PHYSICAL CHEMISTRY

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Physical Chemistry

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CHAPTER OVERVIEW

1: The Basics

Physical Chemistry: Thermodynamics
Patrick Fleming

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Physical chemistry is concerned with the gray area that lies between physics (the study of energy) and chemistry (the study of matter). As such, physical chemistry is all about how energy can be stored through, extracted from, and used to drive chemical reactions and chemical systems. A major topic that focuses on how energy and matter interact and affect one another is thermodynamics. But before diving into thermodynamics, it is important to set down a few definitions that make it possible to begin slicing up the topic.

Thumbnail: Frying an egg is an example of a chemical change induced by the addition of thermal enegy (via heat). Image used iwth permission (CC BY-SA 3.0; Managementboy).

1.1: The System and the Surroundings

The Zeroth Law of Thermodynamics deals with the temperature of a system. And while it may seem intuitive as to what terms like "temperature" and "system" mean, it is important to define these terms. The easiest terms to define are the ones used to describe the system of interest and the surroundings, both of which are subsets of the universe.

- **Universe** – everything
- **System** – subset of the universe that is being studied and/or measured
- **Surroundings** – every part of the universe that is not the system itself.

As it turns out, there can be several types of systems, depending on the nature of the boundary that separates the system from the surroundings, and specifically whether or not it allows to the transmittance of matter or energy across it.

- **Open System** – allows for both mass and energy transfer across its boundary
- **Closed System** – allows for energy transfer across its boundary, but not mass transfer
- **Isolated System** – allows neither mass nor energy transfer across its boundary

Further, systems can be **homogeneous** (consisting of only a single phase of matter, and with uniform concentration of all substances present throughout) or **heterogeneous** (containing multiple phases and/or varying concentrations of the constituents throughout.) A very important variable that describes a system is its composition, which can be specified by the number of moles of each component or the concentration of each component. The number of moles of a substance is given by the ratio of the number of particles to Avogadro's number

$$n = \frac{N}{N_A}$$

where n is the number of moles, N is the number of particles (atoms, molecules, or formula units) and N_A is Avogadro's number (N_A = 6.022 x 10^{23} mol^{-1}).

Other important variables that are used to describe a system include the important variables of pressure, temperature, and volume. Other variables may also be important, but can often be determined if these **state variables** are known. Oftentimes, knowing a small number of state variables is all that is required to determine all of the other properties of a system. The relationship that allows for the determination of these properties from the values of a couple of state variables is called an **equation of state**.

Variables that describe a system can be either **intensive** (independent of the amount of any given substance present in the system) or **extensive** (dependent on the amount of substance present in the system.) Temperature and color are examples of intensive variables, whereas volume and mass are examples of extensive variables. The value of intensive properties is that they can be conveniently tabulated for various substances, whereas extensive properties would be specific to individual systems.

Oftentimes it is the case that the ratio of two extensive variables results in an intensive variable (since the amount of substance cancels out.) An example of this is density, which is the ratio of mass and volume. Another example is molar volume (V_m) which is the ratio of volume and number of moles of substance. For a given substance, the molar volume is inversely proportional to the density of the substance.

In a homogeneous system, an intensive variable will describe not just the system as a whole, but also any subset of that system. However, this may not be the case in a heterogeneous system!

1.2: Pressure and Molar Volume

Italian physicist Evangelista Torricelli (1608 – 1647) (Evangelista Torricelli) was the inventor of an ingenious device that could be used to measure air **pressure**. Basically, he took a glass tube closed at one end, and filled it with mercury. He then inverted it, submerging the open end below the surface level in a pool of mercury. The mercury in the glass tube was then allowed to drain, leaving a vacuum (known as a "Torrocellian vacuum") in the open space at the closed end of the tube.

Figure 1.2.1: Evangelista Torricelli (1608 - 1647). Evangelista Torricelli portrayed on the frontpage of Lezioni d'Evangelista Torricelli. (Public Domain).

Remarkably, the tube did not drain completely! Torricelli, was able to use the residual column height to measure the pressure of the air pushing down on the surface of the pool of mercury. The larger the pressure pushing down on the exposed surface, the larger the column height is observed to be. The ambient air pressure can be computed by equating the force generated by the mass of the mercury in the column to the force generated by ambient air pressure (after normalizing for surface area). The resulting relationship is

$$p = \rho g h$$

where ρ is the density of the mercury (13.1 g/cm^3), g is the acceleration due to gravity, and h is the height of the column. Torricelli found that at sea level, the height of the column was 76 cm.

$$p = (13.1\, g/cm^3)(9.8\, m/s)(76\, cm)\left(\frac{100^2 cm^2}{m^2}\right)\left(\frac{1\, kg}{1000\, g}\right)\left(\frac{1 kg\, m/s^2}{N}\right)$$

$$100,000 N/m^2 = 1 \times 10^5 Pa$$

A force of 1 N acting on an area of 1 m^2 is a Pascal (Pa). A standard atmosphere is 101,325 Pa (101.325 kPa), or 76.0 cm Hg (760 mm Hg.) Another commonly used unit of pressure is the bar:

$$1\, bar = 100,000\, Pa$$

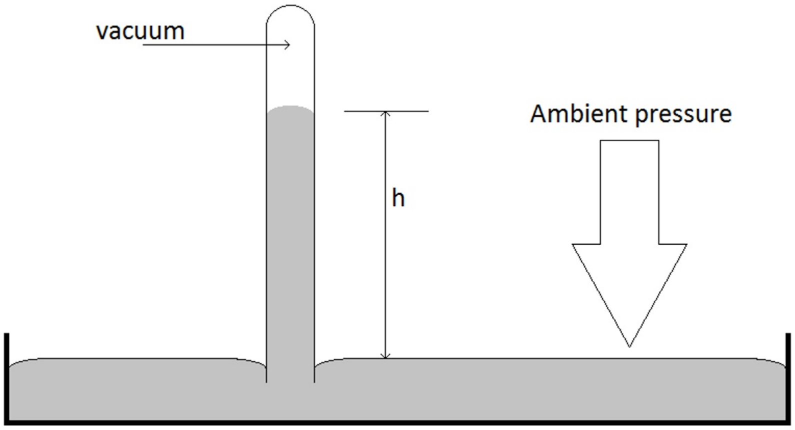

Figure 1.2.2: : Set up for the Torricelli barometer.

1.3: Temperature

Another important variable that describes the state of a system it the system’s **temperature**. Like pressure, temperature scales experienced an important process of development over time. Three of the most important temperature scales in US culture are the Fahrenheit, Celsius, and Kelvin scales.

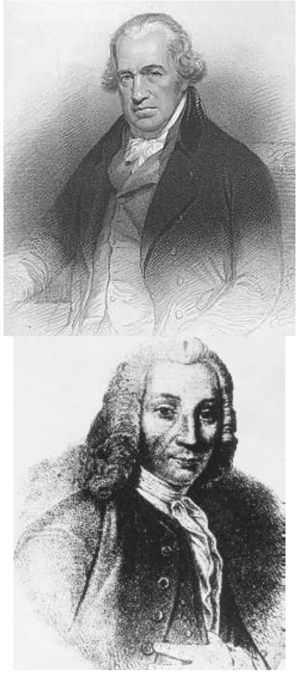

Figure 1.3.1: (left) G. Daniel Fahrenheit (1686 – 1736). (CC BY 4.0) and (right) Anders Celsius (1700 - 1780)

G. Daniel Fahrenheit wanted to develop a temperature scale that would be convenient to use in his laboratory. He wanted it to be of convenient magnitude and wanted to avoid having to use any negative values for temperature. So he define the zero of his temperature scale to be the lowest temperature he could create in his laboratory, which was in a saturated brine/water/ice slurry. He then defined 100 °F as his own body temperature. As a result, using his temperature scale, water has a normal melting point (the temperature at 1.00 atm pressure at which water ice melts) of 32 °F. Similarly, water boils (again at 1 atm pressure) at a temperature of 212 °F. The difference between these values is 180 °F.

Anders Celsius also thought a 100 degree temperature scale made sense, and was given the name “the centigrade scale”. He defined 0 °C on his scale as the normal boiling point of water, and 100 °C as the normal freezing point. By today’s standards, this inverted temperature scale makes little sense. The modern Celsius temperature scale defines 0 °C as the normal freezing point of water and 100 °C as the normal boiling point. The difference is 100 °C. Comparing this to the Fahrenheit scale, one can easily construct a simple equation to convert between the two scales.

$$212\,^\circ F = 100\,^\circ C(m) + b$$

$$32\,^\circ F = 0\,^\circ C(m) + b$$

Solving these equations for m and b yields

$$m = \frac{9\,^\circ F}{5\,^\circ C}$$

$$b = 32\,^\circ F$$

And so conversion between the two scales is fairly simple.

$$y\,^\circ F = x\,^\circ \cancel{C}\left(\frac{9\,^\circ F}{5\,^\circ \cancel{C}}\right) + 32\,^\circ F$$

$$x\ ^{\circ}C = (y\ ^{\circ}\cancel{F} - 32\ ^{\circ}\cancel{F})\left(\frac{5\ ^{\circ}C}{9\ ^{\circ}\cancel{F}}\right)$$

Many physical properties of matter suggest that there is an absolute minimum temperature that can be attained by any sample. This minimum temperature can be shown by several types or experiments to be -273.15 °C. An absolute temperature scale is one that assigns the minimum temperature a value of 0. One particularly useful scale is named after William Lord Kelvin (Kelvin, Lord William Thomson (1824-1907) , 2007).

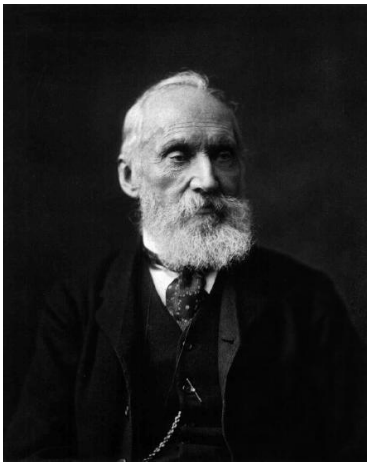

Figure 1.3.2. William Lord Kelvin (1824 - 1907)

The Kelvin scale fixes the normal melting temperature of water at 273.15 K and the boiling point at 373.15 K. As such, temperatures can be converted using the following expression:

$$z\,K = x\ ^{\circ}\cancel{C}\left(\frac{1\ K}{1\ ^{\circ}\cancel{C}}\right) + 273.15\ K$$

1.4: The Zeroth Law of Thermodynamics

Temperature is an important property when it comes to measuring energy flow through a system. But how does one use or measure temperature? Fortunately, there is a simple and intuitive relationship which can be used to design a thermometer – a device to be used to measure temperature and temperature changes. The zeroth law of thermodynamics can be stated as follows:

> *If a system A is in thermal equilibrium with a system B, which is also in thermal equilibrium with system C, then systems A and C share a property called temperature.*

This basic principle has been used to define standard temperature scales by the International Committee on Weights and Measures (BIPM) to guide the adoption of the International Practical Temperature Scale of 1990 (Mangum & Furukawa, 1990). IPT-90 is defined by using various physical properties of substances (such as the triple point of water) which occur at ver specific temperatures and pressures, and then assigning the measurable values such as the resistance on a standard **platinum resistance thermometer** (Strouse, 2008).

1.5: Work and Energy

Temperature, pressure and volume are important variables in the description of physical systems. They will also be important to describe how energy flows from one system to another. Generally, energy can flow in two important forms: 1) work and 2) heat. The bookkeeping needed to track the flow of energy is what the subject of Thermodynamics is all about, so these topics will be discussed at length in subsequent chapters. However, a little bit of review is in order, just to set the foundation for the discussions that are forthcoming.

Energy

Energy is an important entity in the modern world. We use energy to light our homes, drive our cars, and power our electronic devices. According to Richard Smalley, co-winner of the 1996 Nobel Prize in Chemistry, energy is one of the (if not the biggest) challenge we face moving into the 21st century *(energy.senate.gov, 2004)*:

> *Energy is at the core of virtually every problem facing humanity. We cannot afford to get this wrong. … Somehow we must find the basis for energy prosperity for ourselves and the rest of humanity for the 21st century. By the middle of this century we should assume we will need to at least double world energy production from its current level, with most of this coming from some clean, sustainable, CO_2-free source. For worldwide peace and prosperity it needs to be cheap.- Richard Smalley, Testimony to the Senate Committee on Energy and Natural Resources, April 26, 2004*

Energy can be measured in a multitude of different units, including joules (J), kilojoules (kJ), calories (cal), kilocalories (kcal), as well as several other set of units such as kJ/mol or kcal/mol.

A **calorie (cal)** was once defined as the amount of energy needed to raise the temperature of 1 g of water by 1 °C. This definition suggests a convenient property of water called the **specific heat**:

$$C = \frac{1\, cal}{g\, ^{\circ}C}$$

The modern definition of a calorie is 4.184 **joule**,

$$1\, J = 1\, N \cdot m = \frac{1\, kg\, m^2}{s^2}$$

where a joule is the energy necessary to move a mass a distance of 1 m against a resisting force of 1 N.

> *A dietary **Calorie (Cal)** is equal to 1000 cal, or 1 kcal, and is often listed on the labels of food containers to indicate the energy content of the food inside.*

Energy can take the form of **potential energy** (stored energy) and **kinetic energy** (realized energy) forms. Kinetic energy is the energy of motion. On the other hand, potential energy can be defined as the energy stored in a system that can be converted to kinetic energy someplace in the universe. Kinetic energy of a particle can be expressed as

$$E_{kin} = \frac{1}{2} m v^2 \tag{1.5.1}$$

where m is the mass of the particle, and v is the magnitude of its velocity (or speed). Equation 1.5.1 describes the kinetic energy associated with translation; other expressions exist for different motions (e.g., rotation or vibration).

An example of a system in which energy is converted between kinetic energy and potential energy is a Hooke's Law oscillator. According to Hooke's Law, the force acting on an object is proportional in magnitude to the displacement of the object from an equilibrium position, and opposite in sign.

$$F = -kx \tag{1.5.2}$$

In this equation, F is the force, x is the displacement from equilibrium, and k is the constant of proportionality. The negative sign is necessary to insure that the force acting on the object is one that will tend to restore it to an equilibrium position ($x = 0$)

irrespective of whether x is positive or negative.

As the object that follows Hooke's Law moves from its equilibrium position, the kinetic energy of its motion is converted into potential energy until there is no more kinetic energy left. At this point, the change in displacement will change direction, returning the object to the equilibrium position by converting potential energy back into kinetic energy.

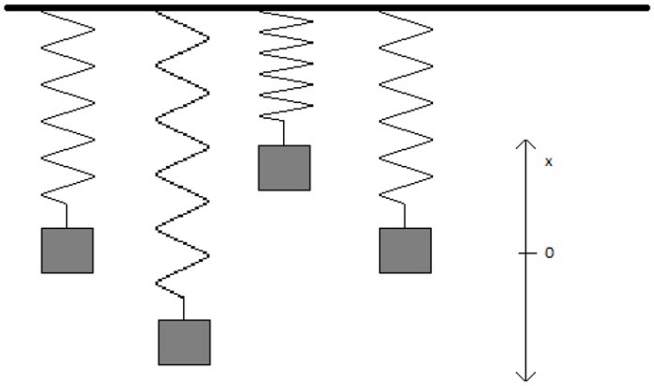

Figure 1.5.1: An example of a harmonic oscillator.

As the object is displaced in the along the x-axis (in the case shown in Figure 1.5.1, this would be accomplished by stretching or compressing the spring), the potential energy increases. The force acting on the object will also increase as the object is displaced and will be directed opposite of the direction of displacement (Equation 1.5.2). According to Newtonian physics, the potential energy $U(x)$ is given by the negative integral of the force with respect to position:

$$U(x) = -\int F(x)dx \tag{1.5.3}$$

Substituting Equation 1.5.2 in Equation 1.5.3 yields

$$U(x) = -\int (-kx)dx$$

$$= \frac{1}{2}kx^2 + constant$$

With the proper choice of coordinate system and other definitions, the constant of integration can be arbitrarily made to be zero (for example, by choosing it to offset any other forces acting on the object, such as the force due to gravity.) The kinetic energy is then given by the total energy minus the potential energy (since the total energy must be constant due to the conservation of energy in the system!)

$$E_{kin} = E_{tot} - U(x)$$

Work

Work is defined as the amount of energy expended to move a mass against a resisting force. For a mass being moved along a surface, the amount of energy expended must be sufficient to overcome the resisting force (perhaps due to friction) and also sufficient to cause motion along the entire path.

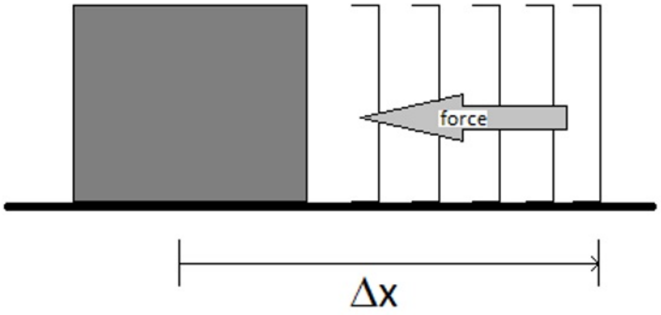

Figure 1.5.2: The work of displacement.

The energy expended as work in this case (if the force is independent of the position of the object being moved) is given by

$$w = -F\,\Delta x$$

where F is the magnitude of the resisting force, and Dx is the displacement of the object. The negative sign is necessary since the force is acting in the opposite direction of the motion. A more general expression, and one that can be used if the force is not constant over the entire motion is

$$dw = -F\,dx$$

This expression can then be integrated, including any dependence F might have on x as needed for a given system.

Another important way that work can be defined includes that for the expansion of a gas sample against an external pressure. In this case, the displacement is defined by a change in volume for the sample:

$$dw = -p_{ext}\,dV$$

This is a very convenient expression and will be used quite often when discussing the work expended in the expansion of a gas.

The conversion of potential energy into kinetic energy generally is accomplished through work which is done someplace in the universe. As such, the concepts of energy and work are inexorably intertwined. They will be central to the study of thermodynamics.

The work of a “reversible” expansion

An important case of **limiting ideal behavior[1]** is that of the **reversible expansion**. For a change to be reversible there can be no net force pushing the change in one direction or the other. In order for this to be the case, the internal pressure (that of the system) and external pressure (that of the surroundings) must be the same.

$$p_{int} = p_{ext} = p$$

In this case, the work of expansion can be calculated by integrating the expression for dw.

$$w = \int dw = -\int p dV$$

Making a simple substitution from the **ideal gas law**

$$p = \frac{nRT}{V} \tag{1.5.4}$$

allows for the expression in terms of volume and temperature. If the temperature is constant (so that it can be placed before the integral) the expression becomes

$$w = -nRT\int_{V_1}^{V_2}\frac{dV}{V} = -nRT\ln\left(\frac{V_2}{V_1}\right) \tag{1.5.5}$$

where V_1 and V_2 are the initial and final volumes of the expansion respectively.

✓ Example 1.5.1:

Consider 1.00 mol of an ideal gas, expanding isothermally at 273 K, from an initial volume of 11.2 L to a final volume of 22.4 L. What is the final pressure of the gas? Calculate the work of the expansion if it occurs

a. against a constant external pressure equal to the final pressure you have calculated.
b. reversibly.

Solution

First, let’s calculate the final pressure via Equation 1.5.4:

$$p = \frac{nRT}{V} = \frac{(1.00\,mole)(0.08206\,atm\,L\,mol^{-1}K^{-1})(273\,K)}{22.4\,L} = 1.00\,atm$$

(This may be a relationship you remember from General Chemistry – that 1 mole of an idea gas occupies 22.4 L at 0 °C!)

Okay – now for the irreversible expansion against a constant external pressure:

$$dw = -p_{ext}\, dV$$

so

$$w = -p_{exp}\int_{V_1}^{V_2} dV = -p_{ext}\,\Delta V$$

$$w = -(1.00\, atm)(22.4\, L - 11.2\, L) = -11.2\, atm\, L$$

But what the heck is an *atm L*? It is actually a fairly simply thing to convert from units of *atm L* to J by using the **ideal gas law constant**.

$$w = -(11.2\, atm\ L)\left(\frac{8.314\,\frac{J}{mol\ K}}{0.08206\,\frac{atm\ L}{mol\ K}}\right) = -1130\, J$$

Note that the negative sign indicated that the system is expending energy by doing work on the surroundings. (This concept will be vital in the Chapter 3!)

Now for the reversible pathway. The work done by the system can be calculated for this change using Equation 1.5.5:

$$w = -(1.00\, mol)(8.314 J\, mol^{-1}\, K^{-1})(273\, K)\ln\left(\frac{22.4\, L}{11.2\, L}\right) = -1570\, J$$

Notes:

- First notice how the value for the gas law constant, R, was chosen in order to match the units required in the problem. (Read and recite that previous sentence to yourself a few times. The incorrect choice of the value of R is one of the most common errors made by students in physical chemistry! By learning how the units will dictate your choice of R, you will save yourself a considerable number of headaches as you learn physical chemistry!)
- Second, You may note that the magnitude of work done by the system in the reversible expansion is larger than that of the irreversible expansion. This will always be the case!

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[1] There are many cases of “limiting ideal behavior” which we use to derive and/or explore the nature of chemical systems. The most obvious case, perhaps, is that of the **Ideal Gas Law**.

1.E: The Basics (Exercises)

Q1.1

Convert the temperatures indicated to complete the following table

°F	°C	K
	25	
98.6		
		373.15
	-40	
32		

Q1.2

Make a graph representing the potential energy of a harmonic oscillator as a function of displacement from equilibrium. On the same graph, include a function describing the kinetic energy as a function of displacement from equilibrium as well as the total energy of the system.

Q1.3

Calculate the work required to move a 3.2 kg mass 10.0 m against a resistive force of 9.80 N.

Q1.4

Calculate the work needed for a 22.4 L sample of gas to expand to 44.8 L against a constant external pressure of 0.500 atm.

Q1.5

If the internal and external pressure of an expanding gas are equal at all points along the entire expansion pathway, the expansion is called "reversible." Calculate the work of a reversible expansion for 1.00 mol of an ideal gas expanding from 22.4 L at 273 K to a final volume of 44.8 L.

1.S: The Basics (Summary)

Learning Objectives

Upon mastering the material covered in this chapter, one should be able to do the following:

1. Write down expressions from which work of motion and of expansion can be calculated.
2. Express the “Zeroth Law of Thermodynamics.
3. Convert between temperatures on several scales that are commonly used.
4. Define boundaries that differentiate between a system and its surroundings.
5. Perform calculations involving Specific Heat and understand how the specific heat governs temperature changes for the flow of a given amount of energy.

Vocabulary and Concepts

- calorie (cal)
- Calorie (Cal)
- closed system
- energy
- equation of state
- extensive
- heterogeneous
- homogeneous
- Ideal Gas Law
- ideal gas law constant
- intensive
- isolated system
- joule
- kinetic energy
- limiting ideal behavior
- open system
- platinum resistance thermometer
- potential energy
- pressure
- reversible expansion
- specific heat
- state variables
- surroundings
- system
- temperature
- universe
- work

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CHAPTER OVERVIEW

2: Gases

Physical Chemistry: Thermodynamics
Patrick Fleming

Gases comprise a very important type of system that can be modeled using thermodynamics. This is true because gas samples can be described by very simple equations of state, such as the ideal gas law. In this chapter, both macroscopic and microscopic descriptions of gases will be used to demonstrate some of the important tools of thermodynamics.

2.1: 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.

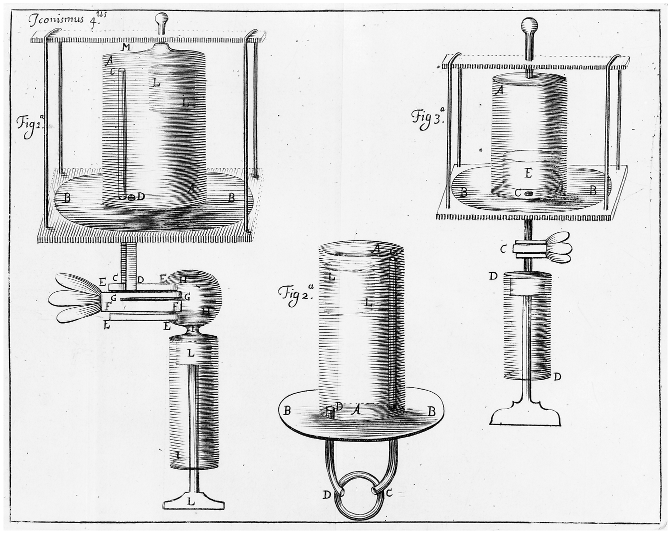


Figure 2.1.1: An apparatus similar to that used by Robert Boyle (1627 - 1691). Image taken from (Fazio, 1992).

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 2.1.2: Amedeao Avogadro (1776 - 1856)

2.2: 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.

$$pV = nRT$$

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!

2.3: 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.

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

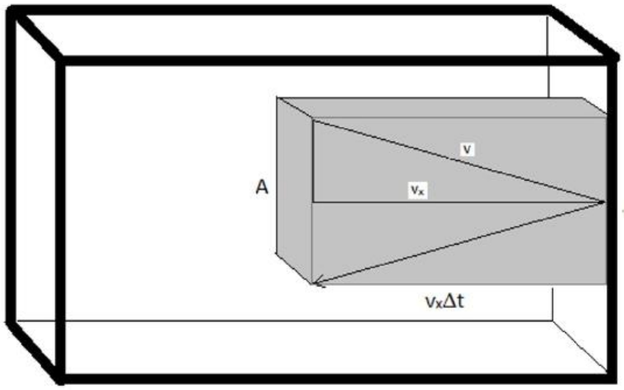


Figure $2.3.1$: The "collision volume" is the subset of the total volume that contains molecules that will actually collide with area A in the time interval Δt.

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

$$\begin{align} F_{tot} &= N_{col} \frac{2(mv_x)}{\Delta t} \tag{2.3.1} \\ &= \frac{1}{2} N_{tot} \left[\frac{(v_x \Delta t) A}{V}\right] \left[\frac{2(mv_x)}{\Delta t}\right] \tag{2.3.2} \\ &= N_{tot} \left(\frac{mv_x^2}{V}\right) A \tag{2.3.3} \end{align}$$

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 $\langle v_x \rangle^2$.

$$p = \frac{N_{tot} m}{V} \langle v_x \rangle^2 \tag{2.3.4}$$

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

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

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

$$\int_{-\infty}^{\infty} f(v_x) dv_x = 1 \tag{2.3.5}$$

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 2.3.5 must be true. So if the form of $f(v_x)$ is assumed to be

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

The normalization constant N can be found from

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

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

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

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

$$f(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(\frac{m v_x^2}{2 k_B T}\right) \tag{2.3.6}$$

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 2.3.4) 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 2.3.6) took the following form

$$f(v) = N v^2 \exp\left(\frac{mv^2}{2k_BT}\right) \tag{2.3.7}$$

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 (½mv^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

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

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

$$N = 4\pi\sqrt{\left(\frac{m}{2\pi k_BT}\right)^3} v^2 \exp\left(\frac{mv^2}{2k_BT}\right) \tag{2.3.8}$$

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).

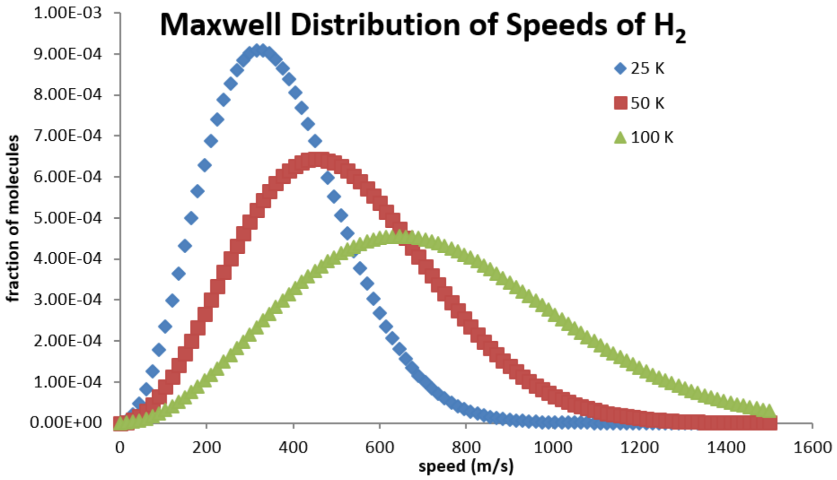


Figure 2.3.1: Maxwell Distribution of speeds for hydrogen molecules at differing temperatures.

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.

$$\langle v \rangle = \int_{-\infty}^{\infty} v\, f(v) dv \tag{2.3.9}$$

$$= \int_{-\infty}^{\infty} v\, 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3}\, v^2 \exp\left(\frac{mv^2}{2k_BT}\right)\, dv \tag{2.3.10}$$

$$= 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \int_{-\infty}^{\infty} v^3 \exp\left(\frac{mv^2}{2k_BT}\right)\, dv \tag{2.3.11}$$

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

$$\langle v \rangle = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \left[\frac{1}{2\left(\frac{m}{2k_BT}\right)^2}\right]$$

Which simplifies to

$$\langle v \rangle = \left(\frac{8k_BT}{\pi m}\right)^{1/2}$$

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 2.3.1:

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

Solution

$$\langle v^2\rangle = \int_{-\infty}^{\infty} v^2\, f(v)dv \tag{2.3.12}$$

$$= \int_{-\infty}^{\infty} v^2\, 4\pi\sqrt{\left(\frac{m}{2\pi k_BT}\right)^3}\, v^2 \exp\left(\frac{mv^2}{2k_BT}\right)\, dv \tag{2.3.13}$$

$$= 4\pi\sqrt{\left(\frac{m}{2\pi k_BT}\right)^3}\int_{-\infty}^{\infty} v^4 \exp\left(\frac{mv^2}{2k_BT}\right)\, dv \tag{2.3.14}$$

A table of integrals indicates that

$$\int_0^{\infty} x^{2n}e^{-ax^2}dx = \frac{1\cdot 3\, cdot5\ldots(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}}$$

Substitution (noting that $n=2$) yields

$$\langle v^2\rangle = 4\pi\sqrt{\left(\frac{m}{2\pi k_BT}\right)^3}\left[\frac{1\cdot 3}{2^3\left(\frac{m}{2k_BT}\right)^2}\sqrt{\frac{\pi}{\left(\frac{m}{2k_BT}\right)}}\right]$$

which simplifies to

$$\langle v^2\rangle = \frac{3k_BT}{m}$$

Note: The square root of this average squared speed is called the **root mean square** (RMS) speed, and has the value

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

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).

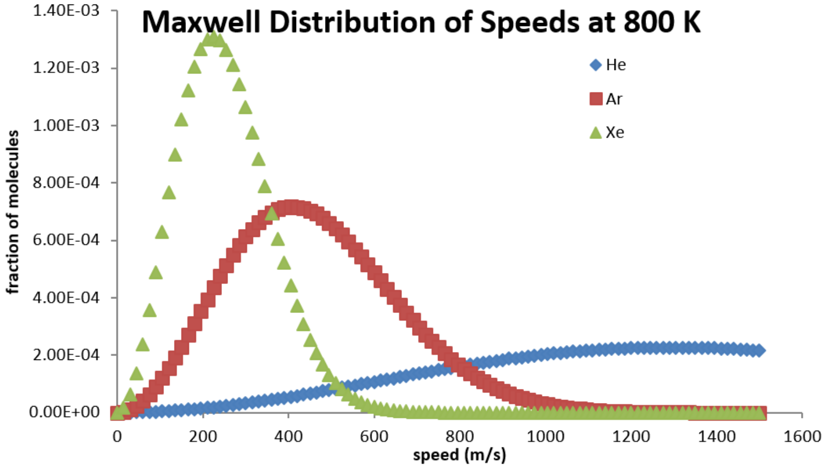


Figure 2.3.2: Maxwell Distribution of speeds at 800 K for different gasses of differing molecular masses.

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.

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

2.4: 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

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

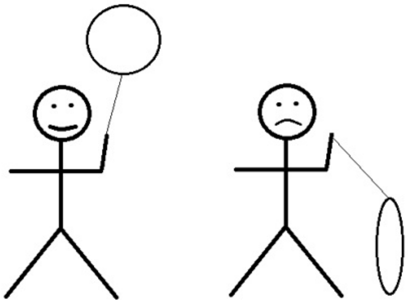
and so

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

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.

2.5: 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.

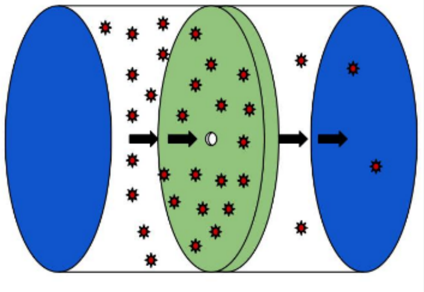


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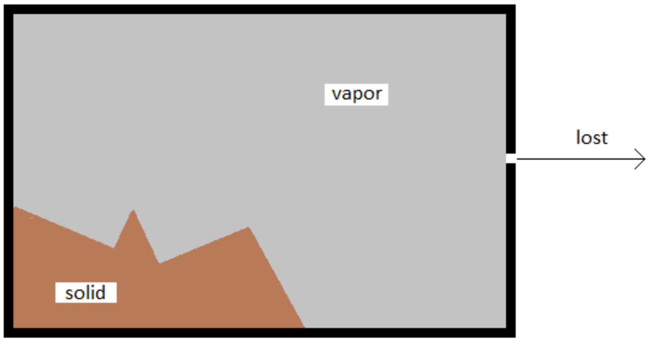
Figure 2.5.1: Effusion of gas particles through an orifice. (CC BY-SA 3.0; Astrang13).

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

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

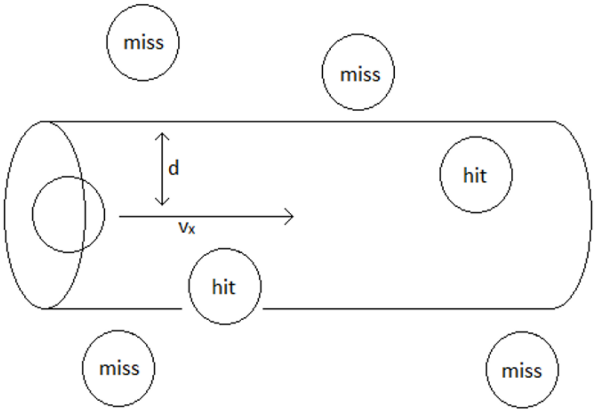
where g is the mass lost, A is the area of the orifice, Δt is the time the effusion is allowed to proceed, T is the temperature and MW is the molar mass of the compound in the vapor phase. The pressure is then given by p. A schematic of what a Knudsen cell might look like is given below.


vapor
lost
solid

2.6: 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.)

2.7: 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)

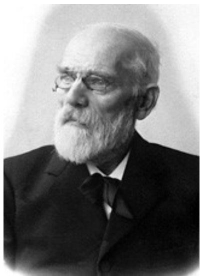


Figure $2.7.1$: Johannes van der Waals (1837 – 1923)

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.

$$\left(p+\frac{a}{V_m^2}\right)(V_m-b)=RT \tag{2.7.1}$$

or

$$p=\frac{RT}{V_m-b}-\frac{a}{V_m^2} \tag{2.7.2}$$

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 $2.7.1$.

Table $2.7.1$: 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 $2.7.2$). 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 $2.7.2$: 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)	$p=\frac{RT}{V_m-b}\exp\left(\frac{-a}{V_mRT}\right)$
Clausius	$p=\frac{RT}{V_m-b}-\frac{a}{T(V_m+c)^2}$
Virial Equations	$p=\frac{RT}{V_m}\left(1+\frac{B(T)}{V_m}+\frac{C(T)}{V_m}\dots\right)$

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.

$$p=\frac{RT}{V_m}\left(1+\frac{B(T)}{V_m}+\frac{C(T)}{V_m^2}\dots\right) \tag{2.7.3}$$

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

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

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.

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

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.

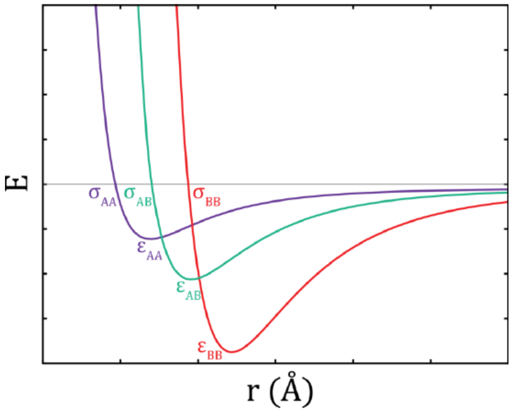


Figure 2.7.2: The estimation of Lennard-Jones potential parameters for mixed pairs of atoms. (CC BY-SA 4.0; Cnrowley).

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 2.7.2). 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

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

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

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

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

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.

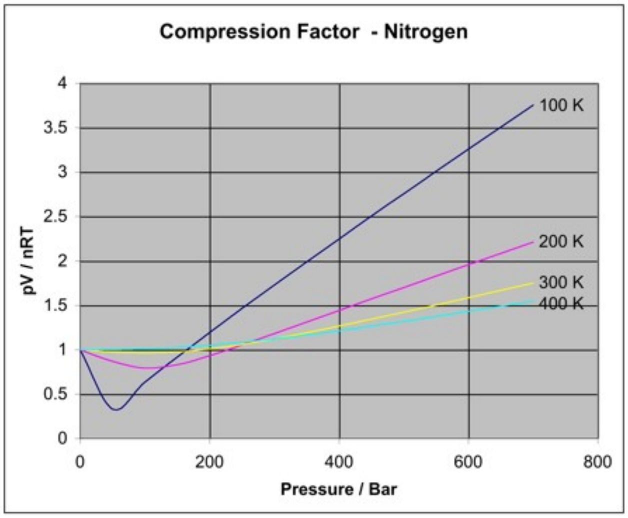


Figure 2.7.3: Compressibility of select gases as a function of applied pressure.

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 2.7.3), the Boyle temperature can be expressed in terms of the virial coefficients. Starting with the compression factor

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

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:

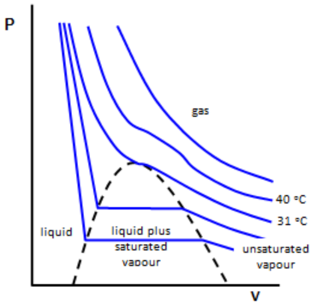


Figure 2.7.4: Condensation of a van der Waal gas.

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.

2.E: Gases (Exercises)

Q2.1

Assuming the form of the Maxwell distribution allowing for motion in three directions to be

$$f(v) = Nv^2 \exp\left(\frac{mv^2}{2k_BT}\right) \tag{2.E.1}$$

derive the correct expression for N such that the distribution is normalized. Hint: a table of definite integrals indicates

$$\int_0^\infty x^{2n} e^{-ax^2}\,dx = \frac{1}{4}\frac{\sqrt{\pi}}{a^{3/2}} \tag{2.E.2}$$

Q2.2

Dry ice (solid CO_2) has a density of 1.6 g/cm^3. Assuming spherical molecules, estimate the collisional cross section for CO_2. How does it compare to the value listed in the text?

Q2.3

Calculate the pressure exerted by 1.00 mol of Ar, N_2, and CO_2 as an ideal gas, a van der Waals gas, and a Redlich-Kwong gas, at 25 °C and 24.4 L.

Q2.4

The compression factor Z for CO_2 at 0 °C and 100 atm is 0.2007. Calculate the volume of a 2.50 mole sample of CO_2 at 0 °C and 100 atm.

Q2.5

	Ar	N_2	CO_2
ideal			
van der Waals			
Redlich-Kwong			

Q2.6

What is the maximum pressure that will afford a N_2 molecule a mean-free-path of at least 1.00 m at 25 °C?

Q2.7

In a Knudsen cell, the effusion orifice is measured to be 0.50 mm^2. If a sample of naphthalene is allowed to effuse for 1.0 hr at a temperature of 40.3 °C, the cell loses 0.0236 g. From this data, calculate the vapor pressure of naphthalene at this temperature.

Q2.8

The vapor pressure of scandium was determined using a Knudsen cell [Kirkorian, *J. Phys. Chem.*, **67**, 1586 (1963)]. The data from the experiment are given below.

Vapor Pressure of Scandium	
Temperature	1555.4 K
Time	110.5 min
Mass loss	9.57 mg
Diameter of orifice	0.2965 cm

From this data, find the vapor pressure of scandium at 1555.4 K.

Q2.9

A thermalized sample of gas is one that has a distribution of molecular speeds given by the Maxwell-Boltzmann distribution. Considering a sample of N_2 at 25 ^{c}C what fraction of the molecules have a speed less than

a. the most probably speed
b. the average sped
c. the RMS speed?
d. The RMS speed of helium atoms under the same conditions?

Q2.10

Assume that a person has a body surface area of 2.0 m^2. Calculate the number of collisions per second with the total surface area of this person at 25 °C and 1.00 atm. (For convenience, assume air is 100% N_2)

Q2.11

Two identical balloons are inflated to a volume of 1.00 L with a particular gas. After 12 hours, the volume of one balloon has decreased by 0.200 L. In the same time, the volume of the other balloon has decreased by 0.0603 L. If the lighter of the two gases was helium, what is the molar mass of the heavier gas?

Q2.12

Assuming it is a van der Waals gas, calculate the critical temperature, pressure and volume for CO_2.

Q2.13

Find an expression in terms of van der Waals coefficients for the Boyle temperature. (*Hint*: use the viral expansion of the van der Waals equation to find an expression for the second viral coefficient!)

Q2.14

Consider a gas that follows the equation of state

$$p = \frac{RT}{V_m - b} \tag{2.E.3}$$

Using a virial expansion, find an expression for the second virial coefficient.

Q2.15

Consider a gas that obeys the equation of state

$$p = \frac{nRT}{V_m - b} \tag{2.E.4}$$

where a and b are non-zero constants. Does this gas exhibit critical behavior? If so, find expressions for p_c, V_c, and T_c in terms of the constants a, b, and R.

Q2.16

Consider a gas that obeys the equation of state

$$p = \frac{nRT}{V - nB} - \frac{an}{V} \tag{2.E.5}$$

a. Find an expression for the *Boyle temperature* in terms of the constant a, b, and R.
b. Does this gas exhibit critical behavior? If so, find expressions for p_c, V_c, and T_c in terms of the constants a, b, and R.

2.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

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CHAPTER OVERVIEW

3: First Law of Thermodynamics

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.

3.1: 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.)

3.2: 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.

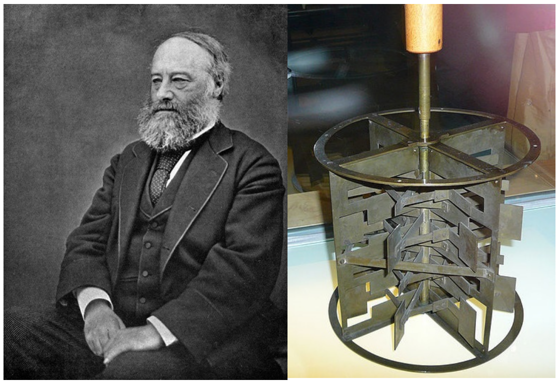


Figure $3.2.1$: (left) James Prescott Joule (1818 - 1889) (right) Joule's apparatus for measuring the work equivalent of heat. (CC BY-SA 3.0; Dr. Mirko Junge)

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

$$\Delta U = U_f - U_i \tag{3.2.1}$$

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 3.2.1: 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

$$\begin{aligned} q &= mC\Delta T \\ &= (5.0\ \cancel{g})(4.184 \frac{J}{\cancel{g}\ \cancel{^\circ C}})(25.0\ \cancel{^\circ C} - 21.0\ \cancel{^\circ C}) \\ &= 84\ J \end{aligned}$$

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

$$\left(\frac{\partial f}{\partial x_i}\right)_{x_j \neq i} = \lim_{\Delta_i \rightarrow 0}\left(\frac{f(x_1+\Delta x_1, x_2+\Delta x_2, \ldots, x_i+\Delta x_i, \ldots x_n+\Delta x_n) - f(x_1, x_2, \ldots x_i, \ldots x_n)}{\Delta x_i}\right)$$

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.

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2} \tag{3.2.2}$$

and

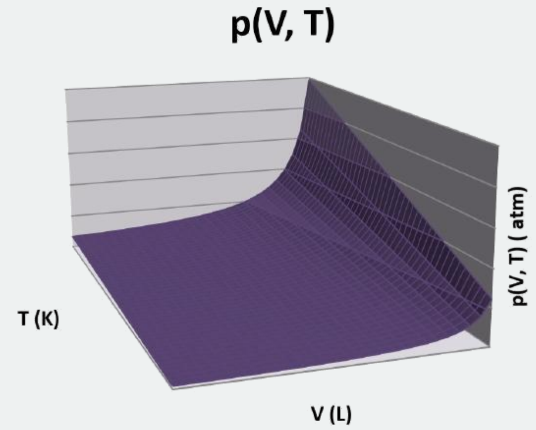
$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} \tag{3.2.3}$$

So that the change in pressure can be expressed

$$dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT \tag{3.2.4}$$

or by substituting Equations 3.2.2 and 3.2.3

$$dp = \left(-\frac{RT}{V^2}\right) dV + \left(\frac{R}{V}\right) dT$$



Macroscopic changes can be expressed by integrating the individual pieces of Equation 3.2.4 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

$$\begin{aligned}\Delta p &= \int_{200\,K}^{400,\,K}\left(\frac{R}{1.0\,L/mol}\right)dT + \int_{1.0\,L/mol}^{3.0\,L/mol}\left(-\frac{R(400\,K)}{V^2}\right)dV \\ &= \left[\frac{RT}{1.0\,L/mol}\right]_{200\,K}^{400\,K} + \left[\frac{R(400\,K)}{V}\right]_{1.0\,L/mol}^{3.0\,L/mol} \\ &= R\left[\left(\frac{400\,K}{1.0\,L/mol} - \frac{200\,K}{1.0\,L/mol}\right) + \left(\frac{400\,K}{3.0\,L/mol} - \frac{400\,K}{1.0\,L/mol}\right)\right] \\ &= -5.47\,atm\end{aligned}$$

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 3.2.2: 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

$$\begin{aligned}w &= -p_{exp}\int_{V_1}^{V_2} dV \\ &= -p_{exp}(V_2 - V_1) \\ &= -(0.500\,am)(44.8\,L - 22.4\,L)\left(\frac{8.314\,J}{0.08206\,atm\,L}\right) \\ &= -1130\,J = -1.14\,kJ\end{aligned}$$

Note: The ratio of gas law constants can be used to convert between atm·L and J quite conveniently!

3.3: 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.

$$w = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln\left(\frac{V_2}{V_1}\right) \tag{3.3.1}$$

Equation 3.3.1 is derived for ideal gases only; a van der Waal gas would result in a different version.

✓ Example 3.3.1: 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?

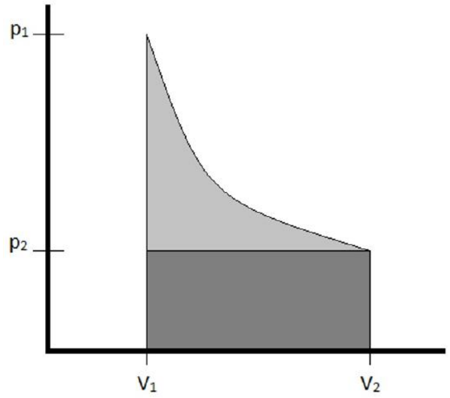
Solution

Using Equation 3.3.1 to calculate this

$$\begin{aligned} w &= -(1.00\ \cancel{mol})\left(8.314\ \frac{J}{\cancel{mol}\ \ \cancel{K}}\right)(273\ \ \cancel{K})\ln\left(\frac{44.8\,L}{22.4\,L}\right) \\ &= -1570\,J = 1.57\ kJ \end{aligned}$$

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 $3.3.1$ 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

$$dq = \frac{dq}{\partial T} dT = C\, dt \tag{3.3.2}$$

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 3.3.2 is integrated the

$$q = \int_{T_1}^{T_2} nC_V dt \tag{3.3.3}$$

✓ Example 3.3.2: 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 3.3.3 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

$$dH = dq + dw + pdV + Vdp \tag{3.3.4}$$

$$= dq - \cancel{pdV} + \cancel{pdV} + \cancelto{0}{Vdp} \tag{3.3.5}$$

$$= dq \tag{3.3.6}$$

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 3.3.3: 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 3.3.6 (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 3.3.4: 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, Equation3.3.1 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

$$dw = nC_v dT \tag{3.3.7}$$

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

$$T_1\left(\frac{V_1}{V_2}\right)^{-\frac{R}{C_V}} = T_2 \tag{3.3.8}$$

Once ΔT is known, it is easy to calculate w, ΔU and ΔH.

✓ Example 3.3.5:

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 3.3.8

$$\begin{aligned} T_2 &= T_1 \left(\frac{V_1}{V_2}\right)^{-\frac{R}{C_V}} \\ &= (273\ K)\left(\frac{22.4\ L}{44.8\ L}\right)^{2/3} \\ &= 172\ K \end{aligned}$$

So

$$\Delta T = 172\ K - 273\ K = -101\ K$$

For calculating work, we integrate Equation 3.3.7 to get

$$\begin{aligned} w &= \Delta U = nC_v \Delta T \\ &= (1.00\ mol)\left(\frac{3}{2} 8.314\ \frac{J}{mol\ K}\right)(-101\ K) \\ &= 1.260\ kJ \end{aligned}$$

$$\begin{aligned} \Delta H &= \Delta U + nR\Delta T \\ &= -1260\ J + (1.00\ mol)\left(\frac{3}{2} 8.314\ \frac{J}{mol\ K}\right)(-101\ K) \\ &= -2100\ J \end{aligned}$$

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

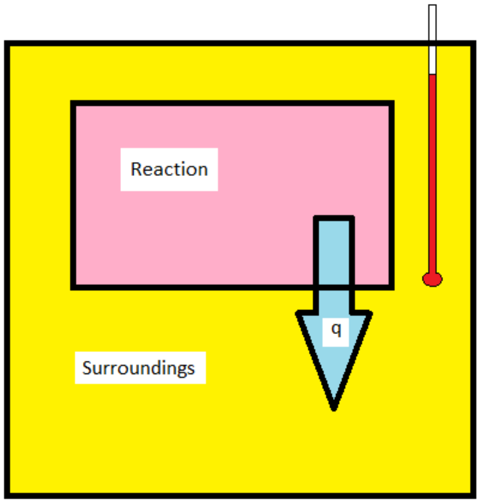
Pathway	q	w	ΔU	ΔH
Isothermal	$nRT\ln(V_2/V_1)$	$-nRT\ln(V_2/V_1)$	0	0
Isochoric	$C_V\Delta T$	0	$C_V\Delta T$	$C_V\Delta T + V\Delta p$
Isobaric	$C_p\Delta T$	$-p\Delta V$	$C_p\Delta T - p\Delta V$	$C_p\Delta T$
adiabatic	0	$C_V\Delta T$	$C_V\Delta T$	$C_p\Delta T$

3.4: 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.

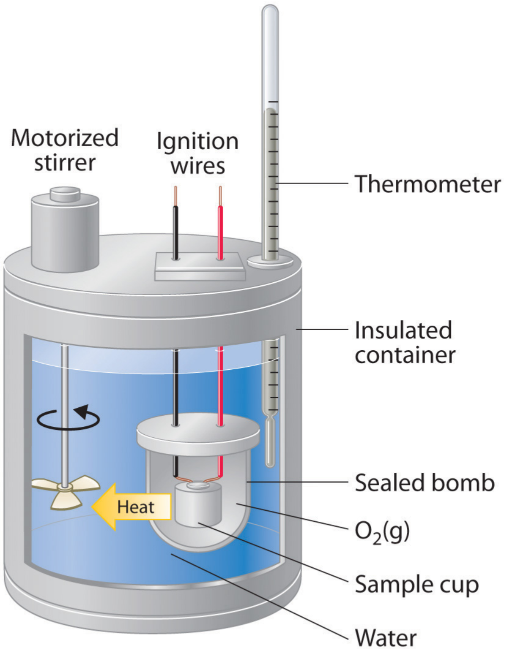


Figure 3.4.1: A Bomb Calorimeter. After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released 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 ^{o}C), 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

$$C_6H_5COOH(s) + \frac{15}{2}O_2(g) \longrightarrow 7\,CO_2(g) + 3\,H_2O(l)$$

it can be seen that Δn_{gas} is -0.5 mol of gas for every mole of benzoic acid reacted.

✓ Example 3.4.1: Combustion of Naphthalene

A student burned a 0.7842 g sample of benzoic acid ($C_7H_6O_2$) 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 ($C_{10}H_8$) (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:

$$C_{10}H_8(s) + 12\,O_2(g) \longrightarrow 10\,CO_2(g) + 4\,H_2O(l)$$

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!

3.5: Temperature Dependence of Enthalpy

It is often required to know thermodynamic functions (such as enthalpy) at temperatures other than those available from tabulated data. Fortunately, the conversion to other temperatures is not difficult.

At constant pressure

$$dH = C_p\, dT$$

And so for a temperature change from T_1 to T_2

$$\Delta H = \int_{T_2}^{T_2} C_p\, dT \tag{3.5.1}$$

Equation 3.5.1 is often referred to as *Kirchhoff's Law*. If C_p is independent of temperature, then

$$\Delta H = C_p\, \Delta T \tag{3.5.2}$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral in Equation 3.5.1. A common *empirical* model used to fit heat capacities over broad temperature ranges is

$$C_p(T) = a + bT + \frac{c}{T^2} \tag{3.5.3}$$

After combining Equations 3.5.3 and 3.5.1, the enthalpy change for the temperature change can be found obtained by a simple integration

$$\Delta H = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2}\right) dT \tag{3.5.4}$$

Solving the definite integral yields

$$\Delta H = \left[aT + \frac{b}{2}T^2 - \frac{c}{T}\right]_{T_1}^{T_2} \tag{3.5.5}$$

$$= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{3.5.6}$$

This expression can then be used with experimentally determined values of a, b, and c, some of which are shown in the following table.

Table 3.5.1*: Empirical Parameters for the temperature dependence of* C_p

Substance	a (J mol^{-1} K^{-1})	b (J mol^{-1} K^{-2})	c (J mol^{-1} K)
C(gr)	16.86	4.77 x 10^{-3}	-8.54 x 10^{5}
CO_2(g)	44.22	8.79 x 10^{-3}	-8.62 x 10^{5}
H_2O(l)	75.29	0	0
N_2(g)	28.58	3.77 x 10^{-3}	-5.0 x 10^{4}
Pb(s)	22.13	1.172 x 10^{-2}	9.6 x 10^{4}

✓ Example 3.5.1: Heating Lead

What is the molar enthalpy change for a temperature increase from 273 K to 353 K for Pb(s)?

Solution

The enthalpy change is given by Equation 3.5.1 with a temperature dependence C_p given by Equation 3.5.1 using the parameters in Table 3.5.1. This results in the integral form (Equation 3.5.6):

$$\Delta H = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

when substituted with the relevant parameters of Pb(s) from Table $3.5.1$.

$$\begin{aligned}\Delta H = &\left(22.14\,\frac{J}{mol\,K}\right)(353\,K - 273\,K)\\ &+ \frac{1.172\times 10^{-2}\,\frac{J}{mol\,K^2}}{2}\left((353\,K)^2 - (273\,K)^2\right)\\ &- 9.6\times 10^4\,\frac{J\,K}{mol}\left(\frac{1}{(353\,K)} - \frac{1}{(273\,K)}\right)\\ \Delta H = &\ 1770.4\,\frac{J}{mol} + 295.5\,\frac{J}{mol} + 470.5\,\frac{J}{mol}\\ =&\,2534.4\,\frac{J}{mol}\end{aligned}$$

For chemical reactions, the reaction enthalpy at differing temperatures can be calculated from

$$\Delta H_{rxn}(T_2) = \Delta H_{rxn}(T_1) + \int_{T_1}^{T_2} \Delta C_p \Delta T$$

✓ Example 3.5.2: Enthalpy of Formation

The enthalpy of formation of NH_3(g) is -46.11 kJ/mol at 25 ^{o}C. Calculate the enthalpy of formation at 100 ^{o}C.

Solution

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)}$$

with $\Delta H\,(298\,K) = -46.11\,kJ/mol$

Compound	Cp (J mol^{-1} K^{-1})
N_2(g)	29.12
H_2(g)	28.82
NH_3(g)	35.06

$$\begin{aligned}\Delta H(373\,K) &= \Delta H(298\,K) + \Delta C_p \Delta T\\ &= -46110 + \frac{J}{mol}\left[2\left(35.06\,\frac{J}{mol\,K}\right) - \left(29.12\,\frac{J}{mol\,K}\right) - 3\left(28.82\,\frac{J}{mol\,K}\right)\right](373\,K - 298\,K)\\ &= -49.5\,\frac{kJ}{mol}\end{aligned}$$

3.6: 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 3.6.1:

Find ΔH_{rxn} for the reaction

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

Given

$$C(gr) + \tfrac{1}{2}O_2(g) \rightarrow CO(g)$$

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^o}). 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

$$\begin{align} \Delta_{rxn} &= (1\, mol)\left(\Delta H_f^o(CO_2)\right) + (2\, mol)\left(\Delta H_f^o(H_2O)\right) - (1\, mol)\left(\Delta H_f^o(CH_4)\right) \tag{3.6.1} \\ &= (1\, mol)(-393.5\, kJ/mol) + (2\, mol)\,(-285.8\, kJ/mol) - (1\, mol)\,(-74.6\, kJ/mol) \tag{3.6.2} \\ &= -890.5\, kJ/mol \tag{3.6.3} \end{align}$$

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

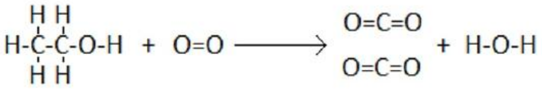
$$XY(g) \rightarrow X(g) + Y(g)$$

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

$$\begin{aligned} \Delta H_c &= 5(413\,kJ/mol) + 1(348\,kJ/mol) + 1(358\,kJ/mol) \\ &\quad + 1(495\,kJ/mol) - 4(799\,kJ/mol) - 2(463\,kJ/mol) \\ &= -856\,kJ/mol \end{aligned} \tag{3.6.4}$$

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%.

3.7: 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

$$\mathrm{NaCl(s)} \rightarrow \mathrm{Na^+(g)} + \mathrm{Cl^-(g)}$$

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.

$$\mathrm{Na(s)} + \tfrac{1}{2}\mathrm{Cl_2} \rightarrow \mathrm{NaCl(s)}$$

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.

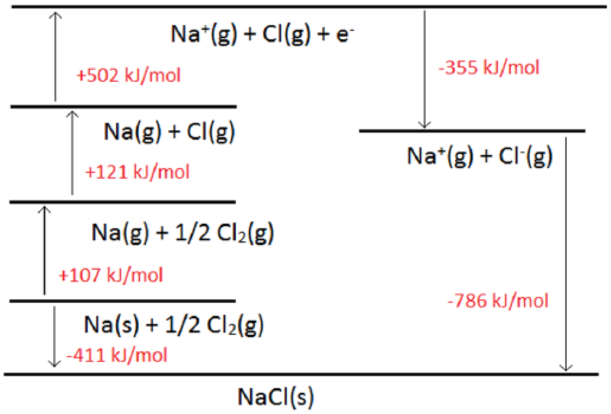


Figure 3.6.1: the Born-Haber Cycle for NaCl.

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 3.7.1: 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

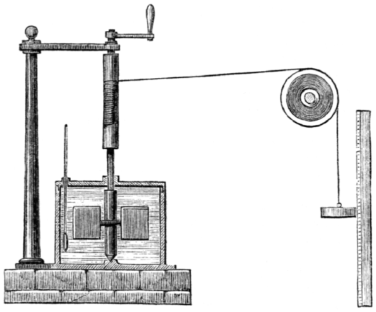
$\Delta H_f = -246\, kJ/mol$

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!

3.E: First Law of Thermodynamics (Exercises)

Q3.1

In the attempt to measure the heat equivalent of mechanical work (as Joule did in his famous experiment) a student uses an apparatus similar to that shown below:



The 1.50 kg weight is lifted 30.0 cm against the force due to gravity (9.8 N). If the specific heat of water is 4.184 J/(g °C), what is the expected temperature increase of the 1.5 kg of water in the canister?

Q3.2

1.00 mol of an ideal gas, initially occupying 12.2 L at 298 K, expands isothermally against a constant external pressure of 1.00 atm until the pressure of the gas is equal to the external pressure. Calculate Δp, q, w, ΔU, and ΔH for the expansion.

Q3.3

Consider 1.00 mol of an ideal gas expanding isothermally at 298 K from an initial volume of 12.2 L to a final volume of 22.4 L. Calculate Δp, q, w, ΔU, and ΔH for the expansion.

Q3.4

Consider 1.00 mol of an ideal gas (C_V = 3/2 R) Occupying 22.4 L that undergoes an isochoric (constant volume) temperature increase from 298 K to 342 K. Calculate Δp, q, w, ΔU, and ΔH for the change.

Q3.5

Consider 1.00 mol of an ideal gas (C_p = 5/2 R) initially at 1.00 atm that undergoes an isobaric expansion from 12.2 L to 22.4 L. Calculate ΔT, q, w, ΔU, and ΔH for the change.

Q3.6

Consider 1.00 mol of an ideal gas (C_V = 3/2 R) initially at 12.2 L that undergoes an adiabatic expansion to 22.4 L. Calculate ΔT, q, w, ΔU, and ΔH for the change.

Q3.7

Derive an expression for the work of an isothermal, reversible expansion of a gas that follows the equation of state (in which a is a parameter of the gas)

$$pV = nRT - \frac{an^2}{V} \tag{3.E.1}$$

from V_1 to V_2.

Q3.8

Use the following data [Huff, Squitieri, and Snyder, J. Am. Chem. Soc., **70**, 3380 (1948)] to calculate the standard enthalpy of formation of tungsten carbide, $WC(s)$.

Reaction	ΔH^o (kJ)
$C(gr) + O_2(g) \rightarrow CO_2(g)$	-393.51
$WC(s) + 5/2O_2(g) \rightarrow WO_3(s) + CO_2(g)$	-1195.79
$W(s) + 3/2O_2(g) \rightarrow WO_3(s)$	-837.42

Q3.9

The standard molar enthalpy of combustion (ΔH_c) of propane gas is given by

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) \tag{3.E.2}$$

with $\Delta H_c = -2220\, kJ/mol$

The standard molar enthalpy of vaporization (ΔH_{vap}) for liquid propane

$$C_3H_8(l) \rightarrow C_3H_8(g) \tag{3.E.3}$$

with $\Delta H_{vap} = 15\, kJ/mol$

a. Calculate the standard enthalpy of combustion of liquid propane.
b. Calculate the standard internal energy change of vaporization (ΔU_{vap}) for liquid propane.
c. Calculate the standard internal energy change of combustion (ΔH_c) for liquid propane.

Q3.10

The enthalpy of combustion (ΔH_c) of aluminum borohydride, $Al(BH_4)_3(l)$, was measured to be -4138.4 kJ/mol [Rulon and Mason, *J. Am. Chem. Soc.*, **73**, 5491 (1951)]. The combustion reaction for this compound is given by

$$Al(BH_4)_3(l) + 6O_2(g) \rightarrow ½Al_2O_3(s) + 3/2B_2O_3(s) + 6H_2O(l) \tag{3.E.4}$$

Given the following additional data, calculate the enthalpy of formation of $Al(BH_4)_3(g)$.

- $Al_2O_3(s)$: $\Delta H_f = -1669.8\, kJ/mol$
- $B_2O_3(s)$: $\Delta H_f = -1267.8\, kJ/mol$
- $H_2O(l)$: $\Delta H_f = -285.84\, kJ/mol$
- $Al(BH_4)_3(l)$: $\Delta H_{vap} = 30.125\, kJ/mol$

Q3.11

The standard enthalpy of formation (ΔH_f^o) for water vapor is -241.82 kJ/mol at 25 °C. Use the data in the following table to calculate the value at 100 °C.

Substance	C_p (J mol^{-1} K^{-1})
H_2(g)	28.84
O_2(g)	29.37
H_2O(g)	33.58

Q3.12

$\Delta C_p = (1.00 + 2.00 \times 10^{-3} T)\, J/K$ and $\Delta H_{298} = -5.00\, kJ$ for a dimerization reaction

$$2A \rightarrow A_2 \tag{3.E.5}$$

Find the temperature at which \(\Delta H = 0\).

Q3.13

From the following data, determine the lattice energy of $BaBr_2$.

$$Ca(s) \rightarrow Ca(g) \tag{3.E.6}$$

with $\Delta H_{sub} = 129 \, kJ/mol$

$$Br_2(l) \rightarrow Br_2(g) \tag{3.E.7}$$

with $\Delta H_{vap} = 31 \, kJ/mol$

$$Br_2(g) \rightarrow 2Br(g) \tag{3.E.8}$$

with $D(Br-Br) = 193 \, kJ/mol$

$$Ca(g) \rightarrow Ca^+(g) + e^- \tag{3.E.9}$$

with $1^{st} \, IP(K) = 589.8 \, kJ/mol$

$$Ca^+(g) \rightarrow Ca^{2+}(g) + e^- \tag{3.E.10}$$

with $2^{nd} IP(K) = 1145.4 \, kJ/mol$

$$Br(g) + e^- \rightarrow Br-(g) \tag{3.E.11}$$

with $1^{st} EA(Br) = 194 \, kJ/mol$

$$Ca(s) + Br_2^-(l) \rightarrow CaBr_2(s) \tag{3.E.12}$$

with $\Delta H_f = -675 \, kJ/mol$

Q3.15

Using average bond energies (Table T3) estimate the reaction enthalpy for the reaction

$$C_2H_4 + HBr \rightarrow C_2H_5Br \tag{3.E.13}$$

Contributors and Attributions

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3.S: 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

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CHAPTER OVERVIEW

4: Putting the First Law to Work

Physical Chemistry: Thermodynamics
Patrick Fleming

4.1: Prelude to Putting the First Law to Work

As has been seen in previous chapters, may important thermochemical quantities can be expressed in terms of partial derivatives. Two important examples are the molar heat capacities C_p and C_V which can be expressed as

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

and

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

These are properties that can be measured experimentally and tabulated for many substances. These quantities can be used to calculate changes in quantities since they represent the slope of a surface (H or U) in the direction of the specified path (constant p or V). This allows us to use the following kinds of relationships:

$$dH = \left(\frac{\partial H}{\partial T} \right)_p dT$$

and

$$\Delta H = \int \left(\frac{\partial H}{\partial T} \right)_p dT$$

Because thermodynamics is kind enough to deal in a number of **state variables**, the functions that define how those variable change must behave according to some very well determined mathematics. This is the true power of thermodynamics!

4.2: Total and Exact Differentials

The fact that we can define the *constant volume heat capacity* as

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V \tag{4.2.1}$$

suggests that the internal energy depends very intimately on two variables: volume and temperature. In fact, we will see that for a single component system, state variables are always determined when two state variables are defined. In the case of internal energy, we might write $U = f(V,T)$ or $U(V,T)$.

This suggests that the way to change U is to change either V or T (or both!) And if there is a mathematical function that relates the internal energy to these two variables, it should easy to see how it changes when either (or both!) are changed. This can be written as a total differential:

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \tag{4.2.2}$$

Even without knowing the actually mathematical function relating the variables to the property, we can imagine how to calculate changes in the property from this expression.

$$\Delta U = \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV + \int_{T_1}^{T_2} \left(\frac{\partial U}{\partial T}\right)_V dT$$

In words, this implies that we can think of a change in U occurring due to an *isothermal change* followed by an *isochoric change*. And all we need to know is the slope of the surface in each pathway direction. There are a couple of very important experiments people have done to explore the measurement of those kinds of slopes. Understanding them, it turns out, depends on two very important physical properties of substances.

Exact Differentials

We have seen that the total differential of $U(V,T)$ can be expressed as Equation 4.2.2. In general, if a differential can be expressed as

$$df(x,y) = P\,dx + Q\,dy$$

the differential will be an **exact differential** if it follows the **Euler relation**

$$\left(\frac{\partial P}{\partial y}\right)_x = \left(\frac{\partial Q}{\partial x}\right)_y \tag{4.2.3}$$

In order to illustrate this concept, consider $p(V,T)$ using the ideal gas law.

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

The total differential of p can be written

$$dp = \left(-\frac{RT}{V^2}\right) dV + \left(\frac{R}{V}\right) dT \tag{4.2.4}$$

✓ Example 4.2.1: Euler Relation

Does Equation 4.2.4 follow the Euler relation (Equation 4.2.3)?

Solution

Let's confirm!

$$\left[\frac{1}{\partial T}\left(-\frac{RT}{V^2}\right)\right]_V \overset{?}{=} \left[\frac{1}{\partial V}\left(\frac{R}{V}\right)\right]_T$$

$$\left(-\frac{R}{V^2}\right) \overset{\checkmark}{=} \left(-\frac{R}{V^2}\right)$$

dp is, in fact, an exact differential.

The differentials of all of the **thermodynamic functions** that are **state functions** will be exact. Heat and work are not exact differential and dw and dq are called *inexact differentials* instead.

4.3: Compressibility and Expansivity

Isothermal Compressibility (κ_T)

A very important property of a substance is how compressible it is. Gases are very compressible, so when subjected to high pressures, their volumes decrease significantly (think Boyle's Law!) Solids and liquids however are not as compressible. However, they are not entirely incompressible! High pressure will lead to a decrease in volume, even if it is only slight. And, of course, different substances are more compressible than others.

To quantify just how compressible substances are, it is necessary to define the property. The **isothermal compressibility** is defined by the fractional differential change in volume due to a change in pressure.

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{4.3.1}$$

The negative sign is important in order to keep the value of κ_T positive, since an increase in pressure will lead to a decrease in volume. The $1/V$ term is needed to make the property intensive so that it can be tabulated in a useful manner.

Isobaric Thermal Expansivity (α)

Another very important property of a substance is how its volume will respond to changes in temperature. Again, gases respond profoundly to changes in temperature (think Charles' Law!) whereas solids and liquid will have more modest (but not negligible) responses to changes in temperature. (For example, If mercury or alcohol didn't expand with increasing temperature, we wouldn't be able to use those substances in thermometers.)

The definition of the **isobaric thermal expansivity** (or sometimes called the expansion coefficient) is

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{4.3.2}$$

As was the case with the compressibility factor, the $1/V$ term is needed to make the property intensive, and thus able to be tabulated in a useful fashion. In the case of expansion, volume tends to increase with increasing temperature, so the partial derivative is positive.

Deriving an Expression for a Partial Derivative (Type I): The reciprocal rule

Consider a system that is described by three variables, and for which one can write a mathematical constraint on the variables

$$F(x,y,z) = 0$$

Under these circumstances, one can specify the state of the system varying only two parameters independently because the third parameter will have a fixed value. As such one could define two functions: $z(x,y)$ and $y(x,z)$.

This allows one to write the total differentials for dz and dy as follows

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{4.3.3}$$

and

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \tag{4.3.4}$$

Substituting the Equation 4.3.4 expression into Equation 4.3.3:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left[\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz\right] \tag{4.3.5}$$

$$= \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x dz \tag{4.3.6}$$

If the system undergoes a change following a pathway where x is held constant ($dx = 0$), this expression simplifies to

$$dz = \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x dz$$

And so for changes for which $dz \neq 0$,

$$\left(\frac{\partial z}{\partial y}\right)_x = \frac{1}{\left(\frac{\partial y}{\partial z}\right)_x}$$

This *reciprocal rule* is very convenient in the manipulation of partial derivatives. But it can also be derived in a straightforward, albeit less rigorous, manner. Begin by writing the total differential for $z(x, y)$ (Equation 4.3.3):

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Now, divide both sides by dz and constrain to constant x.

$$\left.\frac{dz}{dz}\right|_x = \left(\frac{\partial z}{\partial x}\right)_y \left.\frac{dx}{dz}\right|_x + \left(\frac{\partial z}{\partial y}\right)_x \left.\frac{dy}{dz}\right|_x \tag{4.3.7}$$

Noting that

$$\left.\frac{dz}{dz}\right|_x = 1$$

$$\left.\frac{dx}{dz}\right|_x = 0$$

and

$$\left.\frac{dy}{dz}\right|_x = \left(\frac{\partial y}{\partial z}\right)_x$$

Equation 4.3.7 becomes

$$1 = \left(\frac{\partial z}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x$$

or

$$\left(\frac{\partial z}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial z}\right)_x}$$

This “formal” method of partial derivative manipulation is convenient and useful, although it is not mathematically rigorous. However, it does work for the kind of partial derivatives encountered in thermodynamics because the variables are **state variables** and the differentials are **exact**.

Deriving an Expression for a Partial Derivative (Type II): The Cyclic Permutation Rule

This alternative derivation follow the initial steps in the derivation above to Equation 4.3.6:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x dz$$

If the system undergoes a change following a pathway where z is held constant ($dz = 0$), this expression simplifies to

$$0 = \left(\frac{\partial z}{\partial x}\right)_y dy + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z dx$$

And so for and changes in which $dx \neq 0$

$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

This *cyclic permutation rule* is very convenient in the manipulation of partial derivatives. But it can also be derived in a straight-forward, albeit less rigorous, manner. As with the derivation above, we wegin by writing the total differential of $z(x, y)$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Now, divide both sides by dx and constrain to constant z.

$$\left.\frac{dz}{dx}\right|_z = \left(\frac{\partial z}{\partial x}\right)_y \left.\frac{dx}{dx}\right|_z + \left(\frac{\partial z}{\partial y}\right)_x \left.\frac{dy}{dx}\right|_z \tag{4.3.8}$$

Note that

$$\left.\frac{dz}{dx}\right|_z = 0$$

$$\left.\frac{dx}{dx}\right|_z = 1$$

and

$$\left.\frac{dy}{dx}\right|_z = \left(\frac{\partial y}{\partial x}\right)_z$$

Equation 4.3.8 becomes

$$0 = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

which is easily rearranged to

$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

This type of transformation is very convenient, and will be used often in the manipulation of partial derivatives in thermodynamics.

✓ Example 4.3.1: Expanding Thermodynamic Functions

Derive an expression for

$$\frac{\alpha}{\kappa_T}. \tag{4.3.9}$$

in terms of derivatives of thermodynamic functions using the definitions in Equations 4.3.1 and 4.3.2.

Solution

Substituting Equations 4.3.1 and 4.3.2 into the Equation 4.3.9

$$\frac{\alpha}{\kappa_T} = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p}{-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T}$$

Simplifying (canceling the $1/V$ terms and using transformation Type I to invert the partial derivative in the denominator) yields

$$\frac{\alpha}{\kappa_T} = -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T$$

Applying Transformation Type II give the final result:

$$\frac{\alpha}{\kappa_T} = \left(\frac{\partial p}{\partial T}\right)_V$$

4.4: 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)

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

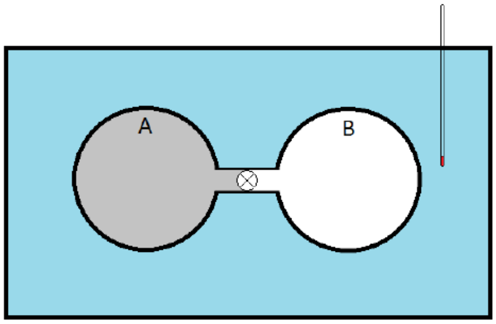
one quickly recognizes one of the terms as the constant volume heat capacity, C_V. And so the expression can be re-written

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + C_V dT$$

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

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{4.4.1}$$

Application to an Ideal Gas

For an ideal gas $p = RT/V$, so it is easy to show that

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} \tag{4.4.2}$$

so combining Equations 4.4.1 and 4.4.2 together to get

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V} - p \tag{4.4.3}$$

And since also becuase $p = RT/V$, then Equation 4.4.3 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,

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \tag{4.4.4}$$

so

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b} \tag{4.4.5}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{R}{V-b} - p \tag{4.4.6}$$

Substitution of the expression for p (Equation 4.4.4) into this Equation 4.4.6

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

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)!

4.5: The Joule-Thomson Effect

In 1852, working with William Thomson (who would later become Lord Kelvin), Joule conducted an experiment in which they pumped gas at a steady rate through a lead pipe that was cinched to create a construction. On the upstream side of the constriction, the gas was at a higher pressure than on the downstream side of the constriction. Also, the temperature of the gas was carefully monitored on either side of the construction. The cooling that they observed as the gas expanded from a high pressure region to a lower pressure region was extremely important and lead to a common design of modern refrigerators.

Not all gases undergo a cooling effect upon expansion. Some gases, such as hydrogen and helium, will experience a warming effect upon expansion under conditions near room temperature and pressure. The direction of temperature change can be determined by measuring the Joule-Thomson coefficient, μ_{JT}. This coefficient has the definition

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial p}\right)_H$$

Schematically, the Joule-Thomson coefficient can be measured by measuring the temperature drop or increase a gas undergoes for a given pressure drop (Figure $4.5.1$). The apparatus is insulated so that no heat can be transferred in or out, making the expansion isenthalpic.

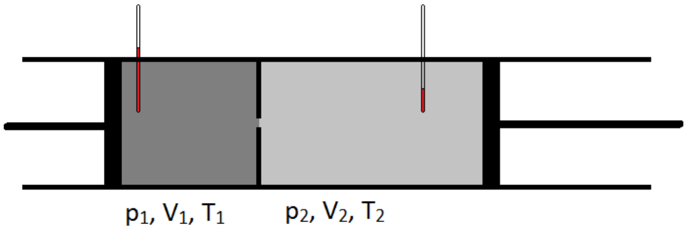


Figure $4.5.1$:

The typical behavior of the Joule-Thomson coefficient can be summarized in Figure $4.5.2$. At the combinations of T and p for which $\mu_{JT} > 0$ (inside the shaded region), the sample will cool upon expansion. At those p and T conditions outside of the shaded region, where $\mu_{JT} < 0$, the gas will undergo a temperature increase upon expansion. And along the boundary, a gas will undergo neither a temperature increase not decrease upon expansion. For a given pressure, there are typically two temperatures at which μ_{JT} changes sign. These are the upper and lower inversion temperatures.

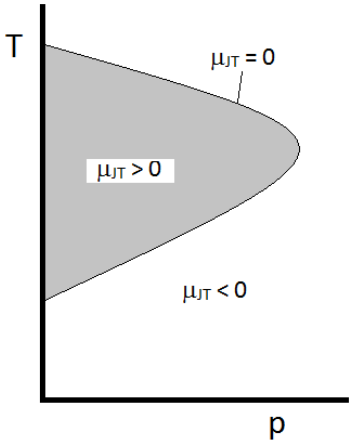


Figure $4.5.2$: The typical behavior of the Joule-Thomson coefficient at different temperatures and pressures.

Using the tools of mathematics, it is possible to express the Joule-Thomson coefficient in terms of measurable properties. Consider enthalpy as a function of pressure and temperature: $H(p,T)$. This suggests that the total differential dH can be expressed

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT \tag{4.5.1}$$

It will be shown later (again, once we develop the *Maxwell Relations*) that

$$\left(\frac{\partial H}{\partial p}\right)_T dp = -T\left(\frac{\partial V}{\partial T}\right)_p + V$$

A simple substitution shows

$$\left(\frac{\partial H}{\partial p}\right)_T dp = -TV\alpha + V = V(1 - T\alpha)$$

So

$$dH = V(1 - T\alpha)dP + C_p dT$$

For an ideal gas, $\alpha = 1/T$, so

$$dH = \cancelto{0}{V\left(1 - T\frac{1}{T}\right)dP} + C_p dT$$

which causes the first term to vanish. So for constant enthalpy expansion ($dH = 0$), there can be no change in temperature ($dT = 0$). This will mean that gases will only show non-zero values for μ_{JT} only because they deviate from ideal behavior!

✓ Example $4.5.1$:

Derive an expression for μ_{JT} in terms of α, C_p, V, and T.

Solution

Using the total differential for $H(p, T)$ (Equation $4.5.1$):

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT$$

Dividing by dp and constraining to constant H:

$$\left.\frac{dH}{dp}\right|_H = \left(\frac{\partial H}{\partial p}\right)_T \left.\frac{dp}{dp}\right|_H + \left(\frac{\partial H}{\partial T}\right)_p \left.\frac{dT}{dp}\right|_H$$

Noting that

$$\left.\frac{dH}{dp}\right|_H = 0$$

$$\left.\frac{dp}{dp}\right|_H = 1$$

and

$$\left.\frac{dT}{dp}\right|_H = \left(\frac{\partial T}{\partial p}\right)_H$$

so

$$0 = \left(\frac{\partial H}{\partial p}\right)_T + \left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H$$

We can then use the following substitutions:

$$\left(\frac{\partial H}{\partial p}\right)_T = V(1 - T\alpha)$$

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

$$\left(\frac{\partial T}{\partial p}\right)_H = \mu_{JT}$$

To get

$$0 = V(1 - T\alpha) + C_p\mu_{JT}$$

And solving for μ_{JT} gives

$$\mu_{JT} = \frac{V}{C_p}(T\alpha - 1)$$

4.6: Useful Definitions and Relationships

In this chapter (and in the previous chapter), several useful definitions have been stated.

Toolbox of useful Relationships

The following "measurable quantities" have been defined:

- **Heat Capacities**:

  $$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V$$

  and

  $$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p$$

- **Coefficient of Thermal Expansion**:

  $$\alpha \equiv \left(\frac{\partial V}{\partial T}\right)_p$$

  or

  $$\left(\frac{\partial V}{\partial T}\right)_p = V\alpha$$

- **Isothermal Compressibility:**

  $$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

  or

  $$\left(\frac{\partial V}{\partial p}\right)_T = -V\kappa_T$$

The following relation has been derived:

$$\frac{\alpha}{\kappa_T} = \left(\frac{\partial p}{\partial T}\right)_V$$

And the following relationships were given without proof (yet!):

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

and

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p - p$$

Together, these relationships and definitions make a powerful set of tools that can be used to derive a number of very useful expressions.

Example 4.6.1: Expanding Thermodynamic Function

Derive an expression for $\left(\frac{\partial H}{\partial V}\right)_T$ in terms of measurable quantities.

Solution 1:

Begin by using the total differential of $H(p,T)$:

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT$$

Divide by dV and constrain to constant T (to generate the partial of interest on the left):

$$\left.\frac{dH}{dV}\right|_T = \left(\frac{\partial H}{\partial p}\right)_T \left.\frac{dp}{dV}\right|_T + \left(\frac{\partial H}{\partial T}\right)_p \cancelto{0}{\left.\frac{dT}{dV}\right|_T}$$

The last term on the right will vanish (since $dT = 0$ for constant T). After converting to partial derivatives

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T \tag{4.6.1}$$

This result is simply a demonstration of the "chain rule" on partial derivatives! But now we are getting somewhere. We can now substitute for $\left(\frac{\partial H}{\partial V}\right)_T$ using our "toolbox of useful relationships":

$$\left(\frac{\partial H}{\partial V}\right)_T = \left[-T\left(\frac{\partial V}{\partial T}\right)_p + V\right]\left(\frac{\partial p}{\partial V}\right)_T$$

Using the *distributive property of multiplication*, this expression becomes

$$\left(\frac{\partial H}{\partial V}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T + V\left(\frac{\partial p}{\partial V}\right)_T \tag{4.6.2}$$

Using the *cyclic permutation rule* (Transformation Type II), the middle term of Equation 4.6.2 can be simplified

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cyclic permutation rule? Where is that on the Libraries?

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V + V\left(\frac{\partial p}{\partial V}\right)_T$$

And now all of the partial derivatives on the right can be expressed in terms of α and κ_T (along with T and V, which are also "measurable properties".

$$\left(\frac{\partial H}{\partial V}\right)_T = T\frac{\alpha}{\kappa_T} + V\frac{1}{-V\kappa_T}$$

or

$$\left(\frac{\partial H}{\partial V}\right)_T = \frac{1}{\kappa_T}(T\alpha - 1)$$

✓ Example 4.6.2: Isothermal Compression

Calculate ΔH for the isothermal compression of ethanol which will decrease the molar volume by $0.010\, L/mol$ at 300 K. (For ethanol, $\alpha = 1.1\times 10^{-3} K^{-1}$ and $\kappa_T = 7.9\times 10^{-5} atm^{-1}$).

Solution

Integrating the total differential of H at constant temperature results in

$$\Delta H = \left(\frac{\partial H}{\partial V}\right)_T \Delta V$$

From Example 4.6.1, we know that

$$\left(\frac{\partial H}{\partial V}\right)_T = \frac{1}{\kappa_T}(T\alpha - 1)$$

so

$$\Delta H = \left[\frac{1}{7.9\times 10^{-5} atm^{-1}}\left((300\,K)(1.1\times 10^{-3} K^{-1}) - 1\right)\right](-0.010\,L/mol)$$

$$\Delta H = \left(84.81\,\frac{atm\,\cancel{L}}{mol}\right)\underbrace{\left(\frac{8.314\,J}{0.8206\ atm\,\cancel{L}}\right)}_{\text{conversion factor}} = 9590\,J/mol$$

Contributors

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4.E: Putting the First Law to Work (Exercises)

Q4.1

Given the relationship

$$\left(-\frac{\partial U}{\partial V}\right)_T = T\left(-\frac{\partial p}{\partial T}\right)_V - p \tag{4.E.1}$$

show that

$$\left(-\frac{\partial U}{\partial V}\right)_T = 0 \tag{4.E.2}$$

for an ideal gas.

Q4.2

Determine if the following differential is exact, and if so, find the function $z(x, y)$ that satisfies the expression.

$$dz = 4xy\,dz + 2x^2 dy \tag{4.E.3}$$

Q4.3

For a van der Waals gas,

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{an^2}{V^2}\right) \tag{4.E.4}$$

Find an expression in terms of a, n, V, and R for

$$\left(\frac{\partial T}{\partial V}\right)_U \tag{4.E.5}$$

if $C_V = 3/2R$. Use the expression to calculate the temperature change for 1.00 mol of Xe (*a* = 4.19 atm L^2 mol $^{-2}$) expanding *adiabatically* against a vacuum from 10.0 L to 20.0 L.

Q4.4

Given the following data, calculate the change in volume for 50.0 cm^3 of

a. neon and
b. copper

due to an increase in pressure from 1.00 atm to 0.750 atm at 298 K.

Substance	T (at 1.00 atm and 298 K)
Ne	1.00 atm^{-1}
Cu	0.735 x 10^{-6} atm^{-1}

Q4.5

Consider a gas that follows the equation of state

$$p = \frac{nRT}{V - nb} \tag{4.E.6}$$

derive an expression for

a. the isobaric thermal expansivity, α
b. the Joule-Thomson coefficient, μ_{JT}

$$\mu_{JT} = \frac{V}{C_p}(T\alpha - 1) \tag{4.E.7}$$

Q4.6

Given

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V \tag{4.E.8}$$

derive an expression for

$$\left(\frac{\partial U}{\partial p}\right)_T \tag{4.E.9}$$

in terms of measurable properties. Use your result to calculate the change in the internal energy of 18.0 g of water when the pressure is increased from 1.00 atm to 20.0 atm at 298 K.

Q4.7

Derive an expression for

$$\left(\frac{\partial U}{\partial T}\right)_p \tag{4.E.10}$$

Begin with the definition of enthalpy, in order to determine

$$dH = dU + pdV + Vdp \tag{4.E.11}$$

Finish by dividing by dT and constraining to constant pressure. Make substitutions for the measurable quantities, and solve for

$$\left(\frac{\partial U}{\partial T}\right)_p. \tag{4.E.12}$$

Q4.8

Derive an expression for the difference between C_p and C_V in terms of the internal pressure, α, p and V. Using the definition for H as a starting point, show that

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \tag{4.E.13}$$

Now, find an expression for by starting with $U(V,T)$ and writing an expression for the total differential $dU(V,T)$.

Divide this expression by dp and constrain to constant T. Substitute this into the previous expressions and solve for

$$\left(\frac{\partial G}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V. \tag{4.E.14}$$

Q4.9

Evaluate the expression you derived in problem 8 for an ideal, assuming that the internal pressure of an ideal gas is zero.

Contributors and Attributions

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4.S: Putting the First Law to Work (Summary)

Learning Objectives

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

1. Express the total differential of a thermodynamic function in terms of partial differentials involving two independent state variables:
$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \tag{4.S.1}$$
2. Utilize the Euler relation to define an exact differential.
3. Derive and utilize partial differential transformation types I and II:
$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$
and
$$\left(\frac{\partial z}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial z}\right)_x}$$
4. Define and describe the meaning of the **isobaric thermal expansivity** coefficient (α) and the **isothermal compressibility** coefficient (κ_T).
5. Derive expressions for α and κ_T for gases based on an assumed equation of state.
6. Define **internal pressure** and describe the experiment Joule used to attempt to measure it.
7. Calculate a value for the internal pressure based on α and κ_T for a given substance.
8. Derive an expression for the internal pressure of a gas based on an assumed equation of state, given
$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\alpha}{\kappa_T} - p$$
9. Demonstrate theat the internal pressure of an ideal gas is zero.
10. Define and describe the physical meaning the Joule-Thomson coefficient.
11. Derive an expression for the Joule-Thomson coefficient in terms of α, C_p, V, and T given
$$\left(\frac{\partial H}{\partial V}\right)_T = \frac{1}{\kappa_T}(T\alpha - 1)$$
12. Demonstrate that the Joule-Thomson coefficient (μ_{JT} for an ideal gas is zero.
13. Derive expressions for the temperature and pressure dependence of enthalpy and internal energy in terms of measurable properties. Use these expressions to calculate changes in enthalpy and internal energy for specific substances based on the values of those measurable properties when the temperature or pressure is changed.

Vocabulary and Concepts

- Euler relation
- exact differential
- internal pressure
- isobaric thermal expansivity
- isothermal compressibility
- Joule-Thomson coefficient
- total differential

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CHAPTER OVERVIEW

5: The Second Law

Physical Chemistry: Thermodynamics
Patrick Fleming

5.1: 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

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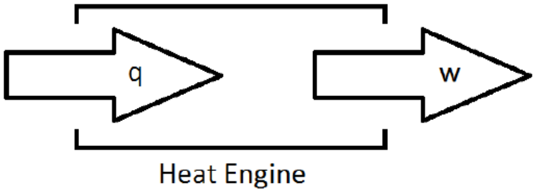
5.2: Heat Engines and the Carnot Cycle

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 5.2.1: Sadi Carnot (1796 - 1832)

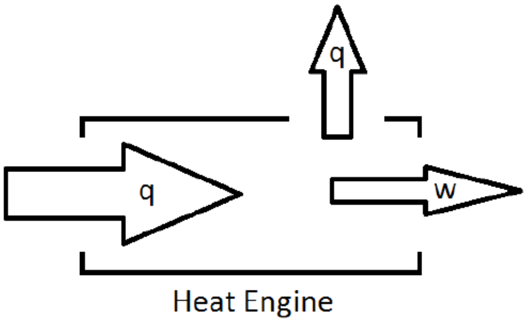
To simplify his analysis of the inner workings of an engine, Carnot devised a useful construct for examining what affect engine efficiency. His construct is the **heat engine**. The idea behind a heat engine is that it will take energy in the form of heat, and transform it into an equivalent amount of 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.*

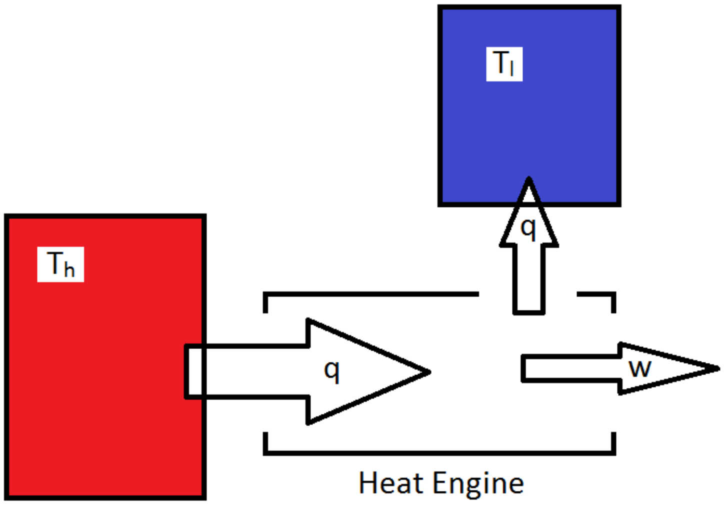
As such, a more reasonable picture of the heat engine is one which will allow for losses of energy to the surroundings.



The fraction of energy supplied to the engine that can be converted to work defines the efficiency of the engine.

The Carnot Cycle

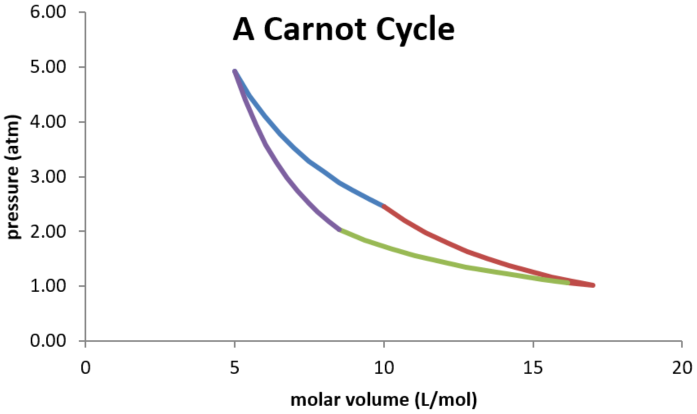
The Carnot cycle is a theoretical cyclic heat engine that can used to examine what is possible for an engine for which the job is convert heat into work. For simplicity, all energy provided to the engine occurs isothermally (and reversibly) at a temperature T_h and all of the energy lost to the surroundings 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

$$\epsilon = \frac{nRT_h \ln\left(\frac{V_2}{V_1}\right) + nRT_l \ln\left(\frac{V_4}{V_3}\right)}{nRT_h \ln\left(\frac{V_2}{V_1}\right)} \tag{5.2.1}$$

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 5.2.1) becomes

$$\epsilon = \frac{n\cancel{R}T_h \ln\cancel{\left(\frac{V_2}{V_1}\right)} + n\cancel{R}T_l \ln\cancel{\left(\frac{V_2}{V_1}\right)}}{n\cancel{R}T_h \ln\cancel{\left(\frac{V_2}{V_1}\right)}}$$

Canceling terms in the numerator and denominator yields

$$\epsilon = \frac{T_g - T_l}{T_h} \tag{5.2.2}$$

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 5.2.1:

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^{o}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 5.2.2 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.

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5.3: 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.

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5.4: 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

$$\Delta S = \int \frac{dq}{T} = nR\int_{V_1}^{V_2}\frac{dV}{V} = nR\ln\left(\frac{V_2}{V_1}\right) \tag{5.4.1}$$

✓ Example 5.4.1: 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 5.4.1

$$\begin{aligned}\Delta S &= nR\ln\left(\frac{V_2}{V_1}\right)\\ &= (1.00\,mol)(8.314J/(mol\,K))\ln\left(\frac{44.8\,L}{22.4\,L}\right)\\ &= 5.76\,J/K\end{aligned}$$

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

$$\Delta S = \frac{q}{T} = \frac{\Delta H_{phase}}{T} \tag{5.4.2}$$

✓ Example 5.4.2: 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 5.4.2:

$$\begin{aligned} \Delta S &= \frac{(1\, mol)(6010\, J/mol)}{273\, K} \\ &= 22\, J/K \end{aligned}$$

5.5: 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 5.5.1

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 5.5.2

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 5.5.1*: Summary of different ways to calculate ΔS depending on the pathway.*

Pathway	$\boldsymbol{\Delta S_{sys} = \ln \frac{dQ_{rev}}{T_{sys}}}$	$\boldsymbol{\Delta S_{surr} = \frac{q_{sys}}{T_{surr}}}$
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	$\frac{\Delta H_{phase}}{T}$	
**for an ideal gas.*		

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.

Contributors

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5.6: 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:

$$S = k_b \ln(W) \tag{5.6.1}$$

This rather famous equation is etched on Boltzmann's grave marker in commemoration of his profound contributions to the science of thermodynamics (Figure $5.6.1$).

Figure $5.6.1$: Ludwig Boltzmann (1844 - 1906)

Example $5.6.1$:

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 $5.6.1$):

$$S = nK\ln(W)$$

And using $W = 2$, the calculation is straightforward.

$$\begin{aligned} S &= \left(1.00\, mol \cot \frac{6.022 \times 10^{23}}{1\, mol}\right)(1.38 \times 10^{-23} J/K)\ln 2 \\ &= 5.76\, J/K \end{aligned}$$

5.7: 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 5.7.1

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!

5.8: 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:

$$\kappa_S = \frac{1}{V}\frac{\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial T}{\partial V}\right)_p} \tag{5.8.1}$$

The utility here is that

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \tag{5.8.2}$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \tag{5.8.3}$$

This means that Equation 5.8.1 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

$$\left(\frac{\partial V}{\partial p}\right)_S = -\frac{\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial S}\right)_p}{\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial T}{\partial S}\right)_V} \tag{5.8.4}$$

And as before, noting that the relationships in Equations 5.8.2 and 5.8.3, Equation 5.8.4 can be simplified to

$$\begin{aligned}\left(\frac{\partial V}{\partial p}\right)_S &= -\frac{C_V}{C_p}\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_V \\ &= \frac{C_V}{C_p}\left(\frac{\partial V}{\partial p}\right)_T \end{aligned}\tag{5.8.5}$$

Or defining $\gamma = C_p/C_V$, Equation 5.8.5 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.

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5.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

$$p = a + bT \tag{5.E.1}$$

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

$$C_p(T) = aT^3 \tag{5.E.2}$$

holds at low temperatures, calculate the molar entropy of the substance at 12.0 K.

5.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

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CHAPTER OVERVIEW

6: Putting the Second Law to Work

6.1: 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

$$\Delta H - T\Delta S \leq 0 \tag{6.1.1}$$

A similar derivation for constant volume processes results in the expression (at constant volume and temperature)

$$\Delta U - T\Delta S \leq 0 \tag{6.1.2}$$

> Equation 6.1.1 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 6.1.1 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

$$dH - TdS \leq 0 \tag{6.1.3}$$

and

$$dU - TdS \leq 0 \tag{6.1.4}$$

The Gibbs and Helmholtz Functions

Equation 6.1.3 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 6.1.1:

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.

6.2: 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 $dU = dq + dw$):

$$dU = TdS - pdV \tag{6.2.1}$$

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 6.2.1 can be expressed:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{6.2.2}$$

Also, by inspection (comparing the two expressions for dU in Equations 6.2.1 and 6.2.2) it is apparent that:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{6.2.3}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \tag{6.2.4}$$

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 6.2.3 and 6.2.4, 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.

$$dH = TdS + Vdp \tag{6.2.5}$$

And much as in the case of internal energy, this suggests that the natural variables of H are S and p. Or

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dV \tag{6.2.6}$$

Comparing Equations 6.2.5 and 6.2.6 show that

$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{6.2.7}$$

and

$$\left(\frac{\partial H}{\partial p}\right)_S = V \tag{6.2.8}$$

It is worth noting at this point that both Equation 6.2.3

$$\left(\frac{\partial U}{\partial S}\right)_V$$

and Equation 6.2.7

$$\left(\frac{\partial H}{\partial S}\right)_p$$

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 6.2.1.

Table 6.2.1: 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 6.2.1

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!

6.3: 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

$$dG = T\cancel{dS} - p\cancel{dV} + dw_e + p\cancel{dV} + Vdp - T\cancel{dS} - SdT$$

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.

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6.4: 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:

$$\Delta A = \int_{V_1}^{V_2} \left(\frac{\partial A}{\partial V}\right)_T dV \tag{6.4.1}$$

But how does one derive an expression for the partial derivative in Equation 6.4.1? 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

$$dA = dU - TdS - SdT \tag{6.4.2}$$

Now, it is convenient to use the combined first and second laws

$$dU = TdS - pdV \tag{6.4.3}$$

which assumes:

1. a reversible change and
2. only pV work is being done.

Substituting Equation 6.4.3 into Equation 6.4.2 yields

$$dA = \cancel{TdS} - pdV - \cancel{TdS} - SdT \tag{6.4.4}$$

Canceling the TdS terms gives the important result

$$dA = -pdV - SdT \tag{6.4.5}$$

The natural variables of A are therefore V and T! So the total differential of A is conveniently expressed as

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT \tag{6.4.6}$$

and by simple comparison of Equations 6.4.5 and 6.4.6, 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 6.4.1 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 6.4.1: 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 6.4.1)

$$\Delta A = \int_{V_1}^{V_2} \left(\frac{\partial A}{\partial V}\right)_T dV$$

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!

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

6.5: 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.

$$G = U + pV - TS \tag{6.5.1}$$

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

$$dG = V\,dp – S\,dT \tag{6.5.2}$$

This suggests that the natural variables of G are p and T. So the total differential dG can also be expressed

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT \tag{6.5.3}$$

And by inspection of Equations 6.5.2 and 6.5.3, 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

$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{6.5.4}$$

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 6.5.1: 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 6.5.4, 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.

$$\Delta G = \left(\frac{197.0\,g}{mol} \times \frac{1}{19.32\,g} \times \frac{1\,L}{1000\,cm^3}\right)(2.00\,atm - 1.00\,atm)\underbrace{\left(\frac{8.315\,J}{0.08206\,atm\,L}\right)}_{\text{conversion unit}} \tag{6.5.5}$$

$$= 1.033\,J \tag{6.5.6}$$

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6.6: 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

$$\int_{T_1}^{T_2} d\left(\frac{\Delta G}{T}\right) = \Delta H \int_{T_1}^{T_2} d\left(\frac{1}{T}\right)$$

$$\frac{\Delta G_{T_2}}{T_2} - \frac{\Delta G_{T_1}}{T_1} = \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{6.6.1}$$

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

$$\frac{\Delta A_{T_2}}{T_2} - \frac{\Delta A_{T_1}}{T_1} = \Delta U\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{6.6.2}$$

✓ Example 6.6.1:

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 6.6.1 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!

6.7: 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.

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT \tag{6.7.1}$$

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 6.7.1: 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:

$$\begin{align} \Delta S_{T_1 \rightarrow T_2} &= \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T}\right)_V dT \tag{6.7.2} \\ &= \int_{T_1}^{T_2} \frac{nC_V}{T} dT \tag{6.7.3} \\ &= nC_V \ln\left(\frac{T_2}{T_1}\right) \tag{6.7.4} \\ &= (1.00\, mol)\left(\frac{3}{2}\cdot 8.314 \frac{J}{mol\ K}\right) \ln\left(\frac{297\ K}{273\ K}\right) \tag{6.7.5} \\ &= 13.57\ J/K \tag{6.7.6} \end{align}$$

The second term is the contribution due to an isothermal expansion:

$$\Delta S_{V_1 \to V_2} = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V} \right)_T dV \tag{6.7.7}$$

From the Maxwell relation on A

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$$

So Equation 6.7.7 becomes

$$\Delta S_{V_1 \to V_2} = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial T} \right)_V dV \tag{6.7.8}$$

$$= \int_{V_1}^{V_2} \left(\frac{nR}{V} \right) dV \tag{6.7.9}$$

$$= nR \ln \left(\frac{V_2}{V_1} \right) \tag{6.7.10}$$

$$= (1.00\, mol) \left(8.314 \frac{J}{mol\, K} \right) \ln \left(\frac{22.0\, L}{10.0\, L} \right) \tag{6.7.11}$$

$$= 6.56\, J/K \tag{6.7.12}$$

And the total entropy change is

$$\Delta S_{tot} = \Delta S_{V_1 \to V_2} + \Delta S_{V_1 \to V_2} \tag{6.7.13}$$

$$= 13.57\, J/K + 6.56\, J/K \tag{6.7.14}$$

$$= 20.13\, J/K \tag{6.7.15}$$

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:

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \tag{6.7.16}$$

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

$$dz = \left(\frac{\partial z}{\partial x} \right)_w dx + \left(\frac{\partial z}{\partial w} \right)_x dy \tag{6.7.17}$$

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 $dw = 0$.

$$\left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy = \left(\frac{\partial z}{\partial x} \right)_w dx \tag{6.7.18}$$

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 6.7.18, yields

$$\left(\frac{\partial z}{\partial x}\right)_y dx+\left(\frac{\partial z}{\partial y}\right)_x\left[-\left(\frac{\partial w}{\partial x}\right)_y\left(\frac{\partial y}{\partial w}\right)_x dx\right]=\left(\frac{\partial z}{\partial x}\right)_w dx \tag{6.7.19}$$

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

$$\left(\frac{\partial z}{\partial x}\right)_y=\left(\frac{\partial z}{\partial x}\right)_w+\left(\frac{\partial z}{\partial w}\right)_x\left(\frac{\partial w}{\partial x}\right)_y \tag{6.7.20}$$

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

$$\left(\frac{\partial z}{\partial x}\right)_y=\left(\frac{\partial z}{\partial x}\right)_w+\left(\frac{\partial z}{\partial w}\right)_x\left(\frac{\partial w}{\partial x}\right)_y \tag{6.7.21}$$

which agrees with the previous result (Equation 6.7.20)! 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**.

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6.8: 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:

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \tag{6.8.1}$$

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 6.8.1 becomes

$$C_p = \left(\frac{\partial U}{\partial T}\right)_p + pV\alpha \tag{6.8.2}$$

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

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial U}{\partial T}\right)_V \tag{6.8.3}$$

(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 6.8.3 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

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p \tag{6.8.4}$$

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 6.8.4 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 6.8.3 to get

$$\begin{aligned}\left(\frac{\partial U}{\partial T}\right)_p &= \left[T\frac{\alpha}{\kappa_T} - p\right]V\alpha + C_V \\ &= \frac{TV\alpha^2}{\kappa_T} - pV\alpha + C_V\end{aligned}$$

This can now be substituted into the Equation 6.8.2 yields

$$C_p = \left[\frac{TV\alpha^2}{\kappa_T} - p\cancel{V\alpha} + C_V\right] + p\cancel{V\alpha}$$

The $pV\alpha$ terms will cancel. And subtracting C_V from both sides gives the desired result:

$$C_p - C_V = \frac{TV\alpha^2}{\kappa_T} \tag{6.8.5}$$

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 6.8.5 yields

$$\begin{aligned}C_p - C_V &= \frac{TV\left(\frac{1}{T}\right)^2}{\left(\frac{1}{p}\right)} \\ &= \frac{pV}{T} \\ &= R\end{aligned}$$

So for an ideal gas, $C_p - C_V = R$. That is good to know, no?

✓ Example 6.8.1

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

$$\left.\frac{dH}{dT}\right|_V = \left.\frac{dU}{dT}\right|_V + p\left.\frac{dV}{dT}\right|_V + V\left.\frac{dp}{dT}\right|_V$$

$$\left(\frac{dH}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V + V\left(\frac{dp}{dT}\right)_V \tag{6.8.6}$$

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.

$$dH = \left(\frac{dH}{dp}\right)_T dp + \left(\frac{dH}{dT}\right)_p dT$$

$$\left(\frac{dH}{dT}\right)_V = \left(\frac{dH}{dp}\right)_T \left(\frac{dp}{dT}\right)_V + \left(\frac{dH}{dT}\right)_p \tag{6.8.7}$$

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

$$\left.\frac{dH}{dp}\right|_T = T\left.\frac{dS}{dp}\right|_T + V\left.\frac{dp}{dp}\right|_T$$

$$\left(\frac{dH}{dp}\right)_T = T\left(\frac{dS}{dp}\right)_T + V \tag{6.8.8}$$

Using the Maxwell Relation on G, we can substitute

$$-\left(\frac{dV}{dT}\right)_p = \left(\frac{dS}{dp}\right)_T$$

So Equation 6.8.8 becomes

$$\left(\frac{dH}{dp}\right)_T = -T\left(\frac{dV}{dT}\right)_p + V$$

Now, substitute this back into the expression for (Equation 6.8.7):

$$\left(\frac{dH}{dT}\right)_V = \left[-T\left(\frac{dV}{dT}\right)_p + V\right]\left(\frac{dp}{dT}\right)_V + \left(\frac{dH}{dT}\right)_p$$

$$\left(\frac{dH}{dT}\right)_V = -T\left(\frac{dV}{dT}\right)_p\left(\frac{dp}{dT}\right)_V + V\left(\frac{dp}{dT}\right)_V + \left(\frac{dH}{dT}\right)_p$$

This can now substituted for the right-hand side of the initial expression for $\left(\frac{dH}{dT}\right)_V$ back into Equation 6.8.6:

$$-T\left(\frac{dV}{dT}\right)_p\left(\frac{dp}{dT}\right)_V + V\cancel{\left(\frac{dp}{dT}\right)_V} + \left(\frac{dH}{dT}\right)_p = \left(\frac{dU}{dT}\right)_V + V\cancel{\left(\frac{dp}{dT}\right)_V} \tag{6.8.9}$$

Several terms cancel one another. Equation 6.8.9 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 6.8.5)!

6.E: Putting the Second Law to Work (Exercises)

Q6.1

Using Table T1, calculate the standard reaction Gibbs functions (\(\Delta G^o\)) for the following reactions at 298 K.

a. $CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
b. $C_6H_{12}O_6(s) + 6O_2 \rightarrow 6CO_2(g) + 6H_2O(l)$
c. $2POCl_3(l) \rightarrow 2PCl_3(l) + O_2(g)$
d. $2KBr(s) + Cl_2(g) \rightarrow 2KCl(s) + Br_2(l)$
e. $SiH_4(g) + 2Cl(g) \rightarrow SiCl_4(l) + 2H_2(g)$

Q6.2

Estimate \(\Delta G\) at 1000 K from its value at 298 K for the reaction

$$C(s) + 2H_2(g) \rightarrow CH_4(g) \tag{6.E.1}$$

with $\Delta G = -50.75\, kJ\, at\, 298\, K/$

Q6.3

The standard Gibbs function for formation (ΔG_f^o) of $PbO_2(s)$ is -217.4 kJ/mol at 298 K. Assuming O_2 is an ideal gas, find the standard Helmholtz function for formation (ΔA_f^o for PbO_2 at 298K.

Q6.4

Calculate the entropy change for 1.00 mol of an ideal monatomic gas (C_V = 3/2 R) undergoing an expansion and simultaneous temperature increase from 10.0 L at 298 K to 205.0 L at 455 K.

Q6.5

Consider a gas that obeys the equation of state

$$p = \frac{nRT}{V - nb} \tag{6.E.2}$$

a. Find expressions for α and κ_T for this gas.
b. Evaluate the difference between C_p and C_V for the gas.

Q6.6

Show that

$$\left(\frac{\partial C_p}{\partial p}\right)_T = 0 \tag{6.E.3}$$

for an ideal gas.

Q6.7

Derive the thermodynamic equation of state

$$\left(\frac{\partial H}{\partial p}\right)_T = V(1 - T\alpha) \tag{6.E.4}$$

Q6.8

Derive the thermodynamic equation of state

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\alpha}{\kappa_T} - p \tag{6.E.5}$$

Q6.9

The “Joule Coefficient” is defined by

$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U \tag{6.E.6}$$

Show that

$$\mu_J = \frac{1}{C_V}\left(p - \frac{T\alpha}{\kappa_T}\right) \tag{6.E.7}$$

and evaluate the expression for an ideal gas.

Q6.10

Derive expressions for the pressure derivatives

$$\left(\frac{\partial X}{\partial p}\right)_T \tag{6.E.8}$$

where$X$ is U, H, A, G, and S at constant temperature in terms of measurable properties. (The derivation of $\left(\frac{\partial H}{\partial p}\right)_T$ was done in problem Q6.7).

Evaluate the expressions for

- $\left(\frac{\partial S}{\partial p}\right)_T$
- $\left(\frac{\partial H}{\partial p}\right)_T$
- $\left(\frac{\partial U}{\partial p}\right)_T$

for a van der Waals gas.

Q6.11

Derive expressions for the volume derivatives

$$\left(\frac{\partial X}{\partial V}\right)_T \tag{6.E.9}$$

where X is U, H, A, G, and S at constant temperature in terms of measurable properties. (The derivation of $\left(\frac{\partial U}{\partial V}\right)_T$ was done in problem Q8.8.)

Evaluate the expressions for

- $\left(\frac{\partial X}{\partial V}\right)_T$
- $\left(\frac{\partial X}{\partial V}\right)_T$

for a van der Waals gas.

Q6.12

Evaluate the difference between C_p and C_V for a gas that obeys the equation of state

$$p = \frac{nRT}{V - nb} \tag{6.E.10}$$

Q6.13

The adiabatic compressibility (k_S) is defined by

$$\kappa_S = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S \tag{6.E.11}$$

Show that for an ideal gas,

$$\kappa_S = \frac{1}{p\gamma} \tag{6.E.12}$$

6.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 ($\Delta G_f^O o$

CHAPTER OVERVIEW

7: Mixtures and Solutions

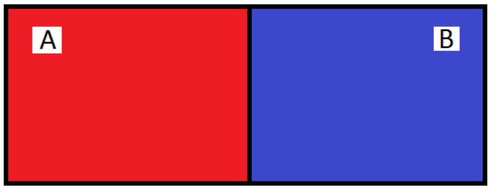
Physical Chemistry: Thermodynamics
Patrick Fleming

I II III IV V VI VII VIII IX X XI XII • **Homework Exercises**

Up until this point, we have conserved single-component systems which do not change in composition. By and large, nature consists of much more complicated systems, containing many components and continually undergoing changes in composition through phase changes or chemical reactions or both! In order to expand our thermodynamic toolbox, we will begin by discussing mixtures.

7.1: 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

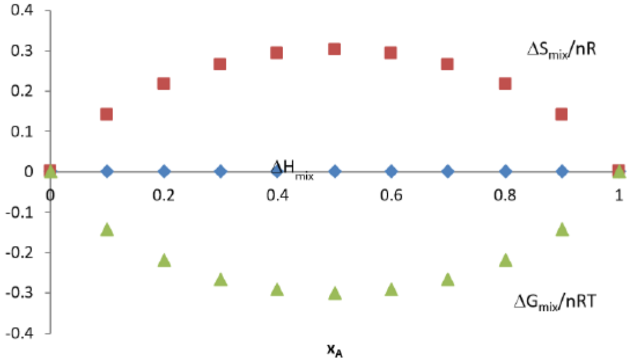
Calculating ΔG_{mix} should be no more difficult than calculating ΔS_{mix}. For *isothermal mixing* and constant total pressure

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$$

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.*

7.2: 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.

7.3: 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:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j\neq i} \tag{7.3.1}$$

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:

$$dG = V dp - S dT + \sum_i \mu_i dn_i$$

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 7.3.1: 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 7.3.1). As the partial most Gibbs function, it is easy to show that

$$d\mu = V dp - S dT$$

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

$$\int_{\mu^o}^{\mu} d\mu = \int_{p^o}^{p} V\, dp \tag{7.3.2}$$

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 7.3.2 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 7.3.2 then becomes

$$\int_{\mu^o}^{\mu} d\mu = RT int_{p^o}^{p} \frac{dp}{p} \tag{7.3.3}$$

or

$$\mu = \mu^o + RT \ln\left(\frac{p}{p^o}\right)$$

7.4: The Gibbs-Duhem Equation

For a system at **equilibrium**, the Gibbs-Duhem equation must hold:

$$\sum_i n_i d\mu_i = 0 \tag{7.4.1}$$

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

$$\sum_i n_i d\mu_i + \sum_i \cancel{\mu_i dn_i} = Vdp - sdT + \sum_i \cancel{\mu_i dn_i}$$

And after canceling terms, one gets

$$\sum_i n_i d\mu_i = Vdp - sdT \tag{7.4.2}$$

For a system at constant temperature and pressure

$$Vdp - sdT = 0 \tag{7.4.3}$$

Substituting Equation 7.4.3 into 7.4.2 results in the **Gibbs-Duhem equation** (Equation 7.4.1). 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)

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

7.5: 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

$$d\mu - V\,dp - SdT$$

and so

$$\left(\frac{\partial\mu}{\partial p}\right)_T = V \tag{7.5.1}$$

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 $p \rightarrow 0$ 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 7.5.1 holds even for gases that deviate from ideal behavior!

7.6: 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

$$\mu_A = \mu_A^o + RT \ln \chi_A \tag{7.6.1}$$

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 7.6.1, 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.

$$\left[\frac{\partial}{\partial T}\left(\frac{\mu_A - \mu_A^o}{RT}\right)\right]_p = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

$$-\frac{\mu_A - \mu_A^o}{RT^2} + \frac{1}{RT}\left[\left(\frac{\partial \mu_A}{\partial T}\right)_p - \left(\frac{\partial \mu_A^o}{\partial T}\right)_p\right] = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p \tag{7.6.2}$$

Recalling that

$$\mu = H = TS$$

and

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S$$

Equation 7.6.2 becomes

$$-\frac{(H_A - TS_A - H_A^o + TS_A^o)}{RT^2} + \frac{1}{RT}\left[-S_A + S_A^o\right] = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p \tag{7.6.3}$$

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 7.6.3 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.

$$\int_{T^o}^{T} \frac{\Delta H_{fus}}{RT^2} dT = \int d \ln \chi_A \tag{7.6.4}$$

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 7.6.4:

$$-\frac{\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T^o}\right) = \ln \chi_A \tag{7.6.5}$$

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 7.6.5 becomes

$$-\frac{\Delta H_{fus}}{R(T^o)^2} \Delta T = \ln \chi_A \tag{7.6.6}$$

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 7.6.1:

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)

$$\mu^o_{vap} + RT \ln \frac{p'}{p^o} = \mu^o_A + RT \ln \chi_A \tag{7.6.7}$$

Where p' is the vapor pressure of the solvent over the solution. Similarly, for the pure solvent in equilibrium with its vapor

$$\mu^o_A = \mu^o_{vap} + RT \ln \frac{p_A}{p^o} \tag{7.6.8}$$

where p^o is the standard pressure of 1 atm, and p_A is the vapor pressure of the pure solvent. Substituting Equation 7.6.8 into Equation 7.6.7 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

$$p' = \chi_A p_A \tag{7.6.9}$$

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 7.6.2:

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 7.6.9)

$$p_A = (0.400)(150\, Toor) = 60.0\, Torr$$

$$p_B = (0.600)(300\, Toor) = 180.0\, Torr$$

$$p_{tot} = p_A + p_B = 240\, Torr$$

To get the mole fractions in the gas phase, one can use Dalton's Law of partial pressures.

$$\chi_A = \frac{p_A}{p_{tot}} = \frac{60.0\,Torr}{240\,Torr} = 0.250$$

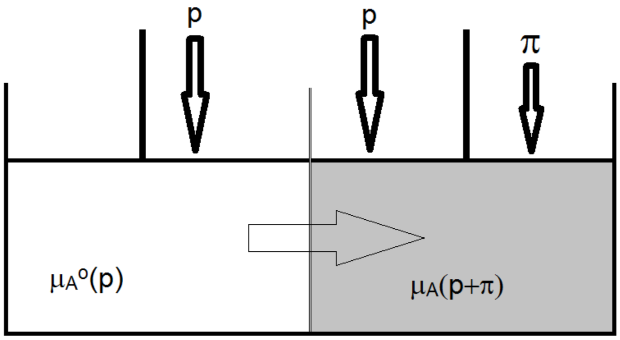
$$\chi_B = \frac{p_B}{p_{tot}} = \frac{180.0\,Torr}{240\,Torr} = 0.750$$

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.

$$\int_p^{\pi} V\, dP = V p|_p^{p+\pi} = V\pi$$

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.

7.7: 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.

7.8: 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

$$M_x X_y(s) \rightarrow x M^{y+}(aq) + y X^{x-}(aq)$$

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

$$\log_{10}\gamma_{\pm} = \frac{1.824\times 10^{6}}{(\epsilon T)^{3/2}}|z_{+}+z_{-}|\sqrt{I}$$

where ϵ is the dielectric constant of the solvent, T is the temperature in K, z_{+} and z_{-} are the charges on the ions, and I is the **ionic strength** of the solution. I is given by

$$I = \frac{1}{2}\frac{m_{+}z_{+}^{2}+m_{-}z_{-}^{2}}{m^{o}}$$

For a solution in water at 25 ^{o}C,

7.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

$$\pi V = \chi_B RT \tag{7.E.1}$$

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

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7.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

CHAPTER OVERVIEW

8: Phase Equilibrium

Physical Chemistry: Thermodynamics
Patrick Fleming

8.1: Prelude to Phase Equilibrium

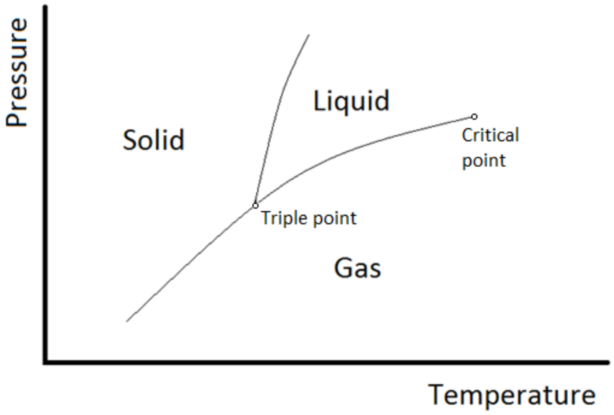
From the very elementary stages of our journey to describe the physical nature of matter, we learn to classify mater into three (or more) phases: solid, liquid, and gas. This is a fairly easy classification system that can be based on such simple ideas as shape and volume.

Phase	Shape	Volume
Solid	Fixed	Fixed
Liquid	Variable	Fixed
Gas	Variable	Variable

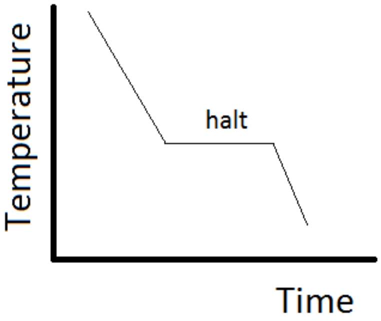
As we have progressed, we have seen that solids and liquids are not completely incompressible as they may have non-zero values of κ_T. And we learn that there are a number of finer points to describing the nature of the phases about which we all learn in grade school. In this chapter, we will employ some of the tools of thermodynamics to explore the nature of phase boundaries and see what we can conclude about them.

8.2: 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.

8.3: 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.

$$\begin{aligned} F &= 2 + P(C-1) - C(P-1) \\ &= 2 + PC - P - PC + C \\ &= 2 + C - P \end{aligned} \tag{8.3.1}$$

Equation 8.3.1 is the Gibbs phase rule.

✓ Example 8.3.1:

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.

8.4: 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.

$$\mu_\alpha = \mu_\beta \tag{8.4.1}$$

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.

$$\mu_\alpha + d\mu_\alpha = \mu_\beta + d\mu_\beta \tag{8.4.2}$$

Taking the difference between these Equations 8.4.1 and 8.4.2 shows that

$$d\mu_\alpha = d\mu_\beta$$

And since $d\mu$ can be expressed in terms of molar volume and molar entropy

$$d\mu = V\,dp - SdT$$

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

$$\Delta V\,dp = \Delta SdT$$

or

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} \tag{8.4.3}$$

Equation 8.4.3 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

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} \tag{8.4.4}$$

✓ Example 8.4.1: 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 8.4.4) 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)!

8.5: 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 (solid $\rightarrow$ gas) or vaporization (liquid $\rightarrow$ 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.

$$dp = \frac{p\Delta H_{vap}}{R}\frac{dT}{T^2} \tag{8.5.1}$$

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,

$$\int_{p_1}^{p_2} \frac{dp}{p} = -\frac{\Delta H_{vap}}{R}\int_{T_1}^{T_2} d\left(\frac{1}{T}\right)$$

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{8.5.2}$$

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 8.5.1

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 8.5.2). 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 $8.5.1$ is very useful when there are several pairs of measurements of vapor pressure and temperature. Such a plot is shown below for water.

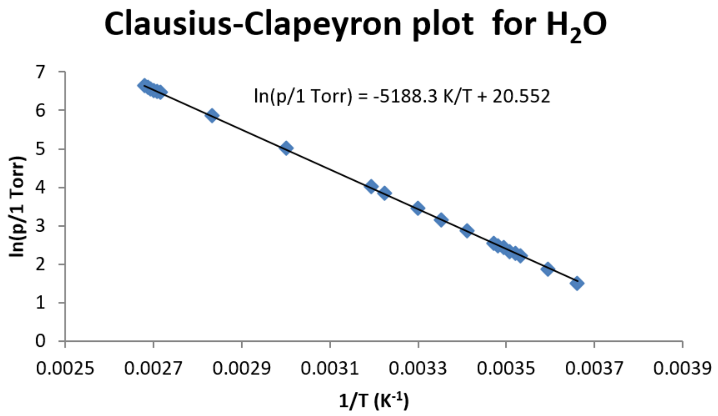


Figure $8.5.1$

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 $8.5.1$) 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 ^{o}C included in the fit. A larger temperature dependence would be found if the higher-temperature data were included in the fit.

8.6: 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.

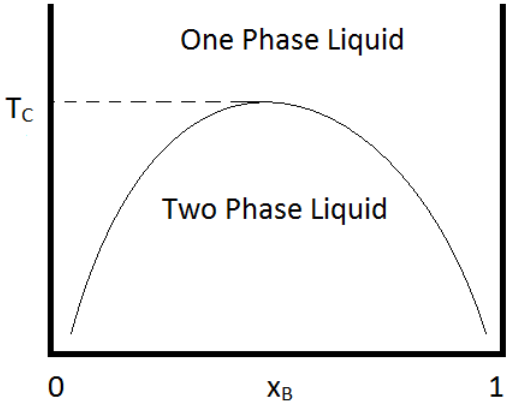


Figure 8.6.1 :

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 8.6.1. 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.

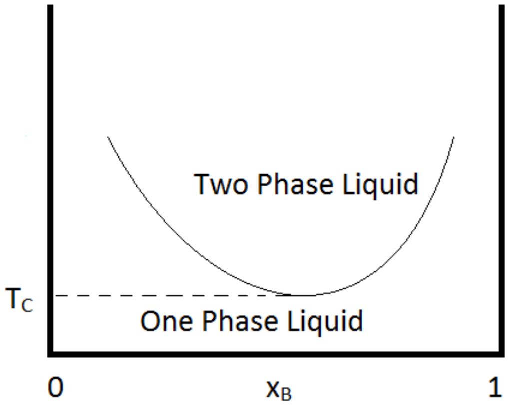


Figure 8.6.2 :

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 $8.6.2$. 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.

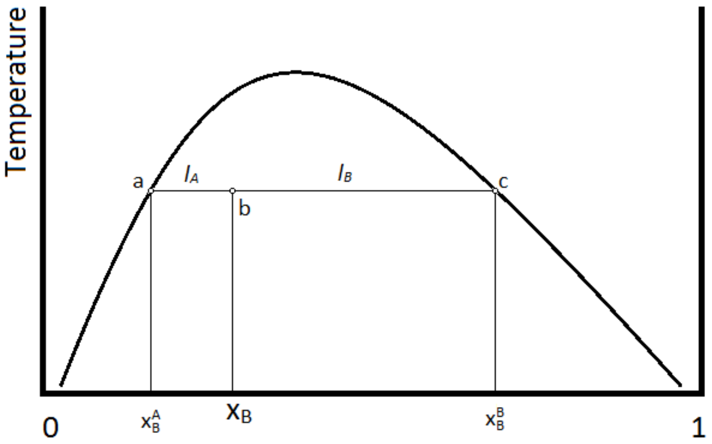


Figure $8.6.3$:

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.

$$\frac{n_A}{n_B} = \frac{l_B}{l_A} = \frac{\chi_B^B - \chi_B}{\chi_B - \chi_B^A}$$

8.7: 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 $8.7.1$, the liquid phase is represented at the top of the graph where the pressure is higher.

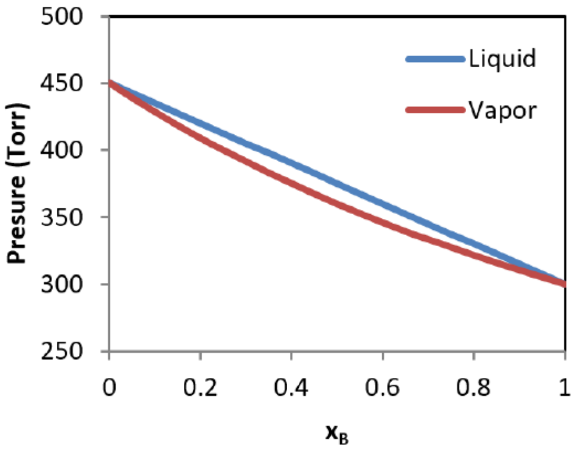


Figure $8.7.1$: The liquid phase is represented at the top of the graph where the pressure is higher

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 $8.7.2$ for an ideal mixture of two volatile liquids.

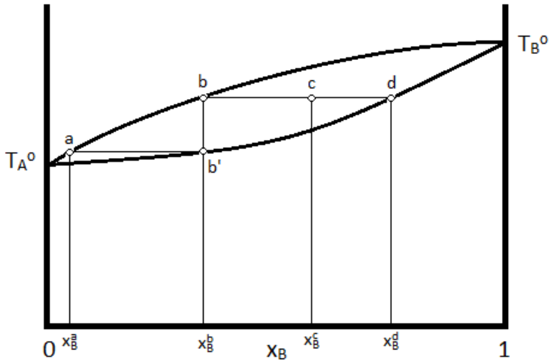


Figure $8.7.2$: *A typical temperature vs. composition diagram.*

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 reevaporating 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.

8.8: 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 8.8.1.

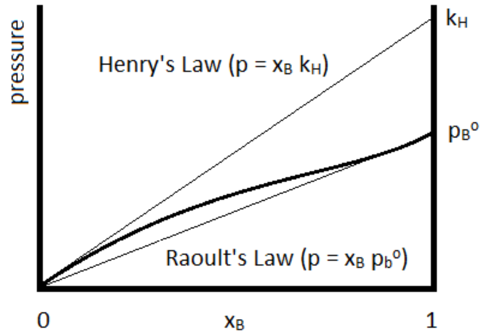


Figure 8.8.1: The relationship between Raoult's Law and Henry's Law for a binary mixture.

Henry’s Law is depicted by the upper straight line and Raoult’s Law by the lower.

✓ Example 8.8.1: 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:

$$\frac{3.32 \times 10^{-2} mol}{L} \cdot 1\, L = 3.32 \times 10^{-2} mol\, CO_2$$

and so the mol fraction of CO_2 is

$$\chi_b = \frac{3.32 \times 10^{-2} mol}{55.5\, mol} = 5.98 \times 10^{-4}$$

And so

$$10^5\ Pa = 5.98 \times 10^{-4} k_H$$

or

$$k_H = 1.67 \times 10^9\ Pa$$

Azeotropes

An azeotrope is defined as the common composition of vapor and liquid when they have the same composition.

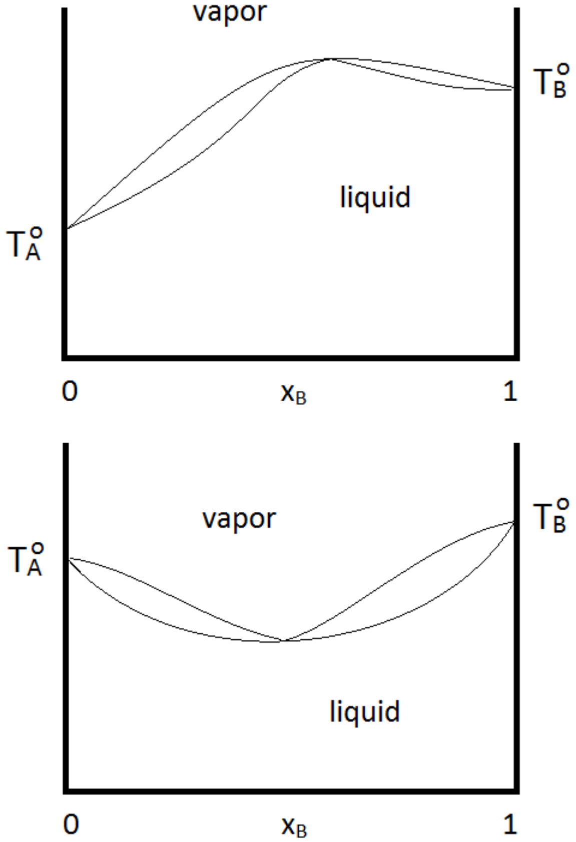


Figure $8.8.2$: Phase diagrams for (left) a maximum boiling point azeotrope and (right) Ta maximum boiling point azeotrope.

Azeotropes can be either maximum boiling or minimum boiling, as show in Figure $8.8.2; left$. 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 $8.8.2; right$.

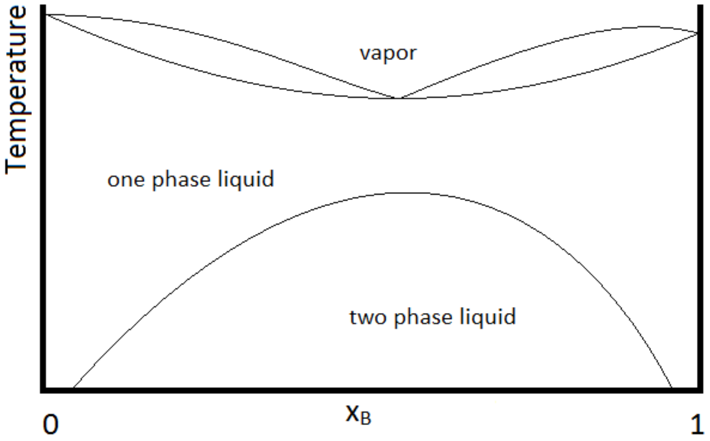
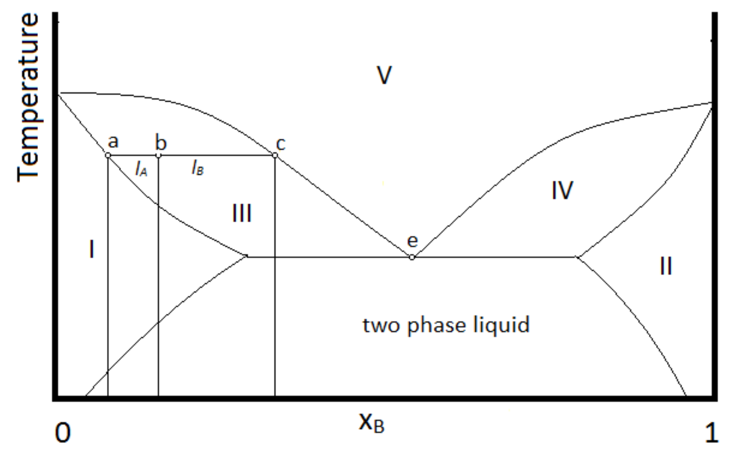


Figure $8.8.3$: *Phase diagram for a binary solution with the boiling point of a minimum boiling azeotrope that is higher that when components are miscible (single phase).*

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 $8.8.3$.

Example 8.8.1:

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.

8.9: Solid-Liquid Systems - Eutectic Points

A phase diagram for two immiscible solids and the liquid phase (which is miscible in all proportions) is shown in Figure 8.9.1. The point labeled “e_2” is the **eutectic point**, meaning the composition for which the mixture of the two solids has the lowest melting point. The four main regions can be described as below:

I. Two-phase solid
II. Solid (mostly A) and liquid (A and B)
III. Solid (mostly B) and liquid (A and B)
IV. Single phase liquid (A and B)

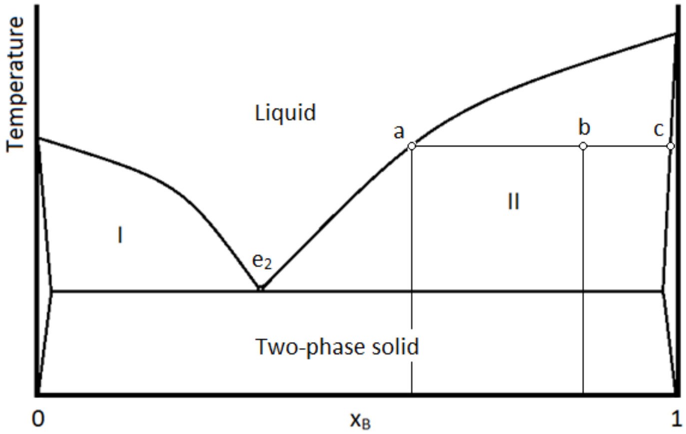


Figure 8.9.1: Phase diagram of a two-component system that exhibits an eutectic point.

The unlabeled regions on the sides of the diagram indicate regions where one solid is so miscible in the other, that only a single phase solid forms. This is different than the “two-phase solid” region where there are two distinct phases, meaning there are regions (crystals perhaps) that are distinctly A or B, even though they are intermixed within on another. Region I contains two phases: a solid phase that is mostly compound A, and a liquid phase which contains both A and B. A sample in region II (such as the temperature/composition combination depicted by point b) will consist of two phases: 1 is a liquid mixture of A and B with a composition given by that at point a, and the other is a single phase solid that is mostly pure compound B, but with traces of A entrained within it. As always, the lever rule applies in determining the relative amounts of material in the two phases.

In the case where the widths of the small regions on either side of the phase diagram are negligibly small, a simplified diagram with a form similar to that shown in Figure 8.9.2 can be used. In this case, it is assumed that the solids never form a single phase! The tin-lead system exhibits such behavor.

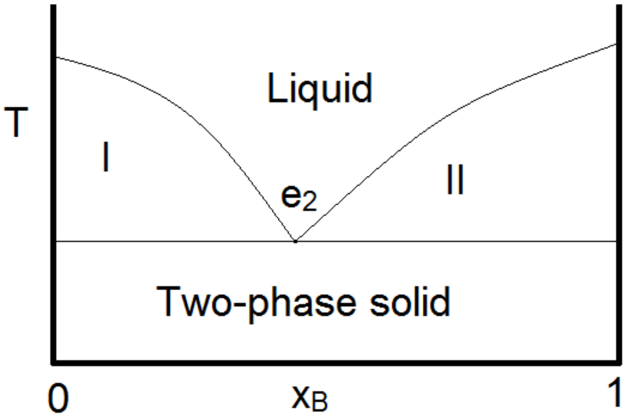


Figure 8.9.2: A simplified phase diagram of a two-component system that exhibits an eutectic point.

Another important case is that for which the two compounds A and B can react to form a third chemical compound C. If the compound C is stable in the liquid phase (does not decompose upon melting), the phase diagram will look like Figure 8.9.3.

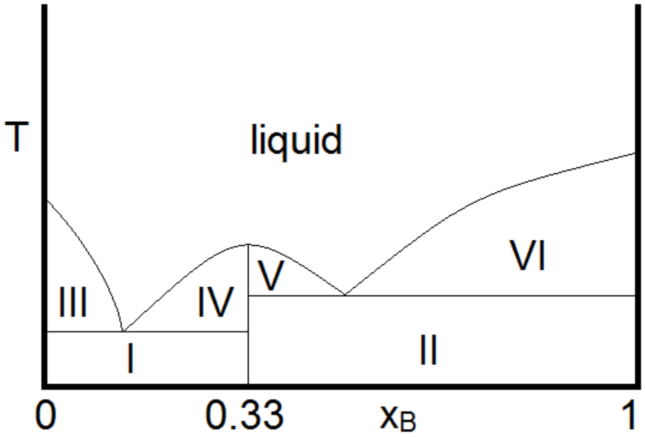


Figure 8.9.3: A simplified phase diagram of a two-component system that exhibits an eutectic point.

In this diagram, the vertical boundary at $\chi_B = 0.33$ is indicative of the compound C formed by A and B. From the mole fraction of B, it is evident that the formula of compound C is A_2B. The reaction that forms compound C is

$$2A + B \rightarrow C$$

Thus, at overall compositions where $\chi_B < 0.33$, there is excess compound A (B is the limiting reagent) and for χ_B there is an excess of compound B (A is now the limiting reagent.) With this in mind, the makeup of the sample in each region can be summarized as

I. Two phase solid (A and C)
II. Two phase solid (C and B)
III. Solid A and liquid (A and C)
IV. Solid C and liquid (A and C)
V. Solid C and liquid (C and B)
VI. Solid B and liquid (C and B)
VII. **liquid**. Single phase liquid (A and C or C and B, depending on which is present in excess)

Zinc and Magnesium are an example of two compounds that demonstrate this kind of behavior, with the third compound having the formula Zn_2Mg (Ghosh, Mezbahul-Islam, & Medraj, 2011).

Incongruent Melting

Oftentimes, the stable compound formed by two solids is only stable in the solid phase. In other words, it will decompose upon melting. As a result, the phase diagram will take a lightly different form, as is shown in Figure 8.9.4.

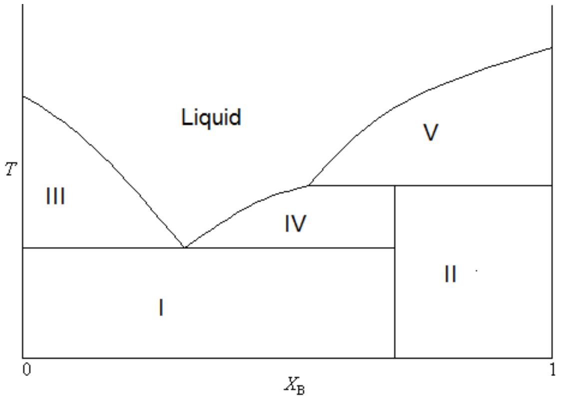


Figure 8.9.4: A phase diagram of a two-component system that exhibits incongruent melting.

In this diagram, the formula of the stable compound is AB_3 (consistent with $\chi_B < 0.75$). But you will notice that the boundary separating the two two-phase solid regions does not extend all of the way to the single phase liquid portion of the diagram. This is because the compound will decompose upon melting. The process of decomposition upon melting is also called **incongruent melting**. The makeup of each region can be summarized as

I. Two phase solid (A and C)
II. Two phase solid (C and B)
III. Solid A and liquid (A and B)
IV. Solid C and liquid (A and B)
V. Solid B and liquid (A and B)

There are many examples of pairs of compounds that show this kind of behavior. One combination is sodium and potassium, which form a compound (Na_2K) that is unstable in the liquid phase and so it melts incongruently (Rossen & Bleiswijk, 1912).

8.10: Cooling Curves

The method that is used to map the phase boundaries on a phase diagram is to measure the rate of cooling for a sample of known composition. The rate of cooling will change as the sample (or some portion of it) begins to undergo a phase change. These "breaks" will appear as changes in slope in the temperature-time curve. Consider a binary mixture for which the phase diagram is as shown in Figure $8.10.1A$. A cooling curve for a sample that begins at the temperature and composition given by point a is shown in Figure $8.10.1B$.

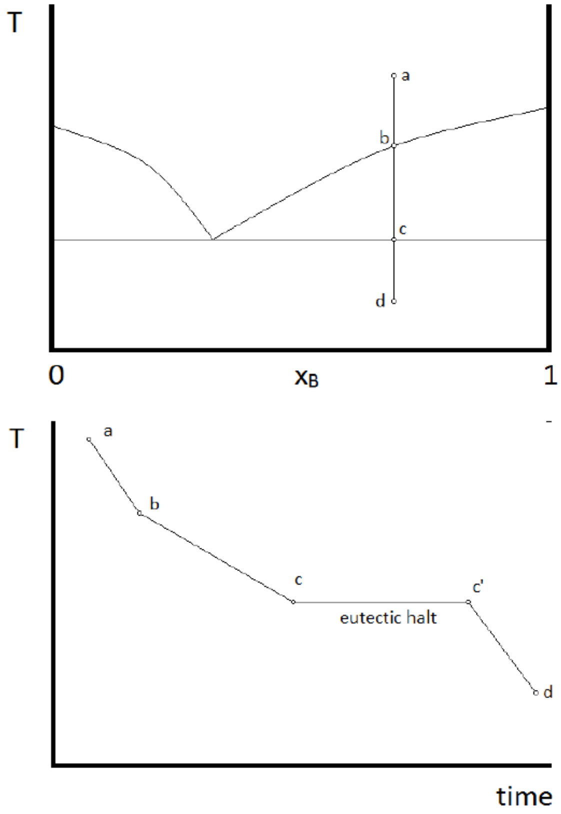


Figure 8.10.1: (A) cooling of a two-component system from liquid to solid. (B) Cooresponding cooling curve for this process.

As the sample cools from point a, the temperature will decrease at a rate determined by the sample composition, and the geometry of the experiment (for example, one expects more rapid cooling is the sample has more surface area exposed to the cooler surroundings) and the temperature difference between the sample and the surroundings.

When the temperature reaches that at point b, some solid compound B will begin to form. This will lead to a slowing of the cooling due to the exothermic nature of solid formation. But also, the composition of the liquid will change, becoming richer in compound A as B is removed from the liquid phase in the form of a solid. This will continue until the liquid attains the composition at the eutectic point (point c in the diagram.)

When the temperature reaches that at point c, both compounds A and B will solidify, and the composition of the liquid phase will remain constant. As such, the temperature will stop changing, creating what is called the **eutectic halt**. Once all of the material has solidified (at the time indicated by point c'), the cooling will continue at a rate determined by the heat capacities of the two solids A and B, the composition, and (of course) the geometry of the experimental set up. By measuring cooling curves for samples of varying composition, one can map the entire phase diagram.

8.E: Phase Equilibrium (Exercises)

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8.S: Phase Equilibrium (Summary)

Learning Objectives

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

1. State the thermodynamic criterion for equilibrium in terms of chemical potential.
2. Derive and interpret the Gibbs Phase Rule.
3. Derive the Clapeyron equation from the thermodynamic criterion for equilibrium.
4. Interpret the slope of phase boundaries on a pressure-temperature phase diagram in terms of the relevant changes in entropy and molar volume for the given phase change.
5. Derive the Clausius-Clapeyron equation, stating all of the necessary approximations.
6. Use the Clausius-Clapeyron equation to calculate the vapor pressure of a substance or the enthalpy of a phase change from pressure-temperature data.
7. Interpret phase diagrams for binary mixtures, identifying the phases and components present in each region.
8. Perform calculations using Raoult’s Law and Henry’s Law to relate vapor pressure to composition in the liquid phase.
9. Describe the distillation process, explaining how the composition of liquid and vapor phases can differ, and how azeotrope composition place bottlenecks in the distillation process.
10. Describe how cooling curves are used to derive phase diagrams by locating phase boundaries.

Vocabulary and Concepts

- azeotrope
- Clapeyron equation
- Clausius-Clapeyron equation
- compositional degrees of freedom
- cooling curve
- distillation
- eutectic halt
- eutectic point
- Gibbs phase rule
- Henry’s Law
- incongruent melting
- lever rule
- lower critical temperature
- phase diagram
- platinum resistance thermometer
- Raoult’s law
- scanning calorimetry
- thermodynamic constraints
- triple point
- upper critical temperature
- volatile liquid

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CHAPTER OVERVIEW

9: Chemical Equilibria

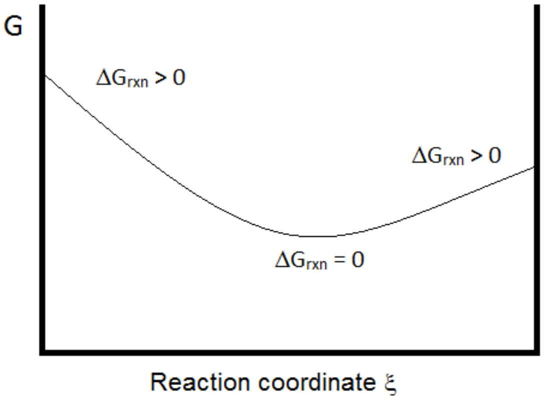
Physical Chemistry: Thermodynamics
Patrick Fleming

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.

9.1: 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.

9.2: 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

$$\mu_A^o + RT\ln\left(\frac{p_A}{p_{tot}}\right) = \mu_B^o + RT\ln\left(\frac{p_B}{p_{tot}}\right) \tag{9.2.1}$$

where Dalton’s Law has been used to express the mole fractions.

$$\chi_i = \frac{p_i}{p_{tot}}$$

Equation 9.2.1 can be simplified by collecting all chemical potentials terms on the left

$$\mu_A^o - \mu_B^o = RT\ln\left(\frac{p_B}{p_{tot}}\right) - RT\ln\left(\frac{p_A}{p_{tot}}\right) \tag{9.2.2}$$

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

$$\Delta G^o_{rxn} = -RT \ln K_p \tag{9.2.3}$$

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 9.2.1:

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 9.2.3.

$$-70040\ J/mol = -(8.314 J/(mol\ K)(298\ K) \ln K_p$$

$$K_p = 1.89 \times 10^{12}$$

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.

9.3: 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,

$$K_p = \prod_i f_i^{\nu_i} \tag{9.3.1}$$

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 9.3.1) becomes

$$K_p = \prod_i (RT[X_i])^{\nu_i} \tag{9.3.2}$$

And since for a given temperature, RT is a constant and can be factored out of the expression, leaving

$$K_p = \left(\prod_i (RT)^{\nu_i}\right)\left(\prod_i [X_i]^{\nu_i}\right) \tag{9.3.3}$$

$$= (RT)^{\sum \nu_i} \prod [X_i]^{\nu_i} \tag{9.3.4}$$

$$= (RT)^{\sum \nu_i} K_c \tag{9.3.5}$$

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.

9.4: 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 9.4.1:

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 9.4.2:

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.

$$\chi_A = \frac{0.154\,atm}{0.154 atm + 0.692\,atm + 1.000\,atm} = 0.08341$$

$$\chi_B = \frac{0.692\,atm}{0.154 atm + 0.692\,atm + 1.000\,atm} = 0.08341$$

$$\chi_{Ar} = \frac{1.000\,atm}{0.154 atm + 0.692\,atm + 1.000\,atm} = 0.08341$$

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.

9.5: 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

$$\begin{aligned} \chi_A &= \frac{n(1-\alpha)}{n(1-\alpha)+2n\alpha} \\ &= \frac{1-\alpha}{1+\alpha} \\ \chi_B &= \frac{2\alpha}{1+\alpha} \end{aligned}$$

Based on these mole fractions

$$K_x = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2}{\frac{1-\alpha}{1+\alpha}} \tag{9.5.1}$$

$$= \frac{4\alpha^2}{1-\alpha^2} \tag{9.5.2}$$

And so K_p, which can be expressed as

$$K_p = K_x (p_{tot})^{\sum \nu_i} \tag{9.5.3}$$

is given by

$$K_p = \frac{4\alpha^2}{(1-\alpha^2)}(p_{tot})$$

✓ Example 9.5.1

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

$$\begin{aligned} \Delta G^o_f &= -RT \ln K_p \\ 2800\,kJ/mol &= -(8.314 J/(mol\,K)(298\,K) \ln K_p \\ K_p &= 0.323\,atm \end{aligned}$$

The degree of dissociation can then be calculated from the ICE tables at the top of the page for the dissociation of $N_2O_4(g)$:

$$\begin{aligned} K_p &= \frac{4\alpha^2}{1-\alpha^2}(p_{tot}) \\ 0.323\,atm &= \frac{4\alpha^2}{1-\alpha^2}(1.00\,atm) \end{aligned}$$

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 9.5.2

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 9.5.3, 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

$$\begin{aligned} \Delta G^o_{rxn} &= -(8.314\,J/(mol\,K))(1350\,K)\ln(0.792) \\ &= 2590\,J/mol \end{aligned}$$

9.6: 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_{rxm} 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.

$$\ln \left(\frac{K_2}{K_1} \right) = -\frac{\Delta H^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{9.6.1}$$

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 9.6.1

A certain reaction has a value of $K_p = 0.0260$ at 25 °C and $\Delta H^o_{rxm} = 32.4\, kJ/mol$. 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
- $\Delta H^o_{rxm} = 32.4\, kJ/mol$
- K_1 = 0.0260
- K_2 = ?

So Equation 9.6.1 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 9.6.2

Given the following average bond enthalpies for $P-Cl$ and $Cl-Cl$ bonds, predict whether or not an increase in temperature will lead to a larger or smaller degree of dissociation for the reaction

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

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.

9.7: 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

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \tag{9.7.1}$$

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.

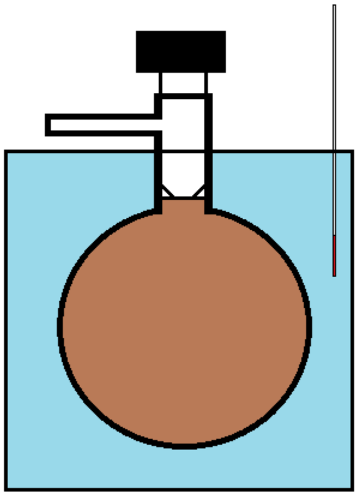


Figure 9.7.1:

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.

9.8: 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

$$pH \equiv -\log a(\mathrm{H}^+) \approx -\log[\mathrm{H}^+] \tag{9.8.1}$$

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

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{9.8.2}$$

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 9.8.1: 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!

	$[\boldsymbol{HOAc}]$	$[\boldsymbol{H}^+]$	$[\boldsymbol{OAc}^-]$
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 9.8.1) 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

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \tag{9.8.3}$$

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.

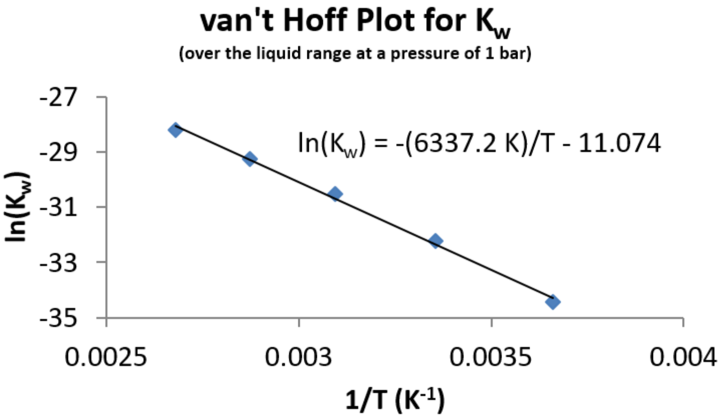


Figure 9.8.1: van't Hoff plot for the autoionization of water.

There is some curvature to the line, suggesting some (albeit small) temperature dependence for ΔH_{rxn} for Equation 9.8.3. 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 9.8.2: 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 9.8.1, 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 9.8.1):

$$pH = -\log_{10}(1.456 \times 10^{-7}) = 6.84$$

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 9.8.2),

$$K_a K_b = \left(\frac{[H^+][A^-]}{[HA]}\right)\left(\frac{[HA][OH^-]}{[A^-]}\right) = [H^+][OH^-] = K_w$$

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 9.8.3:

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 9.8.1):

$$pH = -\log_{10}(6.71 \times 10^{-9}) = 8.17$$

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.

9.9: 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 9.9.1:

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.

9.10: Solubility of Ionic Compounds

The solubility of ionic compounds in water can also be described using the concepts of equilibrium. If you consider the dissociation of a generic salt MX

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$$

The equilibrium expression is

$$K_{sp} = [M^+][X^-]$$

K_{sp} is the **solubility product** and is the equilibrium constant that describes the solubility of an electrolyte. And again, the pure solid MX is not included in the expression since it has unit activity throughout the establishment of equilibrium.

✓ Example 9.10.1:

What is the maximum solubility of CuS at 25 °C? ($K_{sp} = 1 \times 10^{-36}\ M^2$)

Solution

Yup – time for an ICE table.

	CuS	Cu^{2+}	S^{2-}
Initial		0	0
Change		+x	+x
Equilibrium		x	x

So the equilibrium expression is

$$1 \times 10^{-36} M^2 = x^2$$

$$x = \sqrt{1 \times 10^{-36}\ M^2} = 1 \times 10^{-18}\ M$$

✓ Example 9.10.2: Common Ion

What is the maximum solubility of CuS at 25 °C in 0.100 M NaS with ($K_{sp} = 1 \times 10^{-36}\ M^2$)?

Solution

In this problem we need to consider the existence of S^{2-}(aq) from the complete dissociation of the strong electrolyte NaS. An ICE table will help, as usual.

	CuS	Cu^{2+}	S^{2-}
Initial		0	0.100 M
Change		+x	+x
Equilibrium		x	0.100 M + x

Given the miniscule magnitude of the solubility product, x will be negligibly small compared to 0.100 MS the equilibrium expression is

$$1 \times 10^{-36} M^2 = x(0.100\ M)$$

$$1 \times 10^{-35}\ M$$

The huge reduction in solubility is due to the common ion effect. The existence of sulfide in the solution due to sodium sulfide greatly reduces the solutions capacity to support additional sulfide due to the dissociation of CuS.

9.E: Chemical Equilibria (Exercises)

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9.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

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CHAPTER OVERVIEW

10: Electrochemistry

Physical Chemistry: Thermodynamics
Patrick Fleming

I II III IV V VI VII VIII IX X XI XII • **Homework Exercises**

Elon Musk, an innovator in the field of harnessing renewable sources to generate electric power see a huge potential for electric cars to change the way Americans drive.

> - *Selling an electric sports car creates an opportunity to fundamentally change the way America drives.- Elon Musk*
> - *I've actually made a prediction that within 30 years a majority of new cars made in the United States will be electric. And I don't mean hybrid, I mean fully electric.- Elon Musk*

Given the importance of energy production (and in particular, production from renewable sources) alluded to by Richard Smalley in his address to the United States Congress (see Chapter 1), Elon Musk's vision seems well-aligned with Smalley's priority. The generation and consumption of electrical energy and how it is harnessed to do work in the universe lends itself very nicely to discussion within the framework of thermodynamics. In this chapter, we will use some of the tills we have developed to relate electrochemical processes to thermodynamic variables, and to frame discussions of a few important topics.

10.1: Electricity

Electricity has been known for some time. Ancient Egyptians, for example, referred to electric fish in the Nile River as early as 2750 BC (Moller & Kramer, 1991). In 1600, William Gilbert studied what would later be seen to be electrostatic attraction, by creating static charges rubbing amber (Stewart, 2001). And Benjamin Franklin’s famous experiment (although it is actually uncertain if he performed the experiment) of attaching a metal key to a kite string occurred in 1752, and showed that lightening is an electrical phenomenon (Uman, 1987).

One of the biggest breakthroughs in the study of electricity as a chemical phenomenon was made by Alessandro Volta, who in 1799 showed that electricity could be generated by stacking copper and zinc disks submerged in sulfuric acid (Routledge, 1881). The reactions that Volta produced in his **voltaic pile** included both **oxidation** and **reduction** processes that could be considered as **half-reactions**. The half-reactions can be classified as **oxidation** (the loss of electrons) which happens at the **anode** and **reduction** (the gain of electrons) which occurs at the **cathode**. Those half reactions were

$$\underbrace{Zn \rightarrow Zn^{2+} + 2e^-}_{\text{aanode}}$$

$$\underbrace{2H^+ + 2e^- \rightarrow H_2}_{\text{cathode}}$$

The propensity of zinc to oxidize coupled with that of hydrogen to reduce creates a potential energy difference between the electrodes at which these processes occur. And like any potential energy difference, it can create a force which can be used to do work. In this case, the work is that of pushing electrons through a circuit. The work of such a process can be calculated by integrating

$$dw_e - -E\,dQ$$

where E is the potential energy difference, and dQ is an infinitesimal amount of charge carried through the circuit. The infinitesimal amount of charge carried through the circuit can be expressed as

$$dQ = e\,dN$$

where e is the charge carried on one electron ($1.6 \times 10^{-19} C$) and dN is the infinitesimal change in the number of electrons. Thus, if the potential energy difference is constant

$$w_e = -e\,E \int_o^N dN = -N\,e\,E$$

But since the number of electrons carried through a circuit is an enormous number, it would be far more convenient to express this in terms of the number of moles of electrons carried through the circuit. Noting that the number of moles (n) is given by

$$n = \frac{N}{N_A}$$

and that the charge carried by one mole of electrons is given by

$$F = N_A e = 96484\,C$$

where F is **Faraday's constant** and has the magnitude of one Faraday (or the total charge carried by one mole of electrons.) The Faraday is named after Michael Faraday (1791-1867) (Doc, 2014), a British physicist who is credited with inventing the electric motor, among other accomplishments.

Putting the pieces together, the total electrical work accomplished by pushing n moles of electrons through a circuit with a potential difference E, is

$$w_e = -nFE$$

10.2: The connection to ΔG

Recall that in addition to being used as a criterion for spontaneity, ΔG also indicated the maximum amount of non p-V work a system could produce at constant temperature and pressure. And since w_e is non p-V work, it seems like a natural fit that

$$\Delta G = -nFE$$

If all of the reactants and products in the electrochemical cell are in their standard states, it follows that

$$\Delta G^o = -nFE^o$$

where E^o is the **standard cell potential**. Noting that the molar Gibbs function change can be expressed in terms of the reaction quotient Q by

$$\Delta G = \Delta G^o + RT \ln Q$$

it follows that

$$-nFE = -nFE^o + RT \ln Q$$

Dividing by $-nF$ yields

$$E = E^o - \frac{RT}{nF} \ln Q$$

which is the **Nernst equation**. This relationship allows one to calculate the cell potential of a electrochemical cell as a function of the specific activities of the reactants and products. In the Nernst equation, n is the number of electrons transferred per reaction equivalent. For the specific reaction harnessed by Volta in his original battery, E^o = 0.763 V (at 25 ^oC) and $n = 2$. So if the Zn^{2+} and H^+ ions are at a concentration that gives them unit activity, and the H_2 gas is at a partial pressure that gives it unit fugacity:

$$E = 0.763\, V - \frac{RT}{nF} \ln(1) = 0/763$$

10.3: Half Cells and Standard Reduction Potentials

Much like G itself, E can only be measured as a *difference*, so a convention is used to set a zero to the scale. Toward this end, convention sets the reduction potential of the standard hydrogen electrode (SHE) to 0.00 V.

$$\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2\,\mathrm{e}^-$$

wtih $E^o_{ox} = 0.763\, V$

$$2\,\mathrm{H}^+ + 2\,\mathrm{e}^- \rightarrow \mathrm{H}_2$$

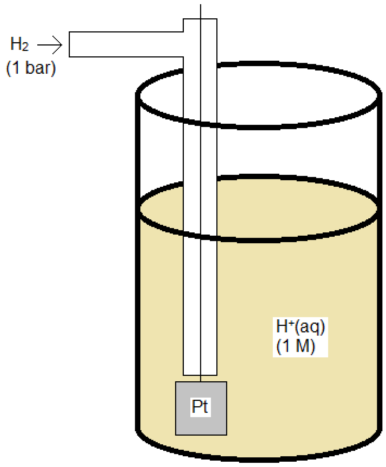
with $E^o_{red} = 0.000\, V$

Standard Hydrogen Electrode

The standard hydrogen electrode is constructed so that H_2 gas flows over an inert electrode made of platinum, and can interact with an acid solution which provides H^+ for the half reaction

$$2\,\mathrm{H}^+(aq) + 2\,\mathrm{e}^- \longrightarrow \mathrm{H}_2(g)$$

Both H^+ and H_2 need to have unit activity (or fugacity), which if the solution and gas behave ideally means a concentration of 1 M and a pressure of 1 bar.



Electrochemical Cells

Standard reduction potentials can be measured relative to the convention of setting the reduction potential of the **Standard Hydrogen Electrode** (SHE) to zero. A number of values are shown in Table P1.

✓ Example 10.3.1: Cell Potential and Spontaneity

Which pair of reactants will produce a spontaneous reaction if everything is present in its standard state at 25 °C?

- Fe and Cu^{2+} or
- Fe^{2+} and Cu

Solution

The species with the standard reduction potential (Table P1) will force the other to oxidize.

From the table,

$$\mathrm{Cu}^{2+} + 2\,\mathrm{e}^- \rightarrow \mathrm{Cu}$$

with $0.337\, V$

$$\mathrm{Fe}^{2+} + 2\,\mathrm{e}^- \rightarrow \mathrm{Fe}$$

with $-0.440\,V$

So the iron half-reaction will flip (so that iron is oxidizing) and the spontaneous reaction under standard conditions will be

$$Cu^{2+} + Fe \rightarrow Cu + Fe^{2+}$$

with $E^o = 0.777\,V$

Calculating Cell Potentials

Using values measured relative to the SHE, it is fairly easy to calculate the standard cell potential of a given reaction. For example, consider the reaction

$$2\,\mathrm{Ag^+(aq)} + \mathrm{Cu(s)} \rightarrow 2\,\mathrm{Ag(s)} + \mathrm{Cu^{2\,+}(aq)}$$

Before calculating the cell potential, we should review a few definitions. The anode half reaction, which is defined by the half-reaction in which oxidation °Ccurs, is

$$\mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2\,+}(aq)} + 2\,\mathrm{e^-}$$

And the cathode half-reaction, defined as the half-reaction in which reduction takes place, is

$$\mathrm{Ag^+(aq)} + \mathrm{e^-} \rightarrow \mathrm{Ag(s)}$$

Using **standard cell notation**, the conditions (such as the concentrations of the ions in solution) can be represented. In the standard cell notation, the anode is on the left-hand side, and the cathode on the right. The two are typically separated by a **salt bridge**, which is designated by a double vertical line. A single vertical line indicates a phase boundary. Hence for the reaction above, if the silver ions are at a concentration of 0.500 M, and the copper (II) ions are at a concentration of 0.100 M, the standard cell notation would be

✓ Example 10.3.2: Cell Potential Under nonstadard Conditions

Calculate the cell potential at 25 °C for the cell indicated by

$$\mathrm{Cu(s)|Cu^{2\,+}(aq,\ 0\cdot100\ M)||Ag^+(aq,\ 0\cdot500\ M)|Ag(s)}$$

Solution

In order to calculate the cell potential (E), the standard cell potential must first be obtained. The standard cell potential at 25 °C is given by

$$\begin{aligned} E_{cell} &= E^o_{cathode} - E^o_{anode} \\ &= 0.799\,V - 0.337\,V \\ &= 0.462\,V \end{aligned}$$

And for a cell at non-standard conditions, such as those indicated above, the Nernst equation can be used to calculate the cell potential. At 25 °C, The cell potential is given by

$$\begin{aligned} E_{cell} &= E^o_{cell} - \frac{RT}{nF}\ln\left(\frac{[Cu^{2+}]}{[Ag^+]}\right) \\ &= 0.462\,V - \frac{(8.314\,J/(mol\,K)(298\,K)}{2(96484\,C)}\ln\left(\frac{0.100\,M}{0.500\,M}\right) \end{aligned}$$

Noting that $1\,J/C = 1\,V$,

$$E = 0.483\,V$$

✓ Example 10.3.3: Cell Potential under Non-Standard Conditions

Calculate the cell potential at 25 °C for the cell defined by

$$Ni(s)|Ni^{2+}\,(aq,\,0.500\,M)||Cu(s)|Cu^{2+}(aq,\,0.100\,M)$$

Solution

We will use the Nernst equation. First, we need to determine E^o. Using Table P1, it is apparent that

$$\mathrm{Cu^{2\,+}2\,e^{-} \rightarrow Cu}$$

$E^o = 0.337\,V$

$$\mathrm{Ni^{2\,+} + 2\,e^{-} \rightarrow Ni}$$

with $E^o = -0.250\,V$

So copper, having the larger reduction potential will be the cathode half-reaction while forcing nickel to oxidize, making it the anode. So E^o for the cell will be given by

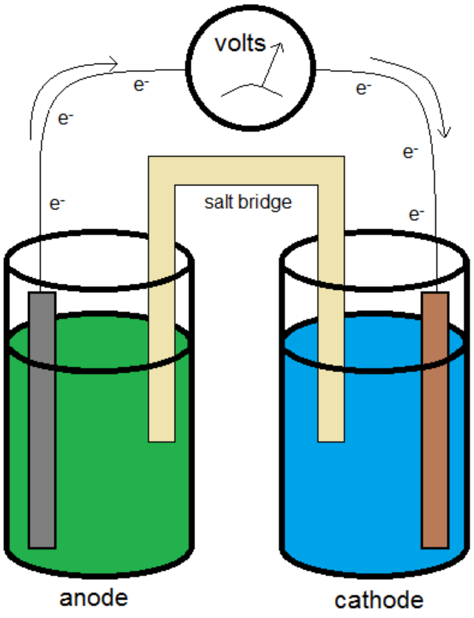
$$\begin{aligned} E_{cell} &= E^o_{cathode} - E^o_{anode} \\ &= 0.337\,V - (-0.250\,V) \\ &= 0.587\,V \end{aligned}$$

And the cell potential is then given by the Nernst Equation

$$\begin{aligned} E_{cell} &= E^o_{cell} - \frac{RT}{nF}\ln Q \\ &= 0.587 - \frac{(8.314\,J/(mol\,K)(298\,K)}{2(96484\,C)}\ln\left(\frac{0.500\,M}{0.100\,M}\right) \\ &= 0.566\,V \end{aligned}$$

Measuring the Voltage

A typical galvanic electrochemical cell can be constructed similar to what is shown in the diagram above. The electrons flow from the anode (the electron source) to the cathode (the electron sink.) The salt bridge allows for the flow of ions to complete the circuit while minimizing the introduction of a junction potential.



10.4: Entropy of Electrochemical Cells

The Gibbs function is related to entropy through its temperature dependence

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S$$

A similar relationship can be derived for the temperature variance of E^o.

$$nF\left(\frac{\partial E^o}{\partial T}\right)_p = \Delta S \tag{10.4.1}$$

Consider the following data for the Daniel cell (Buckbeei, Surdzial, & Metz, 1969) which is defined by the following reaction

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

T (°C)	0	10	20	25	30	40
Eo (V)	1.1028	1.0971	1.0929	1.0913	1.0901	1.0887

From a fit of the data to a quadratic function, the temperature dependence of

$$\left(\frac{\partial E^o}{\partial T}\right)_p$$

is easily established.

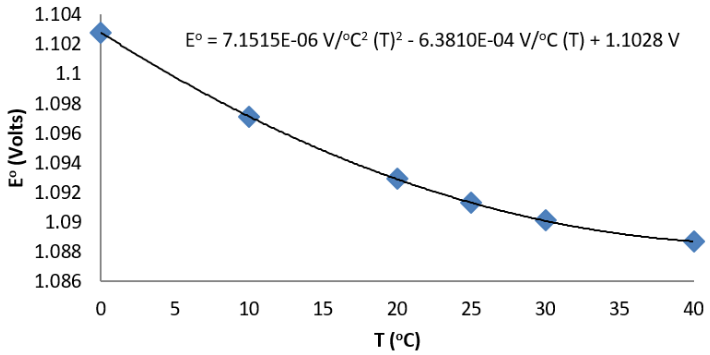


Figure 10.4.1: Temperature dependence of the cell potential for a Daniel cell.

The quadratic fit to the data results in

$$\left(\frac{\partial E^o}{\partial T}\right)_p = 3.8576 \times 10^{-6} \frac{V}{^\circ C^2}(T) - 6.3810 \times 10^{-4} \frac{V}{^\circ C}$$

So, at 25 °C,

$$\left(\frac{\partial E^o}{\partial T}\right)_p = -54166 \times 10^{-4} V/K$$

noting that K can be substituted for $^\circ C$ since in difference they have the same magnitude. So the entropy change is calculated (Equation 10.4.1) is

$$\Delta S = nF\left(\frac{\partial E^o}{\partial T}\right)_p = (2\, mol)(95484\, C/mol)(-5.4166 \times 10^{-4} V/K)$$

Because

$$1\, C \times 1\, V = 1\, J$$

The standard entropy change for the Daniel cell reaction at 25 °C is

$$\Delta S = -104.5\, J/(mol\, K).$$

It is the negative entropy change that leads to an increase in standard cell potential at lower temperatures. For a reaction such as

$$Pb(s) + 2H^+(aq) \rightarrow Pb^{2+}(aq) + H_2(g)$$

which has a large increase in entropy (due to the production of a gas-phase product), the standard cell potential decreases with decreasing temperature. As this is the reaction used in most car batteries, it explains why it can be difficult to start ones car on a very cold winter morning. The topic of temperature dependence of several standard cell potentials is reported and discussed by Bratsch (Bratsch, 1989).

10.5: Concentration Cells

The generation of an electrostatic potential difference is dependent on the creation of a difference in chemical potential between two half-cells. One important manner in which this can be created is by creating a concentration difference. Using the Nernst equation, the potential difference for a concentration cell (one in which both half-cells involve the same half-reaction) can be expressed

$$E = -\frac{RT}{nF}\ln\frac{[\text{oxdizing}]}{[\text{reducing}]}$$

✓ Example 10.5.1

Calculate the cell potential (at 25 °C) for the concentration cell defined by

$$Cu(s)|Cu^{2+}(aq,\, 0.00100\, M)||Cu^{2+}(aq,\, 0.100\, M)|Cu(s)$$

Solution

Since the oxidation and reduction half-reactions are the same,

$$E^o_{cell} = 0\, V$$

The cell potential at 25 °C is calculated using the Nernst equation:

$$E = -\frac{RT}{nF}\ln Q$$

Substituting the values from the problem:

$$\begin{aligned} E_{cell} &= -\frac{(8.314\, J/(mol\, K)(298\, K)}{2(96484\, C)}\ln\left(\frac{0.00100\, M}{0.100\, M}\right) \\ &= 0.059\, V \end{aligned}$$

10.E: Electrochemistry (Exercises)

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10.S: Electrochemistry (Summary)

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Vocabulary and Concepts

- anode
- cathode
- concentration cell
- half-reactions
- Nernst equation
- oxidation
- reduction
- salt bridge
- standard cell notation
- standard cell potential
- Standard Hydrogen Electrode
- voltaic pile

Learning Objectives

CHAPTER OVERVIEW

11: Chemical Kinetics I

Physical Chemistry: Thermodynamics
Patrick Fleming

Chemical kinetics is the study of how fast chemical reactions proceed from reactants to products. This is an important topic because while thermodynamics will tell us about the direction of spontaneous change, it is silent as to how fast processes will occur. But additionally, the power of studying reaction rates is that it gives us insight into the actual pathways chemical processes follow to proceed from reactants to products.

11.1: Reaction Rate

The rate of a chemical reaction (or the **reaction rate**) can be defined by the time needed for a change in concentration to occur. But there is a problem in that this allows for the definition to be made based on concentration changes for either the reactants or the products. Plus, due to stoichiometric concerns, the rates at which the concentrations are generally different! Toward this end, the following convention is used.

For a general reaction

$$aA + bB \rightarrow cC + dD$$

the reaction rate can be defined by any of the ratios

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{dt} = -\frac{1}{b}\frac{\Delta[B]}{dt} = +\frac{1}{c}\frac{\Delta[C]}{dt} = +\frac{1}{d}\frac{\Delta[D]}{dt}$$

Or for infinitesimal time intervals

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[C]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

Example 11.1.1:

Under a certain set of conditions, the rate of the reaction

$$N_2 + 3H_2 \rightarrow 2NH_3$$

the reaction rate is $6.0 \times 10^{-4}\ M/s$. Calculate the time-rate of change for the concentrations of N_2, H_2, and NH_3.

Solution

Due to the stoichiometry of the reaction,

$$\text{rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

so

$$\frac{d[N_2]}{dt} = -6.0 \times 10^{-4}\ M/s$$

$$\frac{d[H_2]}{dt} = -2.0 \times 10^{-4}\ M/s$$

$$\frac{d[NH_3]}{dt} = 3.0 \times 10^{-4}\ M/s$$

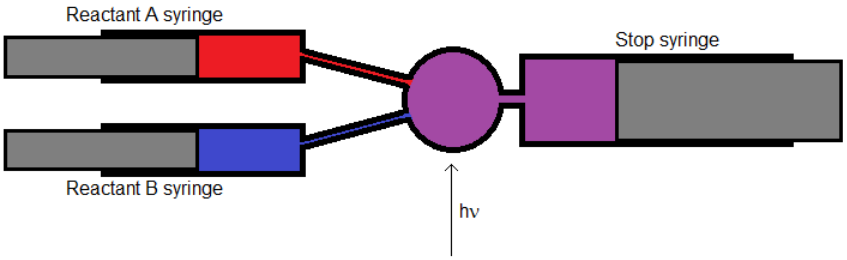
Note: The time derivatives for the reactants are negative because the reactant concentrations are decreasing, and those of products are positive since the concentrations of products increase as the reaction progresses.

11.2: Measuring Reaction Rates

There are several methods that can be used to measure chemical reactions rates. A common method is to use spectrophotometry to monitor the concentration of a species that will absorb light. If it is possible, it is preferable to measure the appearance of a product rather than the disappearance of a reactant, due to the low background interference of the measurement. However, high-quality kinetic data can be obtained either way.

The Stopped-Flow Method

The **stopped-flow method** involves using flow control (which can be provided by syringes or other valves) to control the flow of reactants into a mixing chamber where the reaction takes place. The reaction mixture can then be probed spectrophotometrically. Stopped-flow methods are commonly used in physical chemistry laboratory courses (Progodich, 2014).



Some methods depend on measuring the initial rate of a reaction, which can be subject to a great deal of experimental uncertainty due to fluctuations in instrumentation or conditions. Other methods require a broad range of time and concentration data. These methods tend to produce more reliable results as they can make use of the broad range of data to smooth over random fluctuations that may affect measurements. Both approaches (initial rates and full concentration profile data methods) will be discussed below.

11.3: Rate Laws

A rate law is any mathematical relationship that relates the concentration of a reactant or product in a chemical reaction to time. Rate laws can be expressed in either derivative (or ratio, for finite time intervals) or integrated form. One of the more common general forms a rate law for the reaction

$$A + B \rightarrow products$$

may take is

$$\text{rate} = k[A]^{\alpha}[B]^{\beta}$$

where k, α, and β are experimentally determined values. However, a rate law can take many different forms, some of which can be quite intricate and complex. The powers α and β need not be integers. For example

$$\text{rate} = k[A]^{\alpha}[B]^{1/2} \tag{11.3.1}$$

is a rate law that is observed for some reactions. Sometimes, the concentrations of products must be included.

$$\text{rate} = \frac{k[A]^{1/2}[B]}{[P]}$$

In some cases, the concentration for a catalyst or enzyme is important. For example, many enzyme mitigated reactions in biological systems follow the Michaelis-Menten rate law, which is of the form

$$\text{rate} = \frac{V_{max}[S]}{K_m + [S]}$$

where V_{max} and K_M are factors that are determined experimentally, and $[S]$ is the concentration of the substrate in the reaction.

Order

For those cases where the rate law can be expressed in the form

$$\text{rate} = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}$$

where A, B, and C are reactants (or products or catalysts, etc.) involved in the reaction, the reaction is said to be of α order in A, β order in B, and γ order in C. The reaction is said to be $\alpha + \beta + \gamma$ order overall. Some examples are shown in the following table:

Table 11.3.1: Example Rate Laws

Rate law	Order with respect to A	Order with respect to B	Order with respect to C	Overall order
$\text{rate} = k$	0	0	0	0
$\text{rate} = k[A]$	0	0	0	1
$\text{rate} = k[A]^2$	0	0	0	2
$\text{rate} = k[A][B]$	0	1	0	2
$\text{rate} = k[A]^2[B]$	0	1	0	3
$\text{rate} = k[A][B][C]$	0	1	1	3

Reaction orders can also be fractional such as for Equation 11.3.1 which is 1st order in A, and half order in B. The order can also be negative such as

$$\text{rate} = k\frac{[A]}{[B]}$$

which is 1st order in A, and -1 order in B. In this case, an build-up of the concentration of B will retard (slow) the reaction.

In all cases, the order of the reaction with respect to a specific reactant or product (or catalyst, or whatever) must be determined experimentally. As a general rule, the stoichiometry cannot be used to predict the form of the rate law. However, the rate law can be used to gain some insight into the possible pathways by which the reaction can proceed. That is the topic of Chapter 12. For now we will focus on three useful methods that are commonly used in chemistry to determine the rate law for a reaction from experimental data.

Empirical Methods

Perhaps the simplest of the methods to be used are the empirical methods, which rely on the qualitative interpretation of a graphical representation of the concentration vs time profile. In these methods, some function of concentration is plotted as a function of time, and the result is examined for a linear relationship. For the following examples, consider a reaction of the form

$$A + B \rightarrow products$$

in which A is one of the reactants. In order to employ these empirical methods, one must generate the forms of the integrated rate laws.

11.4: 0th order Rate Law

If the reaction follows a zeroth order rate law, it can be expressed in terms of the time-rate of change of [A] (which will be negative since A is a reactant):

$$-\frac{d[A]}{dt}=k$$

In this case, it is straightforward to separate the variables. Placing time variables on the right and [A] on the left

$$d[A]=-k\,dt$$

In this form, it is easy to integrate. If the concentration of A is $[A]_0$ at time t = 0, and the concentration of A is [A] at some arbitrary time later, the form of the integral is

$$\int_{[A]_o}^{[A]} d[A]=-k\int_{t_o}^{t}\,dt$$

which yields

$$[A]-[A]_o=-kt$$

or

$$[A]=[A]_o-kt$$

This suggests that a plot of concentration as a function of time will produce a straight line, the slope of which is –k, and the intercept of which is $[A]_0$. If such a plot is linear, then the data are consistent with 0^{th} order kinetics. If they are not, other possibilities must be considered.

11.5: 1st order rate law

A first order rate law would take the form

$$\frac{d[A]}{dt} = k[A]$$

Again, separating the variables by placing all of the concentration terms on the left and all of the time terms on the right yields

$$\frac{d[A]}{[A]} = -k\,dt$$

This expression is also easily integrated as before

$$\int_{[A]=0}^{[A]} \frac{d[A]}{[A]} = -k\int_{t=0}^{t=t} dt$$

Noting that

$$\frac{dx}{x} = d(\ln x)$$

The form of the integrated rate law becomes

$$\ln[A] - \ln[A]_o = kt$$

or

$$\ln[A] = \ln[A]_o - kt \tag{11.5.1}$$

This form implies that a plot of the natural logarithm of the concentration is a linear function of the time. And so a plot of ln[A] as a function of time should produce a linear plot, the slope of which is -k, and the intercept of which is $\ln[A]_0$.

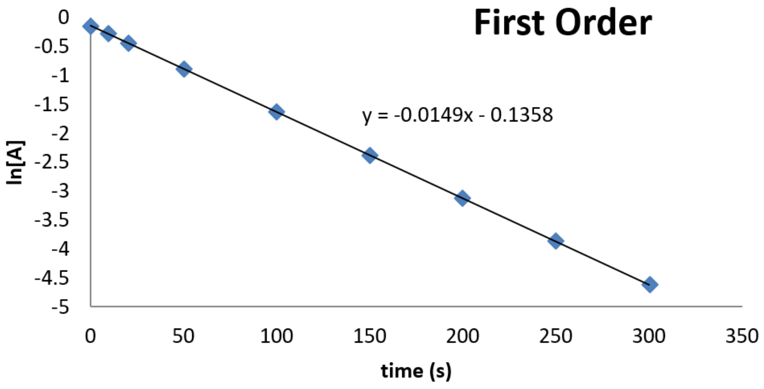
✓ Example 11.5.1:

Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with first order kinetics. Also, if the data are first order, determine the value of the rate constant for the reaction.

Time (s)	0	10	20	50	100	150	200	250	300
[A] (M)	0.873	0.752	0.648	0.414	0.196	0.093	0.044	0.021	0.010

Solution

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.0149 s^{-1}. The concentration at time $t=0$ can also be inferred from the intercept.

It should also be noted that the integrated rate law (Equation 11.5.1) can be expressed in exponential form:

$$[A]=[A]_o e^{-kt}$$

Because of this functional form, 1st order kinetics are sometimes referred to as exponential decay kinetics. Many processes, including radioactive decay of nuclides follow this type of rate law.

11.6: 2nd order Rate Laws

If the reaction follows a second order rate law, the some methodology can be employed. The rate can be written as

$$-\frac{d[A]}{dt}=k[A]^2 \tag{11.6.1}$$

The separation of concentration and time terms (this time keeping the negative sign on the left for convenience) yields

$$-\frac{d[A]}{[A]^2}=k\,dt$$

The integration then becomes

$$-\int_{[A]_o}^{[A]}\frac{d[A]}{[A]^2}=\int_{t=0}^{t}k\,dt \tag{11.6.2}$$

And noting that

$$-\frac{dx}{x^2}=d\left(\frac{1}{x}\right)$$

the result of integration Equation 11.6.2 is

$$\frac{1}{[A]}-\frac{1}{[A]_o}=kt$$

or

$$\frac{1}{[A]}=\frac{1}{[A]_o}+kt$$

And so a plot of $1/[A]$ as a function of time should produce a linear plot, the slope of which is k, and the intercept of which is $1/[A]_0$.

Other 2^{nd} order rate laws are a little bit trickier to integrate, as the integration depends on the actual stoichiometry of the reaction being investigated. For example, for a reaction of the type

$$A+B\rightarrow P$$

That has rate laws given by

$$-\frac{d[A]}{dt}=k[A][B]$$

and

$$-\frac{d[B]}{dt}=k[A][B]$$

the integration will depend on the decrease of [A] and [B] (which will be related by the stoichiometry) which can be expressed in terms the concentration of the product [P].

$$[A]=[A]_o-[P] \tag{11.6.3}$$

and

$$[B]=[B]_o-[P] \tag{11.6.4}$$

The concentration dependence on A and B can then be eliminated if the rate law is expressed in terms of the production of the product.

$$\frac{d[P]}{dt}=k[A][B] \tag{11.6.5}$$

Substituting the relationships for $[A]$ and $[B]$ (Equations 11.6.3 and 11.6.4) into the rate law expression (Equation 11.6.5) yields

$$\frac{d[P]}{dt} = k([A]_o - [P])([B] = [B]_o - [P]) \tag{11.6.6}$$

Separation of concentration and time variables results in

$$\frac{d[P]}{([A]_o - [P])([B] = [B]_o - [P])} = k\,dt$$

Noting that at time $t = 0$, $[P] = 0$, the integrated form of the rate law can be generated by solving the integral

$$\int_{[A]_o}^{[A]} \frac{d[P]}{([A]_o - [P])([B]_o - [P])} = \int_{t=0}^{t} k\,dt$$

Consulting a table of integrals reveals that for $a \neq b$ [1],

$$\int \frac{dx}{(a-x)(b-x)} = \frac{1}{b-a} \ln\left(\frac{b-x}{a-x}\right)$$

Applying the definite integral (as long as $[A]_0 \neq [B]_0$) results in

$$\frac{1}{[B]_0 - [A]_0} \ln\left(\frac{[B]_0 - [P]}{[A]_0 - [P]}\right)\Bigg|_0^{[A]} = k\,t|_0^t$$

$$\frac{1}{[B]_0 - [A]_0} \ln\left(\frac{[B]_0 - [P]}{[A]_0 - [P]}\right) - \frac{1}{[B]_0 - [A]_0} \ln\left(\frac{[B]_0}{[A]_0}\right) = k\,t \tag{11.6.7}$$

Substituting Equations 11.6.3 and 11.6.4 into Equation 11.6.7 and simplifying (combining the natural logarithm terms) yields

$$\frac{1}{[B]_0 - [A]_0} \ln\left(\frac{[B][A]_o}{[A][B]_o}\right) = kt$$

For this rate law, a plot of $\ln([B]/[A])$ as a function of time will produce a straight line, the slope of which is

$$m = ([B]_0 - [A]_0)k.$$

In the limit at $[A]_0 = [B]_0$, then $[A] = [B]$ at all times, due to the stoichiometry of the reaction. As such, the rate law becomes

$$\text{rate} = k[A]^2$$

and integrate direct like in Equation 11.6.1 and the integrated rate law is (as before)

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt$$

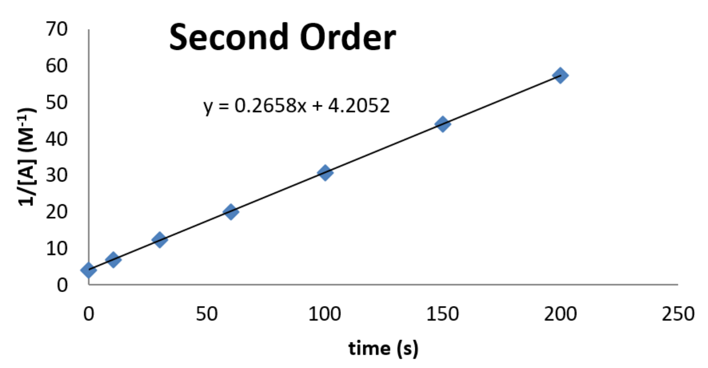
Example 11.6.2: Confirming Second Order Kinetics

Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with second order kinetics. Also, if the data are second order, determine the value of the rate constant for the reaction.

time (s)	0	10	30	60	100	150	200
[A] (M)	0.238	0.161	0.098	0.062	0.041	0.029	0.023

Solution

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.2658 M^{-1} s^{-1}. The concentration at time $t = 0$ can also be inferred from the intercept.

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[1] This integral form can be generated by using the method of partial fractions. See (House, 2007) for a full derivation.

11.7: The Method of Initial Rates

The **method of initial rates** is a commonly used technique for deriving rate laws. As the name implies, the method involves measuring the initial rate of a reaction. The measurement is repeated for several sets of initial concentration conditions to see how the reaction rate varies. This might be accomplished by determining the time needed to exhaust a particular amount of a reactant (preferably one on which the reaction rate does not depend!) A typical set of data for a reaction

$$A + B \rightarrow products$$

might appear as follows:

Run	[A] (M)	[B] (M)	Rate (M/s)
1	0.0100	0.0100	0.0347
2	0.0200	0.0100	0.0694
3	0.0200	0.0200	0.2776

The analysis of this data involves taking the ratios of rates measured where one of the concentrations does not change. For example, assuming a rate law of the form

$$\text{rate} = k[A]^{\alpha}[B]^{\beta} \tag{11.7.1}$$

The ratio of runs i and j generate the following relationship.

$$\frac{\text{rate}_i}{\text{rate}_j} = \frac{k[A]_i^{\alpha}[B]_i^{\beta}}{k[A]_j^{\alpha}[B]_j^{\beta}}$$

So using runs 1 and 2,

$$\frac{0.0347\,M/s}{0.0694\,M/s} = \frac{\cancel{k}(0.01\,M/s)^{\alpha}\ \cancel{(0.01\,M/s)^{\beta}}}{\cancel{k}(0.02\,M/s)^{\alpha}\ \cancel{(0.01\,M/s)^{\beta}}}$$

this simplifies to

$$\frac{1}{2} = \left(\frac{1}{2}\right)^{\alpha}$$

So clearly, \(\alpha = 1\) and the reaction is 1st order in A. Taking the ratio using runs 2 and 3 yields

$$\frac{0.0694\,M/s}{0.2776\,M/s} = \frac{\cancel{k}(0.02\,M)^{\alpha}\ \cancel{(0.01\,M)^{\beta}}}{\cancel{k}(0.02\,M)^{\alpha}\ \cancel{(0.02\,M)^{\beta}}}$$

This simplifies to

$$\frac{1}{4} = \left(\frac{1}{2}\right)^{\beta} \tag{11.7.2}$$

By inspection, one can conclude that \(\beta = 2\), and that the reaction is second order in B. But if it is not so clear (as it might not be if the concentration is not incremented by a factor of 2), the value of \(\beta\) can be determined by taking the natural logarithm of both sides of the Equation 11.7.2.

$$\begin{aligned} \ln \frac{1}{4} &= \ln \left(\frac{1}{2}\right)^{\beta} \\ &= \beta \ln \left(\frac{1}{2}\right) \end{aligned}$$

dividing both sides by $\ln(1/2)$

$$\frac{\ln\left(\frac{1}{4}\right)}{\ln\left(\frac{1}{2}\right)} = \beta \frac{\ln\left(\frac{1}{2}\right)}{\ln\left(\frac{1}{2}\right)}$$

or

$$\beta = \frac{-1.3863}{-0.69315} = 2$$

And so the rate law (Equation 11.7.1) can be expressed as

$$\text{rate} = k[A][B]^2$$

And is 1st order in A, 2nd order in B, and 3rd order overall. The rate constant can then be evaluated by substituting one of the runs into the rate law (or using all of the data and taking an average). Arbitrarily selecting the first run for this,

$$0.0347\ M/s = k(0.01\ M/s)(0.01\ M/s)^2$$

This results in a value of k

$$k = \frac{0.0347\ M/s}{(0.01\ M/s)(0.01\ M/s)^2} = 3.47 \times 10^5\ M^{-2} s^{-1}$$

It is useful to note that the units on k are consistent with a 3rd order rate law.

11.8: The Method of Half-Lives

Another method for determining the order of a reaction is to examine the behavior of the **half-life** as the reaction progresses. The half-life can be defined as the time it takes for the concentration of a reactant to fall to half of its original value. The method of half-lives involved measuring the half-life's dependence on concentration. The expected behavior can be predicted using the integrated rate laws we derived earlier.

Using the definition of the half-life, at time $t_{1/2}$ the concentration $[A]$ drops to half of its original value, $[A]_0$.

$$[A] = \frac{1}{2}[A]_o$$

at $t = t_{1/2}$.

So if the reaction is 0th order in A, after one half-life

$$\frac{1}{2}[A]_o = [A]_o - kt_{1/2}$$

Solving for $t_{1/2}$ reveals the dependence of the half-life on the initial concentration.

$$\frac{[A]_o}{2k} = t_{1/2}$$

So as the original concentration is **decreased**, the half-life of a 0th order reaction will also **decrease**.

Similarly, for a first order reaction,

$$\frac{1}{2}[A]_o = [A]_o e^{-kt_{1/2}}$$

and solving for $t_{1/2}$ results in a concentration independent expression

$$\frac{\ln 2}{k} = t_{1/2}$$

It is because the half-life of a 1st order reaction is **independent** of concentration that it is oftentimes used to describe the rate of first order processes (such as radioactive decay.)

For a 2nd order reaction, the half-life can be expressed based on the integrated rate law.

$$\frac{1}{\frac{1}{2}[A]_o} = \frac{1}{[A]_o} + kt_{1/2}$$

solving for $t_{1/2}$ yields

$$\frac{1}{t_{1/2}} = t_{1/2}$$

In the case of a second order reaction, the half-life **increases** with **decreasing** initial concentration.

Table 11.8.1: Calculated half lives for Reactions following simple Rate Laws

Order	Half-life	Behavior
0th	$\frac{1}{2}[A]_o = [A]_o - kt_{1/2}$	Decreases as the reaction progresses (as [A] decreases
1st	$[\frac{\ln 2}{k} = t_{1/2}$	Remains constant as the reaction progresses (is independent of concentration)
2nd	$\frac{1}{\frac{1}{2}[A]_o} = \frac{1}{[A]_o} + kt_{1/2}$	Increases with decreasing concentration.

For reactions in which the rate law depends on the concentration of more than one species, the half-life can take a much more complex form that may depend on the initial concentrations of multiple reactants, or for that matter, products!

✓ Example 11.8.1: Radiocarbon Dating

Carbon-14 decays into nitrogen-14 with first order kinetics and with a half-life of 5730 years.

$$^{14}\text{C} \rightarrow {}^{14}\text{N}$$

What is the rate constant for the decay process? What percentage of carbon-14 will remain after a biological sample has stopped ingesting carbon-14 for 1482 years?

Solution

The rate constant is fairly easy to calculate:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{5730\,yr} = 1.21 \times 10^{-4}\,yr^{-1}$$

Now the integrated rate law can be used to solve the second part of the problem.

$$[^{14}\text{C}] = [^{14}\text{C}]_o e^{-kt}$$

this can be rewritten in term of relative loss of $[^{14}\text{C}]$.

$$\frac{[^{14}\text{C}]}{[^{14}\text{C}]_o} = e^{-kt}$$

so

$$\frac{[^{14}\text{C}]}{[^{14}\text{C}]_o} = e^{-(1.21 \times 10^{-4}\,yr^{-1})(1482\,ys)} = 0.836$$

So after 1482 years, there is 83.6 % of ^{14}C still left.

✓ Example 11.8.2:

Based on the following concentration data as a function of time, determine the behavior of the half-life as the reaction progresses. Use this information to determine if the following reaction is 0$^{\text{th}}$ order, 1$^{\text{st}}$ order, or 2$^{\text{nd}}$ order in A. Also, use the data to estimate the rate constant for the reaction.

time (s)	[A] (M)
0	1.200
10	0.800
20	0.600
30	0.480
40	0.400
50	0.343
60	0.300
70	0.267
80	0.240
90	0.218
100	0.200

Solution

If the original concentration is taken as 1.200 M, half of the original concentration is 0.600 M. The reaction takes 20 seconds to reduce the concentration to half of its original value. If the original concentration is taken as 0.800 M, it clearly takes 30 seconds for the concentration to reach half of that value. Based on this methodology, the following table is easy to generate:

$[A]_o$ (M)	1.200	0.800	0.600	0.400
$t_{1/2}$ (s)	20	30	40	60

The rate constant can be calculated using any of these values:

$$k = \frac{1}{[A]t_{1/2}} \tag{11.8.1}$$

$$= \frac{1}{(0.8\,M)(30\,s)} \tag{11.8.2}$$

$$= 0.0417\,M^{-1}s^{-1} \tag{11.8.3}$$

11.9: Temperature Dependence

In general, increases in temperature increase the rates of chemical reactions. It is easy to see why, since most chemical reactions depend on molecular collisions. And as we discussed in Chapter 2, the frequency with which molecules collide increases with increased temperature. But also, the kinetic energy of the molecules increases, which should increase the probability that a collision event will lead to a reaction. An empirical model was proposed by Arrhenius to account for this phenomenon. The **Arrhenius model** (Arrhenius, 1889) can be expressed as

$$k = Ae^{-E_a/RT}$$

Although the model is empirical, some of the parameters can be interpreted in terms of the energy profile of the reaction. E_a, for example, is the **activation energy**, which represents the energy barrier that must be overcome in a collision to lead to a reaction.

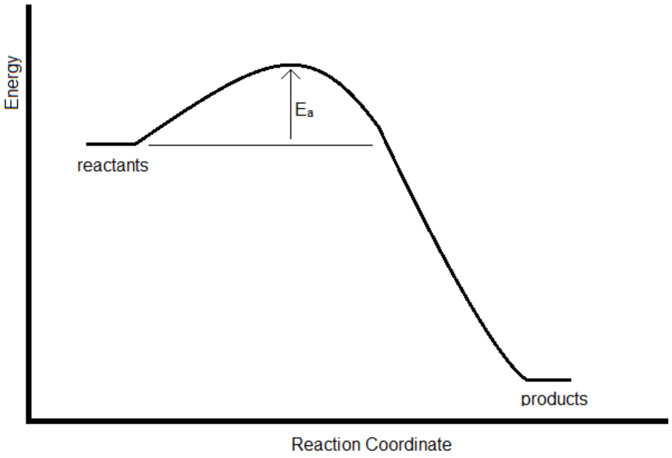


Figure 11.9.1: Reaction profile for an elementary sttep over an activated barrier of height E_a.

If the rate constant for a reaction is measure at two temperatures, the activation energy can be determined by taking the ratio. This leads to the following expression for the Arrhenius model:

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{11.9.1}$$

Example 11.9.1:

For a given reaction, the rate constant doubles when the temperature is increased form 25 °C to 35 °C. What is the Arrhenius activation energy for this reaction?

Solution

The energy of activation can be calculated from the Arrhenius Equation (Equation 11.9.1).

$$\ln\left(\frac{2k_1}{k_1}\right) = -\frac{E_a}{8.314\,\frac{J}{mol\,K}}\left(\frac{1}{308\,K} - \frac{1}{298\,K}\right)$$

From this reaction:

$$E_a = 52.9\,kJ/mol$$

Preferably, however, the rate constant is measured at several temperatures, and then the activation energy can be determined using all of the measurements, by fitting them to the expression

$$\ln(k) = -\frac{E_a}{RT} + \ln(A)$$

This can be done graphically by plotting the natural logarithm of the rate constant as a function of $1/T$ (with the temperature measured in K). The result should be a straight line (for a well-behaved reaction!) with a slope of $-E_a/R$.

There are some theoretical models (such as collision theory and transition state theory) which suggest the form of the Arrhenius model, but the model itself is purely empirical. A general feature, however, of the theoretical approaches is to interpret the activation energy as an energy barrier which a reaction must overcome in order to lead to a chemical reaction.

11.10: Collision Theory

Collision Theory was first introduced in the 1910s by Max Trautz (Trautz, 1916) and William Lewis (Lewis, 1918) to try to account for the magnitudes of rate constants in terms of the frequency of molecular collisions, the collisional energy, and the relative orientations of the molecules involved in the collision.

The rate of a reaction, according to collision theory, can be expressed as

$$\text{rate} = Z_{ab} F \tag{11.10.1}$$

where Z_{AB} is the frequency of collisions between the molecules A and B involved in the reaction, and F is the fraction of those collisions that will lead to a reaction. The factor F has **two** important contributors, the energy of the collision and the orientation of the molecules when they collide. The first term, Z_{AB}, can be taken from the kinetic molecular theory discussed in Chapter 2.

$$Z_{AB} = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} \sigma_{AB}[A][B] \tag{11.10.2}$$

Where the first term is the average relative velocity in which μ is the reduced mass of the A-B collisional system, σ_{AB} is the collisional cross section, and $[A]$ and $[B]$ are the concentrations of A and B.

The factor F depends on the activation energy. Assuming a Boltzmann (or Boltzmann-like) distribution of energies, the fraction of molecular collisions that will have enough energy to overcome the activation barrier is given by

$$F = e^{-E_a/RT} \tag{11.10.3}$$

Combining Equations 11.10.2and 11.10.3, the rate of the reaction (Equation 11.10.1) is predicted by

$$\text{rate} = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} \sigma_{AB} e^{-E_a/RT}[A][B]$$

So if the rate law can be expressed as a second order rate law

$$\text{rate} = k[A][B]$$

it is clear that the rate constant k is given by

$$k = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} \sigma_{AB} e^{-E_a/RT}$$

By comparison, the theory predicts the form of the **Arrhenius prefactor** to be

$$A = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} \sigma_{AB}$$

It should be noted that collision theory appears to apply only to **bimolecular reactions**, since it takes two molecules to collide. But there are many reactions that have first order rate laws, but are initiated by bimolecular steps in the mechanisms. (Reaction mechanisms will form a large part of the discussion in Chapter 12.) Consider as an example, the decomposition of N_2O_5, which follows the reaction

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

Under a certain set of conditions, the following concentrations are observed as a function of time.

time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
0	0.0260	0.0000	0.0000
100	0.0219	0.0081	0.0016
200	0.0185	0.0150	0.0030
300	0.0156	0.0207	0.0041

time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
400	0.0132	0.0256	0.0051
500	0.0111	0.0297	0.0059
600	0.0094	0.0332	0.0066
700	0.0079	0.0361	0.0072

Graphically, these data look as follows:

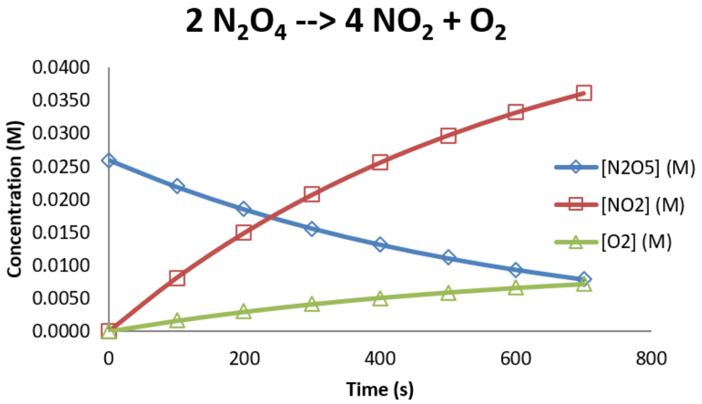
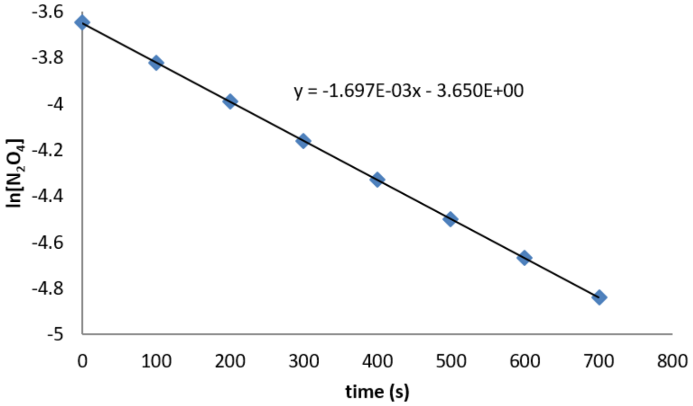


Figure 10.11.1: Concentration kinetics of the thermal decomposition reaction of N_2O_5.

The data for N_2O_5 can be analyzed empirically to show that the reaction is first order in N_2O_5, with a rate constant of 1.697 x 10^{-3} s^{-1}. (The graph is shown below.) So the rate law for the reaction is

$$\text{rate} = 1.697 \times 10^{-3} s^{-1} [N_2O_5]$$

So how can collision theory be used to understand the rate constant? As it turns out, the mechanism for the reaction involves a bimolecular initiation step.



The mechanism for the reaction has a bimolecular initiation step

$$N_2O_5 + M \rightleftharpoons N_2O_5^* + M$$

where $N_2O_5^*$ is an energetically activated form of N_2O_5 which can either relax to reform N_2O_5 or decompose to form the products of the reaction. Because the initiation step is bimolecular, collision theory *can* be used to understand the rate law, but because the product of the unimolecular step undergoes slow conversion to products unimolecularly, the overall rate is observed to be first order in N_2O_5. The analysis of reaction mechanisms, and reconciliation with observed rate laws, form the subjects of Chapter 12.

11.11: Transition State Theory

Transition state theory was proposed in 1935 by Henry Erying, and further developed by Merrideth G. Evans and Michael Polanyi (Laidler & King, 1983), as another means of accounting for chemical reaction rates. It is based on the idea that a molecular collision that leads to reaction must pass through an intermediate state known as the transition state. For example, the reaction

$$A + BC \rightarrow AB + C$$

would have an intermediate (ABC) where the $B-C$ bond is partially broken, and the $A-B$ bond is partially formed.

$$A + B - C \rightarrow (A-B-C)^{\ddagger} \rightarrow A-B+C$$

So the reaction is mediated by the formation of an activated complex (denoted with the double-dagger symbol $\ddagger$) and the decomposition of that complex into the reaction products. Using this theory, the rate of reaction can be expressed as the product of two factors

$$\text{rate} = (\text{transition state concentration}) \times (\text{decomposition frequency})$$

If the formation of the activated complex is considered to reach an equilibrium,

$$K^{\ddagger} = \frac{[ABC]^{\ddagger}}{[A][BC]}$$

So the concentration of the transition state complex can be expressed by

$$[ABC]^{\ddagger} = K^{\ddagger}[A][BC]$$

Using the relationship from Chapter 9 for the equilibrium constant, $K^{\ddagger}$ can be expressed in terms of the free energy of formation of the complex (\(\Delta G^‡\))

$$K^{\ddagger} = e^{-\Delta G^{\ddagger}/RT}$$

And so the reaction rate is given by

$$\text{rate} = (\text{frequency})[A][BC]e^{-\Delta G^{\ddagger}/RT}$$

and the remaining task is to derive an expression for the frequency factor. If the frequency is taken to be equal to the vibrational frequency for the vibration of the bond being broken in the activated complex in order to form the reaction products, it can be expressed in terms of the energy of the oscillation of the bond as the complex vibrates.

$$E = h\nu = k_B T$$

or

$$\nu = \frac{k_B T}{h}$$

The reaction rate is then predicted to be

$$\text{rate} = \frac{k_B T}{h}[A][BC]e^{-\Delta G^{\ddagger}/RT}$$

And the rate constant is thus given by

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT}$$

An alternative description gives the transition state formation equilibrium constant in terms of the partition functions describing the reactants and the transition state:

$$K^{\ddagger} = \frac{Q^{\ddagger}}{Q_A^{\ddagger} Q_{BC}^{\ddagger}} e^{-\Delta G^{\ddagger}/RT}$$

where Q_i is the **partition function** describing the ith species. If the partition function of the transition state is expressed as a product of the partition function excluding and contribution from the vibration leading to the bond cleavage that forms the products and the partition function of that specific vibrational mode

$$Q^{\ddagger} = Q^{\ddagger'} q_v^{\ddagger}$$

In this case, $q_v^{\ddagger}$ can be expressed by

$$q_v^{\ddagger} = \frac{1}{1 - e^{-h\nu^{\ddagger}/RT}} \approx \frac{k_B T}{h\nu^{\ddagger}}$$

So the equilibrium constant can be expressed

$$K^{\ddagger} = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_A^{\ddagger} Q_{BC}^{\ddagger}} e^{-\Delta G^{\ddagger}/RT}$$

And so the rate constant, which is the product of $n^{\ddagger}$ and $K^{\ddagger}$, is given by

$$k = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_A^{\ddagger} Q_{BC}^{\ddagger}} e^{-\Delta G^{\ddagger}/RT}$$

which looks very much like the Arrhenius equation proposed quite a few years earlier! Thus, if one understands the vibrational dynamics of the activated complex, and can calculate the partition functions describing the reactants and the transition state, one can, at least in theory, predict the rate constant for the reaction. In the next chapter, we will take a look at how kinetics studies can shed some light on chemical reaction mechanisms.

11.E: Chemical Kinetics I (Exercises)

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11.S: Chemical Kinetics I (Summary)

The results of the integration of these simple rate laws can be summarized in the following table.

Order	Elementary Reaction	Integrated rate law	Linear plot
0	-	$[A]=[A]_o-kt$	$[A]$ vs. t
1	$A\rightarrow P$	$\ln[A]=\ln[A]_o-kt$ $[[A]=[A]_o e^{-kt}$	$\ln[A]$ vs. t
2	$A+A\rightarrow P$	$\frac{1}{[A]}=\frac{1}{[A]_o}+kt$	$\frac{1}{[A]}$ vs. t
	$A+B\rightarrow P$	$\frac{1}{[B]_0-[A]_0}\ln\left(\frac{[B][A]_o}{[A][B]_o}\right)=kt$	$\ln\left(\frac{[B]}{[A]}\right)$ vs. t

---

CHAPTER OVERVIEW

12: Chemical Kinetics II

In the previous chapter, we discussed the rates of chemical reactions. In this chapter, we will expand on the concepts of chemical reaction rates by exploring what the rate law implies about the mechanistic pathways that reactions actually follow to proceed from reactants to products. Typically, one determines a rate law that describes a chemical reaction, and then suggests a mechanism that can be (or might not be!) consistent with the observed kinetics. This chapter will be concerned with reconciling reaction mechanisms with predicted rate laws.

12.1: Reaction Mechanisms

A **reaction mechanism** is a set of **elementary reactions** steps, that when taken in aggregate define a chemical pathway that connects reactants to products. An elementary reaction is one that proceeds by a single process, such a molecular (or atomic) decomposition or a molecular collision. Typically, elementary reactions only come in **unimolecular**

$$A \rightarrow products$$

and **bimolecular**

$$A + B \rightarrow products$$

form. Occasionally, an elementary step that is **termolecular**

$$A + B + C \rightarrow products$$

(involved the simultaneous collision of three atoms or molecules) but it is generally a pair of bimolecular steps acting in rapid succession, the first forming an activated complex, and the second stabilizing that complex chemically or physically.

$$A + B \rightarrow AB^*$$

$$AB^* + C \rightarrow AB + C^*$$

The wonderful property of elementary reactions is that the **molecularity** defines the order of the rate law for the reaction step.

The Requirements of a Reaction Mechanism

A valid reaction mechanism must satisfy three important criteria:

1. The sum of the steps must yield the overall stoichiometry of the reaction.
2. The mechanism must be consistent with the observed kinetics for the overall reaction.
3. The mechanism must account for the possibility of any observed side products formed in the reaction.

Example 12.1.1:

For the reaction

$$A + B \rightarrow C$$

is the following proposed mechanism valid?

$$A + A \xrightarrow{k_1} A_2$$

$$A_2 + B \xrightarrow{k_1} C + A$$

Solution

Adding both proposed reactions gives

$$\cancel{2}A + \cancel{A_2} + B \rightarrow \cancel{A_2} + C + \cancel{A}$$

Canceling those species that appear on both sides of the arrow leaves

$$A + B \rightarrow C$$

which is the reaction, so the mechanism is at least stoichiometrically valid. However, it would still have to be consistent with the observed kinetics for the reaction and account for any side-products that are observed.

12.2: Concentration Profiles for Some Simple Mechanisms

To illustrate how mechanisms may affect the concentration profile for a reaction, we can examine some simple mechanisms

$A \rightarrow B$

In this type of reaction, one substance is simply converting into another. An example of this type of reaction might be the isomerization of methylisocyanide to form acetonitrile (methylcyanide) (Redmon, Purvis, & Bartlett, 1978). If the reaction mechanism consists of a single unimolecular step, which is characterized by the rate constant k_1:

$$A \xrightarrow{k_1} B$$

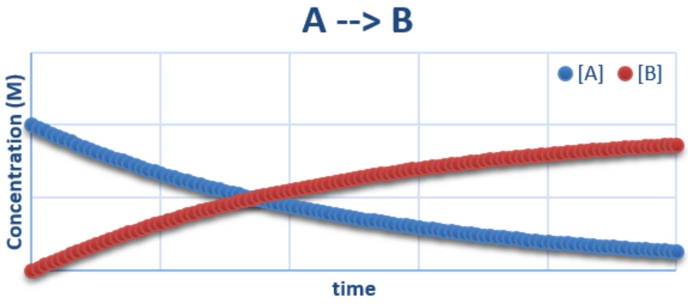
then rate of change of the concentrations of A and B may be written

$$\frac{d[A]}{dt} = -k_1[A]$$

and

$$\frac{d[B]}{dt} = +k_1[A]$$

A plot the concentrations as a function of time would look as follows:



It can be easily seen that the concentration of the reactant (A) decreases as time moves forward, and that of the product (B) increases. This will continue until reactant A is depleted.

$A \rightleftharpoons B$

When the system can establish equilibrium, the rate of change of the concentration of A and B will depend on both the forward and reverse reactions. If k_1 is the rate constant that characterizes the forward reaction

$$A \xrightarrow{k_1} B$$

and k_{-1} that which characterizes the reverse

$$B \xrightarrow{k_{-1}} A$$

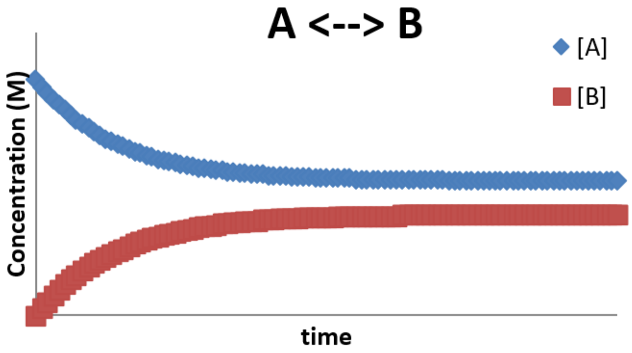
the the rate of change on concentrations of A and B can be expressed

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

and

$$\frac{d[B]}{dt} = +k_1[A] - k_{-1}[B]$$

The concentration profile for this situation looks as follows:



This profile is characterized by the fact that after a certain amount of time, the system achieves equilibrium and the concentrations stop changing (even though the forward and reverse reactions are still taking place. This is the nature of a **dynamic equilibrium** about which we speak off of the time in chemistry. The final concentrations of [A] and [B] once equilibrium is established will depend on the ratio of k_1 and k_-

Since the rate of formation of A (from the reverse step) is equal to the rate of consumption of A (from the forward step, the overall rate of change of the concentration of A is zero once equilibrium has been established. So it should be clear that

$$k_1[A] = k_{-1}[B]$$

or

$$\frac{k_1}{k_{-1}} = \frac{[B]}{[A]}$$

and the ratio o fk_1 to k_{-1} gives the value of the equilibrium constant!

$A + C \rightarrow B + C$

Some reactions require a **catalyst** to mediate the conversion of reactants in to products. The definition of a catalyst is a species that must be added (it is not formed as an intermediate) shows up in the mechanism (usually in a very early step) and this ends up as part of the rate law, but is reformed later on so that it does not appear in the overall stoichiometry. If the reaction

$$A \rightarrow B$$

is aided by a catalyst C, then one possible (single-step) reaction mechanism might be

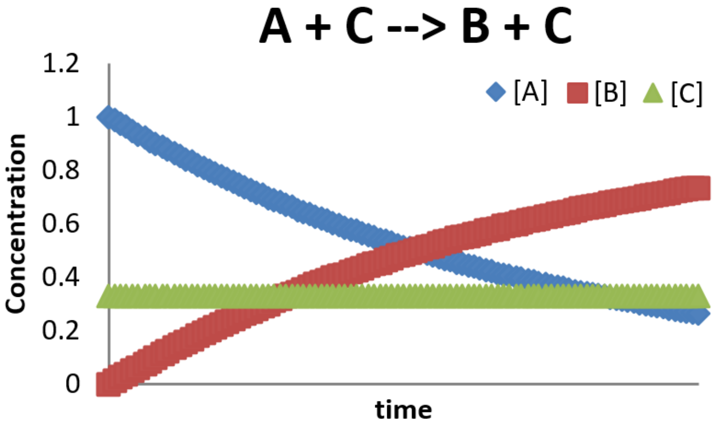
$$A + C \rightarrow B + C$$

In this case, C is acting as a catalyst to the reaction. The rate of change of the concentrations can be found by

$$\frac{[A]}{dt} = -k[A][C]$$

$$\frac{[B]}{dt} = k[A][C]$$

$$\frac{[C]}{dt} = -k[A][C] + k[A][C] = 0$$



This is a very simplified picture of a catalyzed reaction. Generally a catalyzed reaction will require at least two steps:

$$A + C \rightarrow AC$$

$$AC \rightarrow B + C$$

Later, we will see how the steady-state approximation actually predicts the above depicted concentration profile for the two-step mechanism when AC is a short-lived species that can be treated as having a constant and small concentration.

$A \rightarrow B \rightarrow C$

Another important (and very common) mechanistic feature is the formation of an intermediate. This is a species that is formed in at least one of the mechanism step, but does not appear in the overall stoichiometry for the reaction. This is different from a catalyst which must be added to speed the reaction. A simple example of a reaction mechanism involving the formation of a catalyst is

$$A \xrightarrow{k_1} B$$

$$B \xrightarrow{k_2} C$$

In this case, C cannot form until an appreciable concentration of the intermediate B has been created by the first step of the mechanism.

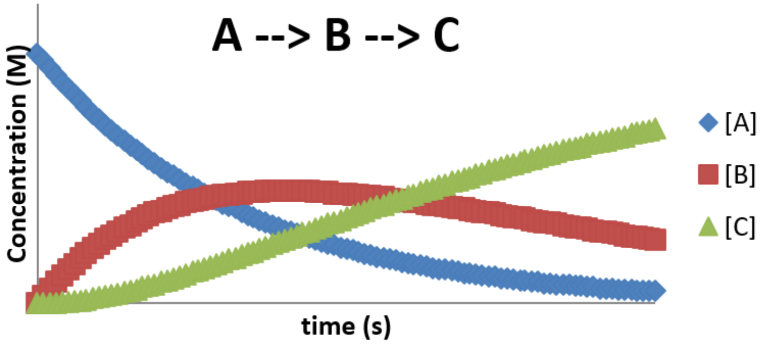
The rate of change of the concentrations of A, B, and C can be expressed

$$\frac{[A]}{dt} = -k_1[A]$$

$$\frac{[B]}{dt} = k_1[A] - k_2[B]$$

$$\frac{[C]}{dt} = k_2[B]$$

The concentration profile is then shown below. Notice the delay in the formation of C.



$A \rightleftharpoons B \rightarrow C$

In many cases, the formation of an intermediate involves a reversible step. This step is sometimes referred to as a **pre-equilibrium** step since it oftentimes will establish a near equilibrium while the reaction progresses. The result of combining a pre-equilibrium with an intermediate produces a profile that shows features of both of the simpler mechanisms. An example of such a mechanism is

$$A \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} B$$

$$B \xrightarrow{k_2} C$$

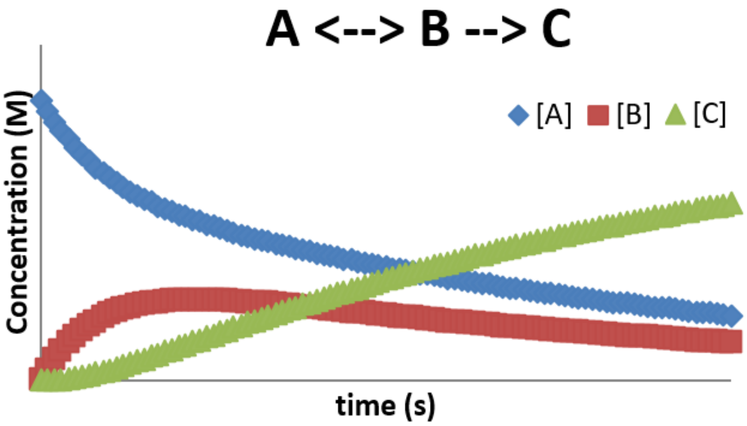
In this case, the rate of change for the concentrations of A, B, and C can be expressed by

$$\frac{[A]}{dt} = -k_1[A] + -k_{-1}[B]$$

$$\frac{[B]}{dt} = k_1[A] - k_{-1}[B] - k_2[B]$$

$$\frac{[C]}{dt} = k_2[B]$$

The concentration profile for this mechanism is shown below. Again, notice the delay in the production of the product C, due to the requirement that the concentration of B be sufficiently high to allow the second step to occur with an appreciable rate.



$A \rightarrow B$ and $A \rightarrow C$

There are many cases where a reactant can follow pathways to different products (or sometimes even the same products!), and those pathways compete with one another. An example is the following simple mechanism:

$$A \xrightarrow{k_{-1}} B$$

$$A \xrightarrow{k_2} C$$

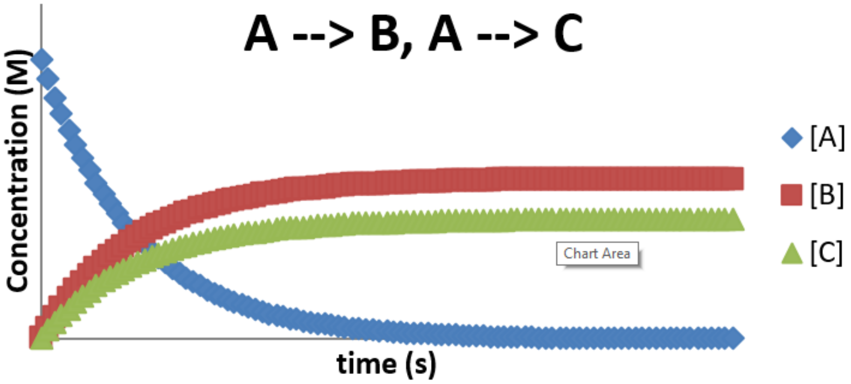
In this case, the rate of change on concentrations can be expressed as

$$\frac{[A]}{dt} = -k_1[A] + -k_2[A]$$

$$\frac{[B]}{dt} = +k_1[A]$$

$$\frac{[C]}{dt} = +k_2[A]$$

Overall, the profile looks like two first order decompositions occurring at the same time, with the final concentration of the product formed with the larger rate constant being favored.



One of the goals of studying chemical kinetics is to understand how to alter reaction condition to favor the production of desirable reaction products. This can be accomplished by a number of means, such as alteration of concentrations, temperature, addition of catalysts, etc. Understanding the basics will (hopefully) lead to a better understanding of how concentration profiles can be altered by changing conditions.

12.3: The Connection between Reaction Mechanisms and Reaction Rate Laws

The great value of chemical kinetics is that it can give us insights into the actual reaction pathways (mechanisms) that reactants take to form the products of reactions. Analyzing a reaction mechanism to determine the type of rate law that is consistent (or not consistent) with the specific mechanism can give us significant insight. For example, the reaction

$$A + B \rightarrow C$$

might be proposed to follow one of two mechanistic pathways:

$$\underbrace{A + A \xrightarrow{k_1} A_2}_{\text{step 1}}$$

$$\underbrace{A_2 + B \xrightarrow{k_2} C}_{\text{step 2}}$$

or

$$\underbrace{A \xrightarrow{k_1} A^*}_{\text{step 1}}$$

$$\underbrace{A^* + B \xrightarrow{k_2} C}_{\text{step 2}}$$

The first rate law will predict that the reaction should be second order in A, whereas the second mechanism predicts that it should be first order in A (in the limit that the steady state approximation, discussed in the following sections, can be applied to A_2 and A^*). Based on the observed rate law being first or second order in A, one can rule out one of the rate laws. Unfortunately, this kind of analysis cannot confirm a specific mechanism. Other evidence is needed to draw such conclusions, such as the spectroscopic observation of a particular reaction intermediate that can only be formed by a specific mechanism.

In order analyze mechanisms and predict rate laws, we need to build a toolbox of methods and techniques that are useful in certain limits. The next few sections will discuss this kind of analysis, specifically focusing on

- the **Rate Determining Step** approximation,
- the **Steady State** approximation, and
- the **Equilibrium** approximation.

Each type of approximation is important in certain limits, and they are oftentimes used in conjunction with one another to predict the final forms of rate laws.

12.4: The Rate Determining Step Approximation

The **rate determining step** approximation is one of the simplest approximations one can make to analyze a proposed mechanism to deduce the rate law it predicts. Simply stated, the rate determining step approximation says that a mechanism can proceed no faster than its slowest step. So, for example, if the reaction

$$A + B \rightarrow C$$

is proposed to follow the mechanism

$$\underbrace{A + A \xrightarrow{k_1} A_2}_{\text{slow}}$$

$$\underbrace{A_2 \xrightarrow{k_2} C + A}_{\text{fast}}$$

the rate determining step approximation suggests that the rate (expressed in terms of the appearance of product C) should be determined by the slow initial step, and so the rate law will be

$$\frac{[C]}{dt} = k_1[A]^2$$

matching the order of the rate law to the molecularity of the slow step. Conversely, if the reaction mechanism is proposed as

$$\underbrace{A \xrightarrow{k_1} A^*}_{\text{slow}}$$

$$\underbrace{A^* + B \xrightarrow{k_2} C}_{\text{fast}}$$

the rate determining step approximation suggests that the rate of the reaction should be

$$\frac{[C]}{dt} = k_1[A]$$

again, with the order of the rate law matching the molecularity of the rate determining step.

12.5: The Steady-State Approximation

One of the most commonly used and most attractive approximations is the **steady state approximation**. This approximation can be applied to the rate of change of concentration of a highly reactive (short lived) intermediate that holds a constant value over a long period of time. The advantage here is that for such an intermediate (I),

$$\frac{d[I]}{dt} = 0$$

So long as one can write an expression for the rate of change of the concentration of the intermediate I, the steady state approximation allows one to solve for its constant concentration. For example, if the reaction

$$A + B \rightarrow C \tag{12.5.1}$$

is proposed to follow the mechanism

$$A + A \xrightarrow{k_1} A_2 \tag{12.5.2}$$

$$A_2 + B \xrightarrow{k_2} C + A \tag{12.5.3}$$

The time-rate of change of the concentration of the intermediate A_2 can be written as

$$\frac{d[A_2]}{dt} = k_1[A]^2 - k_2[A_2][B]$$

In the limit that the steady state approximation can be applied to A_2

$$\frac{d[A_2]}{dt} = k_1[A]^2 - k_2[A_2][B] \approx 0$$

or

$$[A_2] \approx \frac{k_1[A]^2}{k_2[B]}$$

So if the rate of the overall reaction is expressed as the rate of formation of the product C,

$$\frac{d[C]}{dt} = k_2[A_2][B]$$

the above expression for $[A_2]$ can be substituted

$$\frac{d[C]}{dt} = k_2\left(\frac{k_1[A]^2}{k_2[B]}\right)[B]$$

of

$$\frac{d[C]}{dt} = k_1[A]^2$$

and the reaction is predicted to be second order in $[A]$.

Alternatively, if the mechanism for Equation 12.5.1 is proposed to be

$$A \xrightarrow{k_1} A^* \tag{12.5.4}$$

$$A^* + B \xrightarrow{k_2} C \tag{12.5.5}$$

then the rate of change of the concentration of A^* is

$$\frac{[A^*]}{dt} = k_1[A] - k_2[A^*][B]$$

And if the steady state approximation holds, then

$$[A^*] \approx \frac{k_1[A]}{k_2[B]}$$

So the rate of production of C is

$$\frac{d[C]}{dt} = k_2[A^*][B] \tag{12.5.6}$$

$$= \cancel{k_2}\left(\frac{k_1[A]}{\cancel{k_2}\,\cancel{[B]}}\right)\cancel{[B]} \tag{12.5.7}$$

or

$$\frac{d[C]}{dt} = k_1[A]$$

and the rate law is predicted to be first order in A. In this manner, the plausibility of either of the two reaction mechanisms is easily deduced by comparing the predicted rate law to that which is observed. If the prediction cannot be reconciled with observation, then the scientific method eliminates that mechanism from consideration.

12.6: The Equilibrium Approximation

In many cases, the formation of a reactive intermediate (or even a longer lived intermediate) involves a reversible step. This is the case if the intermediate can decompose to reform reactants with a significant probability as well as moving on to form products. In many cases, this will lead to a pre-equilibrium condition in which the **equilibrium approximation** can be applied. An example of a reaction mechanism of this sort is

$$A + B \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} AB$$

$$AB \xrightarrow{k_2} C$$

Given this mechanism, the application of the steady state approximation is cumbersome. However, if the initial step is assumed to achieve equilibrium, an expression can be found for $[AB]$. In order to derive this expression, one assumes that the rate of the forward reaction is equal to the rate of the reverse reaction for the initial step in the mechanism.

$$k_1[A][B] = k_{-1}[AB]$$

or

$$\frac{k_1[A][B]}{k_{-1}} = [AB]$$

This expression can be substituted into an expression for the rate of formation of the product C:

$$\frac{d[C]}{dt} = k_2[AB]$$

or

$$\frac{d[C]}{dt} = \frac{k_2 k_1}{k_{-1}}[A][B]$$

Which predicts a reaction rate law that is first order in A, first order in B, and second order overall.

✓ Example 12.6.1:

Given the following mechanism, apply the equilibrium approximation to the first step to predict the rate law suggested by the mechanism.

$$A + A \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} A_2$$

$$A_2 + B \xrightarrow{k_2} C + A$$

Solution

If the equilibrium approximation is valid for the first step,

$$k_1[A]^2 = k_{-1}[A_2]$$

or

$$\frac{k_1[A]^2}{k_{-1}} \approx [A_2]$$

Plugging this into the rate equation for the second step

$$\frac{d[C]}{dt} = k_2[A_2][B]$$

yields

$$\frac{d[C]}{dt} = \frac{k_2 k_1}{k_{-1}}[A]^2[B]$$

Thus, the rate law has the form

$$\text{rate} = k'[A]^2[B]$$

which is second order in A, first order in B and third order over all, and in which the effective rate constant (k' is

$$k' = \frac{k_2 k_1}{k_{-1}}.$$

Sometimes, the equilibrium approximation can suggest rate laws that have negative orders with respect to certain species. For example, consider the following reaction

$$A + 2B \rightarrow 2C$$

A proposed mechanism for which might be

$$A + B \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} I + C$$

$$I + B \xrightarrow{k_2} C$$

in which I is an intermediate. Applying the equilibrium approximation to the first step yields

$$k_1[A][B] = k_{-1}[I][C]$$

or

$$\frac{k_1[A][B]}{k_{-1}[C]} \approx [I]$$

Substituting this into an expression for the rate of formation of C, one sees

$$\frac{d[C]}{dt} = k_2[I][B]$$

or

$$\frac{d[C]}{dt} = \frac{k_1[A][B]}{k_{-1}[C]}[B] = \frac{k_2 k_1[A][B]}{k_{-1}[C]}$$

The rate law is then of the form

$$\text{rate} = k\frac{[A][B]^2}{[C]}$$

which is first order in A, second order in B, negative one order in C, and second order overall. Also,

$$k' = \frac{k_2 k_1}{k_{-1}}.$$

In this case, the negative order in C means that a buildup of compound C will cause the reaction to slow. These sort of rate laws are not uncommon for reactions with a reversible initial step that forms some of the eventual reaction product.

12.7: The Lindemann Mechanism

The **Lindemann mechanism** (Lindemann, Arrhenius, Langmuir, Dhar, Perrin, & Lewis, 1922) is a useful one to demonstrate some of the techniques we use for relating chemical mechanisms to rate laws. In this mechanism, a reactant is collisionally activated to a highly energetic form that can then go on to react to form products.

$$A + A \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} A^*$$

$$A^* \xrightarrow{k_2} P$$

If the steady state approximation is applied to the intermediate A^*

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] \approx 0$$

an expression can be derived for $[A^*]$.

$$A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2}$$

Substituting this into an expression for the rate of the production of the product P

$$\frac{d[P]}{dt} = k_2[A^*]$$

yields

$$\frac{d[P]}{dt} = \frac{k_2 k_1[A]^2}{k_{-1}[A] + k_2}$$

In the limit that $k_{-1}[A] \ll k_2$, the rate law becomes first order in $[A]$ since $k_{-1}[A] + k_2 \approx k_{-1}[A]$.

$$\frac{d[P]}{dt} = \frac{k_2 k_1}{k_{-1}}[A]$$

This will happen if the second step is very slow (and is the rate determining step), such that the reverse of the first step "wins" in the competition for [A*]. However, in the other limit, that $k_2 \gg k_{-1}[A]$, the reaction becomes second order in $[A]$ since $k_{-1}[A] + k_2 \approx k_2$.

$$\frac{d[P]}{dt} = k_1[A]^2$$

which is consistent with the forward reaction of the first step being the rate determining step, since A^* is removed from the reaction (through the formation of products) very quickly as soon as it is formed.

Third-body Collisions

Sometimes, the **third-body collision** is provided by an inert species M, perhaps by filling the reaction chamber with a heavy non-reactive species, such as Ar. In this case, the mechanism becomes

$$A + M \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} A^* + M$$

$$A^* \xrightarrow{k_2} P$$

And in the limit that $[A^*]$ can be treated using the steady state approximation, the rate of production of the product becomes

$$\frac{d[P]}{dt} = \frac{k_2 k_1[M]}{k_{-1}[M] + k_2}$$

And if the concentration of the third body collider is constant, it is convenient to define an **effective rate constant**, k_{uni} .

$$k_{uni} = \frac{k_2 k_1 [M]}{k_{-1}[M] + k_2}$$

The utility is that important information about the individual step rate constants can be extracted by plotting $1/k_{uni}$ as a function of $1/[M]$.

$$\frac{1}{k_{uni}} = \frac{k_{-1}}{k_2 k_1} + k_2 \left(\frac{1}{[M]} \right)$$

The plot should yield a straight line, the slope of which gives the value of k_2, and the intercept gives $(k_{-1}/k_2 k_1)$.

12.8: The Michaelis-Menten Mechanism

The **Michaelis-Menten** mechanism (Michaelis & Menten, 1913) is one which many enzyme mitigated reactions follow. The basic mechanism involves an enzyme (E, a biological catalyst) and a substrate (S) which must connect to form an enzyme-substrate complex (ES) in order for the substrate to be degraded (or augmented) to form a product (P). The overall reaction is

$$S \rightarrow P$$

And the simple two-step mechanism is given by

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \tag{12.8.1}$$

$$ES \xrightarrow{k_2} P \tag{12.8.2}$$

Notice that the enzyme is necessary for the reaction to proceed, but is not part of the overall stoichiometry (as is the case for any catalyst!).

Equilibrium Approximation Derivation

Applying the equilibrium approximation to the first step

$$k_1[E][S] \approx k_{-1}[ES] \tag{12.8.3}$$

And using a mass conservation relationship on the enzyme (noting that the enzyme must be either in its bare form (E) or complexed with a substrate (ES)):

$$[E]_o = [E] + [ES]$$

or

$$[E] = [E]_o - [ES]$$

Substituting this into the equilibrium expression (Equation 12.8.3) yields

$$k_1([E]_o - [ES])[S] = k_{-1}[ES]$$

Solving this expression for $[ES]$ stepwise reveals

$$k_1[E]_o[S] - k_1[ES][S] = k_{-1}[ES]$$

$$k_1[E]_o[S] = k_{-1}[ES] + k_1[ES][S]$$

$$= (k_{-1} + k_1)[ES]$$

$$\frac{k_1[E]_o[S]}{k_1[S] + k_{-1}} = [ES]$$

Substituting this into the expression for the rate of production of the product P

$$\frac{d[P]}{dt} = k_2[ES] \tag{12.8.4}$$

yields

$$\frac{d[P]}{dt} = \frac{k_2 k_1[E]_o[S]}{k_1[S] + k_{-1}}$$

Multiplying the top and bottom of the expression on the right hand side by $1/\mathrm{k}_1$ gives the result

$$\frac{d[P]}{dt} = \frac{k_2[E]_o[S]}{[S] + \frac{k_1}{k_{-1}}}$$

The ratio of k$_{-1}$/k$_1$ is the equilibrium constant that describes the dissociation of the enzyme-substrate complex, K_d in Equation 12.8.1. Noting that $k_2[E]_0$ gives the maximum rate (V_{max}), and that $\frac{d[P]}{dt}$ is the observed reaction rate, the rate law takes the form

$$\text{rate} = \frac{V_{max}[S]}{K_d + [S]}$$

> This is because the maximum reaction rate is achieved when [ES] is low. As [ES] increases, the likelihood of the complex decomposing to reform reactants is higher, slowing the conversion. [ES] will be low if the concentration of the enzyme is much larger than that of the substrate, so there is never a shortage of enzyme available to form the complex with the substrate. However, if the substrate concentration is higher, the lack of available enzyme active sites will slow the reaction and cause it to become 0th order.

In the limit that the substrate concentration is large compared to K_d (i.e., $K_d + [S] \approx [S]$), the reaction ends up zeroth order in substrate.

$$\text{rate} = \frac{V_{max}[S]}{K_d + [S]} \approx \frac{V_{max}\ \cancel{[S]}}{\cancel{[S]}} = V_{max}$$

Hence, adding more substrate to the system under this limiting condition will have no effect on the observed rate. This is characteristic of a bottleneck in the mechanism, which would happen if there is a shortage of enzyme sites to which the substrate can attach.

In the other extreme, in which K_d is very large compared to the substrate concentration (i.e., $K_d + [S] \approx K_d$), the reaction become first order in substrate.

$$\text{rate} = \frac{V_{max}[S]}{K_d + [S]} \approx \frac{V_{max}[S]}{K_d} = \frac{V_{max}}{K_d}[S]$$

Steady-State Approximation Derivation

In an alternate derivation (Briggs & Haldane, 1925) using the steady state approximation applied to the enzyme-substrate complex

$$\frac{[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] \approx 0$$

Solving for $[ES]$ gives the result

$$ES] = \frac{k_1[E][S]}{k_{-1} + k_2}$$

or

$$[ES] = \frac{[E][S]}{K_m}$$

where

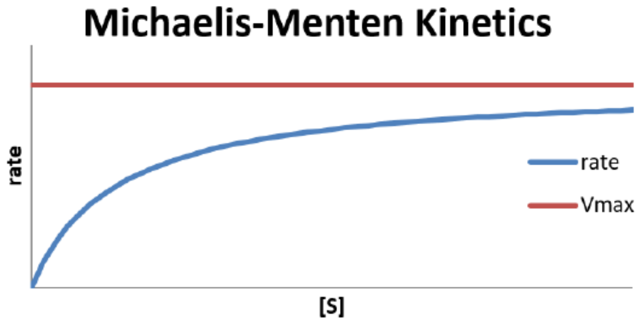
$$K_m = \frac{k_{-1} + K_2}{k_1}$$

K_M is the **Michaelis constant**, which is affected by a number of factors, including pH, temperature, and the nature of the substrate itself. Proceeding as before, though the conservation of mass relationship and substitution into the expression for rate (Equation 12.8.4) results in

$$\frac{d[P]}{dt} = \frac{V_{max}[S]}{K_m + [S]}$$

The advantage to this approach is that it accounts for the loss of ES complex due to the production of products as well as the decomposition to reform the reactants E and S. As before, in the limit that $[S] \gg K_M$, the reaction reaches its maximum rate (

V_{max}) and becomes independent of any concentrations. However in the limit that $[S] \ll K_M$, the reaction becomes 1st order in $[S]$.



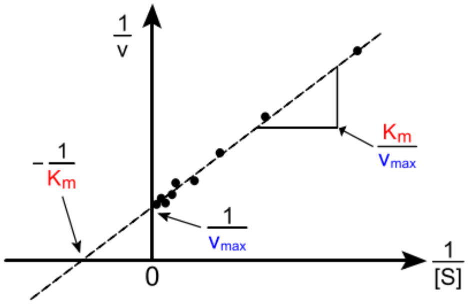
The Michalis constant and V_{max} parameters can be extracted in a number of ways. In the Lineweaver-Burk (Lineweaver & Burk, 1934) method, the reciprocal of the rate law is used to create a linear relationship.

$$\frac{1}{\text{rate}} = \frac{K_m + [S]}{V_{max}[S]}$$

or

$$\frac{1}{\text{rate}} = \frac{K_m}{V_{max}} \frac{1}{[S]} + \frac{1}{V_{max}}$$

So a plot of $1/rate$ as a function of $1/[S]$ results in a straight line, the slope of which is equal to K_M/V_{max} and the intercept is $1/V_{max}$. This is called a Lineweaver–Burk plot.



An example of a Lineweaver-Burk plot. (CC BY-SA 3.0; Diberri).

12.9: Chain Reactions

A large number of reactions proceed through a series of steps that can collectively be classified as a **chain reaction**. The reactions contain steps that can be classified as

- **initiation step** – a step that creates the intermediates from stable species
- **propagation step** – a step that consumes an intermediate, but creates a new one
- **termination step** – a step that consumes intermediates without creating new ones

These types of reactions are very common when the intermediates involved are radicals. An example, is the reaction

$$H_2 + Br_2 \rightarrow 2HBr$$

The observed rate law for this reaction is

$$\text{rate} = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]} \tag{12.9.1}$$

A proposed mechanism is

$$Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Br^{\cdot} \tag{12.9.2}$$

$$2Br^{\cdot} + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HBr + H^{\cdot} \tag{12.9.3}$$

$$H^{\cdot} + Br_2 \xrightarrow{k_3} HBr + Br^{\cdot} \tag{12.9.4}$$

Based on this mechanism, the rate of change of concentrations for the intermediates ($H^{\cdot}$ and $Br^{\cdot}$) can be written, and the steady state approximation applied.

$$\frac{d[H^{\cdot}]}{dt} = k_2[Br^{\cdot}][H_2] - k_{-2}[HBr][H^{\cdot}] - k_3[H^{\cdot}][Br_2] = 0$$

$$\frac{d[Br^{\cdot}]}{dt} = 2k_1[Br_2] - 2k_{-1}[Br^{\cdot}]^2 - k_2[Br^{\cdot}][H_2] + k_{-2}[HBr][H^{\cdot}] + k_3[H^{\cdot}][Br_2] = 0$$

Adding these two expressions cancels the terms involving k_2, k_{-2}, and k_3. The result is

$$2k_1[Br_2] - 2k_{-1}[Br^{\cdot}]^2 = 0$$

Solving for $Br^{\cdot}$

$$Br^{\cdot} = \sqrt{\frac{k_1[Br_2]}{k_{-1}}}$$

This can be substituted into an expression for the $H^{\cdot}$ that is generated by solving the steady state expression for $d[H^{\cdot}]/dt$.

$$[H^{\cdot}] = \frac{k_2[Br^{\cdot}][H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

so

$$[H^{\cdot}] = \frac{k_2\sqrt{\frac{k_1[Br_2]}{k_{-1}}}[H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

Now, armed with expressions for $H^{\cdot}$ and $Br^{\cdot}$, we can substitute them into an expression for the rate of production of the product HBr:

$$\frac{[HBr]}{dt} = k_2[Br^{\cdot}][H_2] + k_3[H^{\cdot}][Br_2] - k_{-2}[H^{\cdot}][HBr]$$

After substitution and simplification, the result is

$$\frac{[HBr]}{dt} = \frac{2k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{1/2}}{1 + \frac{k_{-1}}{k_3}\frac{[HBr]}{[Br_2]}}$$

Multiplying the top and bottom expressions on the right by $[Br_2]$ produces

$$\frac{[HBr]}{dt} = \frac{2k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{3/2}}{[Br_2] + \frac{k_{-1}}{k_3}[HBr]}$$

which matches the form of the rate law found experimentally (Equation 12.9.1)! In this case,

$$k = 2k_2\sqrt{\frac{k_1}{k_{-1}}}$$

and

$$k' = \frac{k_{-2}}{k_3}$$

12.10: Catalysis

There are many examples of reactions that involve catalysis. One that is of current importance to the chemistry of the environment is the catalytic decomposition of ozone (Fahey, 2006). The overall reaction

$$O_3 + O^{\cdot} \rightarrow 2O_2$$

can be catalyze by atomic chlorine by the following mechanism.

$$O_3 + Cl \xrightarrow{k_1} ClO + O_2$$

$$ClO + O \xrightarrow{k_1} Cl + O_2$$

The rate of change of the intermediate (ClO) concentration is given by

$$\frac{[ClO]}{dt} = k_1[O_3][Cl] - k_2[ClO][O]$$

Applying the steady state approximation to this relationship and solving for $[ClO]$ produces

$$ClO] = \frac{[O_3][Cl]}{k_2[O]} \tag{12.10.1}$$

The rate of production of O_2 (which is two times the rate of the reaction) is given by

$$\frac{d[O_2]}{dt} = k_2[O_3][Cl] + k_2[ClO][O]$$

Substituting the expression for $[ClO]$ (Equation 12.10.1) into the above expression yields

$$\begin{aligned} \frac{d[O_2]}{dt} &= k_2[O_3][Cl] + k_2\left(\frac{[O_3][Cl]}{k_2[O]}\right)[O] \\ &= k_1[O_3[Cl] + k_1[O_3][Cl] \\ &= 2k_1[O_3][Cl] \end{aligned}$$

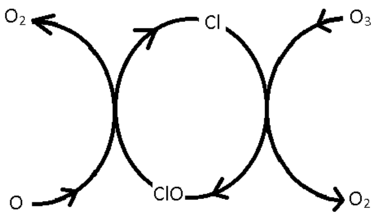
And so the rate of the reaction is predicted to be first order in $[O_3]$, first order in the catalyst $[Cl]$, and second order overall.

$$\text{rate} = k[O_3][Cl]$$

If the concentration of the catalyst is constant, the reaction kinetics will reduce to first order.

$$\text{rate} = k[O_3]$$

This catalytic cycle can be represented in the following diagram:



On the left, atomic oxygen picks up an oxygen atom from ClO to form O_2 and generate a Cl atom, which can then react with O_3 to form ClO and an O_2 molecule. The closed loop in the middle is characteristic of the catalytic cycle involving Cl and ClO. Further, since Cl acts as a catalyst, it can decompose many O_3 molecules without being degraded through side reactions.

The introduction of chlorine atoms into the upper atmosphere is a major environmental problem, leading to the annual thinning and eventual opening of the ozone layer over Antarctica. The source of chlorine is from the decomposition of chlorofluorocarbons which are sued as refrigerants and propellants due to their incredible stability near the Earth's surface. However, in the upper atmosphere, these compounds are subjected to ultraviolet radiation emitted by the sun and decompose to form the radicals responsible for the catalytic decomposition of ozone. The world community addressed this issue by drafting the **Montreal Protocol (Secretariat, 2015)**, which focused on the emission of ozone-destroying compounds. The result of this action has brought about evidence of the Antarctic ozone hole healing (K, 2015). This is one very good example science-guided political, industrial, and economic policies leading to positive changes for our environment.

12.11: Oscillating Reactions

In most cases, the conversion of reactants into products is a fairly smooth process, in that the concentrations of the reactants decrease in a regular manner, and those of the products increase in a similar regular manner. However, some reactions can show irregular behavior in this regard. One particularly peculiar (but interesting!) phenomenon is that of **oscillating reactions**, in which reactant concentrations can rise and fall as the reaction progresses. One way this can happen is when the products of the reaction (or one of the steps) catalyzes the reaction (or one of the steps). This process is called **autocatalysis**.

An example of an autocatalyzed mechanism is the **Lotka-Voltera mechanism**. This is a three-step mechanism defined as follows:

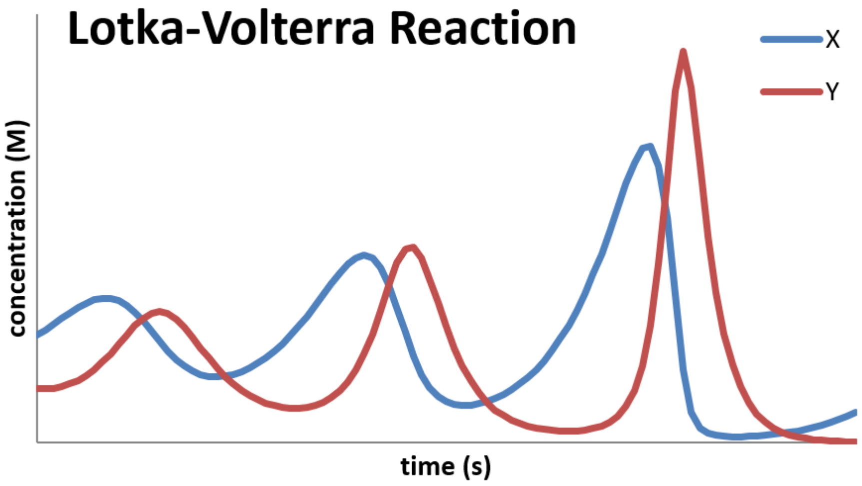
$$A + X \xrightarrow{k_1} X + X$$

$$X + Y \xrightarrow{k_2} Y + Y$$

$$Y \xrightarrow{k_3} B$$

In this reaction, the concentration of reactant A is held constant by continually adding it to the reaction mixture. The first step is **autocatalyzed**, so as it proceeds, it speeds up. However, an increase in the production of X by the first reaction increases the rate of the second reaction as well, which is also autocatalyzed. Finally, the removal of Y through the third reaction brings things to a halt, until the first reaction can again produce a build up of X to start the cycle over.

A plot of the concentration of X and Y as a function of time looks as follows:



This mechanism follows kinetics predicted by what is called the **predator-prey** relationship. In this case, X represents the “prey” and Y represents the “predator”. The population of the predator cannot build up unless there is a significant population of prey on which the predators can feed. Likewise, the population of predators decreases when the population of the prey falls. And finally, there is a lag, as the rise and decline of the prey population controls the rise and fall of the predator population. The equations have been studied extensively and have applications not just in chemical kinetics, but in biology, economics, and elsewhere. One wonders if the equations can be applied to help to understand politics!

12.E: Chemical Kinetics II (Exercises)

In preparation

12.S: Chemical Kinetics II (Summary)

Vocabulary and Concepts

- autocatalysis
- bimolecular
- catalyst
- chain reaction
- dynamic equilibrium
- effect rate constant
- elementary reaction
- equilibrium approximation
- equilibrium constant
- initiation step
- intermediate
- Lindemann mechanism
- Lotka-Voltera mechanism
- Michaelis constant
- Michaelis-Menten
- molecularity
- Montreal Protocol
- oscillating reaction
- predator-prey
- pre-equilibrium
- propagation step
- radical
- rate determining step
- reaction mechanism
- steady state approximation
- termination step
- termolecular
- third-body collision
- unimolecular

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Index

Glossary

Activity | An effective concentration used in non-ideal solutions and gases to account for deviations from ideal behavior.

Adiabatic Process | A thermodynamic process in which no heat is exchanged between a system and its surroundings.

Avogadro's Law | States that equal volumes of gases at the same temperature and pressure contain an equal number of molecules.

Born-Haber Cycle | A thermodynamic cycle used to calculate lattice energy in ionic solids.

Buffer | A solution that resists changes in pH when small amounts of acid or base are added.

Calorimetry | The measurement of heat flow in chemical reactions and physical changes.

Carnot Cycle | A theoretical thermodynamic cycle that describes the most efficient heat engine possible.

Chemical Potential | The change in a system's Gibbs energy with the addition of a mole of a substance, at constant temperature and pressure.

Clapeyron Equation | Describes the relationship between pressure, temperature, and phase equilibrium.

Colligative Properties | Properties of solutions that depend on solute particle number rather than type, such as boiling point elevation.

Degree of Dissociation | The fraction of a dissolved substance that separates into ions in solution.

Electrochemical Cell | A system that generates electrical energy from chemical reactions.

Enthalpy | The heat content of a system at constant pressure.

Entropy | A measure of disorder or randomness in a system.

Equation of State | A mathematical equation that describes the state of matter under given conditions, such as the ideal gas law.

Free Energy | A thermodynamic quantity used to predict whether a reaction is spontaneous at constant pressure and temperature.

Fugacity | A corrected pressure term used to describe real gas behavior.

Gibbs-Duhem Equation | Relates the chemical potentials of components in a mixture.

Graham's Law of Effusion | States that the rate of effusion of a gas is inversely proportional to the square root of its molar mass.

Half-Life | The time required for half of a reactant to be consumed in a reaction.

Helmholtz Energy | A thermodynamic function that measures the work potential of a system at constant volume and temperature.

Ideal Gas Law | An equation describing the state of an ideal gas: $PV=nRT$.

Joule-Thomson Effect | Describes the temperature change of a real gas when it is expanded or compressed without heat exchange.

Kinetic Molecular Theory | A model that explains gas behavior based on particle motion and collisions.

Lattice Energy | The energy required to separate an ionic solid into its gaseous ions.

Le Chatelier's Principle | States that a system at equilibrium will adjust to counteract applied changes.

Maxwell's Relations | A set of thermodynamic equations derived from the symmetry of second derivatives of thermodynamic potentials.

Michaelis-Menten Mechanism | A model describing enzyme-catalyzed reactions.

Non-Ideal Solution | A solution that deviates from Raoult's law due to intermolecular interactions.

Partial Molar Volume | The volume contribution of a component in a mixture.

Phase Diagram | A graphical representation of phase stability as a function of temperature and pressure.

Pressure Dependence of Gibbs Energy | Describes how Gibbs energy varies with pressure.

Raoult's Law | States that the vapor pressure of a solvent is proportional to its mole fraction in solution.

Reaction Mechanism | A step-by-step description of how a chemical reaction occurs.

Reaction Rate | The speed at which reactants are converted to products.

Solubility | The ability of a substance to dissolve in a solvent.

Standard Reduction Potential | A measure of the tendency of a chemical species to gain electrons.

Steady-State Approximation | Assumes that the concentration of reaction intermediates remains constant over time.

Temperature Dependence of Equilibrium Constant | Describes how equilibrium constants change with temperature.

Transition State Theory | A model describing the high-energy transition state of a reaction.

Van 't Hoff Equation | Relates temperature changes to equilibrium constant changes.

Volume Dependence of Helmholtz Energy | Explains how Helmholtz energy changes with volume variations.

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