temperature T_h and all of the energy lost to the surroundings also occurs isothermally and reversibly at temperature T_l. In order to insure this, the system must change between the two temperatures adiabatically.



Thus, the cycle consists of four reversible legs, two of which are isothermal, and two of which are adiabatic.

I. Isothermal expansion from p_1 and V_1 to p_2 and V_2 at T_h.
II. Adiabatic expansion from p_2, V_2, T_h to p_3, V_3, T_l.
III. Isothermal compression from p_3 and V_3 to p_4 and V_4 at T_l.
IV. Adiabatic compression from p_4, V_4, T_l to p_1, V_1, T_h.

Plotted on a pressure-volume diagram, the Carnot cycle looks as follows:



Because this is a closed cycle (the ending state is identical initial state) any state function must have a net change of zero as the system moves around the cycle. Furthermore, the efficiency of the engine can be expressed by the net amount of work the engine produces per unit of heat supplied to power the engine.

$$\epsilon = \frac{w_{net}}{q_h}$$

In order to examine this expression, it is useful to write down expressions fo the heat and work flow in each of the four legs of the engine cycle.

Leg	Heat	Work
I	$q_h = -nRT_h \ln(V_2/V_1)$	$nRT_h \ln(V_2/V_1)$
II	0	$C_V(T_l - T_h)$
III	$q_l = -nRT_l \ln(V_4/V_3)$	$nRT_l \ln(V_4/V_3)$
IV	0	$C_V(T_h - T_l)$

The total amount of work done is given by the sum of terms in the thirst column. Clearly the terms for the two adiabatic legs cancel (as they have the same magnitude, but opposite signs.) So the total work done is given by

$$w_{tot} = nRT_h \ln\left(\frac{V_2}{V_1}\right) + nRT_l \ln\left(\frac{V_4}{V_3}\right)$$

The efficiency of the engine can be defined as the total work produced per unit of energy provided by the high temperature reservoir.

$$\epsilon = \frac{w_{tot}}{q_h}$$

or

$$\epsilon = \frac{nRT_h \ln\left(\frac{V_2}{V_1}\right) + nRT_l \ln\left(\frac{V_4}{V_3}\right)}{nRT_h \ln\left(\frac{V_2}{V_1}\right)} \tag{6.2.1}$$

That expression has a lot of variables, but it turns out that it can be simplified dramatically. It turns out that by the choice of pathways connecting the states places a very important restriction on the relative values of V_1, V_2, V_3 and V_4. To understand this, we must consider how the work of adiabatic expansion is related to the initial and final temperatures and volumes. In Chapter 3, it was shown that the initial and final temperatures and volumes of an adiabatic expansion are related by

$$V_i T_i^{C_V/R} = V_f T_f^{C_V/R}$$

or

$$\frac{V_i}{V_f} = \left(\frac{T_f}{T_i}\right)^{C_V/R}$$

Using the adiabatic expansion and compression legs (II and IV), this requires that

$$\frac{V_2}{V_2} = \left(\frac{T_h}{T_l}\right)^{C_V/R}$$

and

$$\frac{V_4}{V_1} = \left(\frac{T_l}{T_h}\right)^{C_V/R}$$

Since the second terms are reciprocals of one another, the first terms must be as well!

$$\frac{V_2}{V_2} = \frac{V_1}{V_4}$$

A simple rearrangement shows that

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

This is very convenient! It is what allows for the simplification of the efficiency expression (Equation 6.2.1) becomes

$$\epsilon = \frac{\cancel{nRT_h \ln\left(\frac{V_2}{V_1}\right)} + \cancel{nRT_l \ln\left(\frac{V_2}{V_1}\right)}}{\cancel{nRT_h \ln\left(\frac{V_2}{V_1}\right)}}$$

Canceling terms in the numerator and denominator yields

$$\epsilon = \frac{T_g - T_l}{T_h} \tag{6.2.2}$$

This expression gives the maximum efficiency and depends only on the high and low temperatures!

Also, it should be noted that the heat engine can be run backwards. By providing work to the engine, it can be forces to draw heat from the low temperature reservoir and dissipate it into the high temperature reservoir. This is how a refrigerator or heat pump works. The limiting efficiency of such a device can also be calculated using the temperatures of the hot can cold reservoirs.

Example 6.2.1:

What is the maximum efficiency of a freezer set to keep ice cream at a cool -10 ^{o}C, which it is operating in a room that is 25°C? What is the minimum amount of energy needed to remove 1.0 J from the freezer and dissipate it into the room?

Solution

The efficiency is given by Equation 6.2.2 and converting the temperatures to an absolute scale, the efficiency can be calculated as

$$\epsilon = \frac{298\ K - 263\ K}{298\ K}$$

This value can be used in the following manner

$$energy_{transferred} = \epsilon(work_{required})$$

So

$$1.0\ J = 0.1174(w)$$

or

$$w = 8.5\ J$$

It is interesting to note that any arbitrary closed cyclical process can be described as a sum of infinitesimally small Carnot cycles, and so all of the conclusions reached for the Carnot cycle apply to any cyclical process.

Contributors

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)

This page titled 6.2: Heat Engines and the Carnot Cycle is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **5.2: Heat Engines and the Carnot Cycle** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

6.3: Entropy

In addition to learning that the efficiency of a Carnot engine depends only on the high and low temperatures, more interesting things can be derived through the exploration of this system. For example, consider the total heat transferred in the cycle:

$$q_{tot} = nRT_h \ln\left(\frac{V_2}{V_1}\right) - nRT_l \ln\left(\frac{V_4}{V_3}\right)$$

Making the substitution

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

the total heat flow can be seen to be given by

$$q_{tot} = nRT_h \ln\left(\frac{V_4}{V_3}\right) - nRT_l \ln\left(\frac{V_4}{V_3}\right)$$

It is clear that the two terms do not have the same magnitude, unless $T_h = T_l$. This is sufficient to show that q is **not a state function**, since it's net change around a closed cycle is not zero (as any value of a state function must be.) However, consider what happens when the sum of q/T is considered:

$$\begin{aligned}\sum \frac{q}{T} &= \frac{nR\,\cancel{T_h}\ln\left(\frac{V_4}{V_3}\right)}{\cancel{T_h}} - \frac{nR\,\cancel{T_l}\ln\left(\frac{V_4}{V_3}\right)}{\cancel{T_l}} \\ &= nR\ln\left(\frac{V_4}{V_3}\right) - nR\ln\left(\frac{V_4}{V_3}\right) \\ &= 0\end{aligned}$$

This is the behavior expected for a state function! It leads to the definition of entropy in differential form,

$$dS \equiv \frac{dq_{rev}}{T}$$

In general, dq_{rev} will be larger than dq (since the reversible pathway defines the maximum heat flow.) So, it is easy to calculate entropy changes, as one needs only to define a reversible pathway that connects the initial and final states, and then integrate dq/T over that pathway. And since \(\Delta S\) is defined using q for a reversible pathway, ΔS is *independent* of the actual path a system follows to undergo a change.

Contributors and Attributions

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)

This page titled 6.3: Entropy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **5.3: Entropy** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

6.4: Calculating Entropy Changes

Entropy changes are fairly easy to calculate so long as one knows initial and final state. For example, if the initial and final volume are the same, the entropy can be calculated by assuming a reversible, isochoric pathway and determining an expression for $\frac{dq}{T}$. That term can then be integrated from the initial condition to the final conditions to determine the entropy change.

Isothermal Changes

If the initial and final temperatures are the same, the most convenient reversible path to use to calculate the entropy is an isothermal pathway. As an example, consider the isothermal expansion of an ideal gas from V_1 to V_2. As was derived in Chapter 3,

$$dq = nRT\frac{dV}{V}$$

So dq/T is given by

$$\frac{dq}{T} = nR\frac{dV}{V}$$

and so

$$\Delta S = \int \frac{dq}{T} = nR\int_{V_1}^{V_2} \frac{dV}{V} = nR\ln\left(\frac{V_2}{V_1}\right) \tag{6.4.1}$$

Example 6.4.1: Entropy Change for a Gas Expansion

Calculate the entropy change for 1.00 mol of an ideal gas expanding isothermally from a volume of 24.4 L to 48.8 L.

Solution

Recognizing that this is an isothermal process, we can use Equation 6.4.1

$$\begin{aligned}\Delta S &= nR\ln\left(\frac{V_2}{V_1}\right)\\ &= (1.00\,mol)(8.314 J/(mol\,K))\ln\left(\frac{44.8\,L}{22.4\,L}\right)\\ &= 5.76\,J/K\end{aligned}$$

Isobaric Changes

For changes in which the initial and final pressures are the same, the most convenient pathway to use to calculate the entropy change is an isobaric pathway. In this case, it is useful to remember that

$$dq = nC_p dT$$

So

$$\frac{dq}{T} = nC_p\frac{dT}{T}$$

Integration from the initial to final temperature is used to calculate the change in entropy. If the heat capacity is constant over the temperature range

$$\int_{T_1}^{T_2} \frac{dq}{T} = nC_p\int_{T_1}^{T_2} \frac{dT}{T} = nC_p\ln\left(\frac{T_2}{T_1}\right)$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral. For example, if C_p can be expressed as

$$C_p = a + bT + \frac{c}{T^2}$$

ΔS takes the form

$$\int_{T_1}^{T_2} \frac{dq}{T} = n \int_{T_1}^{T_2} \frac{a + bT + \frac{c}{T^2}}{T} dT$$

which simplifies to

$$\Delta S = n \int_{T_1}^{T_2} \left(\frac{a}{T} + bT + \frac{c}{T^3} \right) dT$$

or

$$\Delta S = n \left[a \ln\left(\frac{T_2}{T_1} \right) + b(T_2 - T_1) - \frac{c}{2} \left(\frac{1}{T_2^2} - \frac{1}{T_1^2} \right) \right]$$

Isochoric Changes

Similarly to the cast of constant pressure, it is fairly simple to calculate ΔS. Since

$$dq = nC_V dt$$

$\frac{dq}{T}$ is given by

$$\frac{dq}{T} = nC_V \frac{dT}{T}$$

And so for changes over which C_V is independent of the temperature ΔS is given by

$$\Delta S = nC_v \ln\left(\frac{T_2}{T_1} \right)$$

Adiabatic Changes

The easiest pathway for which to calculate entropy changes is an adiabatic pathway. Since $dq = 0$ for an adiabatic change, then $dS = 0$ as well.

Phase Changes

The entropy change for a phase change at constant pressure is given by

$$\Delta S = \frac{q}{T} = \frac{\Delta H_{phase}}{T} \tag{6.4.2}$$

Example 6.4.2: Entropy Change for Melting Ice

The enthalpy of fusion for water is 6.01 kJ/mol. Calculate the entropy change for 1.0 mole of ice melting to form liquid at 273 K.

Solution

This is a phase transition at constant pressure (assumed) requiring Equation 6.4.2:

$$\begin{aligned} \Delta S &= \frac{(1\,mol)(6010\,J/mol)}{273\,K} \\ &= 22\,J/K \end{aligned}$$

This page titled 6.4: Calculating Entropy Changes is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **5.4: Calculating Entropy Changes** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

6.5: Comparing the System and the Surroundings

It is oftentimes important (for reasons that will be discussed in the next section) to calculate both the entropy change of the system as well as that of the surroundings. Depending on the size of the surroundings, they can provide or absorb as much heat as is needed for a process without changing temperature. As such, it is oftentimes a very good approximation to consider the changes to the surroundings as happening isothermally, even though it may not be the case for the system (which is generally smaller.)

Example 6.5.1

Consider 18.02 g (1.00 mol) of ice melting at 273 K in a room that is 298 K. Calculate DS for the ice, the surrounding room, and of the universe. (DH_{fus} = 6.01 kJ/mol)

Solution

For the process under constant pressure: $q_{ice} = -q_{room}$:

$$q = n\Delta H_{fus} = (1.00\,mol)(6010\,J/mol) = 6010\,J$$

For the ice:

$$\Delta S_{ice} = \frac{q_{ice}}{T_{ice}} = \frac{6010\,J}{273\,K} = 22.0\,J/K$$

For the room:

$$\Delta S_{room} = \frac{q_{room}}{T_{room}} = \frac{-6010\,J}{298\,K} = -20.2\,J/K$$

For the universe:

$$\begin{aligned}\Delta S_{univ} &= \Delta S_{ice} + \Delta S_{room} \\ &= 22.0 J/K - 20.2\,J/K = 1.8\,J/K\end{aligned}$$

Note: ΔS_{univ} is positive, which is characteristic of a spontaneous change!

Example 6.5.2

A 10.0 g piece of metal (C = 0.250 J/g °C) initially at 95 °C is placed in 25.0 g of water initially at 15 °C in an insulated container. Calculate the final temperature of the metal and water once the system has reached thermal equilibrium. Also, calculate the entropy change for the metal, the water, and the entire system.

Solution

Heat will be transferred from the hot metal to the cold water. Since it has nowhere else to go, the final temperature can be calculated from the expression

$$q_w = -q_m$$

where q_w is the heat absorbed by the water, and q_m is the heat lost by the metal. And since

$$q = mC\Delta T$$

it follows that

$$(25\,g)(4.184\,J/g^\circ C))(T_f - 15^\circ C) = -(10.0\,g)(0.250\,J/g^\circ C))(T_f - 95\,J/g^\circ C)$$

A bit of algebra determines the final temperature to be:

$$T_f = 16.9^\circ C.$$

To get the entropy changes, use the expression:

$$\Delta S = mC_p \ln\left(\frac{T_f}{T_i}\right)$$

So, for the water:

$$\begin{aligned}\Delta S_{water} &= (25\ g)(4.184\ J/g^\circ C))\ln\left(\frac{289.9\ K}{288\ K}\right)\\ &= 0.689\ J/K\end{aligned}$$

And for the metal:

$$\begin{aligned}\Delta S_{metal} &= (10.0\ g)(0.250\ J/g^\circ C))\ln\left(\frac{289.9\ K}{368\ K}\right)\\ &= -0.596\ J/K\end{aligned}$$

For the system:

$$\begin{aligned}\Delta S_{sys} &= \Delta S_{water} + \Delta S_{metal}\\ &= 0.689\ J/K + -0.596\ J/K = 0.093\ J/K\end{aligned}$$

Note: The total entropy change is positive, suggesting that this will be a spontaneous process. This should make some sense since one expects heat to flow from the hot metal to the cool water rather than the other way around. Also, note that the sign of the entropy change is positive for the part of the system that is absorbing the heat, and negative for the part losing the heat.

In summary, ΔS can be calculated for a number of pathways fairly conveniently.

Table 6.5.1: Summary of different ways to calculate ΔS depending on the pathway. * for an ideal gas.

Pathway	$\Delta S_{sys} = \frac{dq_{rev}}{T_{sys}}$	$\Delta S_{surr} = \frac{q_{sys}}{T_{surr}}$
Adiabatic	0	$\Delta S_{surr} = \frac{q_{sys}}{T_{surr}}$
Isothermal	$\frac{q_{rev}}{T}$ and $nR\ln\left(\frac{V_2}{V_1}\right)$*	
Isobaric	$mC_p\ln\left(\frac{T_f}{T_i}\right)$	
Isochoric	$mC_V\ln\left(\frac{T_f}{T_i}\right)$	
Phase Change	$\frac{\Delta H_{phase}}{T}$	

And

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}\,.$$

This calculation is important as ΔS_{univ} provides the criterion for spontaneity for which we were searching from the outset. This also suggests a new way to state the second law:

> *The entropy of the universe increases in any spontaneous change.*

If we think of "the direction of spontaneous" to be the natural direction of chance, we can see that entropy and the second law are tied inexorably with the natural direction of the flow of time. Basically, we can expect the entropy of the universe to continue to increase as time flows into the future. We can overcome this natural tendency to greater entropy by doing work on a system. This is why it requires such great effort, for example, to straighten a messy desk, but little effort for the desk to get messy over time.

Clausius Inequality

The Second Law can be summed up in a very simple mathematical expression called the *Clausius Inequality*.

$$\Delta S_{universe} \geq 0$$

which must be true for any spontaneous process. It is not the most convenient criterion for spontaneity, but it will do for now. In the next chapter, we will derive a criterion which is more useful to us as chemists, who would rather focus on the system itself rather than both the system and its surroundings. Another statement of the Clausius theorem is

$$\oint \frac{dq}{T} \geq 0$$

with the only condition of the left hand side equaling zero is if the system transfers all heat reversibly.

This page titled 6.5: Comparing the System and the Surroundings is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **5.5: Comparing the System and the Surroundings** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

6.6: Entropy and Disorder

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:

$$S = k_b \ln(W) \tag{6.6.1}$$

This rather famous equation is etched on Boltzmann's grave marker in commemoration of his profound contributions to the science of thermodynamics (Figure 6.6.1).



Figure 6.6.1: Ludwig Boltzmann (1844 - 1906)

Example 6.6.1:

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 6.6.1):

$$S = nK \ln(W)$$

And using $W = 2$, the calculation is straightforward.

$$\begin{aligned} S &= \left(1.00\, mol \cot \frac{6.022 \times 10^{23}}{1\, mol}\right)(1.38 \times 10^{-23} J/K) \ln 2 \\ &= 5.76\, J/K \end{aligned}$$

This page titled 6.6: Entropy and Disorder is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **5.6: Entropy and Disorder** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

6.7: The Third Law of Thermodynamics

One important consequence of Botlzmann's proposal is that a perfectly ordered crystal (i.e. one that has only one energetic arrangement in its lowest energy state) will have an entropy of 0. This makes entropy qualitatively different than other thermodynamic functions. For example, in the case of enthalpy, it is impossible have a zero to the scale without setting an arbitrary reference (which is that the enthalpy of formation of elements in their standard states is zero.) But entropy has a natural zero! It is the state at which a system has perfect order. This also has another important consequence, in that it suggests that there must also be a zero to the temperature scale. These consequences are summed up in the **Third Law of Thermodynamics**.

> *The entropy of a perfectly ordered crystal at 0 K is zero.*

This also suggests that absolute molar entropies can be calculated by

$$S = \int_o^T \frac{C}{T} dT$$

where C is the heat capacity. An entropy value determined in this manner is called a **Third Law Entropy**.

Naturally, the heat capacity will have some temperature dependence. It will also change abruptly if the substance undergoes a phase change. Unfortunately, it is exceedingly difficult to measure heat capacities very near zero K. Fortunately, many substances follow the **Debye Extrapolation** in that at very low temperatures, their heat capacities are proportional to T^3. Using this assumption, we have a temperature dependence model that allows us to extrapolate absolute zero based on the heat capacity measured at as low a temperature as can be found.

Example 6.7.1

SiO_2 is found to have a molar heat capacity of 0.777 J mol^{-1} K^{-1} at 15 K (Yamashita, et al., 2001). Calculate the molar entropy of SiO_2 at 15 K.

Solution

Using the Debye model, the heat capacity is given by



The value of a can be determined by





The entropy is then calculated by

Calculating a third Law Entropy

Start at 0 K, and go from there!

This page titled 6.7: The Third Law of Thermodynamics is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **5.7: The Third Law of Thermodynamics** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

6.8: Adiabatic Compressibility

In Chapter 4, we learned about the isothermal compressibility, κ_T, which is defined as

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

κ_T is a very useful quantity, as it can be measured for many different substances and tabulated. Also, as we will see in the next chapter, it can be used to evaluate several different partial derivatives involving thermodynamic variables.

In his seminal work, *Philosophiae Naturalis Principia Mathematica* (Newton, 1723), Isaac Newton (1643 - 1727) (Doc) calculated the speed of sound through air, assuming that sound was carried by isothermal compression waves. His calculated value of 949 m/s was about 15% smaller than experimental determinations. He accounted for the difference by pointing to “non-ideal effects”. But it turns out that his error, albeit an understandable one (since sound waves do not appear to change bulk air temperatures) was that the compression waves are adiabatic, rather than isothermal. As such, there are small temperature oscillations that occur due to the adiabatic compression followed by expansion of the gas carrying the sound waves. The oversight was correct by Pierre-Simon Laplace (1749 – 1827) (O'Connor & Robertson, Pierre-Simon Laplace, 1999).

LaPlace modeled the compression waves using the **adiabatic compressibility**, κ_S defined by

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$$

Since the entropy is defined by

$$dS = \frac{dq_{rev}}{T}$$

it follows that any adiabatic pathway ($dq = 0$) is also **isentropic** ($dS = 0$), or proceeds at constant entropy.

> *Adiabatic pathways are also isentropic.*

A couple of interesting conclusions can be reached by following the derivation of an expression for the speed of sound where the sound waves are modeled as adiabatic compression waves. We can begin by expanding the description of κ_S by using Partial Derivative Transformation Type II. Applying this, the adiabatic compressibility can be expressed

$$\kappa_S = \frac{1}{V}\left(\frac{\partial V}{\partial S}\right)_p\left(\frac{\partial S}{\partial p}\right)_V$$

or by using transformation type I

$$\kappa_S = \frac{1}{V}\frac{\left(\frac{\partial S}{\partial p}\right)_V}{\left(\frac{\partial S}{\partial V}\right)_p}$$

Using a simple chain rule, the partial derivatives can be expanded to get something a little easier to evaluate:

$$\kappa_S = \frac{1}{V}\frac{\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial T}{\partial V}\right)_p} \tag{6.8.1}$$

The utility here is that

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \tag{6.8.2}$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \tag{6.8.3}$$

This means that Equation 6.8.1 simplifies to

$$\kappa_S = \frac{C_V}{C_p}\left(\frac{1}{V}\frac{\left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{\partial T}{\partial V}\right)_p}\right)$$

Simplifying what is in the parenthesis yields

$$\kappa_S = \frac{C_V}{C_p}\left(\frac{1}{V}\left(\frac{\partial T}{\partial p}\right)_V\left(\frac{\partial V}{\partial T}\right)_p\right)$$

$$\kappa_S = \frac{C_V}{C_p}\left(-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T\right)$$

$$\kappa_S = \frac{C_V}{C_p}\kappa_T$$

As will be shown in the next chapter, C_p is always bigger than C_V, so κ_S is always smaller than κ_T.

But there is more! We can use this methodology to revisit how pressure affects volume along an adiabat. In order to do this, we would like to evaluate the partial derivative

$$\left(\frac{\partial V}{\partial p}\right)_S$$

This can be expanded in the same way as above

$$\left(\frac{\partial V}{\partial p}\right)_S = -\frac{\left(\frac{\partial V}{\partial S}\right)_p}{\left(\frac{\partial p}{\partial S}\right)_V}$$

And further expand

$$\left(\frac{\partial V}{\partial p}\right)_S = -\frac{\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial S}\right)_p}{\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial T}{\partial S}\right)_V} \tag{6.8.4}$$

And as before, noting that the relationships in Equations 6.8.2 and 6.8.3, Equation 6.8.4 can be simplified to

$$\left(\frac{\partial V}{\partial p}\right)_S = -\frac{C_V}{C_p}\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_V$$

$$= \frac{C_V}{C_p}\left(\frac{\partial V}{\partial p}\right)_T \tag{6.8.5}$$

Or defining $\gamma = C_p/C_V$, Equation 6.8.5 can be easily rearranged to

$$\gamma\left(\frac{\partial V}{\partial p}\right)_S = \left(\frac{\partial V}{\partial p}\right)_T$$

The right-hand derivative is easy to evaluate if we assume a specific equation of state. For an ideal gas,

$$\left(\frac{\partial V}{\partial p}\right)_T = -\frac{nRT}{p^2} = -\frac{V}{p}$$

Substitution yields

$$\gamma\left(\frac{\partial V}{\partial p}\right)_S = -\frac{V}{p}$$

which is now looking like a form that can be integrated. Separation of variables yields

$$\gamma\frac{dV}{V} = \frac{dP}{p}$$

And integration (assuming that g is independent of volume) yields

$$\gamma\int_{V_1}^{V_2}\frac{dV}{V} = \int_{p_1}^{p_2}\frac{dP}{p}$$

or

$$\gamma\ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{p_2}{p_1}\right)$$

which is easily manipulated to show that

$$p_1V_1^{\gamma} = p_2V_2^{\gamma}$$

or

$$pV^{\gamma} = \text{constant}$$

which is what we previously determined for the behavior of an ideal gas along an adiabat.

Finally, it should be noted that the correct expression for the speed of sound is given by

$$v_{sound} = \sqrt{\frac{1}{\rho\,\kappa_S}}$$

where ρ is the density of the medium. For an ideal gas, this expression becomes

$$v_{sound} = \sqrt{\frac{\gamma RT}{M}}$$

where M is the molar mass of the gas. Isaac Newton's derivation, based on the idea that sound waves involved isothermal compressions, would produce a result which is missing the factor of γ, accounting for the systematic deviation from experiment which he observed.

Contributors

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)

This page titled 6.8: Adiabatic Compressibility is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **5.8: Adiabatic Compressibility** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

6.E: The Second Law (Exercises)

Q5.1

What is the minimum amount of work needed to remove 10.0 J of energy from a freezer at -10.0 °C, depositing the energy into a room that is 22.4 °C?

Q5.2

Consider the isothermal, reversible expansion of 1.00 mol of a monatomic ideal gas (C_V = 3/2 R) from 10.0 L to 25.0 L at 298 K. Calculate q, w, ΔU, ΔH, and ΔS for the expansion.

Q5.3

Consider the isobaric, reversible expansion of 1.00 mol of a monatomic ideal gas (C_p = 5/2 R) from 10.0 L to 25.0 L at 1.00 atm. Calculate q, w, ΔU, ΔH, and ΔS for the expansion.

Q5.4

Consider the isochoric, reversible temperature increase of 1.00 mol of a monatomic ideal gas (C_V = 3/2 R) °Ccupying 25.0 L from 298 K to 345 K. Calculate q, w, ΔU, ΔH, and ΔS for this process.

Q5.5

Consider the adiabatic expansion of 1.00 mol of a monatomic ideal gas (C_V = 3/2 R) from 10.0 L at 273 K to a final volume of 45.0 L. Calculate ΔT, q, w, ΔU, ΔH, and ΔS for the expansion.

Q5.6

15.0 g of ice ($\Delta H_{fus} = 6.009\ kJ/mol$) at 0 °C sits in a room that is at 21 °C. The ice melts to form liquid at 0 °C. Calculate the entropy change for the ice, the room, and the universe. Which has the largest magnitude?

Q5.7

15.0 g of liquid water (C_p = 75.38 J mol^{-1} °C^{-1}) at 0 °C sits in a room that is at 21 °C. The liquid warms from 0 °C to 21 °C. Calculate the entropy change for the liquid, the room, and the universe. Which has the largest magnitude?

Q5.8

Calculate the entropy change for taking 12.0 g of H_2O from the solid phase (C_p = 36.9 J mol^{-1} K^{-1}) at -12.0 °C to liquid (C_p = 75.2 J mol^{-1} K^{-1}) at 13.0 °C. The enthalpy of fusion for water is $\Delta H_{fus} = 6.009\ kJ/mol$.

Q5.9

Using Table T1, calculate the standard reaction entropies (ΔS^o) for the following reactions at 298 K.

a. $CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
b. $C_{12}H_{22}O_{11}(s) + 12O_2 \rightarrow 12CO_2(g) + 11H_2O(l)$
c. $2POCl_3(l) \rightarrow 2PCl_3(l) + O_2(g)$
d. $2KBr(s) + Cl2(g) \rightarrow 2KCl(s) + Br_2(l)$
e. $SiH_4(g) + 2Cl(g) \rightarrow SiCl_4(l) + 2H_2(g)$

Q5.10

1.00 mole of an ideal gas is taken through a cyclic process involving three steps:

I. Isothermal expansion from V_1 to V_2 at T_1
II. Isochoric heating from, T_1 to T_2 at V_2
III. Adiabatic compression from V_2 to V_1

a. Graph the process on a V-T diagram.
b. Find q, w, ΔU, and ΔS for each leg. (If you want, you can find ΔH too!)

c. Use the fact that ΔS for the entire cycle must be zero (entropy being a state function and all …), determine the relationship between V_1 and V_2 in terms of C_v, T_1 and T_2.

Q5.11

2.00 moles of a monatomic ideal gas (C_V = 3/2 R) initially exert a pressure of 1.00 atm at 300.0 K. The gas undergoes the following three steps, all of which are reversible:

I. isothermal compression to a final pressure of 2.00 atm,
II. Isobaric temperature increase to a final temperature of 400.0 K, and
III. A return to the initial state along a pathway in which

$$p = a + bT \tag{6.E.1}$$

where a and b are constants. Sketch the cycle on a pressure-temperature plot, and calculate \(\Delta U\) and \(\Delta S\) for each of the legs. Are ΔU and ΔS zero for the sum of the three legs?

Q5.12

A 10.0 g piece of iron (C = 0.443 J/g °C) initially at 97.6 °C is placed in 50.0 g of water (C = 4.184 J/g °C) initially at 22.3 °C in an insulated container. The system is then allowed to come to thermal equilibrium. Assuming no heat flow to or from the surroundings, calculate

a. the final temperature of the metal and water
b. the change in entropy for the metal
c. the change in entropy for the water
d. the change in entropy for the universe

Q5.13

Considers a crystal of $CHFClBr$ as having four energetically equivalent orientations for each molecule. What is the expected residual entropy at 0 K for 2.50 mol of the substance?

Q5.14

A sample of a certain solid is measured to have a constant pressure heat capacity of 0.436 J mol^{-1} K^{-1} at 10.0 K. Assuming the Debeye extrapolation model

$$C_p(T) = aT^3 \tag{6.E.2}$$

holds at low temperatures, calculate the molar entropy of the substance at 12.0 K.

This page titled 6.E: The Second Law (Exercises) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

6.S: The Second Law (Summary)

Learning Objectives

After mastering the material presented in this chapter, one will be able to:

1. Describe a Carnot engine and derive a relationship for its efficiency of converting heat into work, in terms of the two temperatures at which the engine operates.
2. Define entropy and be able to calculate entropy changes for systems (and the surroundings) undergoing changes which are definable as following various pathways, including constant temperature, constant pressure, constant volume, and adiabatic pathways.
3. Relate entropy to disorder in a crystal based on the number of equivalent orientations a single formula unit may take within the crystal.
4. State the Third Law of Thermodynamics, and use it to calculate total entropies for substances at a given temperature.
5. Understand how isothermal compressibility differs from adiabatic compressibility and relate that difference to the measurement of the speed of sound waves traveling through a gas medium.

Vocabulary and Concepts

- adiabatic compressibility
- Carnot cycle
- Clausius theorem
- criterion for spontaneity
- Debye Extrapolation
- efficiency
- entropy
- heat engine
- isentropic
- second law of thermodynamics
- speed of sound
- spontaneous
- spontaneous process
- Third Law Entropy
- Third Law of Thermodynamics

References

1. Biba, E. (2010, February 26). What is Time? One Physicist Hunts for the Ultimate theory. *Wired*. Retrieved from http://www.wired.com/2010/02/what-is-time/
2. Clausius, R. (1879). *The Mechanical Theory of Heat.* London: McMillan and Company.
3. Doc, T. (n.d.). *Isaac Newton*. Retrieved April 2, 2016, from FamousScientists.org: http://www.famousscientists.org/isaac-newton/
4. Mendoza, E. (2016). *Sadi Carnot: French engineer and physicist*. (Encyclopedia Brittanica, Inc.) Retrieved March 30, 2016, from Encyclopædia Britannica Online: http://www.britannica.com/biography/...ench-scientist
5. Newton, I. (1723). *Philosophiae naturalis principia mathematica.* Amstelodamum.
6. O'Connor, J. J., & Robertson, E. F. (1998, September). Retrieved March 30, 2016, from www-groups.dcs.st-and.ac.uk/~...Boltzmann.html
7. O'Connor, J. J., & Robertson, E. F. (1999). *Pierre-Simon Laplace*. Retrieved April 2, 2016, from School of Mathematics and Statistics, University of St Andrews, Scotland: www-groups.dcs.st-and.ac.uk/~...s/Laplace.html
8. Yamashita, I., Tojo, T., Kawaji, H., Atake, T., Linnard, Y., & Richet, P. (2001). Low-temperature heat capacity of sodium borosilicate glasses at temperatures from 13 K to 300 K. *The Journal of Chemical Thermodynamics*, *33*(5), 535-53. doi:10.1006/jcht.2000.0744

This page titled 6.S: The Second Law (Summary) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **5.S: The Second Law (Summary)** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

7: Entropy, Part II



7.1: ntropy Char
7.2: Trouton's rule
7.3: The Third Law of Thermodynamics

Thumbnail: Image used with permission (Guy vandergrift [CC BY-SA 3.0 (https://creativecommons.org/licenses/by-sa/3.0)])

7: Entropy, Part II is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.1: Calculating Entropy Changes

Entropy changes are fairly easy to calculate so long as one knows initial and final state. For example, if the initial and final volume are the same, the entropy can be calculated by assuming a reversible, isochoric pathway and determining an expression for $\frac{dq}{T}$. That term can then be integrated from the initial condition to the final conditions to determine the entropy change.

Isothermal Changes

If the initial and final temperatures are the same, the most convenient reversible path to use to calculate the entropy is an isothermal pathway. As an example, consider the isothermal expansion of an ideal gas from V_1 to V_2. As was derived in Chapter 3,

$$dq = nRT\frac{dV}{V}$$

So dq/T is given by

$$\frac{dq}{T} = nR\frac{dV}{V}$$

and so

$$\Delta S = \int \frac{dq}{T} = nR\int_{V_1}^{V_2} \frac{dV}{V} = nR\ln\left(\frac{V_2}{V_1}\right) \tag{7.1.1}$$

Example 7.1.1: Entropy Change for a Gas Expansion

Calculate the entropy change for 1.00 mol of an ideal gas expanding isothermally from a volume of 24.4 L to 48.8 L.

Solution

Recognizing that this is an isothermal process, we can use Equation 7.1.1

$$\begin{aligned}\Delta S &= nR\ln\left(\frac{V_2}{V_1}\right)\\ &= (1.00\,mol)(8.314 J/(mol\,K))\ln\left(\frac{44.8\,L}{22.4\,L}\right)\\ &= 5.76\,J/K\end{aligned}$$

Isobaric Changes

For changes in which the initial and final pressures are the same, the most convenient pathway to use to calculate the entropy change is an isobaric pathway. In this case, it is useful to remember that

$$dq = nC_p dT$$

So

$$\frac{dq}{T} = nC_p\frac{dT}{T}$$

Integration from the initial to final temperature is used to calculate the change in entropy. If the heat capacity is constant over the temperature range

$$\int_{T_1}^{T_2} \frac{dq}{T} = nC_p\int_{T_1}^{T_2} \frac{dT}{T} = nC_p\ln\left(\frac{T_2}{T_1}\right)$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral. For example, if C_p can be expressed as

$$C_p = a + bT + \frac{c}{T^2}$$

ΔS takes the form

$$\int_{T_1}^{T_2} \frac{dq}{T} = n \int_{T_1}^{T_2} \frac{a + bT + \frac{c}{T^2}}{T} dT$$

which simplifies to

$$\Delta S = n \int_{T_1}^{T_2} \left(\frac{a}{T} + bT + \frac{c}{T^3} \right) dT$$

or

$$\Delta S = n \left[a \ln\left(\frac{T_2}{T_1} \right) + b(T_2 - T_1) - \frac{c}{2} \left(\frac{1}{T_2^2} - \frac{1}{T_1^2} \right) \right]$$

Isochoric Changes

Similarly to the cast of constant pressure, it is fairly simple to calculate ΔS. Since

$$dq = nC_V dt$$

$\frac{dq}{T}$ is given by

$$\frac{dq}{T} = nC_V \frac{dT}{T}$$

And so for changes over which C_V is independent of the temperature ΔS is given by

$$\Delta S = nC_v \ln\left(\frac{T_2}{T_1} \right)$$

Adiabatic Changes

The easiest pathway for which to calculate entropy changes is an adiabatic pathway. Since $dq = 0$ for an adiabatic change, then $dS = 0$ as well.

Phase Changes

The entropy change for a phase change at constant pressure is given by

$$\Delta S = \frac{q}{T} = \frac{\Delta H_{phase}}{T} \tag{7.1.2}$$

Example 7.1.2: Entropy Change for Melting Ice

The enthalpy of fusion for water is 6.01 kJ/mol. Calculate the entropy change for 1.0 mole of ice melting to form liquid at 273 K.

Solution

This is a phase transition at constant pressure (assumed) requiring Equation 7.1.2:

$$\begin{aligned} \Delta S &= \frac{(1\,mol)(6010\,J/mol)}{273\,K} \\ &= 22\,J/K \end{aligned}$$

This page titled 7.1: Calculating Entropy Changes is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **5.4: Calculating Entropy Changes** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

7.2: Trouton's rule

Trouton's rule says that for many (but not all) liquids, the **entropy of vaporization** is approximately the same at ~85 J $mol^{-1}K^{-1}$. The (partial) success of the rule is due to the fact that the entropy of a gas is considerably larger than that of any liquid.

$$S_{gas} \gg S_{liquid} \tag{7.2.1}$$

Therefore, the entropy of the initial state (e.g. the liquid) is negligible in determining the entropy of vaporization

$$\Delta S_{vap} = S_{gas} - S_{liquid} \approx S_{gas} \tag{7.2.2}$$

When a liquid vaporizes its entropy goes from a modest value to a significantly larger one. This is related to the ratio of the enthalpy of vaporization and the temperature of the transition:

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T} \tag{7.2.3}$$

ΔS_{vap} is found to be approximately constant at the boiling point (Figure 7.2.1):

$$\Delta S_{vap} \approx 85\ J\,mol^{-1}\,K^{-1} \tag{7.2.4}$$

This is Trouton's rule, which is valid for many liquids (e.g, the entropy of vaporization of toluene is 87.30 J K^{-1} mol^{-1}, that of benzene is 89.45 J K^{-1} mol^{-1}, and that of chloroform is 87.92 J K^{-1} mol^{-1}). Because of its convenience, the rule is used to estimate the enthalpy of vaporization of liquids whose boiling points are known.

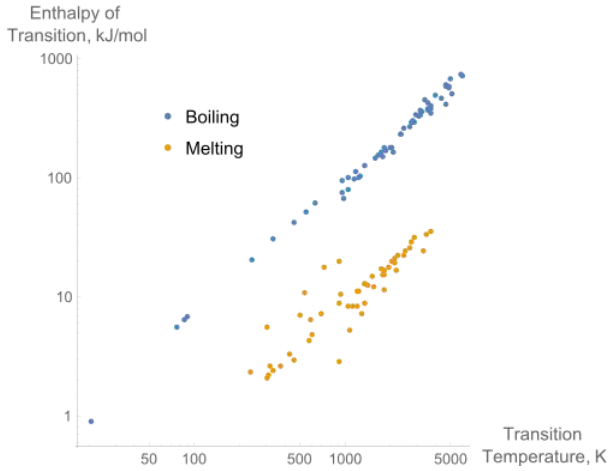


Figure 7.2.1: Enthalpies of melting and boiling for pure elements versus temperatures of transition, demonstrating Trouton's rule (blue data). (CC BY-SA 3.0; Mgibby5).

> *Trouton's rule can be used to estimate the enthalpy of vaporization of liquids whose boiling points are known.*

Experimental values vary rather more than this and for gases such as neon, nitrogen, oxygen and methane whose liquids all boil below 150 K, have values that are in the range 65−75, benzene, many 'normal' liquids and liquid sodium, lithium and iodine, in the range 80−90 and ethanol, water, hydrogen fluoride in the range 105−115 J mol^{-1} K^{-1}. Thus is nothing unusual about 150 K, but rather an influence from intermolecular interactions.

The value of ~85 J $mol^{-1}K^{-1}$ corresponds to a interaction energy of ~9.5kT per molecule and so the boiling point gives an indication of the strength of the cohesive energy holding molecules together in the condensed phase. When the cohesive energy exceeds this value, as in water, then the ratio $\Delta H_{vap}/T$ (Equation 7.2.3) is larger and conversely the ratio is smaller when the cohesive energy is less as in Neon or methane. The ≈9.5kT minimum energy per molecule is quite a modest energy; if a molecule has six near neighbors this corresponds to about 3kT/2 per interaction between two molecules, roughly the average thermal energy.

Melting

There is no universal rule for the entropy of melting since a similar approximate like that used for Trouton's law (Equation 7.2.2) does not exist. However, if the mature of the interactions are consistent between a set of solids, then a crude correlation can be identified (Figure 7.2.1; orange symbols).

Trouton Rule's does not Apply to Structured Liquids

For example, the entropies of vaporization of water, ethanol, formic acid and hydrogen fluoride are far from the predicted values. However, if the liquid presents hydrogen bonding or any other kind of high ordered structure, its entropy will be particularly low and the entropy gain during vaporization will greater, too. The enthalpy of vaporization is greater for hydrogen-bonding molecules than for plain alkanes. For low-molecular weight alcohols, this effect is pronounced. The longer the alkane chain becomes, the more the compound behaves like a pure alkane.

Table 7.2.1: Enthalpy of vaporization in kj/mol

Liquid	ΔH_{vap} (kJ/mol)	ΔH_{vap} (kJ/mol per carbon)
Methanol	38	38
Ethanol	42	21
n-propanol	47	16
n-butanol	52	13
n-pentanol	57	11
n-hexanol	61	10
n-heptanol	67	10
n-octanol	71	9
n-nonanol	77	9
n-decanol	82	8

Data obtained from the NIST Webbook.

Keeping in mind the relative molecular weights of the compounds, you can see there is a decreasing effect of the hydrogen bonding (and other) effects on the n-alcohol series as we move to larger chains and become less alcohol-like (structured liquid) and more alkane-like (unstructure liquid). This is much more obvious when ΔH is normalized to a per-carbon basis.

Table 7.2.1 shows that two different processes control the enthalpy of vaporization, and similarly the saturation vapor concentration (also known as vapor pressure) or boiling point. At the low-molecular weight end, hydrogen bonding dominates, so we see the behavior common to polar, hydrogen-bonding compounds. At the high-molecular weight end, we see the pattern observed for alkanes.

> *Trouton's rule hardly works for high ordered substances exhibiting hydrogen bonding. Other factors like the enthalpy of vaporization for a long chained organic molecule {strength of Van der Waals forces} may also play some significance role.*

Example 7.2.1: Entropy of Waporization for Water

The experimentally determined enthalpy of vaporization if water is $40.7\,kJ\,mol^{-1}$. Does water follow Trouton's rule in predicting the enthalpy of vaporization?

Solution

From Equations 7.2.3 and 7.2.4, we get

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T} \approx 85\ J\,K^{-1}mol^{-1}$$

This predicts that (since water boils at 373.15 K under atmospheric pressure)

$$\Delta H_{vap} \approx (85\ J\,K^{-1}mol^{-1})(373.15\ K) = 31.7\ kJ\,K^{-1}mol^{-1}$$

This deviates from the observed enthalpy change of $40.7\ J\,K^{-1}mol^{-1}$ by 23%, which is a sizable deviation from experiment. So, Trouton's law does not apply to water.

This deviation is similarly observed by comparing the determined entropy of vaporization (Equation 7.2.3) to the estimate from Trouton's law

$$\Delta S_{vap} = \frac{40.7\ kJ\,mol^{-1}}{373.15K} = 109.1 J\,K^{-1}mol^{-1} > 85\ J\,K^{-1}mol^{-1}$$

Example 7.2.1 demostrates the general observation that the S_{liquid} for structured liquids is lower than for unstructured liquids, so the entropy gain during vaporization (i.e., Δ_{vap} in Equation 7.2.2) will be greater.

Trouton Rule's does not Apply to Ordered Gasses

In contrast to water, the entropy of vaporization of formic acid has negative deviance from Trouton's rule. This fact indicates the existence of an orderly structure in the gas phase; it is known that formic acid forms a dimer structure even in the gas phase (Figure 7.2.2). As with water, where hydrogen bonding results in structured phase and reduced entropy of the liquid (positive deviation from Trouton's law), the dimerization in formic acid reduces the entropy of the gas (negative deviation from Trouton's law).

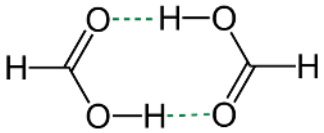


Figure 7.2.2: Cyclic dimer of formic acid; dashed **green** lines represent hydrogen bonds. (Public Domain; Jü).

Negative deviance can also occur as a result of a reduced gas phase entropy owing to a low population of excited rotational states in the gas phase, particularly in small molecules such as methane. Trouton's rule validity can be increased by considering

$$\Delta \bar{S}_{vap} = 4.5R + R\ln T \tag{7.2.5}$$

Contributors and Attributions

- Renato at Chemistry StackExchange
- PHANUEL ALUOMU at Chemistry StackExchange
- porphyrin at Chemistry StackExchange
- airhuff at Chemistry StackExchange
- Wikipedia

7.2: Trouton's rule is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Trouton's rule** is licensed CC BY-NC-SA 4.0.

7.3: The Third Law of Thermodynamics

One important consequence of Botlzmann's proposal is that a perfectly ordered crystal (i.e. one that has only one energetic arrangement in its lowest energy state) will have an entropy of 0. This makes entropy qualitatively different than other thermodynamic functions. For example, in the case of enthalpy, it is impossible have a zero to the scale without setting an arbitrary reference (which is that the enthalpy of formation of elements in their standard states is zero.) But entropy has a natural zero! It is the state at which a system has perfect order. This also has another important consequence, in that it suggests that there must also be a zero to the temperature scale. These consequences are summed up in the **Third Law of Thermodynamics**.

> *The entropy of a perfectly ordered crystal at 0 K is zero.*

This also suggests that absolute molar entropies can be calculated by

$$S = \int_o^T \frac{C}{T} dT$$

where C is the heat capacity. An entropy value determined in this manner is called a **Third Law Entropy**.

Naturally, the heat capacity will have some temperature dependence. It will also change abruptly if the substance undergoes a phase change. Unfortunately, it is exceedingly difficult to measure heat capacities very near zero K. Fortunately, many substances follow the **Debye Extrapolation** in that at very low temperatures, their heat capacities are proportional to T^3. Using this assumption, we have a temperature dependence model that allows us to extrapolate absolute zero based on the heat capacity measured at as low a temperature as can be found.

Example 7.3.1

SiO_2 is found to have a molar heat capacity of 0.777 J mol^{-1} K^{-1} at 15 K (Yamashita, et al., 2001). Calculate the molar entropy of SiO_2 at 15 K.

Solution

Using the Debye model, the heat capacity is given by



The value of a can be determined by





The entropy is then calculated by

Calculating a third Law Entropy

Start at 0 K, and go from there!

This page titled 7.3: The Third Law of Thermodynamics is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **5.7: The Third Law of Thermodynamics** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

8: Gibbs and Helmholtz Energies



8.1: Functions
8.2: Combining the First and Second Laws - Maxwell's Relations
8.3: ΔA, ΔG, and Maximum Work
8.4: Volume Dependence of Helmholtz Energy
8.5: Pressure Dependence of Gibbs Energy
8.6: Temperature Dependence of A and G
8.7: When Two Variables Change at Once
8.8: The Difference between Cp and Cv
8.9: Putting the Second Law to Work (Exercises)
8.S: Putting the Second Law to Work (Summary)

8: Gibbs and Helmholtz Energies is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.1: Free Energy Functions

In the previous chapter, we saw that for a spontaneous process, $\Delta S_{universe} > 0$. While this is a useful criterion for determining whether or not a process is spontaneous, it is rather cumbersome, as it requires one to calculate not only the entropy change for the system, but also that of the surroundings. It would be much more convenient if there was a single criterion that would do the job and focus only on the system. As it turns out, there is.

Since we know that

$$\Delta S_{univ} \geq 0$$

for any natural process, and

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

all we need to do is to find an expression for ΔS_{sys} that can be determined by the changes in the system itself. Fortunately, we have already done that! Recalling that at constant temperature

$$\Delta S = -\frac{q_{rev}}{T}$$

and at constant pressure

$$\Delta H = q_p$$

it follows that at constant temperature and pressure

$$\Delta S_{surr} = -\frac{\Delta H_{sys}}{T}$$

Substitution into the above equations yields an expression for the criterion of spontaneity that depends only on variables describing the changes in the system!

$$\Delta S_{univ} \geq \Delta S_{sys} - \frac{\Delta H_{sys}}{T}$$

so

$$\Delta S_{sys} - \frac{\Delta H_{sys}}{T} \geq 0$$

Multiplying both sides by $-T$ yields

$$\Delta H - T\Delta S \leq 0 \tag{8.1.1}$$

A similar derivation for constant volume processes results in the expression (at constant volume and temperature)

$$\Delta U - T\Delta S \leq 0 \tag{8.1.2}$$

> Equation 8.1.1 is of great use to chemists, as most of chemistry occurs at constant pressure. For geologists, however, who are interested in processes that occur at very high pressures (say, under the weight of an entire mountain) and expansion is not a possibility, the constant volume expression of Equation 8.1.1 may be of greater interest.

All of the above arguments can be made for systems in which the temperature is not constant by considering infinitesimal changes. The resulting expressions are

$$dH - TdS \leq 0 \tag{8.1.3}$$

and

$$dU - TdS \leq 0 \tag{8.1.4}$$

The Gibbs and Helmholtz Functions

Equation 8.1.3 suggests a very convenient thermodynamic function to help keep track of both the effects of entropy and enthalpy changes. This function, the **Gibbs function** (or **Gibbs Free Energy**) is defined by

$$G \equiv H - TS$$

A change in the Gibbs function can be expressed

$$\Delta G = \Delta H - \Delta(TS)$$

Or at constant temperature

$$\Delta G = \Delta H - T\Delta S$$

And the criterion for a process to be spontaneous is the DG < 0. As such, it should be clear spontaneity is not merely a function the enthalpy change (although exothermic processes tend to be spontaneous) but also a function of the entropy change, weighted by the temperature. Going back to an earlier example,

$$NaOH(s) \rightarrow Na^{+}(aq) + OH^{-}(aq)$$

with $\Delta H < 0$.

and

$$NaHCO_3(s) \rightarrow Na^{+}(aq) + HCO_3^{-}(aq)$$

with $\Delta H > 0$.

It is easy to see why both processes are spontaneous. In the first case, the process is exothermic (favorable) and proceeds with an increase in entropy (also favorable) due to the formation of fragments in the liquid phase (more chaotic) from a very ordered solid (more ordered). The second reaction is endothermic (unfavorable) but proceeds with an increase in entropy (favorable). So, so long as the temperature is high enough, the entropy term will overwhelm the enthalpy term and cause the process to be spontaneous. The conditions for spontaneous processes at constant temperature and pressure can be summarized in Table 6.1.1.

Table 6.1.1: Spontaneity Conditions for a Process under Constant Temperature and Pressure

ΔH	ΔS	Spontaneous
> 0	> 0	At high T
> 0	< 0	At no T
< 0	> 0	At all T
< 0	< 0	At low T

Similarly to the Gibbs function, the **Helmholtz function** is defined by

$$A \equiv U - TS$$

and provides another important criterion for spontaneous processes at constant value and temperature. *At constant temperature*, the Helmholtz function can be expressed by

$$\Delta A \equiv \Delta U - T\Delta S$$

Based on similar arguments used for the Gibbs function, the Helmholtz function also can be used to predict which processes will be spontaneous at constant volume and temperature according to Table 6.1.2.

Table 6.1.2: Spontaneity Conditions for a Process under Constant Temperature and Volume

ΔU	ΔS	Spontaneous?
> 0	> 0	At high T
> 0	< 0	At no T

ΔU	ΔS	Spontaneous?
< 0	> 0	At all T
< 0	< 0	At low T

Calculating ΔG for Reactions

Much like in the case of enthalpy (and unlike entropy), free energy functions do not have an unambiguous zero to the energy scale. So, just like in the case of enthalpies of formation, by convention, the standard free energy of formation (ΔG_f^o) for elements in their standard states is defined as zero. This allows for two important things to happen. First, ΔG_f^o can be measured and tabulated for any substance (in principle, at least.) ΔG_f^o is determined to be ΔG_{rxn}^o for the reaction that forms one mole of a compound from elements in their standard states (similarly to how ΔH_f^o is defined.) Secondly, tabulated (ΔG_f^o) can be used to calculate standard reaction free energies (ΔG_{rxn}^o) in much the same way as ΔH_f^o is used for reaction enthalpies.

Example 8.1.1:

Given the following data at 298 K, calculate ΔG^o at 298 K for the following reaction:

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Substance	ΔG_f^o (kJ/mol)
$C_2H_4(g)$	68.4
$C_2H_6(g)$	-32.0

Solution

The ΔG_f^o values can be used to calculate ΔG^o for the reaction in exactly the same method as ΔH_f^o can be used to calculate a reaction enthalpy.

$$\Delta G^o = (1\,mol)(-32.0\,kJ/mol) - (1\,mol)(68.4\,kJ/mol)$$

$$\Delta G^o = 100.4\,kJ$$

Note: $H_2(g)$ is not included in the calculation since ΔG_f^o for $H_2(g)$ is 0 since it is an element in its standard state.

This page titled 8.1: Free Energy Functions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **6.1: Free Energy Functions** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

8.2: Combining the First and Second Laws - Maxwell's 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 $dU = dq + dw$):

$$dU = TdS - pdV \tag{8.2.1}$$

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!

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 8.2.1 can be expressed:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{8.2.2}$$

Also, by inspection (comparing the two expressions for dU in Equations 8.2.1 and 8.2.2) it is apparent that:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{8.2.3}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \tag{8.2.4}$$

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 8.2.3 and 8.2.4, 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.

$$dH = TdS + Vdp \tag{8.2.5}$$

And much as in the case of internal energy, this suggests that the natural variables of H are S and p. Or

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dV \tag{8.2.6}$$

Comparing Equations 8.2.5 and 8.2.6 show that

$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{8.2.7}$$

and

$$\left(\frac{\partial H}{\partial p}\right)_S = V \tag{8.2.8}$$

It is worth noting at this point that both Equation 8.2.3

$$\left(\frac{\partial U}{\partial S}\right)_V$$

and Equation 8.2.7

$$\left(\frac{\partial H}{\partial S}\right)_p$$

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 8.2.1.

Table 8.2.1: Maxwell Relations

Function	Differential	Natural Variables	Maxwell Relation
U	$dU = TdS - pdV$	S, V	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$

Function	Differential	Natural Variables	Maxwell Relation
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 8.2.1

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!

This page titled 8.2: Combining the First and Second Laws - Maxwell's Relations is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **6.2: Combining the First and Second Laws - Maxwell's Relations** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

8.3: ΔA, ΔG, and Maximum Work

The functions A and G are oftentimes referred to as **free energy** functions. The reason for this is that they are a measure of the maximum work (in the case of ΔA) or non p-V work (in the case of ΔG) that is available from a process. To show this, consider the total differentials.

First, consider the differential of A.

$$dA = dU - TdS - SdT$$

Substituting the combined first and second laws for dU, but expressing the work term as dw, yields

$$dA = TdS - dw - TdS - SdT$$

And cancelling the TdS terms gives

$$dA = dw - SdT$$

or at constant temperature ($dT = 0$)

$$dA = dw$$

Since the only assumption made here was that the change is reversible (allowing for the substitution of TdS for dq), and dw for a reversible change is the maximum amount of work, it follows that dA gives the maximum work that can be produced from a process at constant temperature.

Similarly, a simple expression can be derived for dG. Starting from the total differential of G.

$$dG = dU + pdV - pdV + Vdp - TdS - SdT$$

Using an expression for $dU = dq + dw$, where $dq = TdS$ and dw is split into two terms, one (dw_{pV}) describing the work of expansion and the other (dw_e) describing any other type of work (electrical, stretching, etc.)

$$dU - TdS + dW_{pV} + dW_e$$

dG can be expressed as

$$dG = \cancel{TdS} - \cancel{pdV} + dw_e + \cancel{pdV} + Vdp - \cancel{TdS} - SdT$$

Cancelling the TdS and pdV terms leaves

$$dG = +dw_e + Vdp - SdT$$

So at constant temperature ($dT = 0$) and pressure ($dp = 0$),

$$dG = dw_e$$

This implies that dG gives the maximum amount of non p-V work that can be extracted from a process.

This concept of dA and dG giving the maximum work (under the specified conditions) is where the term “free energy” comes from, as it is the energy that is *free* to do work in the surroundings. If a system is to be optimized to do work in the soundings (for example a steam engine that may do work by moving a locomotive) the functions A and G will be important to understand. It will, therefore, be useful to understand how these functions change with changing conditions, such as volume, temperature, and pressure.

Contributors

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)

This page titled 8.3: ΔA, ΔG, and Maximum Work is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **6.3: ΔA, ΔG, and Maximum Work** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

8.4: Volume Dependence of Helmholtz Energy

If one needs to know how the Helmholtz function changes with changing volume at constant temperature, the following expression can be used:

$$\Delta A = \int_{V_1}^{V_2} \left(\frac{\partial A}{\partial V} \right)_T dV \tag{8.4.1}$$

But how does one derive an expression for the partial derivative in Equation 8.4.1? This is a fairly straight forward process that begins with the definition of A:

$$A = U - TS$$

Differentiating (and using the chain rule to evaluate $d(TS)$ yields

$$dA = dU - TdS - SdT \tag{8.4.2}$$

Now, it is convenient to use the combined first and second laws

$$dU = TdS - pdV \tag{8.4.3}$$

which assumes:

1. a reversible change and
2. only pV work is being done.

Substituting Equation 8.4.3 into Equation 8.4.2 yields

$$dA = \cancel{TdS} - pdV - \cancel{TdS} - SdT \tag{8.4.4}$$

Canceling the TdS terms gives the important result

$$dA = -pdV - SdT \tag{8.4.5}$$

The natural variables of A are therefore V and T! So the total differential of A is conveniently expressed as

$$dA = \left(\frac{\partial A}{\partial V} \right)_T dV + \left(\frac{\partial A}{\partial T} \right)_V dT \tag{8.4.6}$$

and by simple comparison of Equations 8.4.5 and 8.4.6, it is clear that

$$\left(\frac{\partial A}{\partial V} \right)_T = -p$$

$$\left(\frac{\partial A}{\partial T} \right)_V = -S$$

And so, one can evaluate Equation 8.4.1 as

$$\Delta A = -\int_{V_1}^{V_2} p\, dV$$

If the pressure is independent of the temperature, it can be pulled out of the integral.

$$\Delta A = -p \int_{V_1}^{V_2} dV = -p(V_2 - V_1)$$

Otherwise, the temperature dependence of the pressure must be included.

$$\Delta A = -\int_{V_1}^{V_2} p(V)\, dV$$

Fortunately, this is easy if the substance is an ideal gas (or if some other equation of state can be used, such as the van der Waals equation.)

Example 8.4.1: Ideal Gas Expansion

Calculate ΔA for the isothermal expansion of 1.00 mol of an ideal gas from 10.0 L to 25.0 L at 298 K.

Solution

For an ideal gas,

$$p = \frac{nRT}{V}$$

So

$$\left(\frac{\partial A}{\partial V}\right)_T = -p$$

becomes

$$\left(\frac{\partial A}{\partial V}\right)_T = -\frac{nRT}{V}$$

And so (Equation 8.4.1)

$$\Delta A = \int_{V_1}^{V_2} \left(\frac{\partial A}{\partial V}\right)_T dV$$

becomes

$$\Delta A = -nRT \int_{V_1}^{V_2} \frac{dV}{V} dT$$

or

$$\Delta A = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

Substituting the values from the problem

$$\Delta A = -(1.00\, mol)(8.314\, J/(mol\, K))(298\, K) \ln\left(\frac{25.0\, L}{10.0\, L}\right)$$

But further, it is easy to show that the Maxwell relation that arises from the simplified expression for the total differential of A is

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

This particular Maxwell relation is exceedingly useful since one of the terms depends only on p, V, and T. As such it can be expressed in terms of our old friends, α and κ_T!

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

This page titled 8.4: Volume Dependence of Helmholtz Energy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **6.4: Volume Dependence of Helmholtz Energy** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

8.5: Pressure Dependence of Gibbs Energy

The pressure and temperature dependence of G is also easy to describe. The best starting place is the definition of G.

$$G = U + pV - TS \tag{8.5.1}$$

Taking the total differential of G yields

$$dG = dU + pdV - pdV + Vdp - TdS - SdT$$

The differential can be simplified by substituting the combined first and second law statement for dU (consider a reversible process and pV work only).

$$dG = \cancel{TdS} - \cancel{pdV} + \cancel{pdV} + Vdp - \cancel{TdS} - SdT$$

Canceling the TdS and pdV terms leaves

$$dG = V\,dp - S\,dT \tag{8.5.2}$$

This suggests that the natural variables of G are p and T. So the total differential dG can also be expressed

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT \tag{8.5.3}$$

And by inspection of Equations 8.5.2 and 8.5.3, it is clear that

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

and

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

It is also clear that the Maxwell relation on G is given by

$$\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial S}{\partial p}\right)_T$$

which is an extraordinarily useful relationship, since one of the terms is expressible entirely in terms of measurable quantities!

$$\left(\frac{\partial V}{\partial T}\right)_p = V\alpha$$

The pressure dependence of G is given by the pressure derivative at constant temperature

$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{8.5.4}$$

which is simply the molar volume. For a fairly incompressible substance (such as a liquid or a solid) the molar volume will be essentially constant over a modest pressure range.

Example 8.5.1: Gold under Pressure

The density of gold is 19.32 g/cm^3. Calculate ΔG for a 1.00 g sample of gold when the pressure on it is increased from 1.00 atm to 2.00 atm.

Solution

The change in the Gibbs function due to an isothermal change in pressure can be expressed as

$$\Delta G = \int_{p_1}^{p_2} \left(\frac{\partial G}{\partial p}\right)_T dp$$

And since substituting Equation 8.5.4, results in

$$\Delta G = \int_{p_1}^{p_2} V dp$$

Assuming that the molar volume is independent or pressure over the stated pressure range, ΔG becomes

$$\Delta G = V(p_2 - p_1)$$

So, the molar change in the Gibbs function can be calculated by substituting the relevant values.

$$\Delta G = \left(\frac{197.0\,g}{mol} \times \frac{1}{19.32\,g} \times \frac{1\,L}{1000\,cm^3}\right)(2.00\,atm - 1.00\,atm)\underbrace{\left(\frac{8.315\,J}{0.08206\,atm\,L}\right)}_{\text{conversion unit}} \tag{8.5.5}$$

$$= 1.033\,J \tag{8.5.6}$$

Contributors

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)

This page titled 8.5: Pressure Dependence of Gibbs Energy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **6.5: Pressure Dependence of Gibbs Energy** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

8.6: Temperature Dependence of A and G

In differential form, the free energy functions can be expressed as

$$dA = -pdV - SdT$$

and

$$dG = -V\,dp - SdT$$

So by inspection, it is easy to see that

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

and

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

And so, it should be fairly straightforward to determine how each changes with changing temperature:

$$\Delta A = -\int_{T_1}^{T_2}\left(\frac{\partial A}{\partial T}\right)_V dT = -\int_{T_1}^{T_2} S\,dT$$

and

$$\Delta G = -\int_{T_1}^{T_2}\left(\frac{\partial G}{\partial T}\right)_p dT = -\int_{T_1}^{T_2} S\,dT$$

But the temperature dependence of the entropy needed to be known in order to evaluate the integral. A convenient work-around can be obtained starting from the definitions of the free energy functions.

$$A = U - TS$$

and

$$G = H - TS$$

Dividing by T yields

$$\frac{A}{T} = \frac{U}{T} - S$$

and

$$\frac{G}{T} = \frac{H}{T} - S$$

Now differentiating each expression with respect to T at constant V or p respectively yields

$$\left(\frac{\partial\left(\frac{A}{T}\right)}{\partial T}\right)_V = -\frac{U}{T^2}$$

and

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_p = -\frac{H}{T^2}$$

Or differentiating with respect to $1/T$ provides a simpler form that is mathematically equivalent:

$$\left(\frac{\partial\left(\frac{A}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_V = U$$

and

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_p = H$$

Focusing on the second expression (since all of the arguments apply to the first as well), we see a system that can be integrated. Multiplying both sides by $d(1/T)$ yields:

$$d\left(\frac{G}{T}\right) = Hd\left(\frac{1}{T}\right)$$

Or for finite changes ΔG and ΔH:

$$d\left(\frac{\Delta G}{T}\right) = \Delta Hd\left(\frac{1}{T}\right)$$

and integration, assuming the *enthalpy change is constant over the temperature* interval yields

$$\int_{T_1}^{T_2} d\left(\frac{\Delta G}{T}\right) = \Delta H \int_{T_1}^{T_2} d\left(\frac{1}{T}\right)$$

$$\frac{\Delta G_{T_2}}{T_2} - \frac{\Delta G_{T_1}}{T_1} = \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{8.6.1}$$

Equation ??? is the **Gibbs-Helmholtz equation** and can be used to determine how ΔG changes with changing temperature. The equivalent equation for the Helmholtz function is

$$\frac{\Delta A_{T_2}}{T_2} - \frac{\Delta A_{T_1}}{T_1} = \Delta U\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{8.6.2}$$

Example 8.6.1:

Given the following data at 298 K, calculate ΔG at 500 K for the following reaction:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + H_2O(g)$$

Compound	ΔG_f^o (kJ/mol)	ΔH_f^o (kJ.mol)
CH_4(g)	-50.5	-74.6
CO_2(g)	-394.4	-393.5
H_2O(g)	-228.6	-241.8

Solution

ΔH and $\Delta G_{298\ K}$ and can be calculated fairly easily. It will be assumed that ΔH is constant over the temperature range of 298 K – 500 K.

$$\Delta H = (1\,mol)(-393.5\,kJ/mol) + (2\,mol)(-241.8\,kJ/mol) - (1\,mol)(-74.5\,kJ/mol) = -820.6\,kJ$$

$$\Delta G_{298} = (1\,mol)(-394.4\,kJ/mol) + (2\,mol)(-228,6\,kJ/mol) - (1\,mol)(-50.5\,kJ/mol) = -801.1\,kJ$$

So using Equation 8.6.1 with the data just calculated gives

$$\frac{\Delta G_{500\ K}}{500\ K} - \frac{-801.1\,kJ}{298\ K} = (-820.6\,kJ)\left(\frac{1}{500\ K} - \frac{1}{298\ K}\right)$$

$$\Delta G_{500\ K} = -787.9\ kJ$$

Note: ΔG became a little bit less negative at the higher temperature, which is to be expected for a reaction which is exothermic. An increase in temperature should tend to make the reaction less favorable to the formation of products, which is exactly what is seen in this case!

This page titled 8.6: Temperature Dependence of A and G is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **6.6: Temperature Dependence of A and G** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

8.7: When Two Variables Change at Once

So far, we have derived a number of expressions and developed methods for evaluating how thermodynamic variables change as one variable changes while holding the rest constant. But real systems are seldom this accommodating. For example, a piece of metal (such as a railroad rail) left in the sun will undergo both an increase in temperature and an expansion due to the absorption of energy from sunlight. So both T and V are changing at the same time! If the change in a thermodynamic variable (such as G) is needed, contributions from both changes are required to be taken into account. We've already seen how to express this in terms of a total differential.

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT \tag{8.7.1}$$

Fortunately, G (like the other thermodynamic functions U, H, S, and A) is kind enough to be a state variable. This means that we can consider the changes independently and then simply add the results. Another way to think of this is that the system may follow either of two pathways to get from the initial conditions to the final conditions:

- *Pathway I:*
    1. An isothermal expansion from V_1 to V_2 at T_1 followed by
    2. An isochoric temperature increase from T_1 to T_2 at V_2
- *Pathway 2:*
    1. An isochoric temperature increase from T_1 to T_2 at V_1 followed by
    2. And isothermal expansion from V_1 to V_2 at T_2

And since G has the good sense to be a state variable, the pathway connecting the initial and final states is unimportant. We are free to choose any path that is convenient to calculate the change.

Example 8.7.1: Non-Isothermal Gas Expansion

Calculate the entropy change for 1.00 mol of a monatomic ideal gas (C_V = 3/2 R) expanding from 10.0 L at 273 K to 22.0 L at 297 K.

Solution

If one considers entropy to be a function of temperature and volume, one can write the total differential of entropy as

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

and thus

$$\Delta S = \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T}\right)_V dT + \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_T dV$$

The first term is the contribution due to an *isochoric temperature* change:

$$\Delta S_{T_1 \rightarrow T_2} = \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T}\right)_V dT \tag{8.7.2}$$

$$= \int_{T_1}^{T_2} \frac{nC_V}{T} dT \tag{8.7.3}$$

$$= nC_V \ln\left(\frac{T_2}{T_1}\right) \tag{8.7.4}$$

$$= (1.00\,mol)\left(\frac{3}{2} \cdot 8.314 \frac{J}{mol\,K}\right) \ln\left(\frac{297\,K}{273\,K}\right) \tag{8.7.5}$$

$$= 13.57\,J/K \tag{8.7.6}$$

The second term is the contribution due to an isothermal expansion:

$$\Delta S_{V_1 \to V_2} = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V} \right)_T dV \tag{8.7.7}$$

From the Maxwell relation on A

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$$

So Equation 8.7.7 becomes

$$\begin{aligned} \Delta S_{V_1 \to V_2} &= \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial T} \right)_V dV && (8.7.8) \\ &= \int_{V_1}^{V_2} \left(\frac{nR}{V} \right) dV && (8.7.9) \\ &= nR \ln \left(\frac{V_2}{V_1} \right) && (8.7.10) \\ &= (1.00\, mol) \left(8.314 \frac{J}{mol\, K} \right) \ln \left(\frac{22.0\, L}{10.0\, L} \right) && (8.7.11) \\ &= 6.56\, J/K && (8.7.12) \end{aligned}$$

And the total entropy change is

$$\begin{aligned} \Delta S_{tot} &= \Delta S_{V_1 \to V_2} + \Delta S_{V_1 \to V_2} && (8.7.13) \\ &= 13.57\, J/K + 6.56\, J/K && (8.7.14) \\ &= 20.13\, J/K && (8.7.15) \end{aligned}$$

Deriving an expression for a partial derivative (Type III)

Thermodynamics involves many variables. But for a single component sample of matter, only two state variables are needed to describe the system and fix all of the thermodynamic properties of the system. As such, it is conceivable that two functions can be specified as functions of the same two variables. In general terms: $z(x, y)$ and $w(x, y)$.

So an important question that can be answered is, "What happens to z if w is held constant, but x is changed?" To explore this, consider the total differential of z:

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \tag{8.7.16}$$

but z can also be considered a function of x and $w(x, y)$. This implies that the total differential can also be written as

$$dz = \left(\frac{\partial z}{\partial x} \right)_w dx + \left(\frac{\partial z}{\partial w} \right)_x dy \tag{8.7.17}$$

and these two total differentials must be equal to one another!

$$= \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy = \left(\frac{\partial z}{\partial x} \right)_w dx + \left(\frac{\partial z}{\partial w} \right)_x dw$$

If we constrain the system to a change in which w remains constant, the last term will vanish since $dw = 0$.

$$\left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy = \left(\frac{\partial z}{\partial x} \right)_w dx \tag{8.7.18}$$

but also, since w is a function x and y, the total differential for w can be written

$$dw = \left(\frac{\partial w}{\partial x} \right)_y dx + \left(\frac{\partial w}{\partial y} \right)_x dy$$

And it too must be zero for a process in which w is held constant.

$$0 = \left(\frac{\partial w}{\partial x}\right)_y dx + \left(\frac{\partial w}{\partial y}\right)_x dy$$

From this expression, it can be seen that

$$dy = -\left(\frac{\partial w}{\partial x}\right)_y \left(\frac{\partial y}{\partial w}\right)_x dx$$

Substituting this into the Equation 8.7.18, yields

$$\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left[-\left(\frac{\partial w}{\partial x}\right)_y \left(\frac{\partial y}{\partial w}\right)_x dx\right] = \left(\frac{\partial z}{\partial x}\right)_w dx \tag{8.7.19}$$

which simplifies to

$$\left(\frac{\partial z}{\partial x}\right)_y dx - \left(\frac{\partial z}{\partial w}\right)_x \left(\frac{\partial w}{\partial x}\right)_y dx = \left(\frac{\partial z}{\partial x}\right)_w dx$$

So for $dx \neq 0$, implies that

$$\left(\frac{\partial z}{\partial x}\right)_y - \left(\frac{\partial z}{\partial w}\right)_x \left(\frac{\partial w}{\partial x}\right)_y = \left(\frac{\partial z}{\partial x}\right)_w$$

or

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial x}\right)_w + \left(\frac{\partial z}{\partial w}\right)_x \left(\frac{\partial w}{\partial x}\right)_y \tag{8.7.20}$$

As with partial derivative transformation types I and II, this result can be achieved in a formal, albeit less mathematically rigorous method.

Consider $z(x, w)$. This allows us to write the total differential for z:

$$dz = \left(\frac{\partial z}{\partial x}\right)_w dx + \left(\frac{\partial z}{\partial w}\right)_x dw$$

Now, divide by dx and constrain to constant y.

$$\left.\frac{dz}{dx}\right|_y = \left(\frac{\partial z}{\partial x}\right)_w \left.\frac{dx}{dx}\right|_y + \left(\frac{\partial z}{\partial w}\right)_x \left.\frac{dw}{dx}\right|_y$$

noting that $dx/dx = 1$ and converting the other ratios to partial derivatives yields

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial x}\right)_w + \left(\frac{\partial z}{\partial w}\right)_x \left(\frac{\partial w}{\partial x}\right)_y \tag{8.7.21}$$

which agrees with the previous result (Equation 8.7.20)! Again, the method is not mathematically rigorous, but it works so long as w, x, y, and z are **state functions** and the total differentials dw, dx, dy, and dz are **exact**.

Contributors

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)

This page titled 8.7: When Two Variables Change at Once is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **6.7: When Two Variables Change at Once** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

8.8: The Difference between Cp and Cv

Constant volume and constant pressure heat capacities are very important in the calculation of many changes. The ratio $C_p/C_V = \gamma$ appears in many expressions as well (such as the relationship between pressure and volume along an adiabatic expansion.) It would be useful to derive an expression for the difference $C_p - C_V$ as well. As it turns out, this difference is expressible in terms of measureable physical properties of a substance, such as α, κ_T, p, V, and T.

In order to derive an expression, let's start from the definitions.

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

and

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

The difference is thus

$$C_p - C_v = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V$$

In order to evaluate this difference, consider the definition of enthalpy:

$$H = U + pV$$

Differentiating this yields

$$dH = dU + pdV + Vdp$$

Dividing this expression by dT and constraining to constant p gives

$$\left.\frac{dH}{dT}\right|_p = \left.\frac{dU}{dT}\right|_p + p\left.\frac{dV}{dT}\right|_p + V\left.\frac{dp}{dT}\right|_p$$

The last term is kind enough to vanish (since $dp = 0$ at constant pressure). After converting the remaining terms to partial derivatives:

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \tag{8.8.1}$$

This expression is starting to show some of the players. For example,

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

and

$$\left(\frac{\partial V}{\partial T}\right)_p = V\alpha$$

So Equation 8.8.1 becomes

$$C_p = \left(\frac{\partial U}{\partial T}\right)_p + pV\alpha \tag{8.8.2}$$

In order to evaluate the partial derivative above, first consider $U(V,T)$. Then the total differential du can be expressed

$$du = \left(\frac{\partial U}{\partial V}\right)_T dV - \left(\frac{\partial U}{\partial T}\right)_V dT$$

Dividing by dT and constraining to constant p will generate the partial derivative we wish to evaluate:

$$\left.\frac{dU}{dT}\right|_p = \left(\frac{\partial U}{\partial V}\right)_T \left.\frac{dV}{dT}\right|_p + \left(\frac{\partial U}{\partial T}\right)_V \left.\frac{dT}{dT}\right|_p$$

The last term will become unity, so after converting to partial derivatives, we see that

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial U}{\partial T}\right)_V \tag{8.8.3}$$

(This, incidentally, is an example of partial derivative transformation type III.) Now we are getting somewhere!

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

and

$$\left(\frac{\partial V}{\partial T}\right)_p = V\alpha$$

So the Equation 8.8.3 can be rewritten

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial V}\right)_T V\alpha + C_V$$

If we can find an expression for

$$\left(\frac{\partial U}{\partial V}\right)_T$$

we are almost home free! Fortunately, that is an easy expression to derive. Begin with the combined expression of the first and second laws:

$$d = TdS - pdV$$

Now, divide both sides by dV and constrain to constant T.

$$\left.\frac{dU}{dV}\right|_T = T\left.\frac{dS}{dV}\right|_T - p\left.\frac{dV}{dV}\right|_T$$

The last term is unity, so after conversion to partial derivatives, we see

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p \tag{8.8.4}$$

A Maxwell relation (specifically the Maxwell relation on A) can be used

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

Substituting this into Equation 8.8.4 yields

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

and since

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

then

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\alpha}{\kappa_T} - p$$

Now, substituting this into the expression into Equation 8.8.3 to get

$$\left(\frac{\partial U}{\partial T}\right)_p = \left[T\frac{\alpha}{\kappa_T} - p\right] V\alpha + C_V$$
$$= \frac{TV\alpha^2}{\kappa_T} - pV\alpha + C_V$$

This can now be substituted into the Equation 8.8.2 yields

$$C_p = \left[\frac{TV\alpha^2}{\kappa_T} - \cancel{pV\alpha} + C_V\right] + \cancel{pV\alpha}$$

The $pV\alpha$ terms will cancel. And subtracting C_V from both sides gives the desired result:

$$C_p - C_V = \frac{TV\alpha^2}{\kappa_T} \tag{8.8.5}$$

And this is a completely general result since the only assumptions made were those that allowed us to use the combined first and second laws in the form

$$dU = TdS - pdV.$$

That means that this expression can be applied to any substance whether gas, liquid, animal, vegetable, or mineral. But what is the result for an ideal gas?

Since we know that for an ideal gas

$$\alpha = \frac{1}{T}$$

and

$$\kappa_T = \frac{1}{p}$$

Substitution back into Equation 8.8.5 yields

$$C_p - C_V = \frac{TV\left(\frac{1}{T}\right)^2}{\left(\frac{1}{p}\right)}$$
$$= \frac{pV}{T}$$
$$= R$$

So for an ideal gas, $C_p - C_V = R$. That is good to know, no?

Example 8.8.1

Derive the expression for the difference between C_p and C_V by beginning with the definition of H, differentiating, dividing by dV (to generate the partial derivative definition of C_V). In this approach, you will need to find expressions for

$$\left(\frac{\partial H}{\partial T}\right)_V$$

and

$$\left(\frac{\partial U}{\partial p}\right)_T$$

and also utilize the Maxwell-Relation on G.

Solution

Begin with the definition of enthalpy.

$$H = U + pV$$

Differentiate the expression.

$$dH = dU + pdV + Vdp$$

Now, divide by dV and constrain to constant T (as described in the instructions) to generate the partial derivative definition of C_V

$$\left.\frac{dH}{dT}\right|_V = \left.\frac{dU}{dT}\right|_V + p\left.\frac{dV}{dT}\right|_V + V\left.\frac{dp}{dT}\right|_V$$

$$\left(\frac{dH}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V + V\left(\frac{dp}{dT}\right)_V \tag{8.8.6}$$

Now what is needed is an expression for

$$\left(\frac{dH}{dT}\right)_V.$$

This can be derived from the total differential for $H(p,T)$ by dividing by dT and constraining to constant V.

$$dH = \left(\frac{dH}{dp}\right)_T dp + \left(\frac{dH}{dT}\right)_p dT$$

$$\left(\frac{dH}{dT}\right)_V = \left(\frac{dH}{dp}\right)_T \left(\frac{dp}{dT}\right)_V + \left(\frac{dH}{dT}\right)_p \tag{8.8.7}$$

This again is an example of partial derivative transformation type III. To continue, we need an expression for

$$\left(\frac{dH}{dp}\right)_T.$$

This can be quickly generated by considering the total differential of $H(p,S)$, its natural variables:

$$dH = TdS + Vdp$$

Dividing by dp and constraining to constant T yields

$$\left.\frac{dH}{dp}\right|_T = T\left.\frac{dS}{dp}\right|_T + V\left.\frac{dp}{dp}\right|_T$$

$$\left(\frac{dH}{dp}\right)_T = T\left(\frac{dS}{dp}\right)_T + V \tag{8.8.8}$$

Using the Maxwell Relation on G, we can substitute

$$-\left(\frac{dV}{dT}\right)_p = \left(\frac{dS}{dp}\right)_T$$

So Equation 8.8.8 becomes

$$\left(\frac{dH}{dp}\right)_T = -T\left(\frac{dV}{dT}\right)_p + V$$

Now, substitute this back into the expression for (Equation 8.8.7):

$$\left(\frac{dH}{dT}\right)_V = \left[-T\left(\frac{dV}{dT}\right)_p + V\right]\left(\frac{dp}{dT}\right)_V + \left(\frac{dH}{dT}\right)_p$$

$$\left(\frac{dH}{dT}\right)_V = -T\left(\frac{dV}{dT}\right)_p\left(\frac{dp}{dT}\right)_V + V\left(\frac{dp}{dT}\right)_V + \left(\frac{dH}{dT}\right)_p$$

This can now substituted for the right-hand side of the initial expression for $\left(\frac{dH}{dT}\right)_V$ back into Equation 8.8.6:

$$-T\left(\frac{dV}{dT}\right)_p\left(\frac{dp}{dT}\right)_V + \cancel{V\left(\frac{dp}{dT}\right)_V} + \left(\frac{dH}{dT}\right)_p = \left(\frac{dU}{dT}\right)_V + \cancel{V\left(\frac{dp}{dT}\right)_V} \tag{8.8.9}$$

Several terms cancel one another. Equation 8.8.9 can then be rearranged to yield

$$\left(\frac{dH}{dT}\right)_p - \left(\frac{dU}{dT}\right)_V = T\left(\frac{dV}{dT}\right)_p\left(\frac{dp}{dT}\right)_V$$

or

$$C_p - C_V = \frac{TV\alpha^2}{\kappa_T}$$

which might look familiar (Equation 8.8.5)!

This page titled 8.8: The Difference between Cp and Cv is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **6.8: The Difference between Cp and Cv** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

8.9: Putting the Second Law to Work (Exercises)

This page titled 8.9: Putting the Second Law to Work (Exercises) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

8.S: Putting the Second Law to Work (Summary)

Learning Objectives

After mastering the material presented in this chapter, one will be able to:

1. Define the free energy functions A and G, and relate changes in these functions to the spontaneity of a given process and constant volume and pressure respectively.
2. Use the definitions of entropy and reversible work of expansion to write an equation that combines the first and second laws of thermodynamics.
3. Utilize the combined first and second law relationship to derive Maxwell Relations stemming from the definitions of U, H, A, and G.
4. Utilize the Maxwell Relations to derive expressions that govern changes in thermodynamic variable as systems move along specified pathways (such as constant temperature, pressure, volume, or adiabatic pathways.)
5. Derive and utilize an expression describing the volume dependence of A.
6. Derive and utilize an expression describing the pressure dependence of G.
7. Derive and utilize expressions that describe the temperature, dependence of A and G.
8. Derive an expression for, and evaluate the difference between C_p and C_V for any substance, in terms of T, V, α, and κ_T.

Vocabulary and Concepts

- free energy
- Gibbs Free Energy
- Gibbs function
- Gibbs-Helmholtz equation
- Helmholtz function
- maximum work
- Maxwell Relation
- standard free energy of formation ($\Delta G_f^o o$

This page titled 8.S: Putting the Second Law to Work (Summary) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **6.S: Putting the Second Law to Work (Summary)** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

9: Phase Equilibria



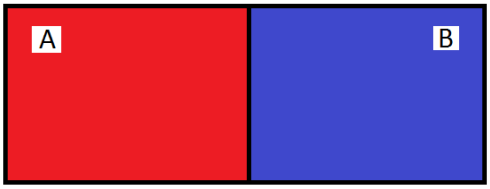
9.1: nics of Mixi
9.2: Partial Molar Volume
9.3: Chemical Potential
9.4: The Gibbs-Duhem Equation
9.5: Non-ideality in Gases - Fugacity
9.6: Colligative Properties
9.7: Solubility
9.8: Non-ideality in Solutions - Activity
9.9: Prelude to Phase Equilibrium
9.E: Mixtures and Solutions (Exercises)
9.E: Phase Equilibrium (Exercises)
9.S: Mixtures and Solutions (Summary)
9.10: Single Component Phase Diagrams
9.11: Criterion for Phase Equilibrium
9.12: The Clapeyron Equation
9.13: The Clausius-Clapeyron Equation

Thumbnail: Image used with permission (Ben FinneyMark Jacobs [CC0])

9: Phase Equilibria is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.1: Thermodynamics of Mixing

A natural place to begin a discussion of mixtures is to consider a mixture of two gases. Consider samples of the two gases filling two partitions in a single container, both at the same pressure, temperature, having volumes V_A and V_B.



After being allowed to mix isothermally, the partial pressures of the two gases will drop by a factor of 2 (although the total pressure will still be the original value) and the volumes occupied by the two gases will double.



Enthalpy of Mixing

Assuming ideal behavior, so that interactions between individual gas molecules are unimportant, it is fairly easy to calculate \(Delta H) for each gas, as it is simply an isothermal expansion. The total enthalpy of mixing is then given by

$$\Delta H_{mix} = \Delta H_A + \Delta H_B$$

And since the enthalpy change for an **isothermal expansion of an ideal gas is zero**,

$$\Delta H_{mix} = 0$$

is a straight-forward conclusion. This will be the criterion for an **ideal mixture**.

In general, real mixtures will deviate from this limiting ideal behavior due to interactions between molecules and other concerns. Also, many substances undergo chemical changes when they mix with other substances. But for now, we will limit ourselves to discussing mixtures in which no chemical reactions take place.

Entropy of Mixing

The entropy change induced due to isothermal mixing (assuming again no interactions between the molecules in the gas mixture) is again going to be the sum of the contributions from isothermal expansions of the two gases. Fortunately, entropy changes for isothermal expansions are easy to calculate for ideal gases.

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$$

If we use the initial volumes V_A and V_B for the initial volumes of gases A and B, the total volume after mixing is $V_A + V_B$, and the total entropy change is

$$\Delta S_{mix} = n_A R\ln\left(\frac{V_A + V_B}{V_A}\right) + n_A R\ln\left(\frac{V_A + V_B}{V_B}\right)$$

Noting that the term

$$\frac{V_A + V_B}{V_A} = \frac{1}{\chi_A}$$

where χ_A is the mole fraction of A after mixing, and that n_A can be expresses as the product of χ_A and the total number of moles, the expression can be rewritten

$$\Delta S_{mix} = n_{tot} R \left[-\chi_A \ln(\chi_A) - \chi_B \ln(\chi_B) \right]$$

It should be noted that because the mole fraction is always between 0 and 1, that $\ln(\chi_B) < 0$. As such, the entropy change for a system undergoing isothermal mixing is always positive, as one might expect (since mixing will make the system less ordered).

> *The entropy change for a system undergoing isothermal mixing is always positive.*

Free Energy of Mixing

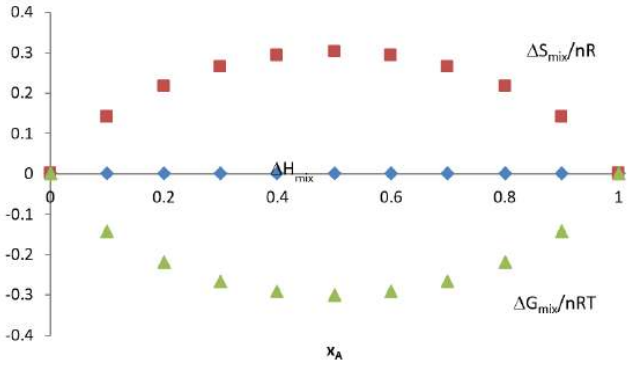
Calculating ΔG_{mix} should be no more difficult than calculating ΔS_{mix}. For *isothermal mixing* and constant total pressure

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

and so it follows from above that for the isothermal mixing of two gases at constant total pressure

$$\Delta G_{mix} = n_{tot} RT \left[-\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B) \right]$$

The relationships describing the isothermal mixing of two ideal gases A and B is summarized in the graph below.



Again, because $\ln(\chi_i) < 0$, then $\Delta G_{mix} < 0$ implying that mixing is **always** a spontaneous process for an *ideal solution*. This is true for gases. But for many combinations of liquids or solids, the strong intermolecular forces may make mixing unfavorable (for example in the case of vegetable oil and water). Also, these interactions may make the volume non-additive as well (as in the case of ethanol and water).

> *Mixing is always a spontaneous process for an ideal solution.*

This page titled 9.1: Thermodynamics of Mixing is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **7.1: Thermodynamics of Mixing** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

9.2: Partial Molar Volume

The **partial molar volume** of compound A in a mixture of A and B can be defined as

$$V_A = \left(\frac{\partial V}{\partial n_A} \right)_{p,T,n_B}$$

Using this definition, a change in volume for the mixture can be described using the total differential of V:

$$dV = \left(\frac{\partial V}{\partial n_A} \right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B} \right)_{p,T,n_A} dn_B$$

or

$$dV = V_a \, dn_A + V_b \, dn_B$$

and integration yields

$$V = \int_0^{n_A} V_a \, dn_A + \int_0^{n_B} V_b \, dn_B$$

$$V = V_a \, n_A + V_b \, n_B$$

This result is important as it demonstrates an important quality of partial molar quantities. Specifically, if ξ_i represents the partial molar property X for component i of a mixture, The total property X for the mixture is given by

$$X = \sum_i \xi_i n_i$$

It should be noted that while the volume of a substance is never negative, the partial molar volume can be. An example of this appears in the dissolution of a strong electrolyte in water. Because the water molecules in the solvation sphere of the ions are physically closer together than they are in bulk pure water, there is a volume decrease when the electrolyte dissolves. This is easily observable at high concentrations where a larger fraction of the water in the sample is tied up in solvation of the ions.

This page titled 9.2: Partial Molar Volume is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **7.2: Partial Molar Volume** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

9.3: Chemical Potential

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:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{p,T,n_{j \neq i}} \tag{9.3.1}$$

This particular 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. And 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. 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 as was done in Chapter 6:

$$dG = Vdp - SdT + \sum_i \mu_i dn_i$$

But as it turns out, the chemical potential can be defined as the partial molar derivative any of the four major thermodynamic functions U, H, A, or G:

Table 9.3.1: 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 9.3.1). 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

$$\int_{\mu^o}^{\mu} d\mu = \int_{p^o}^{p} V \, dp \tag{9.3.2}$$

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 9.3.2 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 a reference pressure (generally the standard pressure of 1 atm) 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 9.3.2 then becomes

$$\int_{\mu^o}^{\mu} d\mu = RTint_{p^o}^{p} \frac{dp}{p} \tag{9.3.3}$$

or

$$\mu = \mu^o + RT \ln\left(\frac{p}{p^o}\right)$$

This page titled 9.3: Chemical Potential is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **7.3: Chemical Potential** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

9.4: The Gibbs-Duhem Equation

For a system at **equilibrium**, the Gibbs-Duhem equation must hold:

$$\sum_i n_i d\mu_i = 0 \tag{9.4.1}$$

This relationship 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,

$$G_{tot} = \sum_i n_i \mu_i$$

Taking the derivative of both sides yields

$$dG_{tot} = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i$$

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

$$\sum_i n_i d\mu_i = Vdp - sdT \tag{9.4.2}$$

For a system at constant temperature and pressure

$$Vdp - sdT = 0 \tag{9.4.3}$$

Substituting Equation 9.4.3 into 9.4.2 results in the **Gibbs-Duhem equation** (Equation 9.4.1). This expression relates how the chemical potential can change for a given composition while the system maintains equilibrium. So for a binary system, consisting of components A and B (the two most often studied compounds in all of chemistry)

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

This page titled 9.4: The Gibbs-Duhem Equation is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **7.4: The Gibbs-Duhem Equation** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

9.5: Non-ideality in Gases - Fugacity

The relationship for chemical potential

$$\mu = \mu^o + RT \ln\left(\frac{p}{p^o}\right)$$

was derived assuming **ideal gas** behavior. But for real gases that deviate widely from ideal behavior, the expression has only limited applicability. In order to use the simple expression on real gases, a "fudge" factor is introduced called **fugacity**. Using fugacity instead of pressure, the chemical potential expression becomes

$$\mu = \mu^o + RT \ln\left(\frac{f}{f^o}\right)$$

where f is the fugacity. Fugacity is related to pressure, but contains all of the deviations from ideality within it. To see how it is related to pressure, consider that a change in chemical potential for a single component system can be expressed as

$$d\mu - V\,dp - S\,dT$$

and so

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V \tag{9.5.1}$$

Differentiating the expression for chemical potential above with respect to pressure at constant volume results in

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \left\{\frac{\partial}{\partial p}\left[\mu^o + RT \ln\left(\frac{f}{f^o}\right)\right]\right\}$$

which simplifies to

$$\left(\frac{\partial \mu}{\partial p}\right)_T = RT\left[\frac{\partial \ln(f)}{\partial p}\right]_T = V$$

Multiplying both sides by p/RT gives

$$\left[\frac{\partial \ln(f)}{\partial p}\right]_T = \frac{pV}{RT} = Z$$

where Z is the compression factor as discussed previously. Now, we can use the expression above to obtain the **fugacity coefficient** γ, as defined by

$$f = \gamma p$$

Taking the natural logarithm of both sides yields

$$\ln f = \ln \gamma + \ln p$$

or

$$\ln \gamma = \ln f - \ln p$$

Using some calculus and substitutions from above,

$$\int \left(\frac{\partial \ln \gamma}{\partial p}\right)_T dp = \int \left(\frac{\partial \ln f}{\partial p} - \frac{\partial \ln p}{\partial p}\right)_T dp$$

$$= \int \left(\frac{Z}{\partial p} - \frac{1}{\partial p}\right)_T dp$$

Finally, integrating from 0 to p yields

$$\ln \gamma = \int_0^p \left(\frac{Z-1}{p}\right)_T dp$$

If the gas behaves ideally, $\gamma = 1$. In general, this will be the limiting value as $p \to 0$ since all gases behave ideal as the pressure approaches 0. The advantage to using the fugacity in this manner is that it allows one to use the expression

$$\mu = \mu^o + RT \ln\left(\frac{f}{f^o}\right)$$

to calculate the chemical potential, insuring that Equation 9.5.1 holds even for gases that deviate from ideal behavior!

This page titled 9.5: Non-ideality in Gases - Fugacity is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **7.5: Non-ideality in Gases - Fugacity** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

9.6: Colligative Properties

Colligative properties are important properties of **solutions** as they describe how the properties of the **solvent** will change as **solute** (or solutes) is (are) added. Before discussing these important properties, let us first review some definitions.

- **Solution** – a homogeneous mixture.
- **Solvent** – The component of a solution with the largest mole fraction
- **Solute** – Any component of a solution that is not the solvent.

Solutions can exist in solid (alloys of metals are an example of solid-phase solutions), liquid, or gaseous forms. For the most part, this discussion will focus on liquid-phase solutions.

Freezing Point Depression

In general (and as will be discussed in Chapter 8 in more detail) a liquid will freeze when

$$\mu_{solid} \leq \mu_{liquid}$$

As such, the freezing point of the solvent in a solution will be affected by anything that changes the chemical potential of the solvent. As it turns out, the chemical potential of the solvent is reduced by the presence of a solute.

In a mixture, the chemical potential of component A can be calculated by

$$\mu_A = \mu_A^o + RT \ln \chi_A \tag{9.6.1}$$

And because χ_A is always less than (or equal to) 1, the chemical potential is always reduced by the addition of another component.

The condition under which the solvent will freeze is

$$\mu_{A,solid} = \mu_{A,liquid}$$

where the chemical potential of the liquid is given by Equation 9.6.1, which rearrangement to

$$\frac{\mu_A - \mu_A^o}{RT} = \ln \chi_A$$

To evaluate the temperature dependence of the chemical potential, it is useful to consider the temperature derivative at constant pressure.

$$\left[\frac{\partial}{\partial T}\left(\frac{\mu_A - \mu_A^o}{RT}\right)\right]_p = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

$$-\frac{\mu_A - \mu_A^o}{RT^2} + \frac{1}{RT}\left[\left(\frac{\partial \mu_A}{\partial T}\right)_p - \left(\frac{\partial \mu_A^o}{\partial T}\right)_p\right] = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p \tag{9.6.2}$$

Recalling that

$$\mu = H = TS$$

and

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S$$

Equation 9.6.2 becomes

$$-\frac{(H_A - TS_A - H_A^o + TS_A^o)}{RT^2} + \frac{1}{RT}\left[-S_A + S_A^o\right] = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p \tag{9.6.3}$$

And noting that in the case of the solvent freezing, H_A^o is the enthalpy of the pure solvent in solid form, and H_A is the enthalpy of the solvent in the liquid solution. So

$$H_A^o - H_a = \Delta H_{fus}$$

Equation 9.6.3 then becomes

$$\frac{\Delta H_{fus}}{RT^2} - \cancel{\frac{-S_A + S_A^o}{RT}} + \cancel{\frac{-S_A + S_A^o}{RT}} = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

or

$$\frac{\Delta H_{fus}}{RT^2} = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

Separating the variables puts the equation into an integrable form.

$$\int_{T^o}^{T} \frac{\Delta H_{fus}}{RT^2} dT = \int d \ln \chi_A \tag{9.6.4}$$

where T^o is the freezing point of the pure solvent and T is the temperature at which the solvent will begin to solidify in the solution. After integration of Equation 9.6.4:

$$-\frac{\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T^o}\right) = \ln \chi_A \tag{9.6.5}$$

This can be simplified further by noting that

$$\frac{1}{T} - \frac{1}{T^o} = \frac{T^o - T}{TT^o} = \frac{\Delta T}{TT^o}$$

where ΔT is the difference between the freezing temperature of the pure solvent and that of the solvent in the solution. Also, for small deviations from the pure freezing point, TT^o can be replaced by the approximate value $(T^o)^2$. So the Equation 9.6.5 becomes

$$-\frac{\Delta H_{fus}}{R(T^o)^2}\Delta T = \ln \chi_A \tag{9.6.6}$$

Further, for dilute solutions, for which χ_A, the mole fraction of the solvent is very nearly 1, then

$$\ln \chi_A \approx -(1 - \chi_A) = -\chi_B$$

where χ_B is the mole fraction of the solute. After a small bit of rearrangement, this results in an expression for freezing point depression of

$$\Delta T = \left(\frac{R(T^o)^2}{\Delta H_{fus}}\right)\chi_B$$

The first factor can be replaced by K_f:

$$\frac{R(T^o)^2}{\Delta H_{fus}} = K_f$$

which is the **cryoscopic constant** for the solvent.

ΔT gives the magnitude of the reduction of freezing point for the solution. Since ΔH_{fus} and T^o are properties of the solvent, the freezing point depression property is independent of the solute and is a property based solely on the nature of the solvent. Further, since χ_B was introduced as $(1 - \chi_A)$, it represents the sum of the mole fractions of all solutes present in the solution.

It is important to keep in mind that for a real solution, freezing of the solvent changes the composition of the solution by decreasing the mole fraction of the solvent and increasing that of the solute. As such, the magnitude of ΔT will change as the freezing process continually removes solvent from the liquid phase of the solution.

Boiling Point Elevation

The derivation of an expression describing boiling point elevation is similar to that for freezing point depression. In short, the introduction of a solute into a liquid solvent lowers the chemical potential of the solvent, cause it to favor the liquid phase over the

vapor phase. As sch, the temperature must be increased to increase the chemical potential of the solvent in the liquid solution until it is equal to that of the vapor-phase solvent. The increase in the boiling point can be expressed as

$$\Delta T = K_b \chi_B$$

where

$$\frac{R(T^o)^2}{\Delta H_{vap}} = K_b$$

is called the **ebullioscopic constant** and, like the cryoscopic constant, is a property of the solvent that is independent of the solute or solutes. A very elegant derivation of the form of the models for freezing point depression and boiling point elevation has been shared by F. E. Schubert (Schubert, 1983).

Cryoscopic and ebullioscopic constants are generally tabulated using molality as the unit of solute concentration rather than mole fraction. In this form, the equation for calculating the magnitude of the freezing point decrease or the boiling point increase is

$$\Delta T = K_f \, m$$

or

$$\Delta T = K_b \, m$$

where m is the concentration of the solute in moles per kg of solvent. Some values of K_f and K_b are shown in the table below.

Substance	K_f (°C kg mol-1)	T_f^o (°C)	K_b (°C kg mol-1)	T_b^o (°C)
Water	1.86	0.0	0.51	100.0
Benzene	5.12	5.5	2.53	80.1
Ethanol	1.99	-114.6	1.22	78.4
CCl_4	29.8	-22.3	5.02	76.8

Example 9.6.1:

The boiling point of a solution of 3.00 g of an unknown compound in 25.0 g of CCl_4 raises the boiling point to 81.5 °C. What is the molar mass of the compound?

Solution

The approach here is to find the number of moles of solute in the solution. First, find the concentration of the solution:

$$(85.5\,^\circ C - 76.8\,^\circ C) = (5.02\,^\circ C\, Kg/mol)\, m$$

$$m = 0.936\, mol/kg$$

Using the number of kg of solvent, one finds the number for moles of solute:

$$\left(0.936\, mol/\ \cancel{kg}\right)(0.02\ \ \cancel{kg}) = 0.0234\, mol$$

The ratio of mass to moles yields the final answer:

$$\frac{3.00\, g}{0.0234} = 128 g/mol$$

Vapor Pressure Lowering

For much the same reason as the lowering of freezing points and the elevation of boiling points for solvents into which a solute has been introduced, the vapor pressure of a volatile solvent will be decreased due to the introduction of a solute. The magnitude of this decrease can be quantified by examining the effect the solute has on the chemical potential of the solvent.

In order to establish equilibrium between the solvent in the solution and the solvent in the vapor phase above the solution, the chemical potentials of the two phases must be equal.

$$\mu_{vapor} = \mu_{solvent}$$

If the solute is not volatile, the vapor will be pure, so (assuming ideal behavior)

$$\mu^o_{vap} + RT \ln \frac{p'}{p^o} = \mu^o_A + RT \ln \chi_A \tag{9.6.7}$$

Where p' is the vapor pressure of the solvent over the solution. Similarly, for the pure solvent in equilibrium with its vapor

$$\mu^o_A = \mu^o_{vap} + RT \ln \frac{p_A}{p^o} \tag{9.6.8}$$

where p^o is the standard pressure of 1 atm, and p_A is the vapor pressure of the pure solvent. Substituting Equation 9.6.8 into Equation 9.6.7 yields

$$\cancel{\mu^o_{vap}} + RT \ln \frac{p'}{p^o} = \left(\cancel{\mu^o_{vap}} + RT \ln \frac{p_A}{p^o} \right) + RT \ln \chi_A$$

The terms for μ^o_{vap} cancel, leaving

$$RT \ln \frac{p'}{p^o} = RT \ln \frac{p_A}{p^o} + RT \ln \chi_A$$

Subtracting $RT \ln(P_A / P^o)$ from both side produces

$$RT \ln \frac{p'}{p^o} - RT \ln \frac{p_A}{p^o} = RT \ln \chi_A$$

which rearranges to

$$RT \ln \frac{p'}{p_A} = RT \ln \chi_A$$

Dividing both sides by RT and then exponentiating yields

$$\frac{p'}{p_A} = \chi_A$$

or

$$p' = \chi_A p_A \tag{9.6.9}$$

This last result is Raoult's Law. A more formal derivation would use the fugacities of the vapor phases, but would look essentially the same. Also, as in the case of freezing point depression and boiling point elevations, this derivation did not rely on the nature of the solute! However, unlike freezing point depression and boiling point elevation, this derivation did not rely on the solute being dilute, so the result should apply the entire range of concentrations of the solution.

Example 9.6.2:

Consider a mixture of two volatile liquids A and B. The vapor pressure of pure A is 150 Torr at some temperature, and that of pure B is 300 Torr at the same temperature. What is the total vapor pressure above a mixture of these compounds with the mole fraction of B of 0.600. What is the mole fraction of B in the vapor that is in equilibrium with the liquid mixture?

Solution

Using Raoult's Law (Equation 9.6.9)

$$p_A = (0.400)(150\,Toor) = 60.0\,Torr$$

$$p_B = (0.600)(300\,Toor) = 180.0\,Torr$$

$$p_{tot} = p_A + p_B = 240\,Torr$$

To get the mole fractions in the gas phase, one can use Dalton's Law of partial pressures.

$$\chi_A = \frac{p_A}{p_{tot}} = \frac{60.0\,Torr}{240\,Torr} = 0.250$$

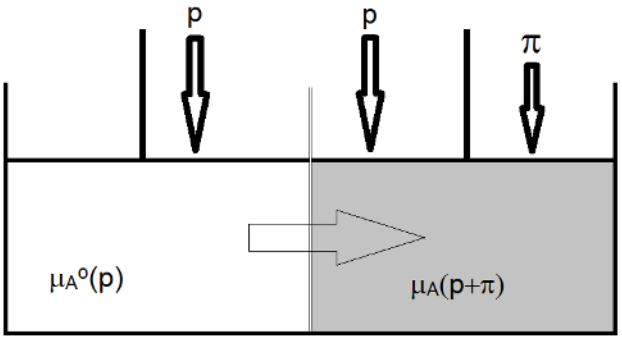
$$\chi_B = \frac{p_B}{p_{tot}} = \frac{180.0\,Torr}{240\,Torr} = 0.750$$

And, of course, it is also useful to note that the sum of the mole fractions is 1 (as it must be!)

$$\chi_A + \chi_B = 1$$

Osmotic Pressure

Osmosis is a process by which solvent can pass through a semi-permeable membrane (a membrane through which solvent can pass, but not solute) from an area of low solute concentration to a region of high solute concentration. The **osmotic pressure** is the pressure that when exerted on the region of high solute concentration will halt the process of osmosis.



The nature of osmosis and the magnitude of the osmotic pressure can be understood by examining the chemical potential of a pure solvent and that of the solvent in a solution. The chemical potential of the solvent in the solution (before any extra pressure is applied) is given by

$$\mu_A = \mu_A^o + RT \ln \chi_A$$

And since $x_A < 1$, the chemical potential is of the solvent in a solution is always lower than that of the pure solvent. So, to prevent osmosis from occurring, something needs to be done to raise the chemical potential of the solvent in the solution. This can be accomplished by applying pressure to the solution. Specifically, the process of osmosis will stop when the chemical potential solvent in the solution is increased to the point of being equal to that of the pure solvent. The criterion, therefore, for osmosis to cease is

$$\mu_A^o(p) = \mu_A(\chi_b, +\pi)$$

To solve the problem to determine the magnitude of p, the pressure dependence of the chemical potential is needed in addition to understanding the effect the solute has on lowering the chemical potential of the solvent in the solution. The magnitude, therefore, of the increase in chemical potential due to the application of excess pressure p must be equal to the magnitude of the reduction of chemical potential by the reduced mole fraction of the solvent in the solution. We already know that the chemical potential of the solvent in the solution is reduced by an amount given by

$$\mu_A^o - \mu_A = RT \ln \chi_A$$

And the increase in chemical potential due to the application of excess pressure is given by

$$\mu(p+\pi) = \mu(p) + \int_p^\pi \left(\frac{\partial \mu}{\partial p}\right)_T dp$$

The integrals on the right can be evaluated by recognizing

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V$$

where V is the molar volume of the substance. Combining these expressions results in

$$-RT \ln \chi_A = \int_p^{p+\pi} V \, dp$$

If the molar volume of the solvent is independent of pressure (has a very small value of κ_T – which is the case for most liquids) the term on the right becomes.

$$\int_p^{\pi} V \, dP = Vp|_p^{p+\pi} = V\pi$$

Also, for values of χ_A very close to 1

$$\ln \chi_A \approx -(1 - \chi_A) = -\chi_B$$

So, for dilute solutions

$$\chi_B RT = V\pi$$

Or after rearrangement

$$\pi \frac{\chi_B RT}{V}$$

again, where V is the molar volume of the solvent. And finally, since χ_B / V is the concentration of the solute B for cases where $n_B \ll n_A$. This allows one to write a simplified version of the expression which can be used in the case of very dilute solutions

$$\pi = [B]RT$$

When a pressure exceeding the osmotic pressure π is applied to the solution, the chemical potential of the solvent in the solution can be made to exceed that of the pure solvent on the other side of the membrane, causing reverse osmosis to occur. This is a very effective method, for example, for recovering pure water from a mixture such as a salt/water solution.

This page titled 9.6: Colligative Properties is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **7.6: Colligative Properties** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

9.7: Solubility

The maximum solubility of a solute can be determined using the same methods we have used to describe colligative properties. The chemical potential of the solute in a liquid solution can be expressed

$$\mu_B(solution) = \mu_B^o(liquid) + RT \ln \chi_B$$

If this chemical potential is lower than that of a pure solid solute, the solute will dissolve into the liquid solvent (in order to achieve a lower chemical potential!) So the point of saturation is reached when the chemical potential of the solute in the solution is equal to that of the pure solid solute.

$$\mu_B^o(solid) = \mu_B^o(liquid) + RT \ln \chi_B$$

Since the mole fraction at saturation is of interest, we can solve for $\ln(\chi_B)$.

$$\ln \chi_B = \frac{\mu_B^o(solid) = \mu_B^o(liquid)}{RT}$$

The difference in the chemical potentials is the molar Gibbs function for the phase change of fusion. So this can be rewritten

$$\ln \chi_B = \frac{-\Delta G_{fus}^o}{RT}$$

It would be convenient if the solubility could be expressed in terms of the enthalpy of fusion for the solute rather than the Gibbs function change. Fortunately, the Gibbs-Helmholtz equation gives us a means of making this change. Noting that

$$\left(\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial T} \right)_p = \frac{\Delta H}{T^2}$$

Differentiation of the above expression for $\ln(\chi_B)$ with respect to T at constant p yields

$$\left(\frac{\partial \ln \chi_B}{\partial T} \right)_p = \frac{1}{R} \frac{\Delta H_{fus}}{T^2}$$

Separating the variables puts this into an integrable form that can be used to see how solubility will vary with temperature:

$$\int_0^{\ln \chi_B} d \ln \chi_B = \frac{1}{R} \int_{T_f}^{T} \frac{\Delta H_{fus} dT}{T^2}$$

So if the enthalpy of fusion is constant over the temperature range of T_f to the temperature of interest,

$$\ln \chi_B = \frac{\Delta H_{fus}}{R} \left(\frac{1}{T_f} - \frac{1}{T} \right)$$

And χ_B will give the mole fraction of the solute in a saturated solution at the temperature T. The value depends on both the enthalpy of fusion, and the normal melting point of the solute.

This page titled 9.7: Solubility is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **7.7: Solubility** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

9.8: Non-ideality in Solutions - Activity

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.

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

$$\gamma_\pm = (\gamma_+^x \gamma_-^y)^{1/x+y}$$

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

$$\log_{10}\gamma_{\pm} = \frac{1.824\times10^{6}}{(\epsilon T)^{3/2}}|z_{+}+z_{-}|\sqrt{I}$$

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 ^{o}C,

This page titled 9.8: Non-ideality in Solutions - Activity is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **7.8: Non-ideality in Solutions - Activity** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

9.9: Prelude to Phase Equilibrium

From the very elementary stages of our journey to describe the physical nature of matter, we learn to classify mater into three (or more) phases: solid, liquid, and gas. This is a fairly easy classification system that can be based on such simple ideas as shape and volume.

Phase	Shape	Volume
Solid	Fixed	Fixed
Liquid	Variable	Fixed
Gas	Variable	Variable

As we have progressed, we have seen that solids and liquids are not completely incompressible as they may have non-zero values of κ_T. And we learn that there are a number of finer points to describing the nature of the phases about which we all learn in grade school. In this chapter, we will employ some of the tools of thermodynamics to explore the nature of phase boundaries and see what we can conclude about them.

This page titled 9.9: Prelude to Phase Equilibrium is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **8.1: Prelude to Phase Equilibrium** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

9.E: Mixtures and Solutions (Exercises)

Q7.1

The compression factor (Z) for O_2 at 200 K is measured to have the following values:

p (atm)	Z
1.000	0.9970
4.000	0.9880
7.000	0.9788
10.000	0.9700

Using numerical integration, calculate the fugacity constant for O_2 at 200 K from these data.

Q7.2

The normal boiling point of ethanol is 78.4 ºC. Its enthalpy of vaporization is 38.6 kJ/mol. Estimate the vapor pressure of ethanol at 24.4 ºC.

Q7.3

When 20.0 grams of an unknown nonelectrolyte compound are dissolved in 500.0 grams of benzene, the freezing point of the resulting solution is 3.77 °C. The freezing point of pure benzene is 5.444 °C and the cryoscopic constant (K_f) for benzene is 5.12 °C/m. What is the molar mass of the unknown compound?

Q7.4

Consider a mixture of two volatile liquids, A and B. The vapor pressure of pure liquid A is 324.3 Torr and that of pure liquid B is 502.3 Torr. What is the total vapor pressure over a mixture of the two liquids for which x_B = 0.675?

Q7.5

Consider the following expression for osmotic pressure

$$\pi V = \chi_B RT \tag{9.E.1}$$

where π is the osmotic pressure, V is the molar volume of the solvent, χ_B is the mole fraction of the solute, R is the gas law constant, and T is the temperature (in Kelvin).

The molar volume of a particular solvent is 0.0180 L/mol. 0.200 g of a solute (B) is dissolved in 1.00 mol of the solvent. The osmotic pressure of the solvent is then measured to be 0.640 atm at 298 K. Calculate the molar mass of the solute.

Q7.6

At 300 K, the vapor pressure of HCl(g) over a solution of HCl in $GeCl_4$ are summarized in the following table. Calculate the Henry's Law constant for HCl based on these data.

χ_{HCl}	P_{HCl} (kPa)
0.005	32.0
0.012	76.9
0.019	121.8

Q7.7

Consider the mixing of 1.00 mol of hexane (C_6H_{12}) with 1.00 mole of benzene (C_6H_6). Calculate \(\Delta H\), \(\Delta S\), and \(\Delta G\) of mixing, of the mixing occurs ideally at 298 K.

Contributors and Attributions

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)

This page titled 9.E: Mixtures and Solutions (Exercises) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

9.E: Phase Equilibrium (Exercises)

This page titled 9.E: Phase Equilibrium (Exercises) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

9.S: Mixtures and Solutions (Summary)

Learning Objectives

After mastering the material in this chapter, one will be able to

1. Describe the thermodynamics of mixing and calculate ΔH, ΔS, and ΔG or mixing for an ideal solution.
2. Define chemical potential, and calculate its value as a function of pressure and composition.
3. Derive expressions for the colligative properties and perform calculations using the relationships.
4. Estimate the maximum solubility of a solute in a solvent based on the concept equality of chemical potential at saturation.
5. Define fugacity and activity.
6. Calculate the mean activity coefficients of ions in solution based on the ionic strength of the solution.

Vocabulary and Concepts

- activity
- activity coefficient
- chemical potential
- cryoscopic constant
- ebullioscopic constant
- enthalpy of mixing
- fugacity
- fugacity coefficient
- Gibbs-Duhem equation
- ideal mixture
- ionic strength
- mean activity coefficient
- osmosis
- osmotic pressure
- Raoult's Law
- solute
- solution
- solvent
- the partial molar Gibbs function

References

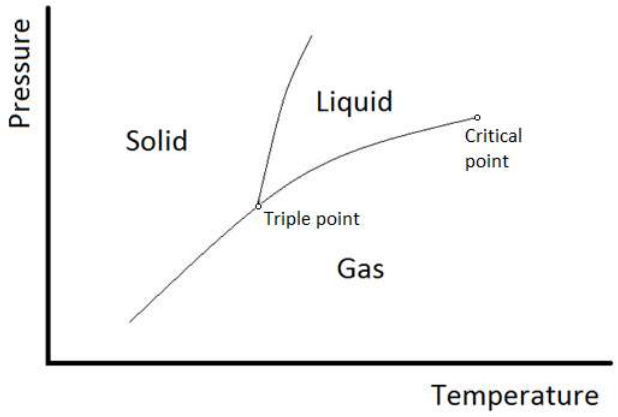
1. Debye, P., & Hückel, E. (1923). Zur Theorie der Electrolyte. *Physikalische Zeitschrift, 24*, 185-206.
2. Schubert, F. E. (1983). Depression of Freezing Point and Elevation of Boiling Point. *Journal of Chemical Education, 60*(1), 88. doi:10.1021/ed060p87.2

This page titled 9.S: Mixtures and Solutions (Summary) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

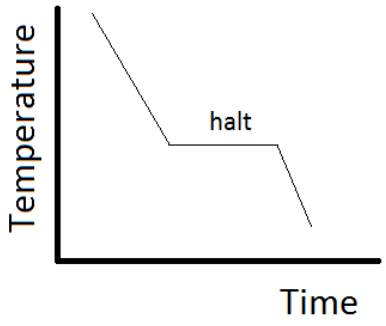
- **7.S: Mixtures and Solutions (Summary)** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

9.10: Single Component Phase Diagrams

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. This can be summarized in a phase diagram like the one shown below.



In this diagram, the phase boundaries can be determined by measuring the rate of cooling at constant temperature. A typical cooling curve is shown below. The temperature will decrease over time as a sample is allowed to cool. When κ_T the substance undergoes a phase change, say from liquid to solid, the temperature will stop changing while heat is extracted due to the phase change. The temperature at which the halt occurs provides one point on the boundary at the temperature of the halt and the pressure at which the cooling curve was measured.



The same data can be obtained by heating the system using a technique such as scanning calorimetry. In this experiment, heat is supplied to a sample at a constant rate, and the temperature of the sample is measured, with breaks occurring at the phase change temperatures.

This page titled 9.10: Single Component Phase Diagrams is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **8.2: Single Component Phase Diagrams** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

9.11: Criterion for Phase Equilibrium

The thermodynamic criterion for phase equilibrium is simple. It is based upon the chemical potentials of the components in a system. For simplicity, consider a system with only one component. For the overall system to be in equilibrium, the chemical potential of the compound in each phase present must be the same. Otherwise, there will be some mass migration from one phase to another, decreasing the total chemical potential of the phase from which material is being removed, and increasing the total chemical potential of the phase into which the material is being deposited. So for each pair of phases present (α and β) the following must be true:

$$\mu_\alpha = \mu_\beta$$

Gibbs Phase Rule

The **Gibbs phase rule** describes the number of compositional and phase variables that can be varied freely for a system at equilibrium. For each phase present in a system, the mole fraction of all but one component can be varied independently. However, the relationship

$$\sum_i \chi_i = 1$$

places a constraint on the last mole fraction. As such, there are $C-1$ compositional degrees of freedom for each phase present, where C is the number of components in the mixture. Similarly, all but one of the chemical potentials of each phase present must be equal, leaving only one that can be varied independently, leading to $P-1$ thermodynamic constraints placed on each component. Finally, there are two state variables that can be varied (such as pressure and temperature), adding two additional degrees of freedom to the system. The net number of degrees of freedom is determined by adding all of the degrees of freedom and subtracting the number of thermodynamic constraints.

$$\begin{aligned} F &= 2 + P(C-1) - C(P-1) \\ &= 2 + PC - P - PC + C \\ &= 2 + C - P \end{aligned} \tag{9.11.1}$$

Equation 9.11.1 is the Gibbs phase rule.

Example 9.11.1:

Show that the maximum number of phases that can co-exist at equilibrium for a single component system is $P = 3$.

Solution

The maximum number of components will occur when the number of degrees of freedom is zero.

$$\begin{aligned} 0 &= 2 + 1 - P \\ P &= 3 \end{aligned}$$

Note: This shows that there can never be a “quadruple point” for a single component system!

Because a system at its triple point has no degrees of freedom, the triple point makes a very convenient physical condition at which to define a temperature. For example, the International Practical Temperature Scale of 1990 (IPT-90) uses the triple points of hydrogen, neon, oxygen, argon, mercury, and water to define several low temperatures. (The calibration of a platinum resistance thermometer at the triple point of argon, for example, is described by Strouse (Strouse, 2008)). The advantage to using a triple point is that the compound sets both the temperature and pressure, rather than forcing the researcher to set a pressure and *then* measure the temperature of a phase change, introducing an extra parameter than can introduce uncertainty into the measurement.

This page titled 9.11: Criterion for Phase Equilibrium is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **8.3: Criterion for Phase Equilibrium** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

9.12: The Clapeyron Equation

Based on the thermodynamic criterion for equilibrium, it is possible to draw some conclusions about the state variables p and T and how they are related along phase boundaries. First, the chemical potentials of the two phases α and β in *equilibrium* with one another must be equal.

$$\mu_\alpha = \mu_\beta \tag{9.12.1}$$

Also, any infinitesimal changes to the chemical potential of one phase must be offset by an infinitesimal change to the chemical potential of the other phase that is equal in magnitude.

$$\mu_\alpha + d\mu_\alpha = \mu_\beta + d\mu_\beta \tag{9.12.2}$$

Taking the difference between these Equations 9.12.1 and 9.12.2 shows that

$$d\mu_\alpha = d\mu_\beta$$

And since $d\mu$ can be expressed in terms of molar volume and molar entropy

$$d\mu = Vdp - SdT$$

It is clear that there will be constraints placed on changes of temperature and pressure while maintaining equilibrium between the phases.

$$V_\alpha dP - S_\alpha dT = V_\beta dP - S_\beta dT$$

Gathering pressure terms on one side and temperature terms on the other

$$(V_\alpha - V_\beta)dP = (S_\alpha - S_\beta)dT$$

The differences $V_\alpha - V_\beta$ and $S_\alpha - S_\beta$ are the changes in molar volume and molar entropy for the phase changes respectively. So the expression can be rewritten

$$\Delta V dp = \Delta S dT$$

or

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} \tag{9.12.3}$$

Equation 9.12.3 is the **Clapeyron equation**. This expression makes it easy to see how the phase diagram for water is qualitatively different than that for most substances. Specifically, the negative slope of the solid-liquid boundary on a pressure-temperature phase diagram for water is very unusual, and arises due to the fact that for water, the molar volume of the liquid phase is smaller than that of the solid phase.

Given that for a phase change

$$\Delta S_{phase} = \frac{\Delta H_{phase}}{T}$$

the Clapeyron equation is sometimes written

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} \tag{9.12.4}$$

Example 9.12.1: Freezing WAter

Calculate the magnitude of the change in freezing point for water ($\Delta H_{fus} = 6.009\, kJ/mol$) and the density of ice is $\rho_{ice} = 0.9167\, g/cm^3$ while that for liquid water is $\rho_{liquid} = 0.9999\, g/cm^3$) for an increase in pressure of $1.00\, atm$ at $273\, K$.

Solution

The molar volume of ice is given by

$$\left(0.9167\ \frac{g}{cm^3}\right)\left(\frac{1\ mol}{18.016\ g}\right)\left(\frac{1000\ cm^3}{1\ L}\right) = 50.88\ \frac{L}{mol}$$

The molar volume of liquid water at 0 °C is given by

$$\left(0.9999\ \frac{g}{cm^3}\right)\left(\frac{1\ mol}{18.016\ g}\right)\left(\frac{1000\ cm^3}{1\ L}\right) = 55.50\ \frac{L}{mol}$$

So ΔV for the phase change of solid $\rightarrow$ liquid (which corresponds to an endothermic change) is

$$50.88\ \frac{L}{mol} - 55.50\ \frac{L}{mol} = -4.62\ \frac{L}{mol}$$

To find the change in temperature, use the *Clapeyron Equation* (Equation 9.12.4) and separating the variables

$$dp = \frac{\Delta H_{fus}}{\Delta V}\frac{dt}{T}$$

Integration (with the assumption that $\Delta H_{fus}/\Delta V$ does not change much over the temperature range) yields

$$\int_{p1}^{p2} dp = \frac{\Delta H_{fus}}{\Delta V}\int_{T1}^{T2}\frac{dt}{T}$$

$$p_2 - p_1 = \Delta p = \frac{\Delta H_{fus}}{\Delta V}\ln\left(\frac{T_2}{T_1}\right)$$

or

$$T_2 = T_1 \exp\left(\frac{\Delta V \Delta p}{\Delta H_{fus}}\right)$$

so

$$T_2 = (273\ K)\exp\left(\frac{(1\ atm)\left(-4.62\ \frac{L}{mol}\right)}{6009\frac{J}{mol}}\underbrace{\left(\frac{8.314\ J}{0.08206\ atm\ L}\right)}_{\text{conversion factor}}\right)$$

$$T_2 = 252.5\ K$$

$$\Delta T = T_2 - T_1 = 252.5\ K - 273\ K = -20.5\ K$$

So the melting point will decrease by 20.5 K. Note that the phase with the smaller molar volume is favored at the higher pressure (as expected from Le Chatelier's principle)!

This page titled 9.12: The Clapeyron Equation is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **8.4: The Clapeyron Equation** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

9.13: The Clausius-Clapeyron Equation

The Clapeyron equation can be developed further for phase equilibria involving the gas phase as one of the phases. This is the case for either sublimation ($\text{solid} \rightarrow \text{gas}$) or vaporization ($\text{liquid} \rightarrow \text{gas}$). In the case of vaporization, the change in molar volume can be expressed

$$\Delta V = V_{gas} - V_{liquid}$$

Since substances undergo a very large increase in molar volume upon vaporization, the molar volume of the condensed phase (liquid in this case) is negligibly small compared to the molar volume of the gas (i.e., $V_{gas} \gg V_{liquid}$). So,

$$\Delta V \approx V_{gas}$$

And if the vapor can be treated as an ideal gas,

$$V_{gas} = \frac{RT}{p}$$

Substitution into the Claperyron equation yields

$$\frac{dp}{dT} = \frac{p\Delta H_{vap}}{RT^2}$$

Separating the variables puts the equation into an integrable form.

$$dp = \frac{p\Delta H_{vap}}{R}\frac{dT}{T^2} \tag{9.13.1}$$

Noting that

$$\frac{dT}{T^2} = -d\left(\frac{1}{T}\right)$$

makes the integration very easy. If the enthalpy of vaporization is *independent* of temperature over the range of conditions,

$$\int_{p_1}^{p_2}\frac{dp}{p} = -\frac{\Delta H_{vap}}{R}\int_{T_1}^{T_2} d\left(\frac{1}{T}\right)$$

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{9.13.2}$$

This is the *Clausius-Clapeyron equation*. It can also be used to describe the boundary between solid and vapor phases by substituting the enthalpy of sublimation (ΔH_{sub})

Example 9.13.1

The vapor pressure of a liquid triples when the temperature is increased from 25 °C to 45 °C. What is the enthalpy of vaporization for the liquid?

Solution

The problem can be solved using the Clausius-Clapeyron equation (Equation 9.13.2). The following values can be used:

$p_2 = 3p_1$	$T_2 = 318\,K$
$p_1 = p_1$	$T_1 = 298\,K$

Substitution into the Clausius-Clapeyron equation yields

$$\ln\left(\frac{3p_1}{p_1}\right) = -\frac{\Delta H_{vap}}{9.314\,\frac{J}{mol\,K}}\left(\frac{1}{318\ K} - \frac{1}{298\ K}\right)$$

$$\Delta H_{vap} = 43280\ \frac{J}{mol} = 43.28\ \frac{kJ}{mol}$$

The Clausius-Clapeyron equation also suggests that a plot of $\ln(p)$ vs. $1/T$ should yield a straight line, the slope of which is $-\Delta H/R$ (provided that ΔH_{vap} is independent of temperature over the range of temperatures involved..

$$\ln(p) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + const.$$

This approach in Example $9.13.1$ is very useful when there are several pairs of measurements of vapor pressure and temperature. Such a plot is shown below for water.

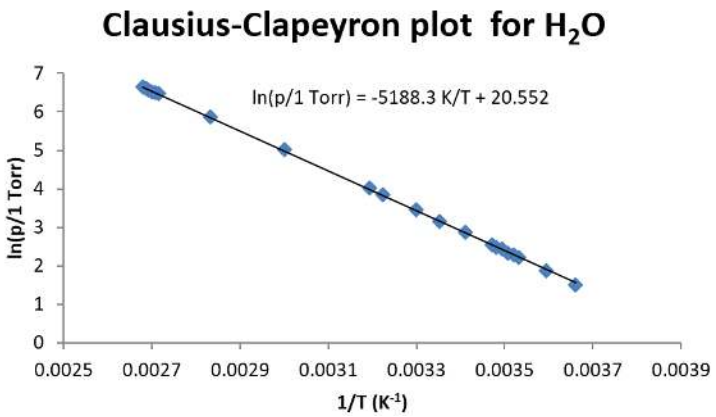


Figure 9.13.1

For water, which has a very large temperature dependence, the linear relationship of $\ln(p)$ vs. $1/T$ holds fairly well over a broad range of temperatures. So even though there is some curvature to the data, a straight line fit still results in a reasonable description of the data (depending, of course, on the precision needed in the experiment.) For this fit of the data, ΔH_{vap} is found to be 43.14 kJ/mol.

Temperature Dependence to ΔH_{vap}

For systems that warrant it, temperature dependence of ΔH_{vap} can be included into the derivation of the model to fit vapor pressure as a function of temperature. For example, if the enthalpy of vaporization is assumed to take the following empirical form

$$\Delta H_{vap} = \Delta H_o + aT + bT^2$$

and substituting it into the differential form of the Clausius-Clapeyron equation (Equation 9.13.1) generates

$$\frac{dp}{p} = \frac{\Delta H_o + aT + bT^2}{R}\frac{dT}{T^2}$$

or

$$\frac{dp}{p} = \frac{\Delta H_o}{R}\frac{dT}{T^2} + \frac{a}{R}\frac{dT}{T} + \frac{b}{R}dT$$

And so the integrated form becomes

$$\ln(p) = -\frac{\Delta H_o}{R}\left(\frac{1}{T}\right) + \frac{a}{R}\ln T + \frac{b}{R}T + constant$$

The results of fitting these data to the temperature dependent model are shown in the table below.

ΔH_0 (J mol^{-1})	a (J mol^{-1} K^{-1})	b (J mol^{-1} K^{-2})	c

ΔH_0 (J mol^{-1})	a (J mol^{-1} K^{-1})	b (J mol^{-1} K^{-2})	c
43080	0.01058	0.000501	20.50

This results in calculated values of ΔH_{vap} of 43.13 kJ/mol at 298 K, and 43.15 kJ/mol at 373 K. The results are a little bit skewed since there is no data above 100 ºC included in the fit. A larger temperature dependence would be found if the higher-temperature data were included in the fit.

This page titled 9.13: The Clausius-Clapeyron Equation is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **8.5: The Clausius-Clapeyron Equation** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

10: Chemical Equilibrium



10.1 hemical Equ
10.2: Chemical Potential
10.3: Activities and Fugacities
10.4: Pressure Dependence of Kp - Le Châtelier's Principle
10.5: Degree of Dissociation
10.6: Temperature Dependence of Equilibrium Constants - the van’t Hoff Equation
10.7: The Dumas Bulb Method for Measuring Decomposition Equilibrium
10.8: Acid-Base Equilibria
10.9: Buffers
10.E: Chemical Equilibria (Exercises)
10.S: Chemical Equilibria (Summary)

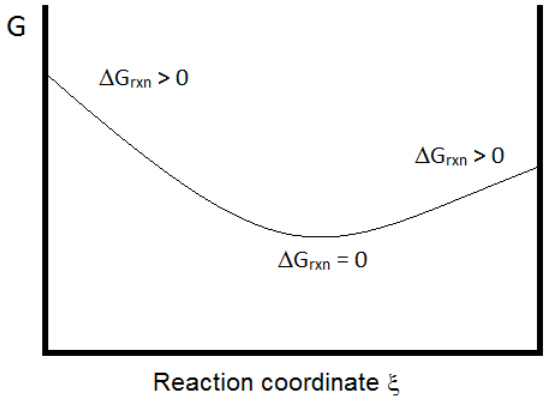
Thumbnail: Image used with permission (L'Aquatique [Public domain])

10: Chemical Equilibrium is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

10.1: Prelude to Chemical Equilibria

> *The small is great, the great is small; all is in equilibrium in necessity... - Victor Hugo in "Les Miserables"*

As was discussed in Chapter 6, the natural tendency of chemical systems is to seek a state of minimum Gibbs function. Once the minimum is achieved, movement in any chemical direction will not be spontaneous. It is at this point that the system achieves a state of equilibrium.



From the diagram above, it should be clear that the direction of spontaneous change is determined by minimizing

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T}.$$

If the slope of the curve is negative, the reaction will favor a shift toward products. And if it is positive, the reaction will favor a shift toward reactants. This is a non-trivial point, as it underscores the importance of the composition of the reaction mixture in the determination of the direction of the reaction.

This page titled 10.1: Prelude to Chemical Equilibria is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **9.1: Prelude to Chemical Equilibria** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

10.2: Chemical Potential

Equilibrium can be understood as accruing at the composition of a reaction mixture at which the aggregate chemical potential of the products is equal to that of the reactants. Consider the simple reaction

$$A(g) \rightleftharpoons B(g)$$

The criterion for equilibrium will be

$$\mu_A = \mu_B$$

If the gases behave ideally, the chemical potentials can be described in terms of the mole fractions of A and B

$$\mu_A^o + RT \ln\left(\frac{p_A}{p_{tot}}\right) = \mu_B^o + RT \ln\left(\frac{p_B}{p_{tot}}\right) \tag{10.2.1}$$

where Dalton's Law has been used to express the mole fractions.

$$\chi_i = \frac{p_i}{p_{tot}}$$

Equation 10.2.1 can be simplified by collecting all chemical potentials terms on the left

$$\mu_A^o - \mu_B^o = RT \ln\left(\frac{p_B}{p_{tot}}\right) - RT \ln\left(\frac{p_A}{p_{tot}}\right) \tag{10.2.2}$$

Combining the logarithms terms and recognizing that

$$\mu_A^o - \mu_B^o - \Delta G^o$$

for the reaction, one obtains

$$-\Delta G^o = RT \ln\left(\frac{p_B}{p_A}\right)$$

And since $p_A / p_B = K_p$ for this reaction (assuming perfectly ideal behavior), one can write

$$\Delta G^o = RT \ln K_p$$

Another way to achieve this result is to consider the Gibbs function change for a reaction mixture in terms of the **reaction quotient**. The reaction quotient can be expressed as

$$Q_p = \frac{\prod_i p_i^{\nu_i}}{\prod_j p_j^{\nu_j}}$$

where ν_i are the stoichiometric coefficients for the products, and ν_j are those for the reactants. Or if the stoichiometric coefficients are defined by expressing the reaction as a sum

$$0 = \sum_i \nu_i X_i$$

where X_i refers to one of the species in the reaction, and ν_i is then the stoichiometric coefficient for that species, it is clear that ν_i will be negative for a reactant (since its concentration or partial pressure will reduce as the reaction moves forward) and positive for a product (since the concentration or partial pressure will be increasing.) If the stoichiometric coefficients are expressed in this way, the expression for the reaction quotient becomes

$$Q_p = \prod_i p_i^{\nu_i}$$

Using this expression, the Gibbs function change for the system can be calculated from

$$\Delta G = \Delta G^o + RT \ln Q_p$$

And since at equilibrium

$$\Delta G = 0$$

and

$$Q_p = K_p$$

It is evident that

$$\Delta G^o_{rxn} = -RT \ln K_p \tag{10.2.3}$$

It is in this simple way that K_p and ΔG^o are related.

It is also of value to note that the criterion for a spontaneous chemical process is that $\Delta G_{rxn} < 0$, rather than ΔG^o_{rxn}, as is stated in many texts! Recall that ΔG^o_{rxn} is a function of all of the reactants and products being in their standard states of unit fugacity or activity. However, the direction of spontaneous change for a chemical reaction is dependent on the composition of the reaction mixture. Similarly, the magnitude of the equilibrium constant is insufficient to determine whether a reaction will spontaneously form reactants or products, as the direction the reaction will shift is also a function of not just the equilibrium constant, but also the composition of the reaction mixture!

Example 10.2.1:

Based on the data below at 298 K, calculate the value of the equilibrium constant (K_p) for the reaction

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

	$NO(g)$	$NO_2(g)$
G^o_f (kJ/mol)	86.55	51.53

Solution

First calculate the value of ΔG^o_{rxn} from the ΔG^o_f data.

$$\Delta G^o_{rxn} = 2 \times (51.53\ kJ/mol) - 2 \times (86.55\ kJ/mol) = -70.04\ kJ/mol$$

And now use the value to calculate K_p using Equation 10.2.3.

$$-70040\ J/mol = -(8.314 J/(mol\ K)(298\ K) \ln K_p$$

$$K_p = 1.89 \times 10^{12}$$

Note: as expected for a reaction with a very large negative ΔG^o_{rxn}, the equilibrium constant is **very** large, favoring the formation of the products.

This page titled 10.2: Chemical Potential is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **9.2: Chemical Potential** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

10.3: Activities and Fugacities

To this point, we have mostly ignored deviations from ideal behavior. But it should be noted that thermodynamic equilibrium constants are not expressed in terms of concentrations or pressures, but rather in terms of activities and fugacities (both being discussed in Chapter 7). Based on these quantities,

$$K_p = \prod_i f_i^{\nu_i} \tag{10.3.1}$$

and

$$K_c = \prod_i a_i^{\nu_i}$$

And since activities and fugacities are unitless, thermodynamic equilibrium constants are unitless as well. Further, it can be noted that the activities of solids and pure liquids are unity (assuming ideal behavior) since they are in their standard states at the given temperature. As such, these species never change the magnitude of the equilibrium constant and are generally omitted from the equilibrium constant expression.

> *Thermodynamic equilibrium constants are unitless.*

K_p and K_c

Oftentimes it is desirable to express the equilibrium constant in terms of concentrations (or activities for systems that deviate from ideal behavior.) To make this conversion, the relationship between pressure and concentration from the ideal gas law can be used.

$$p = RT\left(\frac{n}{V}\right)$$

And noting that the concentration is given by (n/V), the expression for the equilibrium constant (Equation 10.3.1) becomes

$$K_p = \prod_i (RT[X_i])^{\nu_i} \tag{10.3.2}$$

And since for a given temperature, RT is a constant and can be factored out of the expression, leaving

$$K_p = \left(\prod_i (RT)^{\nu_i}\right)\left(\prod_i [X_i]^{\nu_i}\right) \tag{10.3.3}$$

$$= (RT)^{\sum \nu_i} \prod [X_i]^{\nu_i} \tag{10.3.4}$$

$$= (RT)^{\sum \nu_i} K_c \tag{10.3.5}$$

This conversion works for reactions in which all reactants and products are in the gas phase. Care must be used when applying this relationship to heterogeneous equilibria.

This page titled 10.3: Activities and Fugacities is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **9.3: Activities and Fugacities** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

10.4: Pressure Dependence of Kp - Le Châtelier's Principle

Since the equilibrium constant K_p is a function of ΔG^o_{rxn} which is defined for a specific composition (all reactants in their standard states and at unit pressure (or fugacity), changes in pressure have no effect on equilibrium constants for a fixed temperature. However, changes in pressure can have profound effects on the compositions of equilibrium mixtures.

To demonstrate the relationship, one must recall Dalton's law of partial pressures. According to this relationship, the partial pressure of a component of a gas-phase mixture can be expressed

$$p_i = \chi_t p_{tot}$$

It is the combination of mole fractions that describes the composition of the equilibrium mixture.

Substituting the above expression into the expression for K_p yields

$$K_p = \prod_i (\chi_i p_{tot})^{\nu_i}$$

This expression can be factored into two pieces – one containing the mole fractions and thus describing the composition, and one containing the total pressure.

$$K_p = \left(\prod_i \chi_i^{\nu_i}\right)\left(\prod_i p_{tot}^{\nu_i}\right)$$

The second factor is a constant for a given total pressure. If the first term is given the symbol K_x, the expression becomes

$$K_p = K_x (p_{tot})^{\sum_i \nu_i}$$

In this expression, K_x has the same form as an equilibrium constant

$$K_x = \prod \chi_i^{\sum_i \nu_i}$$

but is not itself a constant. The value ofK_x will vary with varying composition, and will *need* to vary with varying total pressure (in most cases) in order to maintain a constant value of K_p.

Example 10.4.1:

Consider the following reaction at equilibrium.

$$A(g) + 2B(g) \rightleftharpoons C(g) + D(g)$$

In which direction will the equilibrium shift if the volume of the reaction vessel is decreased?

Solution

A decrease in the volume will lead to an increase in total pressure. Since the equilibrium constant can be expressed as

$$K_p = \frac{p_C p_D}{p_A p_B^2} = \frac{\chi_p \chi_D}{\chi_A \chi_B^2}(p_{tot})^{-1}$$

An increase in pressure will lead to an increase in K_x to maintain a constant value of K_p. So the reaction will shift to form more of the products C and D.

Note: This should make some sense, since a shift to the side of the reaction with fewer moles of gas will lower the total pressure of the reaction mixture, and thus relieving the stress introduced by increasing the pressure. This is exactly what is expected according to Le Chatelier's principle.

It should be noted that there are several ways one can affect the total pressure of a gas-phase equilibrium. These include the introduction or removal of reactants or products (perhaps through condensation or some other physical process), a change in volume of the reaction vessel, or the introduction of an inert gas that does not participate in the reaction itself. (Changes in the temperature will be discussed in a later section.) The principle of Le Chatelier's can be used as a guide to predict how the equilibrium composition will respond to a change in pressure.

> *Le Chatelier's principle: When a stress is introduced to a system at equilibrium, the system will adjust so as to reduce the stress.*

Le Chatlier's principle is fairly clear on how to think about the addition or removal of reactants or products. For example, the addition of a reactant will cause the system to shift to reduce the partial pressure of the reactant. It can do this by forming more products.

An important exception to the rule that increasing the total pressure will cause a shift in the reaction favoring the side with fewer moles of gas occurs when the total pressure is increased by introducing an inert gas to the mixture. The reason is that the introduction of an inert gas will affect the total pressures *and* the partial pressures of each individual species.

Example 10.4.2:

A 1.0 L vessel is charged with 1.00 atm of A, and the following reaction is allowed to come to equilibrium at 298 K.

$$A(g) \rightleftharpoons 2B(g)$$

with $K_p = 3.10$.

a. What are the equilibrium partial pressures and mole fractions of A and B?
b. If the volume of the container is doubled, what are the equilibrium partial pressures and mole fractions of A and B?
c. If 1.000 atm of Ar (an inert gas) is introduced into the system described in b), what are the equilibrium partial pressures and mole fractions of A and B once equilibrium is reestablished?

Solution

Part a:

First, we can use an ICE[1] table to solve part a).

	A	2 B
Initial	1.00 atm	0
Change	-x	+2x
Equilibrium	1.00 atm - x	2x

So (for convenience, consider K_p to have units of atm)

$$3.10\,atm = \frac{(2x)^2}{1.00\,atm - x}$$

Solving for x yields values of

$$x_1 = -1.349\,atm$$

$$x_1 = 0.574\,atm$$

Clearly, x_1, while a solution to the mathematical problem, is not physically meaningful since the equilibrium pressure of B cannot be negative. So the equilibrium partial pressures are given by

$$p_A = 1.00\,atm - 0.574\,atm = 0.426\,atm$$

$$p_B = 2(0.574\,atm) = 1.148\,atm$$

So the mole fractions are given by

$$chi_A = \frac{0.426\,atm}{0.426\,atm + 1.148\,atm} = 0.271$$

$$\chi_B = 1 - \chi_A = 1 - 0.271 = 0.729$$

Part b:

The volume is doubled. Again, an ICE table is useful. The initial pressures will be half of the equilibrium pressures found in part a).

	A	2 B
Initial	0.213 atm	0.574 atm
Change	-x	+2x
Equilibrium	0.213 atm - x	0.574 atm + 2x

So the new equilibrium pressures can be found from

$$3.10\,atm = \frac{(0.574\,atm + 2x)^2}{0.213\,atm - x}$$

And the values of x that solve the problem are

$$x_1 = -1.4077\,atm$$

$$x_1 = 0.05875\,atm$$

We reject the negative root (since it would cause both of the partial pressures to become negative. So the new equilibrium partial pressures are

$$p_A = 0.154\,atm$$

$$p_B = 0.0692\,atm$$

And the mole fractions are

$$\chi_A = 0.182$$

$$\chi_B = 0.818$$

We can see that the mole fraction of A decreased and the mole fraction B increased. This is the result expected by Le Chatlier's principle since the lower total pressure favors the side of the reaction with more moles of gas.

Part c:

We introduce 1.000 atm of an inert gas. The new partial pressures are

$$p_A = 0.154\,atm$$

$$p_B = 0.692\,atm$$

$$p_{Ar} = 1.000\,atm$$

And because the partial pressures of A and B are unaffected, the equilibrium does not shift! What *is* affected is the composition, and so the mole fractions will change.

$$\chi_A = \frac{0.154\,atm}{0.154atm + 0.692\,atm + 1.000\,atm} = 0.08341$$

$$\chi_B = \frac{0.692\,atm}{0.154atm + 0.692\,atm + 1.000\,atm} = 0.08341$$

$$\chi_{Ar} = \frac{1.000\,atm}{0.154atm + 0.692\,atm + 1.000\,atm} = 0.08341$$

And since

$$K_p = K_x(p_{tot})$$

$$\frac{(0.3749)^2}{0.08342}(1.846\,atm) = 3.1$$

> Within round-off error, the value obtained is the equilibrium constant. So the conclusion is that the introduction of an inert gas, even though it increases the total pressure, does not induce a change in the partial pressures of the reactants and products, so it does not cause the equilibrium to shift.

---

[1] ICE is an acronym for “Initial, Change, Equilibrium”. An ICE table is a tool that is used to solve equilibrium problems in terms of an unknown number of moles (or something proportional to moles, such as pressure or concentration) will shift for a system to establish equilibrium. See (Tro, 2014) or a similar General Chemistry text for more background and information.

This page titled 10.4: Pressure Dependence of Kp - Le Châtelier's Principle is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **9.4: Pressure Dependence of Kp - Le Châtelier's Principle** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

10.5: Degree of Dissociation

Reactions such as the one in the previous example involve the dissociation of a molecule. Such reactions can be easily described in terms of the fraction of reactant molecules that actually dissociate to achieve equilibrium in a sample. This fraction is called the **degree of dissociation**. For the reaction in the previous example

$$A(g) \rightleftharpoons 2B(g)$$

the degree of dissociation can be used to fill out an ICE table. If the reaction is started with n moles of A, and a is the fraction of A molecules that dissociate, the ICE table will look as follows.

	A	$2B$
Initial	n	0
Change	$-\alpha n$	$+2n\alpha$
Equilibrium	$n(1-\alpha)$	$2n\alpha$

The mole fractions of A and B can then be expressed by

$$\chi_A = \frac{n(1-\alpha)}{n(1-\alpha)+2n\alpha}$$
$$= \frac{1-\alpha}{1+\alpha}$$
$$\chi_B = \frac{2\alpha}{1+\alpha}$$

Based on these mole fractions

$$K_x = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2}{\frac{1-\alpha}{1+\alpha}} \tag{10.5.1}$$
$$= \frac{4\alpha^2}{1-\alpha^2} \tag{10.5.2}$$

And so K_p, which can be expressed as

$$K_p = K_x(p_{tot})^{\sum \nu_i} \tag{10.5.3}$$

is given by

$$K_p = \frac{4\alpha^2}{(1-\alpha^2)}(p_{tot})$$

Example 10.5.1

Based on the values given below, find the equilibrium constant at 25 °C and degree of dissociation for a system that is at a total pressure of 1.00 atm for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

	$N_2O_4(g)$	$NO_2(g)$
ΔG_f^o (kJ/mol)	99.8	51.3

Solution

First, the value of K_p can be determined from ΔG^o_{rxn} via an application of Hess' Law.

$$\Delta G^o_{rxn} = 2\,(51.3\,kJ/mol) - 99.8\,kJ/mol \qquad = 2.8\,kJ/mol$$

So, using the relationship between thermodynamics and equilibria

$$\Delta G^o_f = -RT \ln K_p$$

$$2800\,kJ/mol = -(8.314 J/(mol\,K)(298\,K) \ln K_p$$

$$K_p = 0.323\,atm$$

The degree of dissociation can then be calculated from the ICE tables at the top of the page for the dissociation of $N_2O_4(g)$:

$$K_p = \frac{4\alpha^2}{1-\alpha^2}(p_{tot})$$

$$0.323\,atm = \frac{4\alpha^2}{1-\alpha^2}(1.00\,atm)$$

Solving for α,

$$\alpha = 0.273$$

Note: since a represents the fraction of N_2O_4 molecules dissociated, it **must** be a positive number between 0 and 1.

Example 10.5.2

Consider the gas-phase reaction

$$A + 2B \rightleftharpoons 2C$$

A reaction vessel is initially filled with 1.00 mol of A and 2.00 mol of B. At equilibrium, the vessel contains 0.60 mol C and a total pressure of 0.890 atm at 1350 K.

1. How many mol of A and B are present at equilibrium?
2. What is the mole fraction of A, B, and C at equilibrium?
3. Find values for K_x, K_p, and ΔG^o_{rxn}.

Solution

Let's build an ICE table!

	A	2 B	2 C
Initial	1.00 mol	2.00 mol	0
Change	-x	-2x	+2x
Equilibrium	1.00 mol - x	2.00 mol – 2x	2x = 0.60 mol

From the equilibrium measurement of the number of moles of C, x = 0.30 mol. So at equilibrium,

	A	2 B	2 C
Equilibrium	0.70 mol	1.40 mol	0.60 mol

The total number of moles at equilibrium is 2.70 mol. From these data, the mole fractions can be determined.

$$\chi_A = \frac{0.70\,mol}{2.70\,mol} = 0.259$$

$$\chi_B = \frac{1.40\,mol}{2.70\,mol} = 0.519$$

$$\chi_C = \frac{0.60\,mol}{2.70\,mol} = 0.222$$

So K_x is given by

$$K_x = \frac{(0.222)^2}{(0.259)(0.519)^2} = 0.7064$$

And K_p is given by Equation 10.5.3, so

$$K_p = 0.7604(0.890\,atm)^{-1} = 0.792\,atm^{-1}$$

The thermodynamic equilibrium constant is unitless, of course, since the pressures are all divided by 1 atm. So the actual value of K_p is 0.794. This value can be used to calculate ΔG^o_{rxn} using

$$\Delta G^o_{rxn} = -RT \ln K_p$$

so

$$\begin{aligned}\Delta G^o_{rxn} &= -(8.314\,J/(mol\,K))(1350\,K)\ln(0.792) \\ &= 2590\,J/mol\end{aligned}$$

This page titled 10.5: Degree of Dissociation is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **9.5: Degree of Dissociation** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

10.6: Temperature Dependence of Equilibrium Constants - the van't Hoff Equation

The value of K_p is independent of pressure, although the composition of a system at equilibrium may be very much dependent on pressure. Temperature dependence is another matter. Because the value of ΔG^o_{rxn} is dependent on temperature, the value of K_p is as well. The form of the temperature dependence can be taken from the definition of the Gibbs function. At constant temperature and pressure

$$\frac{\Delta G^o_{T_2}}{T_2} - \frac{\Delta G^o_{T_1}}{T_1} = \Delta H^o \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Substituting

$$\Delta G^o = -RT \ln K$$

For the two values of ΔG^o and using the appropriate temperatures, yields

$$\frac{-RT_2 \ln K_2}{T_2} - \frac{-RT_1 \ln K_1}{T_1} = \Delta H^o \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

And simplifying the expression so that only terms involving K are on the left and all other terms are on the right results in the **van 't Hoff equation**, which describes the temperature dependence of the equilibrium constant.

$$\ln\left(\frac{K_2}{K_1} \right) = -\frac{\Delta H^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{10.6.1}$$

Because of the assumptions made in the derivation of the Gibbs-Helmholtz equation, this relationship only holds if ΔH^o is independent of temperature over the range being considered. This expression also suggests that a plot of $\ln(K)$ as a function of $1/T$ should produce a straight line with a slope equal to $-\Delta H^o/R$. Such a plot is known as a **van 't Hoff plot**, and can be used to determine the reaction enthalpy.

Example 10.6.1

A certain reaction has a value of $K_p = 0.0260$ at 25 °C and $\Delta H^o_{rxn} = 32.4\ kJ/mol$. Calculate the value of K_p at 37 °C.

Solution

This is a job for the van 't Hoff equation!

- T_1 = 298 K
- T_2 = 310 K
- $\Delta H^o_{rxn} = 32.4\ kJ/mol$
- K_1 = 0.0260
- K_2 = ?

So Equation 10.6.1 becomes

$$\ln\left(\frac{K_2}{0.0260} \right) = -\frac{32400\ J/mol}{8.314\ K/(mol\ K)} \left(\frac{1}{310\ K} - \frac{1}{298\ K} \right)$$

$$K_2 = 0.0431$$

Note: the value of K_2 **increased** with **increasing** temperature, which is what is expected for an **endothermic** reaction. An increase in temperature should result in an increase of product formation in the equilibrium mixture. But unlike a change in pressure, a change in temperature actually leads to a change in the value of the equilibrium constant!

Example 10.6.2

Given the following average bond enthalpies for $\mathrm{P-Cl}$ and $\mathrm{Cl-Cl}$ bonds, predict whether or not an increase in temperature will lead to a larger or smaller degree of dissociation for the reaction

$$\mathrm{PCl_5 \rightleftharpoons PCl_3 + Cl_2}$$

X-Y	D(X-Y) (kJ/mol)
P-Cl	326
Cl-Cl	240

Solution

The estimated reaction enthalpy is given by the total energy expended breaking bonds minus the energy recovered by the formation of bonds. Since this reaction involves breaking two P-Cl bonds (costing 652 kJ/mol) and the formation of one Cl-Cl bond (recovering 240 kJ/mol), it is clear that the reaction is endothermic (by approximately 412 kJ/mol). As such, an increase in temperature should increase the value of the equilibrium constant, causing the degree of dissociation to be increased at the higher temperature.

This page titled 10.6: Temperature Dependence of Equilibrium Constants - the van't Hoff Equation is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **9.6: Temperature Dependence of Equilibrium Constants - the van 't Hoff Equation** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

10.7: The Dumas Bulb Method for Measuring Decomposition Equilibrium

A classic example of an experiment that is employed in many physical chemistry laboratory courses uses a Dumas Bulb method to measure the dissociation of N_2O_4(g) as a function of temperature (Mack & France, 1934). In this experiment, a glass bulb is used to create a constant volume container in which a volatile substance can evaporate, or achieve equilibrium with other gases present. The latter is of interest in the case of the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \tag{10.7.1}$$

The reaction is endothermic, so at higher temperatures, a larger degree of dissociation is observed.

The procedure is to first calibrate the internal volume of the Dumas bulb. This is done using a heavy gas (such as SF_6) and comparing the mass of the bulb when evacuated to the mass of the bulb full of the calibrant gas at a particular pressure and temperature.

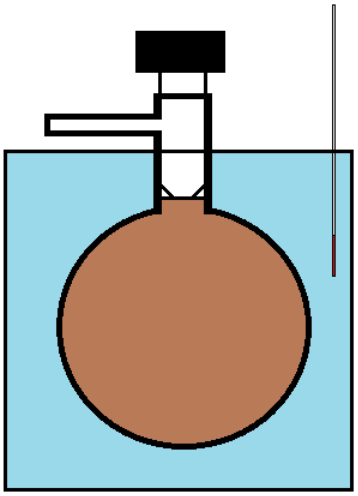


Figure 10.7.1:

The Dumas bulb is then charged with a pure sample of the gas to be investigated (such as N_2O_4) and placed in a thermalized bath. It is then allowed to come to equilibrium. Once Equilibrium is established, the stopcock is opened to allow gas to escape until the internal pressure is set to the pressure of the room. The stopcock is then closed and the bulb weighed to determine the total mass of gas remaining inside. The experiment is repeated at higher and higher temperatures (so that at each subsequent measurement, the larger degree of dissociation creates more molecules of gas and an increase in pressure in the bulb (along with the higher temperature), which then leads to the expulsion of gas when the pressure is equilibrated.

The degree of dissociation is then determined based on the calculated gas density at each temperature.

$$\alpha = \frac{\rho_1 - \rho_2}{\rho_2(n-1)}$$

where ρ_1 is the measured density and ρ_2 is the theoretical density if no dissociation occurs (calculated from the ideal gas law for the given temperature, pressure, and molar mass of the dissociating gas) and n is the number of fragments into which the dissociating gas dissociates (ie.g., $n = 2$ for Equation \req{eq1}). The equilibrium constant is then calculated as

$$K = \frac{4\alpha^2}{1-\alpha^2}\left(\frac{p}{1.00\,atm}\right)$$

Finally, a van't Hoff plot is generated to determine the reaction enthalpy.

This page titled 10.7: The Dumas Bulb Method for Measuring Decomposition Equilibrium is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **9.7: The Dumas Bulb Method for Measuring Decomposition Equilibrium** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

10.8: Acid-Base Equilibria

A great many processes involve proton transfer, or acid-base types of reactions. As many biological systems depend on carefully controlled pH, these types of processes are extremely important. The pH is defined by

$$pH \equiv -\log a(\mathrm{H}^+) \approx -\log[\mathrm{H}^+] \tag{10.8.1}$$

where a is the activity of hydronium ions and $[\mathrm{H}^+]$ is the true concentration of hydronium ions (both in mol/L).

The dissociation of a weak acid in water is governed by the equilibrium defined by

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

The equilibrium constant for such a reaction, K_a, takes the form

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{10.8.2}$$

As is the case for all thermodynamic equilibrium constants, the concentrations are replaced by activities and the equilibrium constant is unitless. However, if all species behave ideally (have unit activity coefficients) the units can be used as a very useful guide in solving problems.

Example 10.8.1: Acetic Acid

What is the pH of a 0.200 M HOAc (acetic acid) solution? (K_a = 1.8 x 10^{-5} M)

Solution

An ICE table will come in very handy here!

	$[HOAc]$	$[H^+]$	$[OAc^-]$
Initial	0.200 M	0	0
Change	-x	+x	+x
Equilibrium	0.200 M - x	x	x

The equilibrium problem can then be set up as

$$K_a = \frac{[H^+][OAc^-]}{[HOAc]}$$

Substituting the values that are known

$$1.8 \times 10^{-5} = \frac{x^2}{0.200\,M - x}$$

This produces a quadratic equation, and thus two values of x which satisfy the relationship.

$$x_1 = -0.001906\,M$$

$$x_2 = 0.001888\,M$$

The negative root is not physically meaningful since the concentrations of H^+ and OAc^- cannot be negative. Using the value of x_2 as $[H^+]$, the pH is then calculated (via Equation 10.8.1) to be

$$pH \approx -\log_{10}(0.001888) = 2.72$$

The Auto-ionization of Water

Water is a very important solvent as water molecules have large dipole moments which create favorable interactions with ionic compounds. Water also has a large dielectric constant which damps the electric field generated by ions in solutions, making the

comparative interactions with water more favorable than with other ions in solution in many cases. But water also dissociates into ions through the reaction

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \tag{10.8.3}$$

The equilibrium constant governing this dissociation is highly temperature dependent. The data below are presented by Bandura and Lvov (Bandura & Lvov, 2006)

T (°C)	0	25	50	75	100
pK_w	14.95	13.99	13.26	12.70	12.25

From these data, a van't Hoff plot can be constructed.

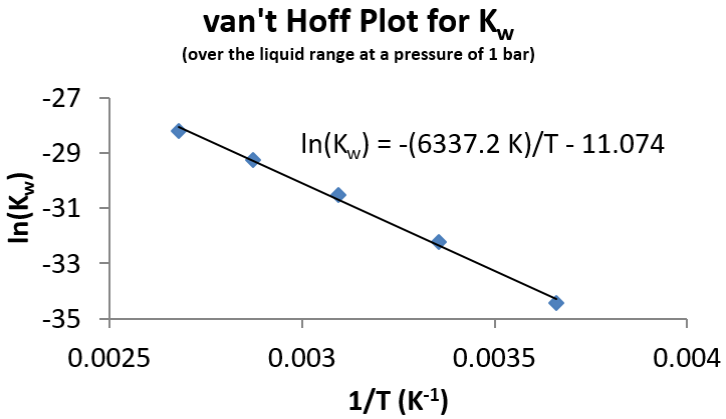


Figure 10.8.1: van't Hoff plot for the autoionization of water.

There is some curvature to the line, suggesting some (albeit small) temperature dependence for ΔH_{rxn} for Equation 10.8.3. However, from the fit of these data, a value of ΔH_{rxn} can be determined to be 52.7 kJ/mol. Of particular note is that the dissociation is **endothermic**, so increases in temperature will lead to a greater degree of dissociation.

Example 10.8.2: Neutral Water

What is the pH of neutral water at 37 °C (normal human body temperature)? Neutral water no excess of $[H^+]$ over $[OH^-]$ or vice versa.

Solution

From the best-fit line in the van't Hoff plot of Figure 10.8.1, the value of K_w can be calculated:

$$\ln(K_w) = -\frac{6338\ K}{310\ K} - 11.04$$

$$K_w = 2.12 \times 10^{-14}\ M^2$$

Since K_w gives the product of $[H^+]$ and $[OH^-]$ (which must be equal in a neutral solution),

$$H^+] = \sqrt{2.12 \times 10^{-14}\ M^2} = 1.456 \times 10^{-7}\ M$$

And the pH is given by (Equation 10.8.1):

$$pH = -\log_{10}(1.456 \times 10^{-7}) = 6.84$$

Note: This is slightly less than a pH of 7.00, which is normally considered to be "neutral." But a pH of 7.00 is only neutral at 25 °C! At higher temperatures, neutral pH is a lower value due to the endothermic nature of the auto-ionization water. While it has a nigher $[H^+]$ concentration, it also has a higher $[OH^-]$ and at the same level, so it is still technically neutral.

The Hydrolysis of a Weak Base

Hydrolysis is defined as a reaction with water that splits a water molecule. The hydrolysis of a weak base defines the equilibrium constant K_b.

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

For this reaction, the equilibrium constant K_b is given by

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

The concentration (or activity) of the pure compound H_2O is not included in the equilibrium expression because, being a pure compound in its standard state, it has unit activity throughout the process of establishing equilibrium. Further, it should be noted that when K_b is combined with the expression for K_a for the weak acid HA (Equation 10.8.2),

$$K_aK_b = \left(\frac{[H^+][A^-]}{[HA]}\right)\left(\frac{[HA][OH^-]}{[A^-]}\right) = [H^+][OH^-] = K_w$$

As a consequence, if one knows K_a for a weak acid, one also knows K_b for its conjugate base, since the product results in K_w.

Example 10.8.3:

What is the pH of a 0.150 M solution of KF? (For HF, pK_a = 3.17 at 25 °C)

Solution

The problem involves the hydrolysis of the conjugate base of HF, F^-. The hydrolysis reaction is

$$F^- + H_2O \rightleftharpoons HF + OH^-$$

An ICE table is in order here.

	F^-	HF	OH^-
Initial	0.150 M	0	0
Change	-x	+x	+x
Equilibrium	0.150 M - x	x	x

So the expression for K_b is

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14} M^2}{10^{3.17} M} = \frac{x^2}{1.50\,M - x}$$

In this case, the small value of K_b insures that the value of x will be negligibly small compared to 0.150 M. In this limit, the value of x (which is equal to $[OH^-]$)

$$x = [OH^-] = 1.49 \times 10^{-6}\ M$$

So $[H^+]$ is given by

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14} M^2}{1.49 \times 10^{-6} M} = 6.71 \times 10^{-9}\ M$$

And the pH is given by (Equation 10.8.1):

$$pH = -\log_{10}(6.71 \times 10^{-9}) = 8.17$$

Note: The pH of this salt solution is slightly basic. This is to be expected as KF can be thought of being formed in the reaction of a weak acid (HF) with a strong base (KOH). In the competition to control the pH, the strong base ends up winning the battle.

This page titled 10.8: Acid-Base Equilibria is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **9.8: Acid-Base Equilibria** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

10.9: Buffers

Buffer solutions, which are of enormous importance in controlling pH in various processes, can be understood in terms of acid/base equilibrium. A buffer is created in a solution which contains both a weak acid and its conjugate base. This creates to absorb excess H^+ or supply H^+ to replace what is lost due to neutralization. The calculation of the pH of a buffer is straightforward using an ICE table approach.

Example 10.9.1:

What is the pH of a solution that is 0.150 M in KF and 0.250 M in HF?

Solution

The reaction of interest is

$$HF \rightleftharpoons H^+ + F^-$$

Let's use an ICE table!

	HF	H^+	F^-
Initial	0.250 M	0	0.150 M
Change	-x	+x	+x
Equilibrium	0.250 M - x	x	0.150 M + x

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

$$10^{-3.17} M = \frac{x(0.150\,M + x)}{0.250\,M - x}$$

This expression results in a quadratic relationship, leading to two values of x that will make it true. Rejecting the negative root, the remaining root of the equation indicates

$$[H^+] = 0.00111\,M$$

So the pH is given by

$$pH = -log_{10}(0.00111) = 2.95$$

For buffers made from acids with sufficiently large values of pK_a the buffer problem can be simplified since the concentration of the acid and its conjugate base will be determined by their pre-equilibrium values. In these cases, the pH can be calculated using the Henderson-Hasselbalch approximation.

If one considers the expression for K_a

$$K_a = \frac{[H^+][A^-]}{[HA]} = [H^+]\frac{[H^-]}{[HA]}$$

Taking the log of both sides and multiplying by -1 yields

$$pK_a = pH - \log_{10}\frac{[A^-]}{[HA]}$$

An rearrangement produces the form of the Henderson-Hasselbalch approxmimation.

$$pH = pK_a - \log_{10}\frac{[A^-]}{[HA]}$$

It should be noted that this approximation will fail if:

1. the pk_a is too small,
2. the concentrations $[A^-]$ is too small, or
3. $[HA]$ is too small,

since the equilibrium concentration will deviate wildly from the pre-equilibrium values under these conditions.

This page titled 10.9: Buffers is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **9.9: Buffers** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

10.E: Chemical Equilibria (Exercises)

This page titled 10.E: Chemical Equilibria (Exercises) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

10.S: Chemical Equilibria (Summary)

Vocabulary and Concepts

- common ion effect
- conjugate base
- degree of dissociation
- dissociation of a weak acid
- Dumas Bulb
- Henderson-Hasselbalch equation
- Le Chatlier's principle
- reaction quotient
- solubility product
- thermodynamic equilibrium constant
- van't Hoff equation
- van't Hoff plot
- weak acid

References

1. Bandura, A. V., & Lvov, S. N. (2006). The Ionization Constant of Water over Wide Ranges of Temperature and Density. *J. Phys. Chem. Ref. Data*, *35*(1), 15-30.
2. Mack, E., & France, W. G. (1934). *A Laboratory Manual of Elementary Physical Chemistry* (2nd ed.). New York: D. Van Nostrand Company, Inc.
3. Tro, N. J. (2014). *Chemistry: a molecular approach* (3rd ed.). Boston: Pearson.

This page titled 10.S: Chemical Equilibria (Summary) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **9.S: Chemical Equilibria (Summary)** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

11: Solutions- Liquid-Liquid Solutions



11.1 ams for Bina

11.2: Liquid-Vapor Systems - Raoult’s Law

11.3: Non-ideality - Henry's Law and Azeotropes

Thumbnail: Image used with permission (Esmu Igors [Public domain])

11: Solutions- Liquid-Liquid Solutions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.1: Phase Diagrams for Binary Mixtures

As suggested by the Gibbs Phase Rule, the most important variables describing a mixture are pressure, temperature and composition. In the case of single component systems, composition is not important so only pressure and temperature are typically depicted on a phase diagram. However, for mixtures with two components, the composition is of vital important, so there is generally a choice that must be made as to whether the other variable to be depicted is temperature or pressure.

Temperature-composition diagrams are very useful in the description of binary systems, many of which will for two-phase compositions at a variety of temperatures and compositions. In this section, we will consider several types of cases where the composition of binary mixtures are conveniently depicted using these kind of phase diagrams.

Partially Miscible Liquids

A pair of liquids is considered partially miscible if there is a set of compositions over which the liquids will form a two-phase liquid system. This is a common situation and is the general case for a pair of liquids where one is polar and the other non-polar (such as water and vegetable oil.) Another case that is commonly used in the organic chemistry laboratory is the combination of diethyl ether and water. In this case, the differential solubility in the immiscible solvents allows the two-phase liquid system to be used to separate solutes using a separatory funnel method.

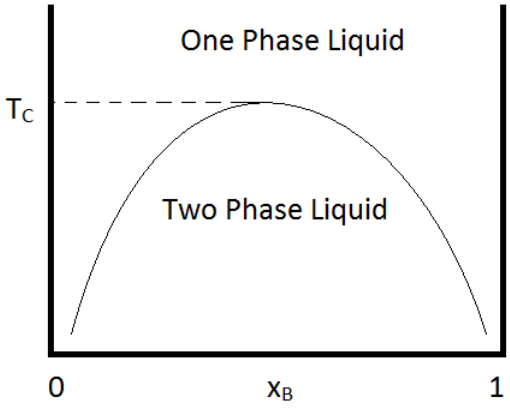


Figure 11.1.1 :

As is the case for most solutes, their solubility is dependent on temperature. For many binary mixtures of immiscible liquids, miscibility increases with increasing temperature. And then at some temperature (known as the upper critical temperature), the liquids become miscible in all compositions. An example of a phase diagram that demonstrates this behavior is shown in Figure 11.1.1. An example of a binary combination that shows this kind of behavior is that of methyl acetate and carbon disufide, for which the critical temperature is approximately 230 K at one atmosphere (Ferloni & Spinolo, 1974). Similar behavior is seen for hexane/nitrobenzene mixtures, for which the critical temperature is 293 K.

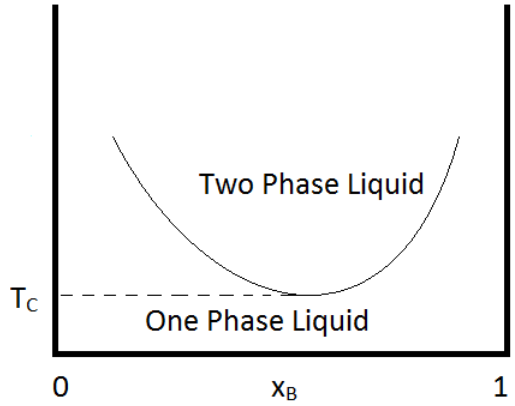


Figure 11.1.2 :

Another condition that can occur is for the two immiscible liquids to become completely miscible below a certain temperature, or to have a lower critical temperature. An example of a pair of compounds that show this behavior is water and trimethylamine. A typical phase diagram for such a mixture is shown in Figure 11.1.2 Some combinations of substances show both an upper and lower critical temperature, forming two-phase liquid systems at temperatures between these two temperatures. An example of a combination of substances that demonstrate the behavior is nicotine and water.

The Lever Rule

The composition and amount of material in each phase of a two phase liquid can be determined using the **lever rule**. This rule can be explained using the following diagram.

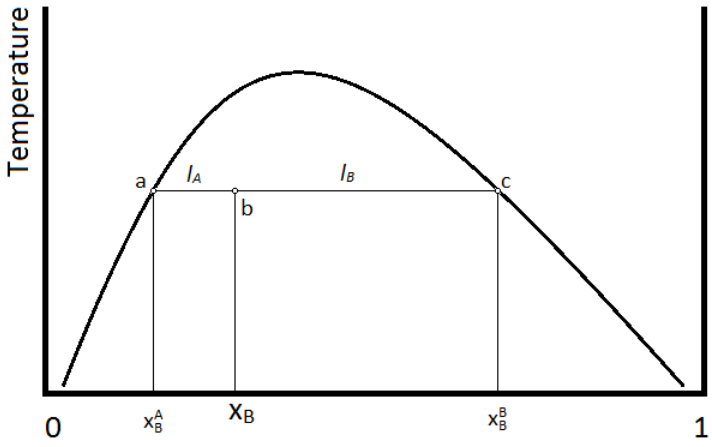


Figure 11.1.3 :

Suppose that the temperature and composition of the mixture is given by point b in the above diagram. The horizontal line segment that passes through point b, is terminated at points a and c, which indicate the compositions of the two liquid phases. Point a indicates the mole faction of compound B (χ_B^A) in the layer that is predominantly A, whereas the point c indicates the composition (χ_B^B)of the layer that is predominantly compound B. The relative amounts of material in the two layers is then inversely proportional to the length of the tie-lines a-b and b-c, which are given by l_A and l_B respectively. In terms of mole fractions,

$$l_A = \chi_B - \chi_B^A$$

and

$$l_A = \chi_B^B - \chi_B$$

The number of moles of material in the A layer (n_A) and the number of moles in the B layer (n_B) are inversely proportional to the lengths of the two lines l_A and l_B.

$$n_A l_A = n_B l_B$$

Or, substituting the above definitions of the lengths l_A and l_B, the ratio of these two lengths gives the ratio of moles in the two phases.

$$\frac{n_A}{n_B} = \frac{l_B}{l_A} = \frac{\chi_B^B - \chi_B}{\chi_B - \chi_B^A}$$

This page titled 11.1: Phase Diagrams for Binary Mixtures is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **8.6: Phase Diagrams for Binary Mixtures** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

11.2: Liquid-Vapor Systems - 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 continuing at least one volatile liquid can be described using Raoult's Law.

Raoult's Law

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 theoretical diagram for an ideal mixture of two compounds, one having a pure vapor pressure of $p_B^o = 450\,Torr$ and the other having a pure vapor pressure of $p_B^o = 350\,Torr$. In Figure 11.2.1, the liquid phase is represented at the top of the graph where the pressure is higher.

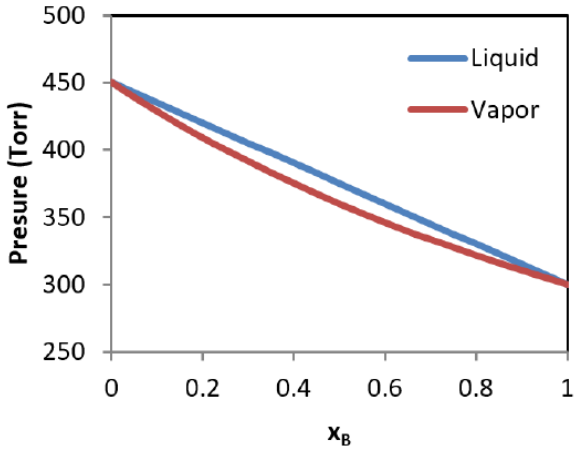


Figure 11.2.1: The liquid phase is represented at the top of the graph where the pressure is higher

Oftentimes, 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 11.2.2 for an ideal mixture of two volatile liquids.

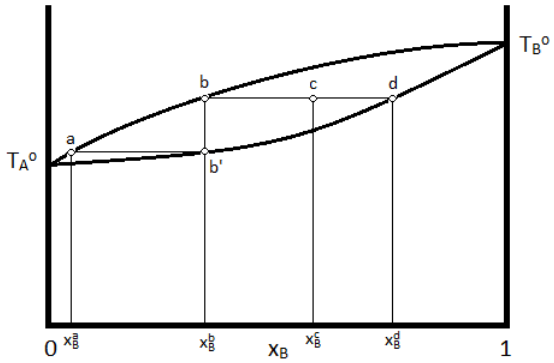


Figure 11.2.2: *A typical temperature vs. composition diagram.*

In this diagram, T_A^o and T_B^o 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 revaporized, 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.

This page titled 11.2: Liquid-Vapor Systems - Raoult's Law is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **8.7: Liquid-Vapor Systems - Raoult's Law** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

11.3: Non-ideality - Henry's Law and Azeotropes

The proceeding discussion was based on the behaviors of ideal solutions of volatile compounds, and for which both compounds follow Raoult's Law. **Henry's Law** can be used to describe these deviations.

$$p_B = k_H p_B^o$$

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 11.3.1.

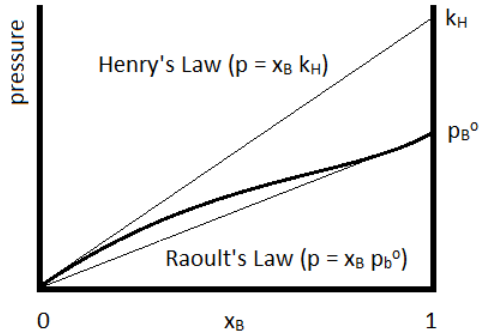


Figure 11.3.1: The relationship between Raoult's Law and Henry's Law for a binary mixture.

Henry's Law is depicted by the upper straight line and Raoult's Law by the lower.

Example 11.3.1: 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

$$k_H = 1.67\times10^9\ Pa$$

Azeotropes

An azeotrope is defined as the common composition of vapor and liquid when they have the same composition.

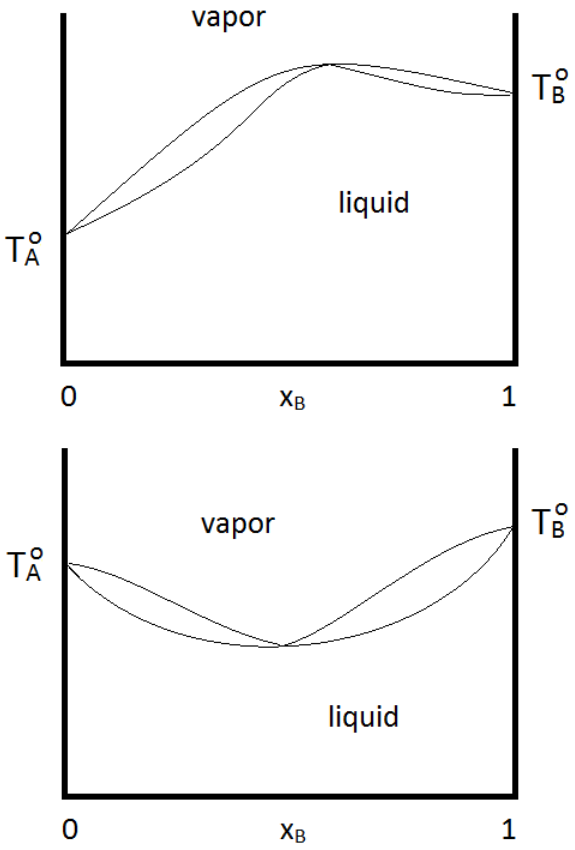


Figure 11.3.2: Phase diagrams for (left) a maximum boiling point azeotrope and (right) Ta maximum boiling point azeotrope.

Azeotropes can be either maximum boiling or minimum boiling, as show in Figure $11.3.2; left$ Regardless, distillation cannot purify past the azeotrope point, since the vapor and quid phases have the same composition. If a system forms a minimum boiling azeotrope and also has a range of compositions and temperatures at which two liquid phases exist, the phase diagram might look like Figure $11.3.2; right$

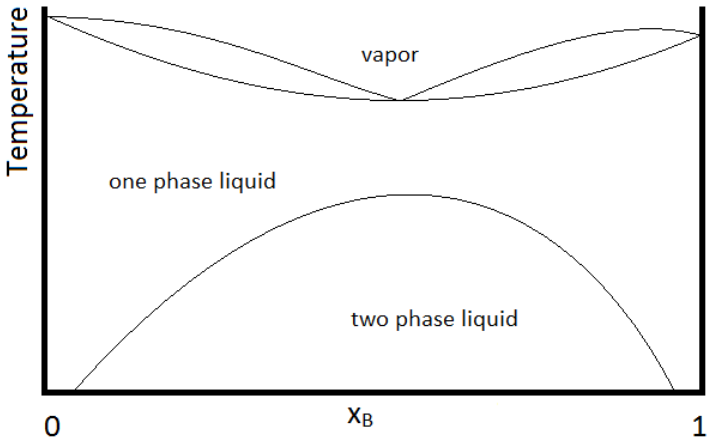
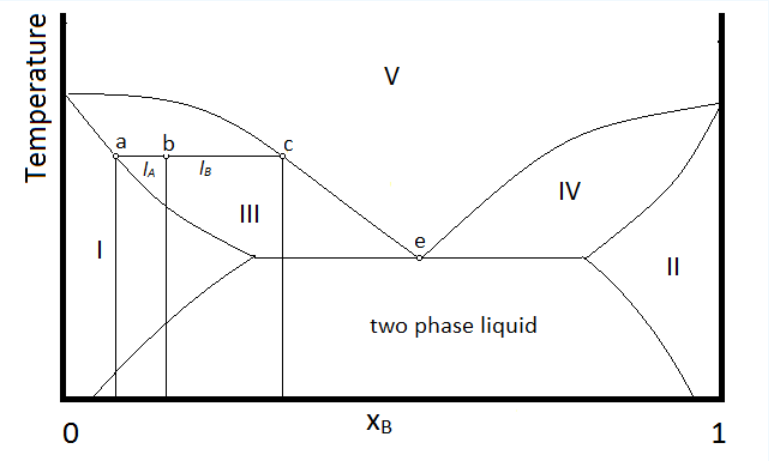


Figure 11.3.3: *Phase diagram for a binary solution with the boiling point of a minimum boiling azeotrope that is higher that when components are miscible (single phase).*

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 $11.3.3$

Example 11.3.1:

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)

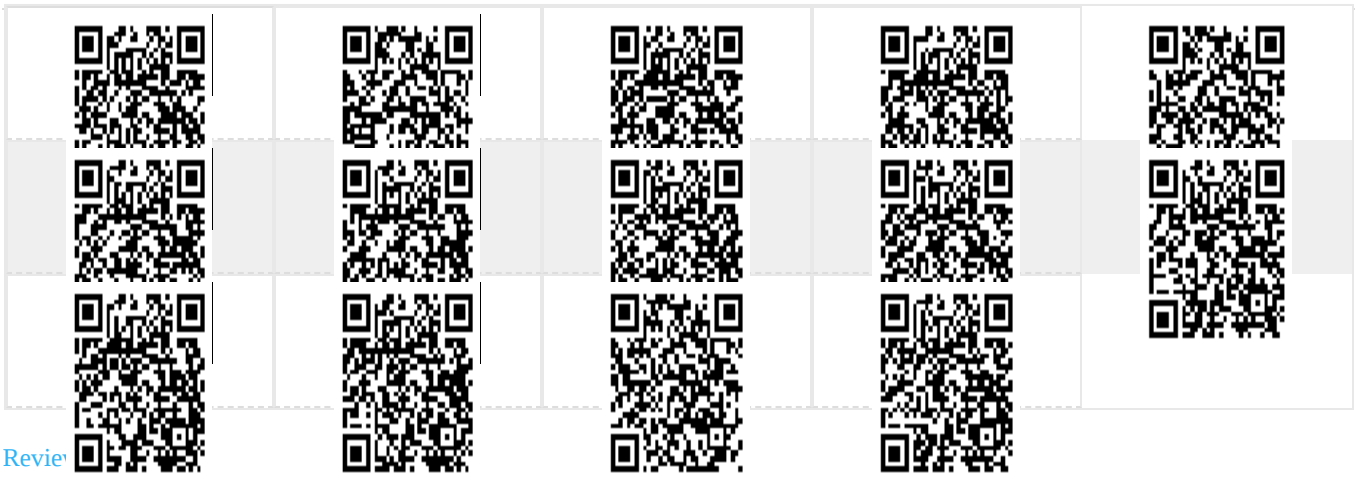
Solution

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.

This page titled 11.3: Non-ideality - Henry's Law and Azeotropes is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Patrick Fleming.

- **8.8: Non-ideality - Henry's Law and Azeotropes** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

Math Review



Revie

Applications: Derivatives

Review: Integrals

Applications: Integrals

Thumbnail: Image used with permission (CC BY-SA 3.0; Nick Youngson)

Math Review is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

Index

A

activity
- 9.8: Non-ideality in Solutions - Activity
- 10.3: Activities and Fugacities

activity coefficient
- 9.8: Non-ideality in Solutions - Activity

Adiabatic Changes
- 5.4: Reversible and Irreversible Pathways
- 6.4: Calculating Entropy Changes
- 7.1: Calculating Entropy Changes

adiabatic compressibility
- 6.8: Adiabatic Compressibility

anharmonicity
- 3.2.3: The Harmonic Oscillator Approximates Vibrations

autoionization
- 10.8: Acid-Base Equilibria

average speed in gas
- 1.3: The Kinetic Molecular Theory of Gases

Avogadro's law
- 1.1: The Empirical Gas Laws

azeotrope
- 11.3: Non-ideality - Henry's Law and Azeotropes

B

boiling point elevation
- 9.6: Colligative Properties

Boltzman Distribution
- 2.2: The Thermal Boltzman Distribution

Boltzmann equation for entropy
- 6.6: Entropy and Disorder

bomb calorimeter
- 5.6: Calorimetry

bond energy
- 5.7: Reaction Enthalpies

Boyle temperature
- 1.7: Real Gases

Boyle's Law
- 1.1: The Empirical Gas Laws

buffer
- 10.9: Buffers

C

calorimetry
- 5.6: Calorimetry

Carnot cycle
- 6.2: Heat Engines and the Carnot Cycle

Charles' Law
- 1.1: The Empirical Gas Laws

Charles's Law
- 1.1: The Empirical Gas Laws

chemical potential
- 9.3: Chemical Potential
- 10.2: Chemical Potential

Clapeyron equation
- 9.12: The Clapeyron Equation

Classical Harmonic Oscillator
- 3.2.1: A Harmonic Oscillator Obeys Hooke's Law

Clausius inequality
- 6.5: Comparing the System and the Surroundings

colligative property
- 9.6: Colligative Properties

collisional cross section
- 1.6: Collisions with Other Molecules

Collisions with wall
- 1.4: Kinetic Energy

combined gas law
- 1.1: The Empirical Gas Laws

commutator
- 3.1.2: Linear Operators in Quantum Mechanics

compressibility factor
- 9.5: Non-ideality in Gases - Fugacity

compression factor
- 1.7: Real Gases

constant pressure heat capacity
- 5.4: Reversible and Irreversible Pathways
- 8.8: The Difference between Cp and Cv

constant volume heat capacity
- 5.4: Reversible and Irreversible Pathways
- 8.8: The Difference between Cp and Cv

cooling curve
- 9.10: Single Component Phase Diagrams

correspondence principle
- 3.1.3: The Schrödinger Equation is an Eigenvalue Problem

cryoscopic constant
- 9.6: Colligative Properties

cyclic boundary condition
- 3.2.8: The Energy Levels of a Rigid Rotor

D

Debye extrapolation
- 6.7: The Third Law of Thermodynamics
- 7.3: The Third Law of Thermodynamics

degeneracy
- 3.1.9: A Particle in a Three-Dimensional Box
- 4.5: Most Molecules are Rotationally Excited at Ordinary Temperatures

degree of dissociation
- 10.5: Degree of Dissociation

Diatomic Vibration
- 3.2.5: The Harmonic Oscillator and Infrared Spectra

dipole
- 1.9.1: Dipole-Dipole Interactions

dipole moment
- 1.9.3: Dipole moments

disorder
- 6.6: Entropy and Disorder

distillation
- 11.2: Liquid-Vapor Systems - Raoult's Law

Dumas Bulb
- 10.7: The Dumas Bulb Method for Measuring Decomposition Equilibrium

E

ebullioscopic constant
- 9.6: Colligative Properties

eigenfunction
- 3.1.3: The Schrödinger Equation is an Eigenvalue Problem

eigenvalue problem
- 3.1.3: The Schrödinger Equation is an Eigenvalue Problem

empirical gas laws
- 1.1: The Empirical Gas Laws

endothermic process
- 5.3: Work and Heat

enthalpy change
- 5.6: Calorimetry

enthalpy of combustion
- 5.6: Calorimetry

enthalpy of mixing
- 9.1: Thermodynamics of Mixing

entropy
- 6.3: Entropy

entropy change of the surroundings
- 6.5: Comparing the System and the Surroundings

entropy change of the system
- 6.5: Comparing the System and the Surroundings

entropy of mixing
- 9.1: Thermodynamics of Mixing

entropy of vaporization
- 7.2: Trouton's rule

EOS
- 5.4: Reversible and Irreversible Pathways

exothermic
- 5.3: Work and Heat

expectation value
- 3.1.7: The Average Momentum of a Particle in a Box is Zero

F

first law of thermodynamics
- 5.3: Work and Heat

free energy
- 8.3: ΔA, ΔG, and Maximum Work

freezing point depression
- 9.6: Colligative Properties

freezing point depression constant
- 9.6: Colligative Properties

frequency of collisions
- 1.6: Collisions with Other Molecules

fugacity
- 9.5: Non-ideality in Gases - Fugacity
- 10.3: Activities and Fugacities

fugacity coefficient
- 9.5: Non-ideality in Gases - Fugacity

G

Gibbs energy of mixing
- 9.1: Thermodynamics of Mixing

Gibbs function
- 8.1: Free Energy Functions

Graham's law
- 1.5: Graham's Law of Effusion

H

harmonic oscillator
- 3.2.3: The Harmonic Oscillator Approximates Vibrations
- 3.2.4: The Harmonic Oscillator Energy Levels
- 3.2.5: The Harmonic Oscillator and Infrared Spectra

heat
- 5.3: Work and Heat

heat capacity
- 6.2: Heat Engines and the Carnot Cycle

heat is not a state function
6.3: Entropy
Heisenberg Uncertainty Principle
3.1.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions
Helmholtz function
8.1: Free Energy Functions
Henry's Law
11.3: Non-ideality - Henry's Law and Azeotropes
Hermite polynomials
3.2.6: The Harmonic-Oscillator Wavefunctions involve Hermite Polynomials
3.2.7: Hermite Polynomials are either Even or Odd Functions
Hermitian operators
3.1.2: Linear Operators in Quantum Mechanics
Hess's law
5.7: Reaction Enthalpies
Hooke's Law
3.2.1: A Harmonic Oscillator Obeys Hooke's Law

I

ideal gas law
1.2: The Ideal Gas Law
intermolecular forces
1.8: Intermolecular Forces
internal energy
5.3: Work and Heat
internal pressure
5.5: The Joule Experiment
ionic strength
9.8: Non-ideality in Solutions - Activity
ionization energy
5.7: Reaction Enthalpies
IR spectra
3.2.5: The Harmonic Oscillator and Infrared Spectra
Isobaric Changes
6.4: Calculating Entropy Changes
7.1: Calculating Entropy Changes
isochoric
5.3: Work and Heat
isothermal
5.3: Work and Heat
Isothermal Changes in Entropy
6.4: Calculating Entropy Changes
7.1: Calculating Entropy Changes

J

Joule Experiment
5.3: Work and Heat
5.5: The Joule Experiment

K

kinetic energy
1.4: Kinetic Energy
Kinetic Molecular Theory of Gases
1.3: The Kinetic Molecular Theory of Gases
Knudsen cell
1.5: Graham's Law of Effusion

L

Lattice Energy
5.8: Lattice Energy and the Born-Haber Cycle
Le Chatelier's principle
10.4: Pressure Dependence of Kp - Le Châtelier's Principle
lever rule
11.1: Phase Diagrams for Binary Mixtures

M

maximum boiling point azeotrope
11.3: Non-ideality - Henry's Law and Azeotropes
Maxwell relations
8.2: Combining the First and Second Laws - Maxwell's Relations
mean activity coefficient
9.8: Non-ideality in Solutions - Activity
mean free path
1.6: Collisions with Other Molecules
microwave spectroscopy
3.2.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule
minimum boiling point azeotrope
11.3: Non-ideality - Henry's Law and Azeotropes
molar heat capacities
4.9: Molar Heat Capacities
Morse potential
3.2.3: The Harmonic Oscillator Approximates Vibrations
3.2.5: The Harmonic Oscillator and Infrared Spectra
most probable speed in gas
1.3: The Kinetic Molecular Theory of Gases

N

natural variable
8.2: Combining the First and Second Laws - Maxwell's Relations
nodes
3.1.7: The Average Momentum of a Particle in a Box is Zero

O

operators
3.1.2: Linear Operators in Quantum Mechanics
orthogonality
3.1.5: The Energy of a Particle in a Box is Quantized
Orthonormality
3.1.5: The Energy of a Particle in a Box is Quantized

P

partial molar volume
9.2: Partial Molar Volume
Partially Miscible Liquids
11.1: Phase Diagrams for Binary Mixtures
Particle in a 3D Box
3.1.9: A Particle in a Three-Dimensional Box
particle in a box
3.1.5: The Energy of a Particle in a Box is Quantized
Partition Function (Rotational)
4.6: Rotational Partition Functions of Diatomic Gases
phase diagram
9.9: Prelude to Phase Equilibrium
9.10: Single Component Phase Diagrams
Phase Rule
9.11: Criterion for Phase Equilibrium
polarizability
1.9.10: Polarizability
Pressure Dependence of Equilibrium Constant
10.4: Pressure Dependence of Kp - Le Châtelier's Principle
Pressure Dependence of Gibbs Energy
8.5: Pressure Dependence of Gibbs Energy
principle of corresponding states
1.7: Real Gases
Probabilistic Interpretation
3.1.4: Wavefunctions Have a Probabilistic Interpretation
probability density
3.1.4: Wavefunctions Have a Probabilistic Interpretation

R

Raoult's law
11.2: Liquid-Vapor Systems - Raoult's Law
reaction enthalpy
5.7: Reaction Enthalpies
reaction quotient
10.2: Chemical Potential
Redox in Acid Solution
3.2.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule
reduced mass
3.2.1: A Harmonic Oscillator Obeys Hooke's Law
reducing agent
3.2.5: The Harmonic Oscillator and Infrared Spectra
rigid rotor
3.2.8: The Energy Levels of a Rigid Rotor
3.2.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule
RMS speed in gas
1.3: The Kinetic Molecular Theory of Gases

S

Schrödinger equation
3.1.1: The Schrödinger Equation
Second Law of Thermodynamics
6.1: Introduction to the Second Law
Second Virial Coefficient
1.7: Real Gases
selection rules
3.2.5: The Harmonic Oscillator and Infrared Spectra
solubility
9.7: Solubility
speed of sound
6.8: Adiabatic Compressibility
spherical harmonics
3.2.8: The Energy Levels of a Rigid Rotor
spontaneous change
6.1: Introduction to the Second Law
standard enthalpy of formation
5.7: Reaction Enthalpies
standard state
5.7: Reaction Enthalpies
symmetry number
4.6: Rotational Partition Functions of Diatomic Gases

T

Temperature Dependence of Equilibrium Constant
10.6: Temperature Dependence of Equilibrium Constants - the van’t Hoff Equation

Temperature Dependence of Gibbs Energy
8.6: Temperature Dependence of A and G

Temperature Dependence of Helmholtz Energy
8.6: Temperature Dependence of A and G

third law entropy
6.7: The Third Law of Thermodynamics
7.3: The Third Law of Thermodynamics

Third Law of Thermodynamics
6.7: The Third Law of Thermodynamics
7.3: The Third Law of Thermodynamics

Transition Energies
3.2.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule

triple point
9.11: Criterion for Phase Equilibrium

Trouton's rule
7.2: Trouton's rule

Two Variables Change at Once
8.7: When Two Variables Change at Once

U

uncertainty
3.1.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions

V

Van der Waals forces
1.8.1: Van der Waals Forces

van’t Hoff equation
10.6: Temperature Dependence of Equilibrium Constants - the van’t Hoff Equation

van’t Hoff plot
10.6: Temperature Dependence of Equilibrium Constants - the van’t Hoff Equation

vapor pressure
9.6: Colligative Properties

viral EOS
1.7: Real Gases

Volume Dependence of Helmholtz Energy
8.4: Volume Dependence of Helmholtz Energy

W

Wavefunction Normalization
3.1.6: Wavefunctions Must Be Normalized

weak acid
10.8: Acid-Base Equilibria

weak bases
10.8: Acid-Base Equilibria

work
5.3: Work and Heat

Glossary

Sample Word 1 | Sample Definition 1

Detailed Licensing

Overview

Title: CHEM 3212: Physical Chemistry II

Webpages: 144

Applicable Restrictions: Noncommercial

All licenses found:

- Undeclared: 50.7% (73 pages)
- CC BY-NC-SA 4.0: 49.3% (71 pages)

By Page

- CHEM 3212: Physical Chemistry II - *Undeclared*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: The Properties of Gases - *Undeclared*
    - 1.E: Gases (Exercises) - *CC BY-NC-SA 4.0*
    - 1.S: Gases (Summary) - *CC BY-NC-SA 4.0*
    - 1.1: The Empirical Gas Laws - *CC BY-NC-SA 4.0*
    - 1.2: The Ideal Gas Law - *CC BY-NC-SA 4.0*
    - 1.3: The Kinetic Molecular Theory of Gases - *CC BY-NC-SA 4.0*
    - 1.4: Kinetic Energy - *CC BY-NC-SA 4.0*
    - 1.5: Graham's Law of Effusion - *CC BY-NC-SA 4.0*
    - 1.6: Collisions with Other Molecules - *CC BY-NC-SA 4.0*
    - 1.7: Real Gases - *CC BY-NC-SA 4.0*
    - 1.8: Intermolecular Forces - *Undeclared*
      - 1.8.1: Van der Waals Forces - *Undeclared*
    - 1.9: Specific Interactions - *Undeclared*
      - 1.9.1: Dipole-Dipole Interactions - *Undeclared*
      - 1.9.2: Dipole Moment - *Undeclared*
      - 1.9.3: Dipole moments - *Undeclared*
      - 1.9.4: Hydrogen Bonding - *Undeclared*
      - 1.9.5: Ion - Dipole Interactions - *Undeclared*
      - 1.9.6: Ion - Induced Dipole Interactions - *Undeclared*
      - 1.9.7: Ion - Ion Interactions - *Undeclared*
      - 1.9.8: Lennard-Jones Potential - *Undeclared*
      - 1.9.9: London Dispersion Interactions - *CC BY-NC-SA 4.0*
      - 1.9.10: Polarizability - *Undeclared*
  - 2: The Boltzmann Factor and Partition Functions - *Undeclared*
    - 2.1: The Boltzmann Factor - *Undeclared*
    - 2.2: The Thermal Boltzman Distribution - *Undeclared*
    - 2.3: The Average Ensemble Energy - *Undeclared*
  - 3: Quantum Review - *Undeclared*
    - 3.1: The Schrödinger Equation and a Particle in a Box - *Undeclared*
      - 3.1.E: The Schrödinger Equation and a Particle in a Box (Exercises) - *Undeclared*
      - 3.1.1: The Schrödinger Equation - *Undeclared*
      - 3.1.2: Linear Operators in Quantum Mechanics - *Undeclared*
      - 3.1.3: The Schrödinger Equation is an Eigenvalue Problem - *Undeclared*
      - 3.1.4: Wavefunctions Have a Probabilistic Interpretation - *Undeclared*
      - 3.1.5: The Energy of a Particle in a Box is Quantized - *Undeclared*
      - 3.1.6: Wavefunctions Must Be Normalized - *Undeclared*
      - 3.1.7: The Average Momentum of a Particle in a Box is Zero - *Undeclared*
      - 3.1.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions - *Undeclared*
      - 3.1.9: A Particle in a Three-Dimensional Box - *Undeclared*
    - 3.2: The Harmonic Oscillator and the Rigid Rotor - *Undeclared*
      - 3.2.E: The Harmonic Oscillator and the Rigid Rotor (Exercises) - *Undeclared*
      - 3.2.1: A Harmonic Oscillator Obeys Hooke's Law - *Undeclared*
      - 3.2.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule - *Undeclared*
      - 3.2.3: The Harmonic Oscillator Approximates Vibrations - *Undeclared*

- 3.2.4: The Harmonic Oscillator Energy Levels - *Undeclared*
- 3.2.5: The Harmonic Oscillator and Infrared Spectra - *Undeclared*
- 3.2.6: The Harmonic-Oscillator Wavefunctions involve Hermite Polynomials - *Undeclared*
- 3.2.7: Hermite Polynomials are either Even or Odd Functions - *Undeclared*
- 3.2.8: The Energy Levels of a Rigid Rotor - *Undeclared*
- 3.2.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule - *Undeclared*

- 4: Partition Functions of Model Systems - *Undeclared*
  - 4.E: Partition Functions and Ideal Gases (Exercises) - *Undeclared*
  - 4.1: Translational Partition Functions of Monotonic Gases - *Undeclared*
  - 4.2: Most Atoms are in the Ground Electronic State - *Undeclared*
  - 4.3: The Energy of a Diatomic Molecule Can Be Approximated as a Sum of Separate Terms - *Undeclared*
  - 4.4: Most Molecules are in the Ground Vibrational State - *Undeclared*
  - 4.5: Most Molecules are Rotationally Excited at Ordinary Temperatures - *Undeclared*
  - 4.6: Rotational Partition Functions of Diatomic Gases - *Undeclared*
  - 4.7: Vibrational Partition Functions of Polyatomic Molecules - *Undeclared*
  - 4.8: Rotational Partition Functions of Polyatomic Molecules - *Undeclared*
  - 4.9: Molar Heat Capacities - *Undeclared*
  - 4.10: Ortho and Para Hydrogen - *Undeclared*
  - 4.11: The Equipartition Principle - *Undeclared*
  - Symmetry and Group Theory - *Undeclared*
- 5: Energy and Enthalpy - *Undeclared*
  - 5.E: First Law of Thermodynamics (Exercises) - *CC BY-NC-SA 4.0*
  - 5.1: First Law of Thermodynamics (Summary) - *CC BY-NC-SA 4.0*
  - 5.2: Prelude to Thermodynamics - *CC BY-NC-SA 4.0*
  - 5.3: Work and Heat - *CC BY-NC-SA 4.0*
  - 5.4: Reversible and Irreversible Pathways - *CC BY-NC-SA 4.0*
  - 5.5: The Joule Experiment - *CC BY-NC-SA 4.0*
  - 5.6: Calorimetry - *CC BY-NC-SA 4.0*
  - 5.7: Reaction Enthalpies - *CC BY-NC-SA 4.0*
  - 5.8: Lattice Energy and the Born-Haber Cycle - *CC BY-NC-SA 4.0*
- 6: Entropy, Part I - *Undeclared*
  - 6.E: The Second Law (Exercises) - *CC BY-NC-SA 4.0*
  - 6.S: The Second Law (Summary) - *CC BY-NC-SA 4.0*
  - 6.1: Introduction to the Second Law - *CC BY-NC-SA 4.0*
  - 6.2: Heat Engines and the Carnot Cycle - *CC BY-NC-SA 4.0*
  - 6.3: Entropy - *CC BY-NC-SA 4.0*
  - 6.4: Calculating Entropy Changes - *CC BY-NC-SA 4.0*
  - 6.5: Comparing the System and the Surroundings - *CC BY-NC-SA 4.0*
  - 6.6: Entropy and Disorder - *CC BY-NC-SA 4.0*
  - 6.7: The Third Law of Thermodynamics - *CC BY-NC-SA 4.0*
  - 6.8: Adiabatic Compressibility - *CC BY-NC-SA 4.0*
- 7: Entropy, Part II - *Undeclared*
  - 7.1: Calculating Entropy Changes - *CC BY-NC-SA 4.0*
  - 7.2: Trouton's rule - *Undeclared*
  - 7.3: The Third Law of Thermodynamics - *CC BY-NC-SA 4.0*
- 8: Gibbs and Helmholtz Energies - *Undeclared*
  - 8.S: Putting the Second Law to Work (Summary) - *CC BY-NC-SA 4.0*
  - 8.1: Free Energy Functions - *CC BY-NC-SA 4.0*
  - 8.2: Combining the First and Second Laws - Maxwell's Relations - *CC BY-NC-SA 4.0*
  - 8.3: ΔA, ΔG, and Maximum Work - *CC BY-NC-SA 4.0*
  - 8.4: Volume Dependence of Helmholtz Energy - *CC BY-NC-SA 4.0*
  - 8.5: Pressure Dependence of Gibbs Energy - *CC BY-NC-SA 4.0*
  - 8.6: Temperature Dependence of A and G - *CC BY-NC-SA 4.0*
  - 8.7: When Two Variables Change at Once - *CC BY-NC-SA 4.0*
  - 8.8: The Difference between Cp and Cv - *CC BY-NC-SA 4.0*
  - 8.9: Putting the Second Law to Work (Exercises) - *CC BY-NC-SA 4.0*
- 9: Phase Equilibria - *Undeclared*
  - 9.E: Mixtures and Solutions (Exercises) - *CC BY-NC-SA 4.0*
  - 9.E: Phase Equilibrium (Exercises) - *CC BY-NC-SA 4.0*
  - 9.S: Mixtures and Solutions (Summary) - *CC BY-NC-SA 4.0*
  - 9.1: Thermodynamics of Mixing - *CC BY-NC-SA 4.0*
  - 9.2: Partial Molar Volume - *CC BY-NC-SA 4.0*
  - 9.3: Chemical Potential - *CC BY-NC-SA 4.0*
  - 9.4: The Gibbs-Duhem Equation - *CC BY-NC-SA 4.0*

- 9.5: Non-ideality in Gases - Fugacity - *CC BY-NC-SA 4.0*
- 9.6: Colligative Properties - *CC BY-NC-SA 4.0*
- 9.7: Solubility - *CC BY-NC-SA 4.0*
- 9.8: Non-ideality in Solutions - Activity - *CC BY-NC-SA 4.0*
- 9.9: Prelude to Phase Equilibrium - *CC BY-NC-SA 4.0*
- 9.10: Single Component Phase Diagrams - *CC BY-NC-SA 4.0*
- 9.11: Criterion for Phase Equilibrium - *CC BY-NC-SA 4.0*
- 9.12: The Clapeyron Equation - *CC BY-NC-SA 4.0*
- 9.13: The Clausius-Clapeyron Equation - *CC BY-NC-SA 4.0*

10: Chemical Equilibrium - *Undeclared*

- 10.E: Chemical Equilibria (Exercises) - *CC BY-NC-SA 4.0*
- 10.S: Chemical Equilibria (Summary) - *CC BY-NC-SA 4.0*
- 10.1: Prelude to Chemical Equilibria - *CC BY-NC-SA 4.0*
- 10.2: Chemical Potential - *CC BY-NC-SA 4.0*
- 10.3: Activities and Fugacities - *CC BY-NC-SA 4.0*
- 10.4: Pressure Dependence of Kp - Le Châtelier's Principle - *CC BY-NC-SA 4.0*
- 10.5: Degree of Dissociation - *CC BY-NC-SA 4.0*
- 10.6: Temperature Dependence of Equilibrium Constants - the van't Hoff Equation - *CC BY-NC-SA 4.0*
- 10.7: The Dumas Bulb Method for Measuring Decomposition Equilibrium - *CC BY-NC-SA 4.0*
- 10.8: Acid-Base Equilibria - *CC BY-NC-SA 4.0*
- 10.9: Buffers - *CC BY-NC-SA 4.0*

11: Solutions- Liquid-Liquid Solutions - *Undeclared*

- 11.1: Phase Diagrams for Binary Mixtures - *CC BY-NC-SA 4.0*
- 11.2: Liquid-Vapor Systems - Raoult's Law - *CC BY-NC-SA 4.0*
- 11.3: Non-ideality - Henry's Law and Azeotropes - *CC BY-NC-SA 4.0*

Math Review - *Undeclared*

Back Matter - *Undeclared*

- Index - *Undeclared*
- Glossary - *Undeclared*
- Detailed Licensing - *Undeclared*