Meredith College

Thermodynamics

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CHAPTER OVERVIEW

1: Fundamental 1 - Measurable Properties

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1.1: Non-Ideal Gas Behavior

Learning Objectives

- Describe the physical factors that lead to deviations from ideal gas behavior
- Explain how these factors are represented in the van der Waals equation
- Define compressibility (Z) and describe how its variation with pressure reflects non-ideal behavior
- Quantify non-ideal behavior by comparing computations of gas properties using the ideal gas law and the van der Waals equation

The ideal gas law, $PV = nRT$, can been applied to a variety of different types of problems, ranging from reaction stoichiometry and empirical and molecular formula problems to determining the density and molar mass of a gas. However, the behavior of a gas is often non-ideal, meaning that the observed relationships between its pressure, volume, and temperature are not accurately described by the gas laws. In this section, the reasons for these deviations from ideal gas behavior are considered.

One way in which the accuracy of PV = nRT can be judged is by comparing the actual volume of 1 mole of gas (its molar volume, $\bar{V}$) to the molar volume of an ideal gas at the same temperature and pressure. This ratio is called the compressibility factor (Z) with:

$$Z = \frac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left(\frac{P\bar{V}}{RT} \right)_{\text{measured}} \tag{1.1.1}$$

Ideal gas behavior is therefore indicated when this ratio is equal to 1, and any deviation from 1 is an indication of non-ideal behavior. Figure 1.1.1 shows plots of Z over a large pressure range for several common gases.
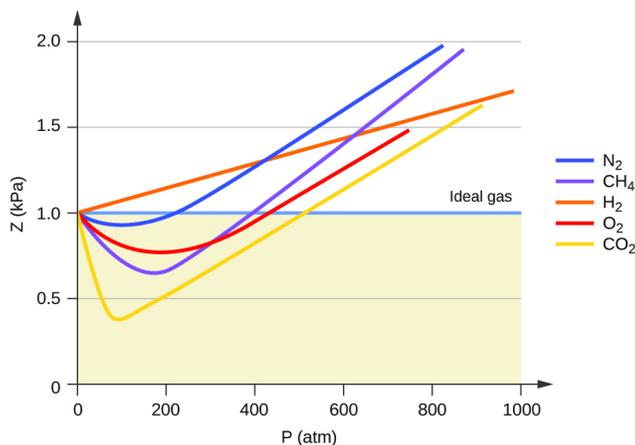
Figure 1.1.1: A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law.

As is apparent from Figure 1.1.1, the ideal gas law does not describe gas behavior well at relatively high pressures. To determine why this is, consider the differences between real gas properties and what is expected of a hypothetical ideal gas.

Particles of a hypothetical ideal gas have **no significant volume** and **do not attract or repel each other**. In general, real gases approximate this behavior at relatively low pressures and high temperatures. However, at high pressures, the molecules of a gas are crowded closer together, and the amount of empty space between the molecules is reduced. At these higher pressures, the volume of the gas molecules themselves becomes appreciable relative to the total volume occupied by the gas (Figure 1.1.2). The gas therefore becomes less compressible at these high pressures, and although its volume continues to decrease with increasing pressure, this decrease is not *proportional* as predicted by Boyle's law.
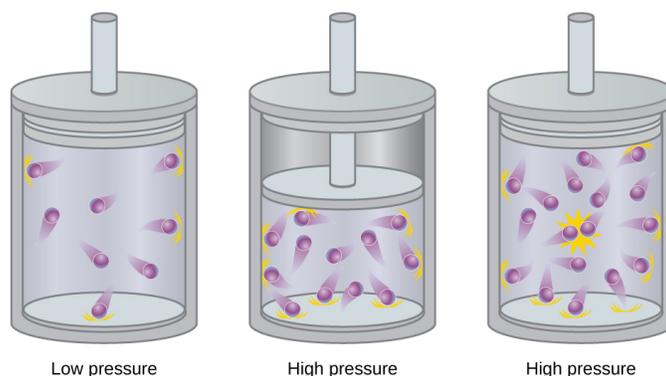
Figure 1.1.2: Raising the pressure of a gas increases the fraction of its volume that is occupied by the gas molecules and makes the gas less compressible.

At relatively low pressures, gas molecules have practically no attraction for one another because they are (on average) so far apart, and they behave almost like particles of an ideal gas. At higher pressures, however, the force of attraction is also no longer insignificant. This force pulls the molecules a little closer together, slightly decreasing the pressure (if the volume is constant) or decreasing the volume (at constant pressure) (Figure 1.1.3). This change is more pronounced at low temperatures because the molecules have lower KE relative to the attractive forces, and so they are less effective in overcoming these attractions after colliding with one another.
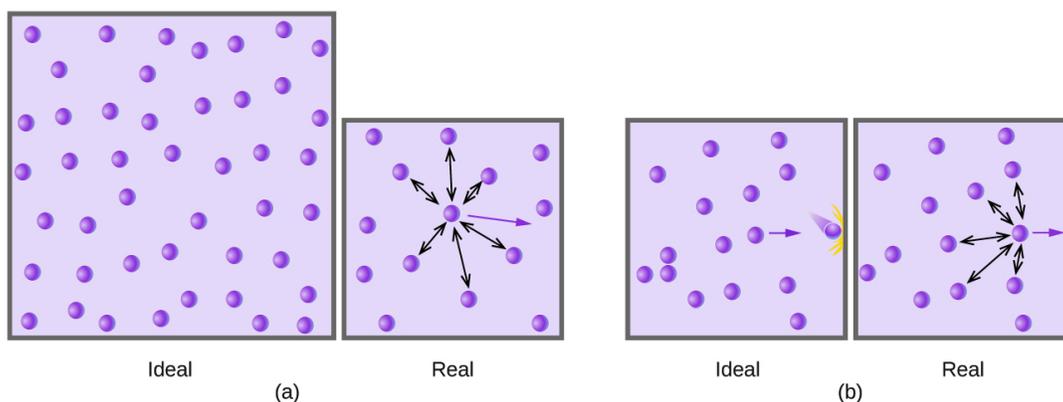
Figure 1.1.3: (a) Attractions between gas molecules serve to decrease the gas volume at constant pressure compared to an ideal gas whose molecules experience no attractive forces. (b) These attractive forces will decrease the force of collisions between the molecules and container walls, therefore reducing the pressure exerted compared to an ideal gas.

There are several different equations that better approximate gas behavior than does the ideal gas law. The first, and simplest, of these was developed by the Dutch scientist Johannes van der Waals in 1879. The van der Waals equation improves upon the ideal gas law by adding two terms: one to account for the volume of the gas molecules and another for the attractive forces between them.

$$PV = nRT \longrightarrow \left(P + \frac{an^2}{V^2} \right)(V - nb) = nRT$$

Correction for molecular attraction

Correction for volume of molecules

The constant a corresponds to the strength of the attraction between molecules of a particular gas, and the constant b corresponds to the size of the molecules of a particular gas. The "correction" to the pressure term in the ideal gas law is $\frac{n^2 a}{V^2}$, and the "correction" to the volume is nb. Note that when V is relatively large and n is relatively small, both of these correction terms become negligible, and the van der Waals equation reduces to the ideal gas law, $PV = nRT$. Such a condition corresponds to a gas in which a relatively low number of molecules is occupying a relatively large volume, that is, a gas at a relatively low pressure. Experimental values for the van der Waals constants of some common gases are given in Table 1.1.1.

Table 1.1.1: Values of van der Waals Constants for Some Common Gases

Gas	a (L^2 atm/mol^2)	b (L/mol)
N$_2$	1.39	0.0391
O$_2$	1.36	0.0318
CO$_2$	3.59	0.0427
H$_2$O	5.46	0.0305
He	0.0342	0.0237
CCl$_4$	20.4	0.1383

At low pressures, the correction for intermolecular attraction, *a*, is more important than the one for molecular volume, *b*. At high pressures and small volumes, the correction for the volume of the molecules becomes important because the molecules themselves are incompressible and constitute an appreciable fraction of the total volume. At some intermediate pressure, the two corrections have opposing influences and the gas appears to follow the relationship given by *PV = nRT* over a small range of pressures. This behavior is reflected by the "dips" in several of the compressibility curves shown in Figure 1.1.1. The attractive force between molecules initially makes the gas more compressible than an ideal gas, as pressure is raised (Z decreases with increasing *P*). At very high pressures, the gas becomes less compressible (Z increases with *P*), as the gas molecules begin to occupy an increasingly significant fraction of the total gas volume.

Strictly speaking, the ideal gas equation functions well when intermolecular attractions between gas molecules are negligible and the gas molecules themselves do not occupy an appreciable part of the whole volume. These criteria are satisfied under conditions of *low pressure and high temperature*. Under such conditions, the gas is said to behave ideally, and deviations from the gas laws are small enough that they may be disregarded—this is, however, very often not the case.

Example 1.1.1: Comparison of Ideal Gas Law and van der Waals Equation

A 4.25-L flask contains 3.46 mol CO$_2$ at 229 °C. Calculate the pressure of this sample of CO$_2$:

a. from the ideal gas law
b. from the van der Waals equation
c. Explain the reason(s) for the difference.

Solution

(a) From the ideal gas law:

$$P = \frac{nRT}{V} = \frac{3.46 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 502 \text{ K}}{4.25 \text{ L}} = 33.5 \text{ atm}$$

(b) From the van der Waals equation:

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

$$P = \frac{3.46 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1}\text{ K}^{-1} \times 502 \text{ K}}{(4.25 \text{ L} - 3.46 \text{ mol} \times 0.0427 \text{ L mol}^{-1})} - \frac{(3.46 \text{ mol})^2 \times 3.59 \text{ L}^2 \text{ atm mol}^2}{(4.25 \text{ L})^2}$$

This finally yields $P = 32.4$ atm.

(c) This is not very different from the value from the ideal gas law because the pressure is not very high and the temperature is not very low. The value is somewhat different because CO_2 molecules do have some volume and attractions between molecules, and the ideal gas law assumes they do not have volume or attractions.

Exercise 1.1.1

A 560-mL flask contains 21.3 g N_2 at 145 °C. Calculate the pressure of N_2:

  a. from the ideal gas law
  b. from the van der Waals equation
  c. Explain the reason(s) for the difference.

Answer a

    46.562 atm

Answer b

    46.594 atm

Answer c

    The van der Waals equation takes into account the volume of the gas molecules themselves as well as intermolecular attractions.

Contributors and Attributions

Summary

Gas molecules possess a finite volume and experience forces of attraction for one another. Consequently, gas behavior is not necessarily described well by the ideal gas law. Under conditions of low pressure and high temperature, these factors are negligible, the ideal gas equation is an accurate description of gas behavior, and the gas is said to exhibit ideal behavior. However, at lower temperatures and higher pressures, corrections for molecular volume and molecular attractions are required to account for finite molecular size and attractive forces. The van der Waals equation is a modified version of the ideal gas law that can be used to account for the non-ideal behavior of gases under these conditions.

Key Equations

- $Z = \dfrac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left(\dfrac{P \times \bar{V}}{R \times T}\right)_{\text{measured}}$
- $\left(P + \dfrac{n^2 a}{V^2}\right) \times (V - nb) = nRT$

Glossary

compressibility factor (Z)

    ratio of the experimentally measured molar volume for a gas to its molar volume as computed from the ideal gas equation

van der Waals equation

    modified version of the ideal gas equation containing additional terms to account for non-ideal gas behavior

Contributors and Attributions

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1.2: Virial Equations

It is often useful to fit accurate pressure-volume-temperature data to polynomial equations. The experimental data can be used to compute a quantity called the **compressibility factor**, Z, which is defined as the pressure–volume product for the real gas divided by the pressure–volume product for an ideal gas at the same temperature.

We have

$$(PV)_{ideal\ gas} = nRT$$

Letting P and V represent the pressure and volume of the real gas, and introducing the molar volume, $\overline{V} = V/n$, we have

$$Z = \frac{(PV)_{real\ gas}}{(PV)_{ideal\ gas}} = \frac{PV}{nRT} = \frac{P\overline{V}}{RT}$$

Since $Z = 1$ if the real gas behaves exactly like an ideal gas, experimental values of Z will tend toward unity under conditions in which the density of the real gas becomes low and its behavior approaches that of an ideal gas. At a given temperature, we can conveniently ensure that this condition is met by fitting the Z values to a polynomial in P or a polynomial in $\overline{V}^{-1}$. The coefficients are functions of temperature. If the data are fit to a polynomial in the pressure, the equation is

$$Z = 1 + B^*(T)P + C^*(T)P^2 + D^*(T)P^3 + \ldots$$

For a polynomial in $\overline{V}^{-1}$, the equation is

$$Z = 1 + \frac{B(T)}{\overline{V}} + \frac{C(T)}{\overline{V}^2} + \frac{D(T)}{\overline{V}^3} + \ldots$$

These empirical equations are called **virial equations**. As indicated, the parameters are functions of temperature. The values of $B^*(T)$, $C^*(T)$, $D^*(T)$, …, and $B(T)$, $C(T)$, $D(T)$,…, must be determined for each real gas at every temperature. (Note also that $B^*(T) \neq B(T)$, $C^*(T) \neq C(T)$, $D^*(T) \neq D(T)$, *etc*. However, it is true that $B^* = B/RT$.) Values for these parameters are tabulated in various compilations of physical data. In these tabulations, $B(T)$ and $C(T)$ are called the second virial coefficient and third virial coefficient, respectively.

2: Extension 1.1 - Kinetic Molecular Theory

2.1: Kinetic Molecular Theory

Learning Objectives

- To understand the significance of the kinetic molecular theory of gases.

The laws that describe the behavior of gases were well established long before anyone had developed a coherent model of the properties of gases. In this section, we introduce a theory that describes why gases behave the way they do. The theory we introduce can also be used to derive laws such as the ideal gas law from fundamental principles and the properties of individual particles.

A Molecular Description

The kinetic molecular theory of gases explains the laws that describe the behavior of gases. Developed during the mid-19th century by several physicists, including the Austrian Ludwig Boltzmann (1844–1906), the German Rudolf Clausius (1822–1888), and the Englishman James Clerk Maxwell (1831–1879), who is also known for his contributions to electricity and magnetism, this theory is based on the properties of individual particles as defined for an ideal gas and the fundamental concepts of physics. Thus the kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following four postulates:

> **four postulates of Kinetic Molecular Theory**
>
> 1. A gas is composed of a large number of particles called molecules (whether monatomic or polyatomic) that move randomly in straight-line, continuous motion.
> 2. Gas molecules collide with one another and with the walls of the container, but these collisions are perfectly elastic; that is, they do not change the average kinetic energy of the molecules.
> 3. Because the distance between gas molecules is much greater than the size of the molecules, the volume of the molecules is negligible. They are considered "point" particles.
> 4. Intermolecular interactions, whether repulsive or attractive, are so weak that they are also negligible.

Although the molecules of real gases have nonzero volumes and exert both attractive and repulsive forces on one another, for the moment we will focus on how the kinetic molecular theory of gases relates to the properties of gases we have been discussing. In the following sections, we explain how this theory must be modified to account for the behavior of real gases.
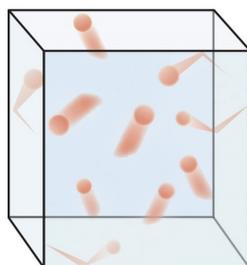
Figure 2.1.1: Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.

Postulates 1 and 2 state that gas molecules are in constant motion and collide frequently with the walls of their containers. The collision of molecules with their container walls results in a **momentum transfer** (impulse) from molecules to the walls (Figure 2.1.2).
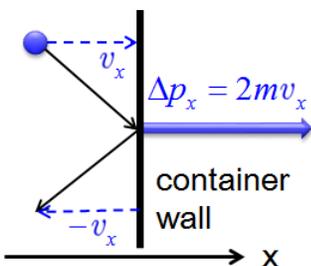
Figure 2.1.2: Momentum transfer (impulse) from a molecule to the container wall as it bounces off the wall. v_x and Δp_x are the x component of the molecular velocity and the momentum transferred to the wall, respectively. The wall is perpendicular to x axis. Since the collisions are elastic, the molecule bounces back with the same velocity in the opposite direction.

The **momentum transfer** to the wall perpendicular to x axis as a molecule with an initial velocity v_x in x direction hits is expressed as:

$$\Delta p_x = 2mv_x \tag{2.1.1}$$

The **collision frequency**, a number of collisions of the molecules to the wall per unit area and per second, increases with the molecular speed and the number of molecules per unit volume.

$$f \propto (v_x) \times \left(\frac{N}{V}\right) \tag{2.1.2}$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mv_x) \times (v_x) \times \left(\frac{N}{V}\right) \propto \left(\frac{N}{V}\right)mv_x^2 \tag{2.1.3}$$

At any instant, however, the molecules in a gas sample are traveling at different speed. Therefore, we must replace v_x^2 in the expression above with the average value of v_x^2, which is denoted by $\langle v_x^2 \rangle$. The overbar designates the average value over all molecules.

The exact expression for pressure is given as :

$$P = \frac{N}{V}m\langle v_x^2 \rangle \tag{2.1.4}$$

Finally, we must consider that there is nothing special about x direction. We should expect that

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3}\langle v^2 \rangle \tag{2.1.5}$$

Here the quantity $\langle v^2 \rangle$ is called the **mean-square speed** defined as the average value of square-speed (v^2) over all molecules. Since

$$v^2 = v_x^2 + v_y^2 + v_z^2 \tag{2.1.6}$$

for each molecule, then

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle \tag{2.1.7}$$

By substituting $\frac{1}{3}\langle v^2 \rangle$ for $\langle v_x^2 \rangle$ in the expression above, we can get the final expression for the pressure:

$$P = \frac{1}{3}\frac{N}{V}m\left\langle v^2 \right\rangle \tag{2.1.8}$$

Because volumes and intermolecular interactions are negligible, postulates 3 and 4 state that all gaseous particles behave identically, regardless of the chemical nature of their component molecules. This is the essence of the ideal gas law, which treats all gases as collections of particles that are identical in all respects except mass. Postulate 3 also explains why it is relatively easy to compress a gas; you simply decrease the distance between the gas molecules.

Additionally, the average kinetic energy of the molecules of any gas depends on only the temperature, and at a given temperature, all gaseous molecules have exactly the same average kinetic energy. This is sometimes considered Postulate 5 of Kinetic Molecular Theory. This postulate provides a molecular explanation for the temperature of a gas. It refers to the *average translational* kinetic energy of the molecules of a gas $\langle E_k \rangle$, which can be represented as *and states that at a given Kelvin temperature* (T), *all gases have the same value of*

$$\langle E_k \rangle = \frac{1}{2}m\left\langle v^2 \right\rangle = \frac{3}{2}\frac{R}{N_A}T \tag{2.1.9}$$

where N_A is the Avogadro's constant. The total translational kinetic energy of 1 mole of molecules can be obtained by multiplying the equation by N_A:

$$N_A \langle E_k \rangle = \frac{1}{2}M\left\langle v^2 \right\rangle = \frac{3}{2}RT \tag{2.1.10}$$

where M is the molar mass of the gas molecules and is related to the molecular mass by $M = N_A m$. By rearranging the equation, we can get the relationship between the root-mean square speed (v_{rms}) and the temperature. The rms speed (v_{rms}) is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{\mathrm{rms}} = \sqrt{\left\langle v^2 \right\rangle} = \sqrt{\frac{v_1^2 + v_2^2 + \cdots v_N^2}{N}} \tag{2.1.11}$$

where N is the number of particles and v_i is the speed of particle i.

The relationship between v_{rms} and the temperature is given by:

$$v_{\mathrm{rms}} = \sqrt{\frac{3RT}{M}} \tag{2.1.12}$$

In Equation 2.1.12, v_{rms} has units of meters per second; consequently, the units of molar mass M are kilograms per mole, temperature T is expressed in kelvins, and the ideal gas constant R has the value 8.3145 J/(K•mol). Equation 2.1.12 shows that v_{rms} of a gas is proportional to the square root of its Kelvin temperature and inversely proportional to the square root of its molar mass. The root mean-square speed of a gas increase with increasing temperature. At a given temperature, heavier gas molecules have slower speeds than do lighter ones.

The rms speed and the average speed do not differ greatly (typically by less than 10%). The distinction is important, however, because the rms speed is the speed of a gas particle that has average kinetic energy. Particles of different gases at the same temperature have the same average kinetic energy, not the same average speed. In contrast, the most probable speed (vp) is the speed at which the greatest number of particles is moving. If the average kinetic energy of the particles of a gas increases linearly with increasing temperature, then Equation 2.1.11 tells us that the rms speed must also increase with temperature because the mass of the particles is constant. At higher temperatures, therefore, the molecules of a gas move more rapidly than at lower temperatures, and vp increases.

> *At a given temperature, all gaseous particles have the same average kinetic energy but not the same average speed.*

Example 2.1.1

The speeds of eight particles were found to be 1.0, 4.0, 4.0, 6.0, 6.0, 6.0, 8.0, and 10.0 m/s. Calculate their average speed (v_{av}) root mean square speed (v_{rms}), and most probable speed (v_{m}).

Given: particle speeds

Asked for: average speed (v_{av}), root mean square speed (v_{rms}), and most probable speed (v_m)

Strategy:

Use Equation 2.1.9 to calculate the average speed and Equation 2.1.11 to calculate the rms speed. Find the most probable speed by determining the speed at which the greatest number of particles is moving.

Solution:

The average speed is the sum of the speeds divided by the number of particles:

$$v_{av} = \frac{(1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0) \text{ m/s}}{8} = 5.6 \text{ m/s}$$

The rms speed is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{rms} = \sqrt{\frac{(1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2) \text{ m}^2/\text{s}^2}{8}} = 6.2 \text{ m/soumber} \qquad (2.1.13)$$

The most probable speed is the speed at which the greatest number of particles is moving. Of the eight particles, three have speeds of 6.0 m/s, two have speeds of 4.0 m/s, and the other three particles have different speeds. Hence $v_m = 6.0$ m/s. The v_{rms} of the particles, which is related to the average kinetic energy, is greater than their average speed.

Distributions of Molecular Speeds

At any given time, what fraction of the molecules in a particular sample has a given speed? Some of the molecules will be moving more slowly than average, and some will be moving faster than average, but how many in each situation? Answers to questions such as these can have a substantial effect on the amount of product formed during a chemical reaction. This problem was solved mathematically by Maxwell in 1866; he used statistical analysis to obtain an equation that describes the distribution of molecular speeds at a given temperature. Typical curves showing the distributions of speeds of molecules at several temperatures are displayed in Figure 2.1.3. Increasing the temperature has two effects. First, the peak of the curve moves to the right because the most probable speed increases. Second, the curve becomes broader because of the increased spread of the speeds. Thus increased temperature increases the *value* of the most probable speed but decreases the relative number of molecules that have that speed. Although the mathematics behind curves such as those in Figure 2.1.3 were first worked out by Maxwell, the curves are almost universally referred to as Boltzmann distributions, after one of the other major figures responsible for the kinetic molecular theory of gases.
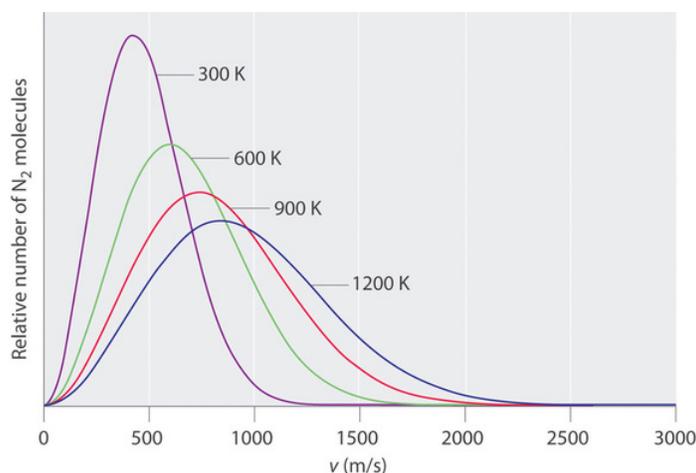
Figure 2.1.3 The Distributions of Molecular Speeds for a Sample of Nitrogen Gas at Various Temperatures. Increasing the temperature increases both the most probable speed (given at the peak of the curve) and the width of the curve.

The Relationships among Pressure, Volume, and Temperature

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

- **Pressure versus Volume**: At constant temperature, the kinetic energy of the molecules of a gas and hence the rms speed remain unchanged. If a given gas sample is allowed to occupy a larger volume, then the speed of the molecules does not change, but the density of the gas (number of particles per unit volume) decreases, and the average distance between the molecules increases. Hence the molecules must, on average, travel farther between collisions. They therefore collide with one another and with the walls of their containers less often, leading to a decrease in pressure. Conversely, increasing the pressure forces the molecules closer together and increases the density, until the collective impact of the collisions of the molecules with the container walls just balances the applied pressure.
- **Volume versus Temperature**: Raising the temperature of a gas increases the average kinetic energy and therefore the rms speed (and the average speed) of the gas molecules. Hence as the temperature increases, the molecules collide with the walls of their containers more frequently and with greater force. This increases the pressure, *unless* the volume increases to reduce the pressure, as we have just seen. Thus an increase in temperature must be offset by an increase in volume for the net impact (pressure) of the gas molecules on the container walls to remain unchanged.
- **Pressure of Gas Mixtures**: Postulate 4 of the kinetic molecular theory of gases states that gas molecules exert no attractive or repulsive forces on one another. If the gaseous molecules do not interact, then the presence of one gas in a gas mixture will have no effect on the pressure exerted by another, and Dalton's law of partial pressures holds.

Example 2.1.2

The temperature of a 4.75 L container of N_2 gas is increased from 0°C to 117°C. What is the qualitative effect of this change on the

- a. average kinetic energy of the N_2 molecules?
- b. rms speed of the N_2 molecules?
- c. average speed of the N_2 molecules?
- d. impact of each N_2 molecule on the wall of the container during a collision with the wall?
- e. total number of collisions per second of N_2 molecules with the walls of the entire container?
- f. number of collisions per second of N_2 molecules with each square centimeter of the container wall?
- g. pressure of the N_2 gas?

Given: temperatures and volume

Asked for: effect of increase in temperature

Strategy:

Use the relationships among pressure, volume, and temperature to predict the qualitative effect of an increase in the temperature of the gas.

Solution:

- a. Increasing the temperature increases the average kinetic energy of the N_2 molecules.
- b. An increase in average kinetic energy can be due only to an increase in the rms speed of the gas particles.
- c. If the rms speed of the N_2 molecules increases, the average speed also increases.
- d. If, on average, the particles are moving faster, then they strike the container walls with more energy.
- e. Because the particles are moving faster, they collide with the walls of the container more often per unit time.
- f. The number of collisions per second of N_2 molecules with each square centimeter of container wall increases because the total number of collisions has increased, but the volume occupied by the gas and hence the total area of the walls are unchanged.
- g. The pressure exerted by the N_2 gas increases when the temperature is increased at constant volume, as predicted by the ideal gas law.

Exercise 2.1.2

A sample of helium gas is confined in a cylinder with a gas-tight sliding piston. The initial volume is 1.34 L, and the temperature is 22°C. The piston is moved to allow the gas to expand to 2.12 L at constant temperature. What is the qualitative effect of this change on the

- a. average kinetic energy of the He atoms?

b. rms speed of the He atoms?

c. average speed of the He atoms?

d. impact of each He atom on the wall of the container during a collision with the wall?

e. total number of collisions per second of He atoms with the walls of the entire container?

 f. number of collisions per second of He atoms with each square centimeter of the container wall?

g. pressure of the He gas?

Answer a

no change

Answer b

no change

Answer c

no change

Answer d

no change

Answer e

decreases

Answer f

decreases

Answer g

decreases

Summary

- The kinetic molecular theory of gases provides a molecular explanation for the observations that led to the development of the ideal gas law.
- **Average kinetic energy:**

$$\langle E_k \rangle = \frac{1}{2} m v_{\mathrm{rms}}{}^2 = \frac{3}{2} \frac{R}{N_A} T n$$

- **Root mean square speed:**

$$v_{\mathrm{rms}} = \sqrt{\frac{v_1^2 + v_2^2 + \cdots v_N^2}{N}}$$

- **Kinetic molecular theory of gases:**

$$v_{\mathrm{rms}} = \sqrt{\frac{3RT}{M}}$$

The behavior of ideal gases is explained by the **kinetic molecular theory of gases**. Molecular motion, which leads to collisions between molecules and the container walls, explains pressure, and the large intermolecular distances in gases explain their high compressibility. Although all gases have the same average kinetic energy at a given temperature, they do not all possess the same **root mean square (rms) speed (v_{rms})**. The actual values of speed and kinetic energy are not the same for all particles of a gas but are given by a **Boltzmann distribution**, in which some molecules have higher or lower speeds (and kinetic energies) than average.

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3: Extension 1.2 - Microscopic Gas Models

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3.1: Van der Waals' Equation

An equation due to van der Waals extends the ideal gas equation in a straightforward way. ***Van der Waals' equation*** is

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

It fits pressure-volume-temperature data for a real gas better than the ideal gas equation does. The improved fit is obtained by introducing two parameters (designated "a" and "b") that must be determined experimentally for each gas. Van der Waals' equation is particularly useful in our effort to understand the behavior of real gases, because it embodies a simple physical picture for the difference between a real gas and an ideal gas.

In deriving Boyle's law from Newton's laws, we assume that the gas molecules do not interact with one another. Simple arguments show that this can be only approximately true. Real gas molecules must interact with one another. At short distances they repel one another. At somewhat longer distances, they attract one another. The ideal gas equation can also be derived from the basic assumptions that we make in §10 by an application of the theory of statistical thermodynamics. By making different assumptions about molecular properties, we can apply statistical thermodynamics to derive[5] van der Waals' equation. The required assumptions are that the molecules occupy a finite volume and that they attract one another with a force that varies as the inverse of a power of the distance between them. (The attractive force is usually assumed to be proportional to r^{-6}.)

To recognize that real gas molecules both attract and repel one another, we need only remember that any gas can be liquefied by reducing its temperature and increasing the pressure applied to it. If we cool the liquid further, it freezes to a solid. Now, two distinguishing features of a solid are that it retains its shape and that it is almost incompressible. We attribute the incompressibility of a solid to repulsive forces between its constituent molecules; they have come so close to one another that repulsive forces between them have become important. To compress the solid, the molecules must be pushed still closer together, which requires inordinate force. On the other hand, if we throw an ice cube across the room, all of its constituent water molecules fly across the room together. Evidently, the water molecules in the solid are attracted to one another, otherwise they would all go their separate ways—throwing the ice cube would be like throwing a handful of dry sand. But water molecules are the same molecules whatever the temperature or pressure, so if there are forces of attraction and repulsion between them in the solid, these forces must be present in the liquid and gas phases also.

In the gas phase, molecules are far apart; in the liquid or the solid phase, they are packed together. At its boiling point, the volume of a liquid is much less than the volume of the gas from which it is condensed. At the freezing point, the volume of a solid is only slightly different from the volume of the liquid from which it is frozen, and it is certainly greater than zero. These commonplace observations are readily explained by supposing that any molecule has a characteristic volume. We can understand this, in turn, to be a consequence of the nature of the intermolecular forces; evidently, these forces become stronger as the distance between a pair of molecules decreases. Since a liquid or a solid occupies a definite volume, the repulsive force must increase more rapidly than the attractive force when the intermolecular distance is small. Often it is useful to talk about the molar volume of a condensed phase. By molar volume, we mean the volume of one mole of a pure substance. The molar volume of a condensed phase is determined by the intermolecular distance at which there is a balance between intermolecular forces of attraction and repulsion.

Evidently molecules are very close to one another in condensed phases. If we suppose that the empty spaces between molecules are negligible, the volume of a condensed phase is approximately equal to the number of molecules in the sample multiplied by the volume of a single molecule. Then the molar volume is Avogadro's number times the volume occupied by one molecule. If we know the density, D, and the molar mass, $\overline{M}$, we can find the molar volume, $\overline{V}$, as

$$\overline{V} = \frac{\overline{M}}{D}$$

The volume occupied by a molecule, $V_{molecule}$, becomes

$$V_{molecule} = \frac{\overline{V}}{\overline{N}}$$

The pressure and volume appearing in van der Waals' equation are the pressure and volume of the real gas. We can relate the terms in van der Waals' equation to the ideal gas equation: It is useful to think of the terms $\left(P + an^2/V^2\right)$ and $(V - nb)$ as the pressure and volume of a *hypothetical ideal gas*. That is

$$P_{ideal\ gas}\,V_{ideal\ gas} = \left(P_{real\ gas} + \frac{an^2}{V^2_{real\ gas}}\right)(V_{real\ gas} - nb)$$

$$= nRT$$

Then we have

$$V_{real\ gas} = V_{ideal\ gas} + nb$$

We derive the ideal gas equation from a model in which the molecules are non-interacting point masses. So the volume of an ideal gas is the volume occupied by a gas whose individual molecules have zero volume. If the individual molecules of a real gas effectively occupy a volume $b/\overline{N}$, then n moles of them effectively occupy a volume

$$\left(b/\overline{N}\right)\left(n\overline{N}\right) = nb.$$

Van der Waals' equation says that the volume of a real gas is the volume that would be occupied by non-interacting point masses, $V_{ideal\ gas}$, plus the effective volume of the gas molecules themselves. (When data for real gas molecules are fit to the van der Waals' equation, the value of b is usually somewhat greater than the volume estimated from the liquid density and molecular weight. See problem 24.)

Similarly, we have

$$P_{\text{real gas}} = P_{\text{ideal gas}} - \frac{an^2}{V^2_{\text{real gas}}}$$

We can understand this as a logical consequence of attractive interactions between the molecules of the real gas. With $a > 0$, it says that the pressure of the real gas is less than the pressure of the hypothetical ideal gas, by an amount that is proportional to $(n/V)^2$. The proportionality constant is a. Since n/V is the molar density (moles per unit volume) of the gas molecules, it is a measure of concentration. The number of collisions between molecules of the same kind is proportional to the square of their concentration. (We consider this point in more detail in Chapters 4 and 5.) So $(n/V)^2$ is a measure of the frequency with which the real gas molecules come into close contact with one another. If they attract one another when they come close to one another, the effect of this attraction should be proportional to $(n/V)^2$. So van der Waals' equation is consistent with the idea that the pressure of a real gas is different from the pressure of the hypothetical ideal gas by an amount that is proportional to the frequency and strength of attractive interactions.

But why should attractive interactions have this effect; why should the pressure of the real gas be less than that of the hypothetical ideal gas? Perhaps the best way to develop a qualitative picture is to recognize that attractive intermolecular forces tend to cause the gas molecules to clump up. After all, it is these attractive forcesattractive force that cause the molecules to aggregate to a liquid at low temperatures. Above the boiling point, the ability of gas molecules to go their separate ways limits the effects of this tendency; however, even in the gas, the attractive forces must act in a way that tends to reduce the volume occupied by the molecules. Since the volume occupied by the gas is dictated by the size of the container—not by the properties of the gas itself—this clumping-up tendency finds expression as a decrease in pressure.
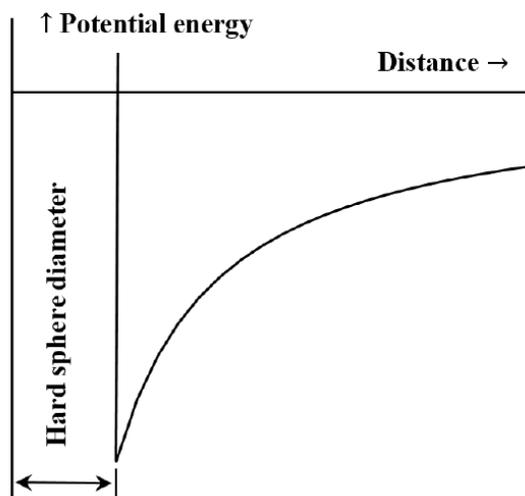
Figure 5. Potential energy versus distance for "hard sphere molecules."

It is frequently useful to describe the interaction between particles or chemical moieties in terms of a potential energy versus distance diagram. The van der Waals' equation corresponds to the case that the repulsive interaction between molecules is non-existent until the molecules come into contact. Once they come into contact, the energy required to move them still closer together becomes arbitrarily large. Often this is described by saying that they behave like "hard spheres". The attractive force between two molecules decreases as the distance between them increases. When they are very far apart the attractive interaction is very small. We say that the energy of interaction is zero when the molecules are infinitely far apart. If we initially have two widely separated, stationary, mutually attracting molecules, they will spontaneously move toward one another, gaining kinetic energy as they go. Their potential energy decreases as they approach one another, reaching its smallest value when the molecules come into contact. Thus, van der Waals' equation implies the potential energy *versus* distance diagram sketched in Figure 5.

CHAPTER OVERVIEW

4: Fundamental 2 - Counting Configurations

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4.1: The Distribution Function as a Summary of Experimental Results

In Section 2.10, we derive Boyle's law from Newton's laws using the assumption that all gas molecules move at the same speed at a given temperature. This is a poor assumption. Individual gas molecules actually have a wide range of velocities. In Chapter 4, we derive the Maxwell–Boltzmann distribution law for the distribution of molecular velocities. This law gives the fraction of gas molecules having velocities in any range of velocities. Before developing the Maxwell–Boltzmann distribution law, we need to develop some ideas about distribution functions. Most of these ideas are mathematical. We discuss them in a non-rigorous way, focusing on understanding what they mean rather than on proving them.

The overriding idea is that we have a real-world source of data. We call this source of data the ***distribution***. We can collect data from this source to whatever extent we please. The datum that we collect is called the distribution's ***random variable***. We call each possible value of the random variable an ***outcome***. The process of gathering a set of particular values of the random variable from a distribution is often called ***sampling*** or ***drawing a sample***. The set of values that is collected is called ***the sample***. The set of values that comprise the sample is often called "the data." In scientific applications, the random variable is usually a number that results from making a measurement on a physical system. Calling this process "drawing a sample" can be inappropriate. Often we call the process of getting a value for the random variable "doing an experiment", "doing a test", or "making a trial".

As we collect increasing amounts of data, the accumulation quickly becomes unwieldy unless we can reduce it to a mathematical model. We call the mathematical model we develop a ***distribution function***, because it is a function that expresses what we are able to learn about the data source—the distribution. A distribution function is an equation that summarizes the results of many measurements; it is a mathematical model for a real-world source of data. Specifically, it models the ***frequency*** of an event with which we obtain a particular outcome. We usually believe that we can make our mathematical model behave as much like the real-world data source as we want if we use enough experimental data in developing it.

Often we talk about ***statistics***. By a statistic, we mean any mathematical entity that we can calculate from data. Broadly speaking a distribution function is a statistic, because it is obtained by fitting a mathematical function to data that we collect. Two other statistics are often used to characterize experimental data: the ***mean*** and the ***variance***. The mean and variance are defined for any distribution. We want to see how to estimate the mean and variance from a set of experimental data collected from a particular distribution.

We distinguish between discrete and continuous distributions. A ***discrete distribution*** is a real-world source of data that can produce only particular data values. A coin toss is a good example. It can produce only two outcomes—heads or tails. A ***continuous distribution*** is a real-world source of data that can produce data values in a continuous range. The speed of an automobile is a good example. An automobile can have any speed within a rather wide range of speeds. For this distribution, the random variable is automobile speed. Of course we can generate a discrete distribution by aggregating the results of sampling a continuous distribution; if we lump all automobile speeds between 20 mph and 30 mph together, we lose the detailed information about the speed of each automobile and retain only the total number of automobiles with speeds in this interval.

4.2: Outcomes, Events, and Probability

We also need to introduce the idea that a function that successfully models the results of past experiments can be used to predict some of the characteristics of future results.

We reason as follows: We have results from drawing many samples of a random variable from some distribution. We suppose that a mathematical representation has been found that adequately summarizes the results of these experiences. If the underlying distribution—the physical system in scientific applications—remains the same, we expect that a long series of future results would give rise to essentially the same mathematical representation. If 25% of many previous results have had a particular characteristic, we expect that 25% of a large number of future trials will have the same characteristic. We also say that there is one chance in four that the next individual result will have this characteristic; when we say this, we mean that 25% of a large number of future trials will have this characteristic, and the next trial has as good a chance as any other to be among those that do. ***The probability that an outcome will occur in the future is equal to the frequency with which that outcome has occurred in the past.***

Given a distribution, the possible outcomes must be mutually exclusive; in any given trial, the random variable can have only one of its possible values. Consequently, a discrete distribution is completely described when the probability of each of its outcomes is specified. Many distributions are comprised of a finite set of N mutually exclusive possible outcomes. If each of these outcomes is equally likely, the probability that we will observe any particular outcome in the next trial is $1/N$.

We often find it convenient to group the set of possible outcomes into subsets in such a way that each outcome is in one and only one of the subsets. We say that such assignments of outcomes to subsets are ***exhaustive***, because every possible outcome is assigned to some subset; we say that such assignments are ***mutually exclusive***, because no outcome belongs to more than one subset. We call each such subset an ***event***. When we partition the possible outcomes into exhaustive and mutually exclusive events, we can say the same things about the probabilities of events that we can say about the probabilities of outcomes. In our discussions, the term "events" will always refer to an exhaustive and mutually exclusive partitioning of the possible outcomes. Distinguishing between outcomes and events just gives us some language conventions that enable us to create alternative groupings of the same set of real world observations.

Suppose that we define a particular event to be a subset of outcomes that we denote as U. If in a large number of trials, the fraction of outcomes that belong to this subset is F, we say that the probability is F that the outcome of the next trial will belong to this event. To express this in more mathematical notation, we write $P(U) = F$. When we do so, we mean that the fraction of a large number of future trials that belong to this subset will be F, and the next trial has as good a chance as any other to be among those that do. In a sample comprising M observations, the best forecast we can make of the number of occurrences of U is $M \times P(U)$, and we call this the ***expected number of occurrences*** of U in a sample of size M.

The idea of grouping real world observations into either outcomes or events is easy to remember if we keep in mind the example of tossing a die. The die has six faces, which are labeled with 1, 2, 3, 4, 5, or 6 dots. The dots distinguish one face from another. On any given toss, one face of the die must land on top. Therefore, there are six possible outcomes. Since each face has as good a chance as any other of landing on top, the six possible outcomes are equally probable. The probability of any given outcome is $1/6$. If we ask about the probability that the next toss will result in one of the even-numbered faces landing on top, we are asking about the probability of an event—the event that the next toss will have the characteristic that an even-numbered face lands on top. Let us call this event X. That is, event X occurs if the outcome is a 2, a 4, or a 6. These are three of the six equally likely outcomes. Evidently, the probability of this event is $3/6 = 1/2$.

Having defined event X as the probability of an even-number outcome, we still have several alternative ways to assign the odd-number outcomes to events. One assignment would be to say that all of the odd-number outcomes belong to a second event—the event that the outcome is odd. The events "even outcome" and "odd outcome" are exhaustive and mutually exclusive. We could create another set of events by assigning the outcomes 1 and 3 to event Y, and the outcome 5 to event Z. Events X, Y, and Z are also exhaustive and mutually exclusive.

We have a great deal of latitude in the way we assign the possible outcomes to events. If it suits our purposes, we can create many different exhaustive and mutually exclusive partitionings of the outcomes of a given distribution. We require that each partitioning of outcomes into events be exhaustive and mutually exclusive, because we want to apply the laws of probability to events.

4.3: Some Important Properties of Events

If we know the probabilities of the possible outcomes of a trial, we can calculate the probabilities for combinations of outcomes. These calculations are based on two rules, which we call **the laws of probability**. If we partition the outcomes into exhaustive and mutually exclusive events, the laws of probability also apply to events. Since, as we define them, "events" is a more general term than "outcomes," we call them the law of the **probability of alternative events** and the law of the **probability of compound events**. These laws are valid so long as three conditions are satisfied. We have already discussed the first two of these conditions, which are that the outcomes possible in any individual trial must be exhaustive and mutually exclusive. The third condition is that, if we make more than one trial, the outcomes must be **independent**; that is, the outcome of one trial must not be influenced by the outcomes of the others.

We can view the laws of probability as rules for inferring information about combinations of events. The law of the probability of alternative events applies to events that belong to the same distribution. The law of the probability of compound events applies to events that can come from one or more distributions. An important special case occurs when the compound events are N successive samplings of a given distribution that we identify as the **parent distribution**. If the random variable is a number, and we average the numbers that we obtain from N successive samplings of the parent distribution, these "averages-of-N" themselves constitute a distribution. If we know certain properties of the parent distribution, we can calculate corresponding properties of the "distribution of averages-of-N values obtained by sampling the parent distribution." These calculations are specified by the **central limit theorem**, which we discuss in Section 3.11.

In general, when we combine events from two distributions, we can view the result as an event that belongs to a third distribution. At first encounter, the idea of combining events and distributions may seem esoteric. A few examples serve to show that what we have in mind is very simple.

Since an event is a set of outcomes, an event occurs whenever any of the outcomes in the set occurs. Partitioning the outcomes of tossing a die into "even outcomes" and "odd outcomes" illustrates this idea. The event "even outcome" occurs whenever the outcome of a trial is 2, 4, or 6. The probability of an event can be calculated from the probabilities of the underlying outcomes. We call the rule for this calculation the law of the probabilities of alternative events. (We create the opportunity for confusion here because we are illustrating the idea of alternative events by using an example in which we call the alternatives "alternative outcomes" rather than "alternative events." We need to remember that "event" is a more general term than "outcome." One possible partitioning is that which assigns every outcome to its own event.) We discuss the probabilities of alternative events further below.

To illustrate the idea of compound events, let us consider a first distribution that comprises "tossing a coin" and a second distribution that comprises "drawing a card from a poker deck." The first distribution has two possible outcomes; the second distribution has 52 possible outcomes. If we combine these distributions, we create a third distribution that comprises "tossing a coin and drawing a card from a poker deck." The third distribution has 104 possible outcomes. If we know the probabilities of the outcomes of the first distribution and the probabilities of the outcomes of the second distribution, and these probabilities are independent of one another, we can calculate the probability of any outcome that belongs to the third distribution. We call the rule for this calculation the law of the probability of compound events. We discuss it further below.

A similar situation occurs when we consider the outcomes of tossing two coins. We assume that we can tell the two coins apart. Call them coin 1 and coin 2. We designate heads and tails for coins 1 and 2 as H_1, T_1, H_2, and T_2, respectively. There are four possible outcomes in the distribution we call "tossing two coins:" H_1H_2, H_1T_2, T_1H_2, and T_1T_2. (If we could not tell the coins apart, H_1T_2 would be the same thing as T_1H_2; there would be only three possible outcomes.) We can view the distribution "tossing two coins" as being a combination of the two distributions that we can call "tossing coin 1" and "tossing coin 2." We can also view the distribution "tossing two coins" as a combination of two distributions that we call "tossing a coin a first time" and "tossing a coin a second time." We view the distribution "tossing two coins" as being equivalent to the distribution "tossing one coin twice." This is an example of **repeated trials**, which is a frequently encountered type of distribution. In general, **we call such a distribution a "distribution of events from a trial repeated N times," and we view this distribution as being completely equivalent to N simultaneous trials of the same kind**. Chapter 19 considers the distribution of outcomes when a trial is repeated many times. Understanding the properties of such distributions is the single most essential element in understanding the theory of statistical thermodynamics. The central limit theorem relates properties of the repeated-trials distribution to properties of the parent distribution.

The Probability of Alternative Events

If we know the probability of each of two mutually exclusive events that belong to an exhaustive set, the probability that one or the other of them will occur in a single trial is equal to the sum of the individual probabilities. Let us call the independent events A and B, and represent their probabilities as $P(A)$ and $P(B)$, respectively. The probability that one of these events occurs is the same thing as the probability that either A occurs or B occurs. We can represent this probability as $P(A \; or \; B)$. The probability of this combination of events is the sum: $P(A) + P(B)$. That is,

$$P\left(A \; or \; B\right) = P\left(A\right) + P(B)$$

Above we define Y as the event that a single toss of a die comes up either 1 or 3. Because each of these outcomes is one of six, mutually-exclusive, equally-likely outcomes, the probability of either of them is $1/6$: $P\left(tossing \; a \; 1\right) = P\left(tossing \; a \; 3\right) = 1/6$. From the law of the probability of alternative events, we have

$$P\left(event \; Y\right) = \left(tossing \; a \; 1 \; or \; tossing \; a \; 3\right)$$
$$= P\left(tossing \; a \; 1\right) \; or P\left(tossing \; a \; 3\right)$$
$$= 1/6 + 1/6$$
$$= 2/6$$

We define X as the event that a single toss of a die comes up even. From the law of the probability of alternative events, we have

$$P\left(event \; X\right) = P\left(tossing \; 2 \; or \; 4 \; or \; 6\right)$$
$$= P\left(tossing \; a \; 2\right) + P\left(tossing \; a \; 4\right) + P\left(tossing \; a \; 6\right)$$
$$= 3/6$$

We define Z as the event that a single toss comes up 5.

$$P\left(event \; Z\right) = P\left(tossing \; a \; 5\right) = 1/6$$

If there are ω independent events (denoted $E_1, E_2, \ldots, E_i, \ldots, E_\omega$), the law of the probability of alternative events asserts that the probability that one of these events will occur in a single trial is

$$P\left(E_1 \; or \; E_2 \; or \ldots E_i \ldots or \; E_\omega\right) = P\left(E_1\right) + P\left(E_2\right) + \cdots + P\left(E_i\right) + \cdots + P\left(E_\omega\right)$$
$$= \sum_{i=1}^{\omega} P\left(E_i\right)$$

If these ω independent events encompass all of the possible outcomes, the sum of their individual probabilities must be unity.
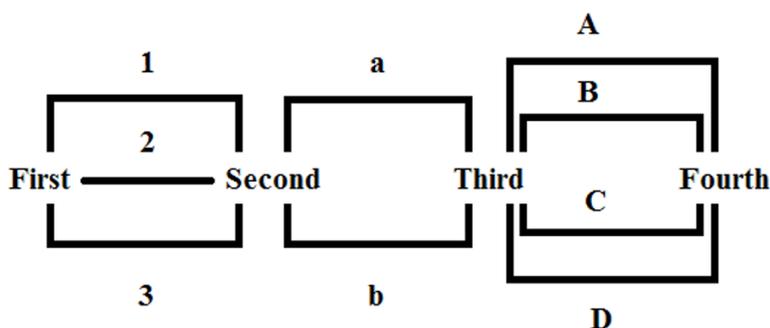
Figure 1. A simple case that illustrates the laws of probability.

The Probability of Compound Events

Let us now suppose that we make two trials in circumstances where event A is possible in the first trial and event B is possible in the second trial. We represent the probabilities of these events by $P\left(A\right)$ and $P(B)$ and stipulate that they are independent of one another; that is, the probability that B occurs in the second trial is independent of the outcome of the first trial. Then, the

probability that A occurs in the first trial and B occurs in the second trial, $P(A\ and\ B)$, is equal to the product of the individual probabilities.

$$P\left(A\ and\ B\right) = P\left(A\right) \times P(B)$$

To illustrate this using outcomes from die-tossing, let us suppose that event A is tossing a 1 and event B is tossing a 3. Then, $P\left(A\right) = 1/6$ and $P\left(B\right) = 1/6$. The probability of tossing a 1 in a first trial and tossing a 3 in a second trial is then

$$P\left(\text{tossing a 1 first and tossing a 3 second}\right) = P\left(\text{tossing a 1}\right) \times P\left(\text{tossing a 3}\right)$$
$$= 1/6 \times 1/6$$
$$= 1/36$$

If we want the probability of getting one 1 and one 3 in two tosses, we must add to this the probability of tossing a 3 first and a 1 second.

If there are ω independent events (denoted $E_1, E_2, \ldots, E_i, \ldots, E_\omega$), the law of the probability of compound events asserts that the probability that E_1 will occur in a first trial, and E_2 will occur in a second trial, *etc.*, is

$$P\left(E_1\ and\ E_2\ and \ldots E_i \ldots and\ E_\omega\right)\ = P\left(E_1\right) \times P\left(E_2\right) \times \cdots \times P\left(E_i\right) \times \cdots \times P\left(E_\omega\right)$$
$$= \prod_{i=1}^{\omega} P(E_i)$$

4.4: Applying the Laws of Probability

The laws of probability apply to events that are independent. If the result of one trial depends on the result of another trial, we may still be able to use the laws of probability. However, to do so, we must know the nature of the interdependence.

If the activity associated with event C precedes the activity associated with event D, the probability of D may depend on whether C occurs. Suppose that the first activity is tossing a coin and that the second activity is drawing a card from a deck; however, the deck we use depends on whether the coin comes up heads or tails. If the coin is heads, we draw a card from an ordinary deck; if the coin is tails, we draw a coin from a deck with the face cards removed. Now we ask about the probability of drawing an ace. If the coin is heads, the probability of drawing an ace is $4/52 = 1/13$. If the coin is tails, the probability of drawing an ace is $4/40 = 1/10$. The combination coin is heads and card is ace has probability: $(1/2)(1/13) = 1/26$. The combination coin is tails and card is ace has probability $(1/2)(1/10) = 1/20$. In this

case, the probability of drawing an ace depends on the modification we make to the deck based on the outcome of the coin toss.

Applying the laws of probability is straightforward. An example that illustrates the application of these laws in a transparent way is provided by villages First, Second, Third, and Fourth, which are separated by rivers. (See Figure 1.) Bridges 1, 2, and 3 span the river between First and Second. Bridges a and b span the river between Second and Third. Bridges A, B, C, and D span the river between Third and Fourth. A traveler from First to Fourth who is free to take any route he pleases has a choice from among $3 \times 2 \times 4 = 24$ possible combinations. Let us consider the probabilities associated with various events:

- There are 24 possible routes. If a traveler chooses his route at random, the probability that he will take any particular route is $1/24$. This illustrates our assumption that each event in a set of N exhaustive and mutually exclusive events occurs with probability $1/N$.
- If he chooses a route at random, the probability that he goes from First to Second by either bridge 1 or bridge 2 is $P(1) + P(2) = 1/3 + 1/3 = 2/3$. This illustrates the calculation of the probability of alternative events.
- The probability of the particular route $2 \to a \to C$ is $P(2) \times P(a) \times P(C) = (1/3)(1/2)(1/4) = 1/24$, and we calculate the same probability for any other route from First to Fourth. This illustrates the calculation of the probability of a compound event.
- If he crosses bridge 1, the probability that his route will be $2 \to a \to C$ is zero, of course. The probability of an event that has already occurred is 1, and the probability of any alternative is zero. If he crosses bridge 1, $P(1) = 1$, and $P(2) = P(3) = 0$.
- Given that a traveler has used bridge 1, the probability of the route $1 \to a \to C$ becomes the probability of path $a \to C$, which is $P(a) \times P(C) = (1/2)(1/4) = 1/8$. Since $P(1) = 1$, the probability of the compound event $1 \to a \to C$ is the probability of the compound event $a \to C$.

The outcomes of rolling dice, rolling provide more illustrations. If we roll two dice, we can classify the possible outcomes according to the sums of the outcomes for the individual dice. There are thirty-six possible outcomes. They are displayed in Table 1.

Table 1: Outcomes from tossing two dice

	Outcome for first die					
	1	2	3	4	5	6
1	2	3	4	5	6	7
2	3	4	5	6	7	8
Outcome for second die 3	4	5	6	7	8	9
4	5	6	7	8	9	10
5	6	7	8	9	10	11
6	7	8	9	10	11	12

Let us consider the probabilities associated with various dice-throwing events:

- The probability of any given outcome, say the first die shows 2 and the second die shows 3, is $1/36$.

- Since the probability that the first die shows 3 while the second die shows 2 is also $1/36$, the probability that one die shows 2 and the other shows 3 is

$$P(3) \times P(2) + P(2) \times P(3) = (1/36) + (1/36) = 1/18.$$

- Four different outcomes correspond to the event that the score is 5. Therefore, the probability of rolling 5 is

$$P(1) \times P(4) + P(2) \times P(3) + P(3) \times P(2) + P(4) \times P(1) = 1/9$$

- The probability of rolling a score of three or less is the probability of rolling 2, plus the probability of rolling 3 which is $(1/36) + (2/36) = 3/36 = 1/12$
- Suppose we roll the dice one at a time and that the first die shows 2. The probability of rolling 7 when the second die is thrown is now $1/6$, because only rolling a 5 can make the score 7, and there is a probability of $1/6$ that a 5 will come up when the second die is thrown.
- Suppose the first die is red and the second die is green. The probability that the red die comes up 2 and the green die comes up 3 is $(1/6)(1/6) = 1/36.$

Above we looked at the number of outcomes associated with a score of 3 to find that the probability of this event is $1/18$. We can use another argument to get this result. The probability that two dice roll a score of three is equal to the probability that the first die shows 1 or 2 times the probability that the second die shows whatever score is necessary to make the total equal to three. This is:

$$P(first\ die\ shows\ 1\ or\ 2) \times (1/6) = [(1/6) + (1/6)] \times 1/6$$
$$= 2/36$$
$$= 1/18$$

Application of the laws of probability is frequently made easier by recognizing a simple restatement of the requirement that events be mutually exclusive. In a given trial, either an event occurs or it does not. Let the probability that an event A occurs be $P(A)$. Let the probability that event A does not occur be $P(\sim A)$. Since in any given trial, the outcome must belong either to event A or to event $\sim A$, we have

$$P(A) + P(\sim A) = 1$$

For example, if the probability of success in a single trial is $2/3$, the probability of failure is $1/3$. If we consider the outcomes of two successive trials, we can group them into four events.

- Event SS: First trial is a success; second trial is a success.
- Event SF: First trial is a success; second trial is a failure.
- Event FS: First trial is a failure; second trial is a success.
- Event FF: First trial is a failure; second trial is a failure.

Using the laws of probability, we have

$$1 = P(Event\ SS) + P(Event\ SF) + P(Event\ FS) + P(Event\ FF)$$
$$= P_1(S) \times P_2(S) + P_1(S) \times P_2(F) + P_1(F) \times P_2(S) + P_1(F) \times P_2(F)$$

where $P_1(X)$ and $P_2(X)$ are the probability of event X in the first and second trials, respectively.

This situation can be mapped onto a simple diagram. We represent the possible outcomes of the first trial by line segments on one side of a unit square $P_1(S) + P_1(F) = 1$. We represent the outcomes of the second trial by line segments along an adjoining side of the unit square. The four possible events are now represented by the areas of four mutually exclusive and exhaustive portions of the unit square as shown in Figure 2.

	$P_1(S)$	$P_1(F)$
$P_2(S)$	Event SS	Event FS
$P_2(F)$	Event SF	Event FF

Figure 2. Success and failure in successive trials.

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4.5: Combinatorics and Multiplicity

Definitions

Combinatorics: a branch of mathematics that deals with the rules for combining different outcomes and events and calculating the probabilities of these combinations.

Probability: The probability of an outcome is a measure of the likelihood that the outcome will occur in comparison to all possible outcomes.

Permutation: one "way" in which all or part of a set of objects can be ordered or arranged.

Combination: one "way" of selecting all or part of a set of objects without regard to the order in which the objects are selected.

Multiplicity: the multiplicity of events is the total number of "ways" in which different outcomes can possibly occur. Represented by the symbol W, and also called ways, permutations, sequences, degeneracy, weight, arrangements, thermodynamic probability, etc. depending on the context.

As you can see from these definitions, ***combinatorics*** is the branch of math related to counting events and outcomes, while ***multiplicity*** is the statistical thermodynamics variable equal to the number of possible outcomes. They are intricately connected.

Depending on the situation, this number of possible outcomes (multiplicity) could be calculated using the fundamental principles of counting, permutation formulas, or combination formulas from the field of combinatorics. Below is a detailed explanation and example of each of these counting methods and when they can be applied.

The Fundamental Principles of Counting

The Multiplication Principle

During restaurant week, you go out to eat for dinner. The restaurant week menu gives you the option to choose between three appetizers, four entrées, and two desserts. You feel a bit overwhelmed by the number of possibilities; how many different meal options are there?

- Each of these selection events has a different number of possible outcomes or options:
  - Appetizer selection = 3 options
  - Entrée selection = 4 options
  - Dessert event = 2 options
- Because you will choose one appetizer AND one entrée AND one dessert, the total number of different ways your meal could be prepared is:

$$W = 3 \times 4 \times 2 = 24 \tag{4.5.1}$$

- One of the Fundamental Principles of Counting, the Multiplication Principle states that if there are n possible outcomes for each event type, i, in a sequence, then the total number of possible outcomes is equal to the values of n multiplied together:

$$W = n_1 n_2 \cdots n_t = \prod_{i=1}^{t} n_i \tag{4.5.2}$$

  where $\prod$ symbol is the product operator (similar to $\sum$ symbol for the sum operator).
- In this context, each n_i represents the number of possible outcomes for each event. Therefore, the multiplicity of each event type, W_i, is equal to n_i, and the total multiplicity, W_{total}, can be determined by:

$$W_{total} = W_1 W_2 \cdots W_3 = \prod_{i=1}^{t} W_i \tag{4.5.3}$$

The Addition Principle

You are looking to buy a new binder to store your class notes. You're torn between a 1" binder and a 1.5" binder. The 1" binder comes in 5 colors and the 1.5" binder comes in 3. How many total binder options are you considering?

- The two binders each has a different number of possible outcomes:
  - 1" binder = 5 outcomes
  - 1.5" binder = 3 outcomes
- Because you will choose a 1" binder <u>OR</u> a 1.5" binder, the total number of different outcomes you are considering is:

$$W = 5 + 3 = 8 \tag{4.5.4}$$

- One of the *Fundamental Principles of Counting*, the **Addition Principle** states that if there are *n* possible outcomes for each event, *i*, and we *cannot do both* at the same time, then the total number of possible outcomes is equal to the values of *n* added together:

$$W = n_1 + n_2 + n_3 \cdots = \sum_{i=1}^{t} n_i \tag{4.5.5}$$

Permutations

Permutations of distinguishable outcomes without repetition: ALL outcomes selected

You decide to take on the challenge of trying each of CookOut's 40 flavors of milkshakes! If you have a different milkshake each day until you've tried them all (no repeats!), how many different *sequences* of milkshakes (i.e., *orders* or *arrangements*) are possible?

- Since you are not repeating any milkshakes during this time, you will choose from 40 milkshakes on day one <u>AND</u> 39 on day two <u>AND</u> 38 on day three, etc. According to the Multiplication Principle above, the total number of sequences is:

$$W = 40 \times 39 \times 38 \times 37 \times \cdots \times 2 \times 1 = 40! = 8.16 \times 10^{47} \tag{4.5.6}$$

- The *order* of the milkshakes matters in this question but no milkshakes are repeated; this is called a *permutation <u>without</u> repetition*:

$$W = N! \tag{4.5.7}$$

where N is the total number of possible outcomes and *all* possible outcomes are sampled (i.e., you will keep selecting milkshakes until you've tried all the milkshakes). Because you can identify which milkshake you are trying each day, the outcomes or options are considered *distinguishable*.

Permutations of distinguishable outcomes without repetition: SOME outcomes only

On second thought, having a different milkshake every day for 40 days may be a bit much… Instead, you decide to have a different milkshake every day for a week. (Then you'll take a break and come back to tackle the rest of the menu in the future!) How many different *arrangements* or *sequences* are possible during the first week?

- The math is similar to the previous question, except that we only need to multiply the first seven of the numbers in the factorial for the first seven days:

$$W = 40 \times 39 \times 38 \times 37 \times 36 \times 35 \times 34 = 93963542400 \tag{4.5.8}$$

- A more general expression for this *permutation <u>without</u> repetition* includes the total number of possible outcomes, *N*, and the total number of selection events, *r*, which is expressed as "*N*, take *r*" (or you may want to think of it as "*N*, arrange *r*"):

$$W = {}_NP_r = \frac{N!}{(N-r)!} \tag{4.5.9}$$

  where ${}_NP_r$ is a common notation for permutation without repetition.
- For our example, this would be:

$$W = {}_{40}P_7 = \frac{40!}{(40-7)!} = \frac{40!}{33!} = \frac{40 \times 39 \times 38 \times 37 \times 36 \times 35 \times 34 \times 33!}{33!} = 93963542400 \tag{4.5.10}$$

- The previous example (with all 40 milkshakes) can also be depicted this way, however, since all items are selected, N and r are equal:

$$W = {}_{40}P_{40} = \frac{40!}{(40-40)!} = \frac{40!}{0!} = 40! \tag{4.5.11}$$

Permutations of distinguishable outcomes with repetition

To help power you through finals, you decide to have a milkshake every day during finals week, but you are not going to bother with trying different ones; you may just decide to have the same one every day! What would the total number of milkshake *sequences* be in this case?

- If every day you have the option of 40 different milkshakes, the number of possible sequences is:

$$W = 40 \times 40 \times 40 \times 40 \times 40 \times 40 \times 40 = 40^7 = 163840000000 \tag{4.5.12}$$

- This is a **permutation __with__ repetition**, and the equation gives the number of possible sequences for *r* events that each have *N* possible outcomes:

$$W = N^r \tag{4.5.13}$$

- The term **repetition** indicates that an outcome or object is not removed from the available pool after selection. Another way to refer to this concept is as **permutation with __replacement__**; after selecting a particular outcome, that outcome is returned to the selection pool so that the available selection options are always the same.

Permutations of indistinguishable outcomes

Over winter break, you purchase an 11 oz bag of Holiday Milk Chocolate Hershey's Kisses. In the bag of 72 kisses, you have 25 red, 23 silver, and 24 green kisses. If you pull the kisses out of the bag one at a time, how many different *sequences* of holiday colors are possible?

- It may seem that this description also refers to calculating the number of permutations for items that repeat (since there are multiple kisses of each wrapper color), and in fact, some resources do refer to the equation that way. However, this scenario does <u>not</u> repeat in the same way as the previous example.
  - The term **repetition** is used for a series of events or set of objects where the outcomes are allowed to repeat **__after__** being selected (i.e., the selection pool does not change because the selected outcome is replaced by another outcome of the same type).
  - In the current scenario, the selected individual kisses do **__not__** "repeat" because they are not returned to the bag; as each kiss is removed, the available selection pool decreases. Instead, there are simply multiple **indistinguishable** items in the selection pool **__before__** the selections begin. This makes a difference in terms of how many items of each type (i.e., kisses of each color) are available to be selected.
- If our kisses were labeled so that each kiss was distinguishable from the others, then our total number of permutations would be calculated as described previously:

$$W = 72! \tag{4.5.14}$$

However, this calculation will count red_A followed by red_B as a different sequence from red_B followed by red_A. These two outcomes are **indistinguishable** without the *A* and *B* labels, so the number of **unique** sequences must be determined by factoring out the number of identical or redundant arrangements.
- The number of possible arrangements for each individual type of kiss is:

$$n_{red} = 25! \tag{4.5.15}$$

$$n_{silver} = 23! \tag{4.5.16}$$

$$n_{green} = 24! \tag{4.5.17}$$

Therefore, our number of unique sequences or arrangements is:

$$W = \frac{N!}{n_{red}! n_{silver}! n_{green}!} = \frac{72!}{25!23!24!} \tag{4.5.18}$$

- Another way to refer to this type of permutation is a **multiset** permutation because the overall set is composed of smaller subsets of indistinguishable outcomes. The general expression for a multiset permutation is:

$$W = \frac{N!}{n_1! n_2! \cdots n_t!} \tag{4.5.19}$$

where each n_i is the number of possible outcomes for each selection type, i, and the total number of outcomes or objects, N, is:

$$N = \sum_{i=1}^{t} n_i \tag{4.5.20}$$

Combinations

Combinations without repetition

In the spring semester, you decide you've had enough CookOut milkshakes for a while. You buy Blue Bell ice cream from the grocery store instead! You stock 5 flavors: cookies and cream (CC), mint chocolate chip (M), strawberry (S), Dutch chocolate (DC), and banana pudding (B). If you always get three scoops of different flavors, how many different combinations are possible?

- Let's list our five available flavors of ice cream:

Available Flavors	Scoops in Bowl
CC, M, S, DC, B	

Assume we choose B for the first scoop. If we cannot have each flavor more than once (i.e., without repetition), then B is no longer an option for the remaining scoops. Therefore, the second scoop only has four choices available to it:

Available Flavors	Scoops in Bowl
CC, M, S, DC, ~~B~~	B

We choose S for the second scoop, and remove it from the available flavors:

Available Flavors	Scoops in Bowl
CC, M, ~~S~~, DC, ~~B~~	B, S

Lastly, we choose DC for the third scoop:

Available Flavors	Scoops in Bowl
CC, M, ~~S~~, ~~DC~~, ~~B~~	B, S, DC

- Thus far, this process looks like a permutation without repeats, and the permutation equation would yield:

$$_5P_3 = \frac{5!}{(5-3)!} = \frac{5!}{2!} = 5 \times 4 \times 3 = 60 \tag{4.5.21}$$

However, the combination {B, S, DC} is ***indistinguishable*** from other combinations of B, S, and DC scooped in a different order. Once in the bowl, ***order does not matter***. The permutation equation would count each <u>sequence</u> of B, S, and DC <u>separately</u>, so we need to correct for the number of duplicate or <u>indistinguishable</u> combinations.

We can illustrate this point further by looking at the example of B, S, and DC in more details:

Permutations or Sequences (order matters)	Composition or Indistinguishable Combinations (order does not matter)
{B, S, DC}	
{B, DC, S}	
{S, B, DC}	
{S, DC, B}	{DC, S, B}
{DC, B, S}	
{DC, S, B}	

There are six distinguishable sequences that produce indistinguishable combinations. We could also calculate this value using the permutation without repetition for the number of scoops:

$$_3P_3 = \frac{3!}{(3-3)!} = \frac{3!}{0!} = 3! = 6 \tag{4.5.22}$$

- To determine the number of unique or distinguishable combinations (where order does not matter), we need to divide our number of distinguishable <u>sequences</u> by the number of sequences that produce indistinguishable <u>combinations</u>:

$$W = \frac{60}{6} = 10 \tag{4.5.23}$$

$$W = \frac{_5P_3}{3!} = \frac{\frac{5!}{(5-3)!}}{3!} = \frac{5!}{(5-3)!3!} = \frac{5!}{2!3!} = 10 \tag{4.5.24}$$

- The general equation for this ***combination without repetition***, which is referred to as "N, choose r" (or in our case "5 ice cream flavors, choose 3") is:

$$W = \,_NC_r = \binom{N}{r} = \frac{_NP_r}{r!} = \frac{N!}{(N-r)!r!} \tag{4.5.25}$$

where $_NC_r$ and $\binom{N}{r}$ are common notations for combination without repetition.

Combinations with repetition

Instead of always doing three different scoops, how many different combinations are possible if you do include ***repetitions*** (i.e. combinations with more than one scoop of a particular flavor)?

- This concept is called ***combination with repetition*** or ***combination with replacement***. In this case, it's easier to think about as ***replacement***.

Let's list our five flavors of ice cream again:

Available Flavors	Scoops in Bowl
CC, M, S, DC, B	

Assume we choose B for the first scoop. However, unlike before, after B has been taken from the available flavors, we will ***replace*** it with another B, leaving the selection options the same:

Available Flavors	Scoops in Bowl
CC, M, S, DC, ~~B~~, B	B

We choose a second scoop of B next, replacing it again with another B:

Available Flavors	Scoops in Bowl
CC, M, S, DC, ~~B~~, ~~B~~, B	B, B

Lastly, we choose DC for the last scoop:

Available Flavors	Scoops in Bowl
CC, M, S, ~~DC~~, ~~B~~, ~~B~~, B	B, B, DC

- What you can see is that, if you have ***repetition*** or ***replacements***, you do not end up with "5, choose 3." Instead, because of the replacements after the first two scoops, you had 7 total available choices during the selection process, making "7, choose 3."

$$W = \,_7C_3 = \frac{7!}{4!3!} = 35 \tag{4.5.26}$$

- In considering this more generally, hopefully you can recognize that, regardless of whatever number of $N_initial$ options you started with, if you allow replacements, you will end up adding $(r-1)$ additional options (one fewer then the number of

selections) by your final choice. Your final number of available options, therefore, becomes:

$$N_{\text{final}} = N_{\text{initial}} + (r-1) \tag{4.5.27}$$

We can take this expression for the final number of available choices and substitute it into the combination formula from the previous example:

$$_NC_r = \frac{N!}{(N-r)!r!} = \frac{N_{\text{final}}!}{(N_{\text{final}}-r)!r!} = \frac{(N_{\text{initial}}+(r-1))!}{(N_{\text{initial}}+(r-1)-r)!r!} = \frac{(N_{\text{initial}}+(r-1))!}{(N_{\text{initial}}-1)!r!} \tag{4.5.28}$$

We can rearrange this equation as:

$$\left(\binom{N}{r}\right) = \frac{((N_{\text{initial}}-1)+r)!}{(N_{\text{initial}}-1)!r!} \tag{4.5.29}$$

where the notation $\left(\binom{N}{r}\right)$ is used to denote a combination with replacement and is called "N, multichoose r."

- This new expression resembles a permutation for two items with indistinguishable outcomes: there are $(N_{\text{initial}}-1)$ indistinguishable outcomes of one item and r of the other. This is from where the line/dot representation comes.

We will develop the system as having $(N_{\text{initial}}-1)$ lines and r dots. Therefore, for our 5 ice cream flavors and 3 scoops, we will use 4 lines and 3 dots:

$$W = \frac{(4+3)!}{4!3!} = 35 \tag{4.5.30}$$

- While this equation gives the correct answer, it may still seem strange to recast the problem in this way. Let's look at it one more time: pretend you had an ice cream scooping machine, and you gave this machine instructions in a code of lines and dots. Each dot represents one scoop of ice cream, and each line separates (or partitions) one flavor from another. In order to communicate the combination of {B, B, DC} to the machine, you send the following code (remembering that order does not matter):

If you wanted {CC, M, DC}, it would be:

And if you wanted all CC:

To demonstrate that the line/dot method works generally, recognize that, for N_{initial} options, there will always be $(N_{\text{initial}}-1)$ lines needed to separate them from one another. For r choices, you will always need a total of r dots, one for each choice. It works to use three dots placed among four lines that separate the five flavors!

Therefore, the "N, multichoose r" combination with replacement equation is equal to the permutation equation for $(N_{\text{initial}}-1)$ lines and r dots, where the lines and dots are indistinguishable:

$$\left(\binom{N}{r}\right) = _{N-1}P_r = \frac{((N-1)+r)!}{(N-1)!r!} \tag{4.5.31}$$

5: Fundamental 4 - Heat Transfer

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5.1: Energy Basics

Chemical changes and their accompanying changes in energy are important parts of our everyday world (Figure 5.1.1). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.

(a)   (b)   (c)

Figure 5.1.1: The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by "Pink Sherbet Photography"/Flickr; credit b: modification of work by Jeffery Turner).

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world's energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called thermochemistry. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. Food scientists use them to determine the energy content of foods. Biologists study the energetics of living organisms, such as the metabolic combustion of sugar into carbon dioxide and water. The oil, gas, and transportation industries, renewable energy providers, and many others endeavor to find better methods to produce energy for our commercial and personal needs. Engineers strive to improve energy efficiency, find better ways to heat and cool our homes, refrigerate our food and drinks, and meet the energy and cooling needs of computers and electronics, among other applications. Understanding thermochemical principles is essential for chemists, physicists, biologists, geologists, every type of engineer, and just about anyone who studies or does any kind of science.

Energy

Energy can be defined as the capacity to supply heat or do work. One type of work (w) is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against the opposing force of the air surrounding the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: potential energy, the energy an object has because of its relative position, composition, or condition, and kinetic energy, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure 5.1.2). A battery has potential energy because the chemicals within it can produce electricity that can do work.

(a)   (b)
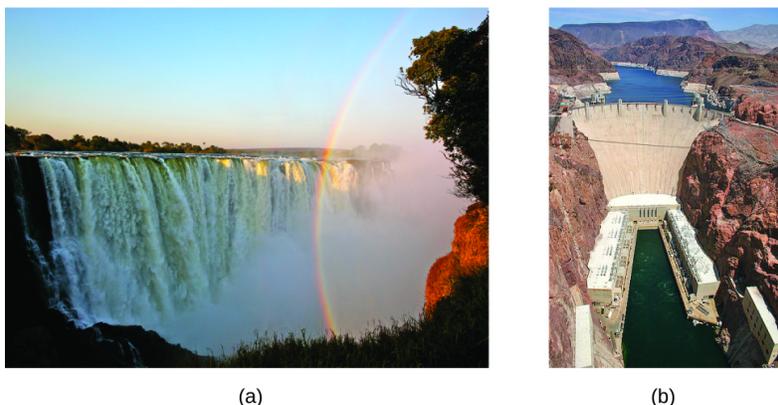
Figure 5.1.2: (a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons).

Two pictures are shown and labeled a and b. Picture a shows a large waterfall with water falling from a high elevation at the top of the falls to a lower elevation. The second picture is a view looking down into the Hoover Dam. Water is shown behind the high wall of the dam on one side and at the base of the dam on the other.

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry. To encompass both chemical and nuclear changes, we combine these laws into one statement: The total quantity of matter and energy in the universe is fixed.

Thermal Energy, Temperature, and Heat

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of "hot" or "cold." When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is "hot." When the atoms and molecules are moving slowly, they have lower KE, and we say that the object is "cold" (Figure 5.1.3). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

Hot water
(a)
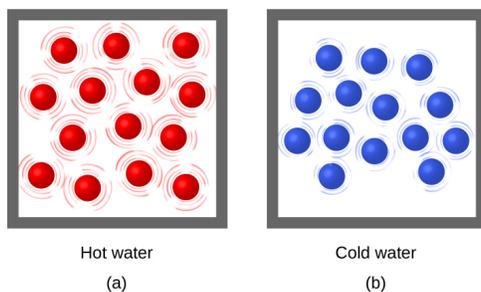
Cold water
(b)

Figure 5.1.3: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Two molecular drawings are shown and labeled a and b. Drawing a is a box containing fourteen red spheres that are surrounded by lines indicating that the particles are moving rapidly. This drawing has a label that reads "Hot water." Drawing b depicts another box of equal size that also contains fourteen spheres, but these are blue. They are all surrounded by smaller lines that depict some particle motion, but not as much as in drawing a. This drawing has a label that reads "Cold water."

States of Matter: Bas
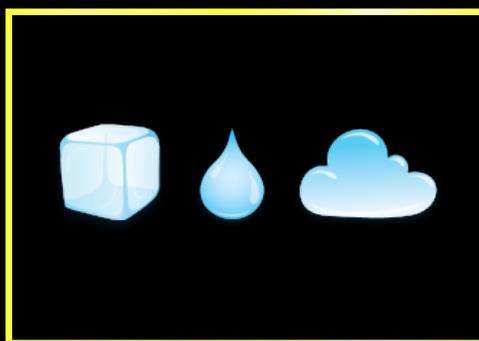
States
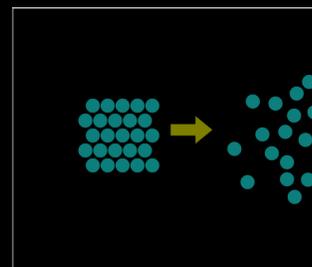
Phase Change

Measuring Energy and Heat Capacity

Historically, energy was measured in units of calories (cal). A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A joule (J) is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m^2/s^2, which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

We now introduce two concepts useful in describing heat flow and temperature change. The heat capacity (C) of a body of matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin)

$$C = \frac{q}{\Delta T} \tag{5.1.1}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an extensive property—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,150 J of energy to raise the temperature of the pan by 50.0 °C

$$C_{\text{small pan}} = \frac{18,140 \text{ J}}{50.0 \text{ }^\circ\text{C}} = 363 \text{ J/}^\circ\text{C} \tag{5.1.2}$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a (proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

$$C_{\text{large pan}} = \frac{90,700 \text{ J}}{50.0 \text{ }^\circ\text{C}} = 1814 \text{ J/}^\circ\text{C} \tag{5.1.3}$$

The specific heat capacity (c) of a substance, commonly called its "specific heat," is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

$$c = \frac{q}{m\Delta T} \tag{5.1.4}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

$$c_{\text{iron}} = \frac{18,140 \text{ J}}{(808 \text{ g})(50.0 \text{ }^\circ\text{C})} = 0.449 \text{ J/g }^\circ\text{C} \tag{5.1.5}$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

$$c_{\text{iron}} = \frac{90,700 \text{ J}}{(4,040 \text{ g})(50.0 \text{ }^\circ\text{C})} = 0.449 \text{ J/g }^\circ\text{C} \tag{5.1.6}$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure 5.1.7).

Figure 5.1.7: Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser).

The picture shows two black metal frying pans sitting on a flat surface. The left pan is about half the size of the right pan.

Liquid water has a relatively high specific heat (about 4.2 J/g °C); most metals have much lower specific heats (usually less than 1 J/g °C). The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in Table 5.1.1.

Table 5.1.1: Specific Heats of Common Substances at 25 °C and 1 bar

Substance	Symbol (state)	Specific Heat (J/g °C)
helium	He(g)	5.193
water	H$_2$O(l)	4.184
ethanol	C$_2$H$_6$O(l)	2.376
ice	H$_2$O(s)	2.093 (at −10 °C)
water vapor	H$_2$O(g)	1.864
nitrogen	N$_2$(g)	1.040
air		1.007
oxygen	O$_2$(g)	0.918
aluminum	Al(s)	0.897
carbon dioxide	CO$_2$(g)	0.853
argon	Ar(g)	0.522
iron	Fe(s)	0.449
copper	Cu(s)	0.385
lead	Pb(s)	0.130
gold	Au(s)	0.129
silicon	Si(s)	0.712

If we know the mass of a substance and its specific heat, we can determine the amount of heat, q, entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost:

$$q = (\text{specific heat}) \times (\text{mass of substance}) \times (\text{temperature change})$$
$$q = c \times m \times \Delta T$$
$$= c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

In this equation, c is the specific heat of the substance, m is its mass, and ΔT (which is read "delta T") is the temperature change, $T_{\text{final}} - T_{\text{initial}}$. If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial

temperature, $T_{\text{final}} - T_{\text{initial}}$ has a positive value, and the value of q is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a negative value, and the value of q is negative.

✔ **Example 5.1.1: Measuring Heat**

A flask containing 8.0×10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 800 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need 800 times as much to heat 800 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need 64 times as much to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using the equation:

$$\begin{aligned}
q &= c \times m \times \Delta T \\
&= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \\
&= (4.184 \text{ J}/\cancel{g} \, ^\circ\text{C}) \times (800 \ \cancel{g}) \times (85 - 21)\, ^\circ\text{C} \\
&= (4.184 \text{ J}/\cancel{g} \, ^\circ \cancel{C}) \times (800 \ \cancel{g}) \times (64)^\circ \, \cancel{C} \\
&= 210,000 \text{ J} (= 210 \text{ kJ})
\end{aligned}$$

Because the temperature increased, the water absorbed heat and q is positive.

? **Exercise 5.1.1**

How much heat, in joules, must be added to a 5.00×10^2 g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.451 J/g °C.

Answer

5.05×10^4 J

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

✔ **Example 5.1.2: Determining Other Quantities**

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C. Determine the specific heat of this metal (which might provide a clue to its identity).

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship:

$$\begin{aligned}
q &= c \times m \times \Delta T \\
&= c \times m \times (T_{\text{final}} - T_{\text{initial}})
\end{aligned}$$

Substituting the known values:

$$6,640 \text{ J} = c \times (348 \text{ g}) \times (43.6 - 22.4) \ ^{\circ}\text{C}$$

Solving:

$$c = \frac{6,640 \text{ J}}{(348 \text{ g}) \times (21.2 \,^{\circ}\text{C})} = 0.900 \text{ J/g} \ ^{\circ}\text{C}$$

Comparing this value with the values in Table 5.1.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

> **? Exercise 5.1.2**
>
> A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C. Determine the specific heat of this metal, and predict its identity.
>
> **Answer**
>
> $c = 0.45 \text{ J/g} \ ^{\circ}\text{C}$; the metal is likely to be iron from checking Table 5.1.1.

Solar Thermal Energy Power Plants

The sunlight that reaches the earth contains thousands of times more energy than we presently capture. Solar thermal systems provide one possible solution to the problem of converting energy from the sun into energy we can use. Large-scale solar thermal plants have different design specifics, but all concentrate sunlight to heat some substance; the heat "stored" in that substance is then converted into electricity.

The Solana Generating Station in Arizona's Sonora Desert produces 280 megawatts of electrical power. It uses parabolic mirrors that focus sunlight on pipes filled with a heat transfer fluid (HTF) (Figure 5.1.8). The HTF then does two things: It turns water into steam, which spins turbines, which in turn produces electricity, and it melts and heats a mixture of salts, which functions as a thermal energy storage system. After the sun goes down, the molten salt mixture can then release enough of its stored heat to produce steam to run the turbines for 6 hours. Molten salts are used because they possess a number of beneficial properties, including high heat capacities and thermal conductivities.

(a)   (b)
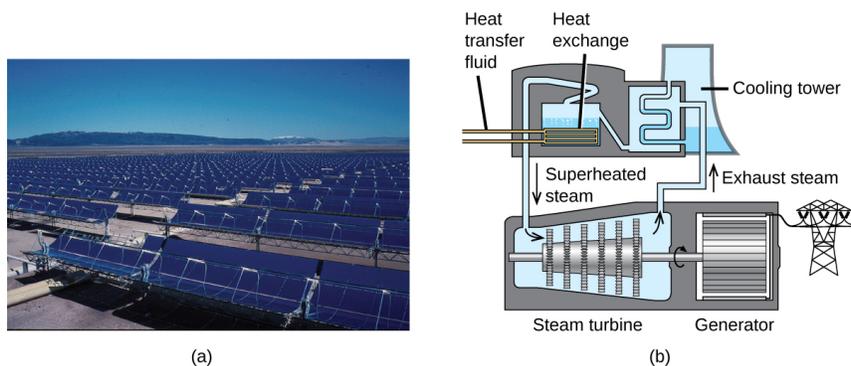
Figure 5.1.8: This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land Management)

This figure has two parts labeled a and b. Part a shows rows and rows of trough mirrors. Part b shows how a solar thermal plant works. Heat transfer fluid enters a tank via pipes. The tank contains water which is heated. As the heat is exchanged from the pipes to the water, the water becomes steam. The steam travels to a steam turbine. The steam turbine begins to turn which powers a generator. Exhaust steam exits the steam turbine and enters a cooling tower.

The 377-megawatt Ivanpah Solar Generating System, located in the Mojave Desert in California, is the largest solar thermal power plant in the world (Figure 5.1.9). Its 170,000 mirrors focus huge amounts of sunlight on three water-filled towers, producing steam at over 538 °C that drives electricity-producing turbines. It produces enough energy to power 140,000 homes. Water is used as the working fluid because of its large heat capacity and heat of vaporization.

<div align="center">(a)   (b)</div>

Figure 5.1.9: (a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border. (credit a: modification of work by Craig Dietrich; credit b: modification of work by "USFWS Pacific Southwest Region"/Flickr)

Two pictures are shown and labeled a and b. Picture a shows a thermal plant with three tall metal towers. Picture b is an arial picture of the mirrors used at the plant. They are arranged in rows.

Summary

Energy is the capacity to do work (applying a force to move matter). Kinetic energy (KE) is the energy of motion; potential energy is energy due to relative position, composition, or condition. When energy is converted from one form into another, energy is neither created nor destroyed (law of conservation of energy or first law of thermodynamics). Matter has thermal energy due to the KE of its molecules and temperature that corresponds to the average KE of its molecules. Heat is energy that is transferred between objects at different temperatures; it flows from a high to a low temperature. Chemical and physical processes can absorb heat (endothermic) or release heat (exothermic). The SI unit of energy, heat, and work is the joule (J). Specific heat and heat capacity are measures of the energy needed to change the temperature of a substance or object. The amount of heat absorbed or released by a substance depends directly on the type of substance, its mass, and the temperature change it undergoes.

Key Equations

- $q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$

Glossary

calorie (cal)

unit of heat or other energy; the amount of energy required to raise 1 gram of water by 1 degree Celsius; 1 cal is defined as 4.184 J

endothermic process

chemical reaction or physical change that absorbs heat

energy

capacity to supply heat or do work

exothermic process

chemical reaction or physical change that releases heat

heat (q)

transfer of thermal energy between two bodies

heat capacity (C)

extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

joule (J)

SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second, 1 J = 1 kg m^2/s and 4.184 J = 1 cal

kinetic energy

energy of a moving body, in joules, equal to $\frac{1}{2}mv^2$ (where m = mass and v = velocity)

potential energy

energy of a particle or system of particles derived from relative position, composition, or condition

specific heat capacity (c)

intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

temperature

intensive property of matter that is a quantitative measure of "hotness" and "coldness"

thermal energy

kinetic energy associated with the random motion of atoms and molecules

thermochemistry

study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

work (w)

energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

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CHAPTER OVERVIEW

6: Fundamental 5 - Entropy

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6.1: Entropy

Learning Objectives

- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (Figure 6.1.2) published the results of an extensive study regarding the efficiency of steam heat engines. In a later review of Carnot's findings, Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (T). The term reversible process refers to a process that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be "reversed") by an infinitesimally small change is some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.
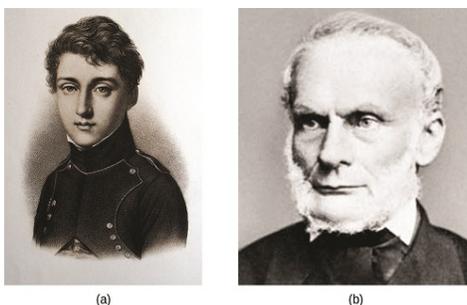
Figure 6.1.1: (a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, and so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property entropy (S) and defined its change for any process as the following:

$$\Delta S = \frac{q_{rev}}{T} \tag{6.1.1}$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the number of *microstates* possible for the system. A microstate is a specific configuration of the locations and energies of the atoms or molecules that comprise a system like the following:

$$S = k \ln W \tag{6.1.2}$$

Here k is the Boltzmann constant and has a value of $1.38 \times 10^{-23} \, J/K$ and W is the microscopic multiplicity.

As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

$$\begin{aligned}
\Delta S &= S_f - S_i \\
&= k \ln W_f - k \ln W_i \\
&= k \ln \frac{W_f}{W_i}
\end{aligned} \tag{6.1.3}$$

For processes involving an increase in the number of microstates of the system, $W_f > W_i$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates in the system, $W_f < W_i$, yield a decrease in system entropy, $\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.
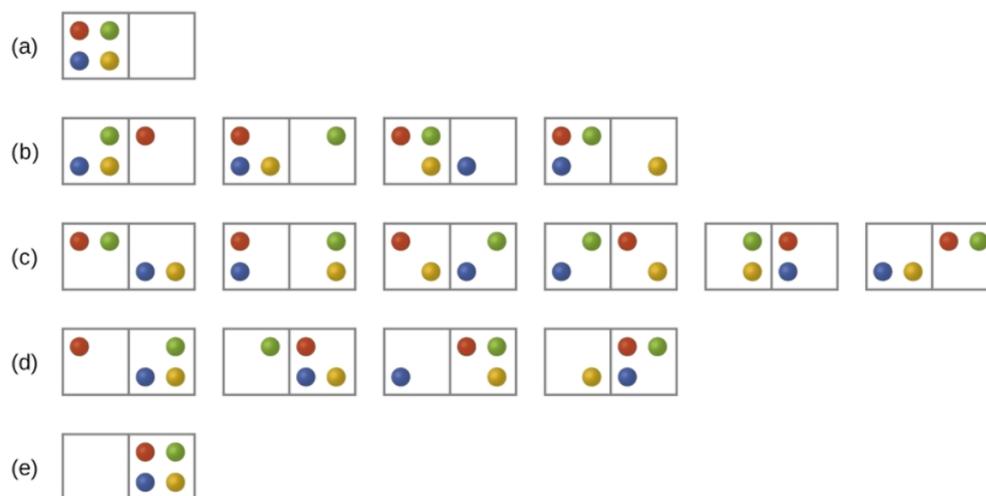
Figure 6.1.2: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

Consider the general case of a system comprised of N particles distributed among n boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in $2^4 = 16$ different microstates as illustrated in Figure 6.1.2. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions* (sometimes called macrostates or configurations). The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is

$$\frac{6}{16} = \frac{3}{8} \tag{6.1.4}$$

The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of

$$\frac{1}{16} \tag{6.1.5}$$

The probability of finding all particles in only one box (either the left box or right box) is then

$$\left(\frac{1}{16} + \frac{1}{16}\right) = \frac{2}{16} = \frac{1}{8} \tag{6.1.6}$$

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

> *The most probable distribution is therefore the one of greatest entropy.*

The previous description of an ideal gas expanding into a vacuum is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. The spontaneous process whereby the gas contained initially in one flask expands to fill both flasks equally therefore yields an increase in entropy for the system.
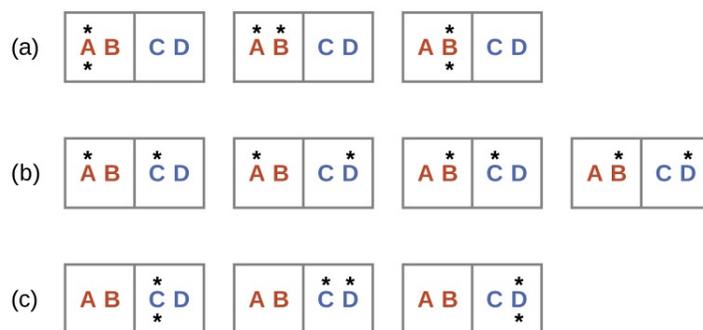
Figure 6.1.3: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of energy (represented as "*") in Figure 6.1.3. The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. And so, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. As for the previous example of matter dispersal, extrapolating this treatment to macroscopic collections of particles dramatically increases the probability of the uniform distribution relative to the other distributions. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects' temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

Example 6.1.1: Determination of ΔS

Consider the system shown here. What is the change in entropy for a process that converts the system from distribution (a) to (c)?
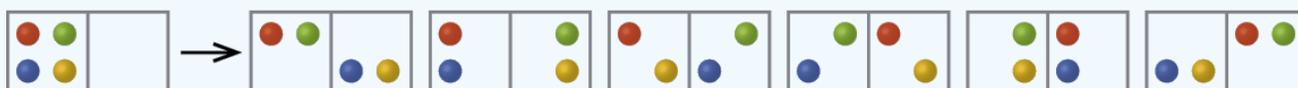
Solution

We are interested in the following change:

The initial number of microstates is one, the final six:

$$\Delta S = k \ln \frac{W_c}{W_a}$$

$$= 1.38 \times 10^{-23} \ J/K \times \ln \frac{6}{1}$$

$$= 2.47 \times 10^{-23} \ J/K$$

The sign of this result is consistent with expectation; since there are more microstates possible for the final state than for the initial state, the change in entropy should be positive.

> ### Exercise 6.1.1
>
> Consider the system shown in Figure 6.1.3. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?
>
> **Answer**
>
>   0 J/K

Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure 6.1.4. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{liquid} > S_{solid}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.
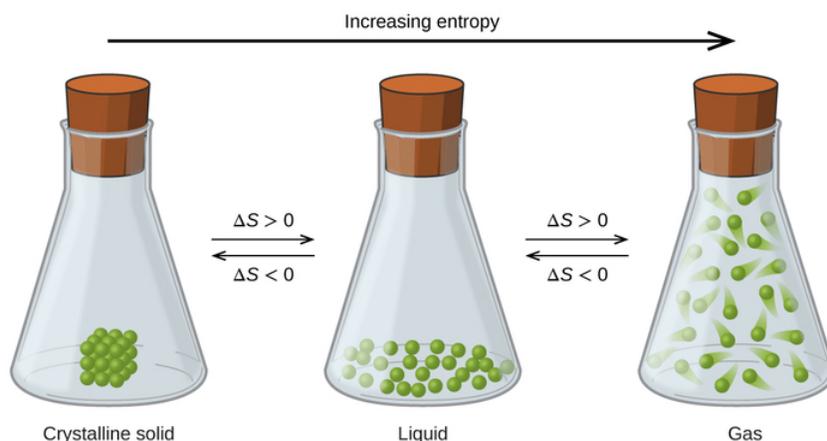
Figure 6.1.4: The entropy of a substance increases (ΔS > 0) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases (ΔS < 0) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the vapor or gas phase. The atoms or molecules occupy a *much* greater volume than in the liquid phase; therefore each atom or molecule can be found in many more locations than in the liquid (or solid) phase. Consequently, for any substance, $S_{gas} > S_{liquid} > S_{solid}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (Figure 6.1.5).
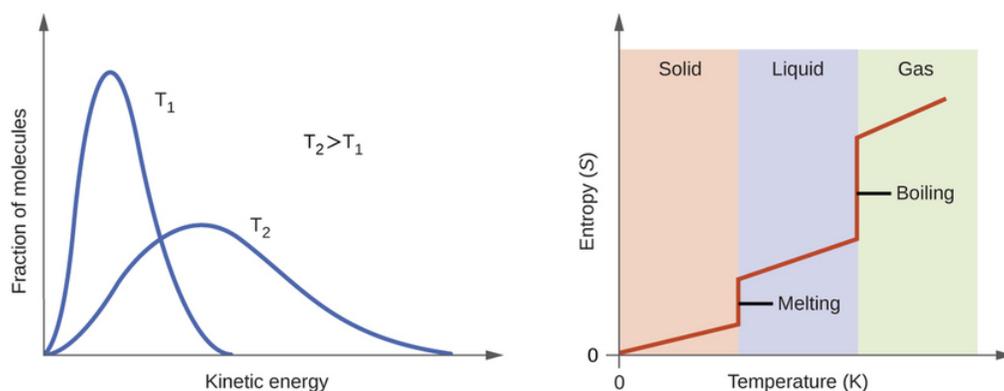
Figure 6.1.5: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.

The entropy of a substance is influenced by structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle's mass and the spacing of quantized translational energy levels (which is a topic beyond the scope of our treatment). For molecules, greater numbers of atoms (regardless of their masses) increase the ways in which the molecules can vibrate and thus the number of possible microstates and the system entropy.

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in Example .

Example 6.1.2: Predicting the Sign of ΔS

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

a. One mole liquid water at room temperature $\longrightarrow$ one mole liquid water at 50 °C
b. $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
c. $C_6H_6(l) + \dfrac{15}{2}O_2(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(l)$
d. $NH_3(s) \longrightarrow NH_3(l)$

Solution

a. positive, temperature increases
b. negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter
c. negative, net decrease in the amount of gaseous species
d. positive, phase transition from solid to liquid, net increase in dispersal of matter

Exercise 6.1.2

Predict the sign of the enthalpy change for the following processes. Give a reason for your prediction.

a. $NaNO_3(s) \longrightarrow Na^+(aq) + NO_3^-(aq)$
b. the freezing of liquid water
c. $CO_2(s) \longrightarrow CO_2(g)$
d. $CaCO(s) \longrightarrow CaO(s) + CO_2(g)$

Answer a

Positive; The solid dissolves to give an increase of mobile ions in solution.

Answer b

Negative; The liquid becomes a more ordered solid.

Answer c

Positive; The relatively ordered solid becomes a gas

Answer d

Positive; There is a net production of one mole of gas.

Contributors and Attributions

Summary

Entropy (S) is a state function that can be related to the number of microstates for a system (the number of ways the system can be arranged) and to the ratio of reversible heat to kelvin temperature. It may be interpreted as a measure of the dispersal or distribution of matter and/or energy in a system, and it is often described as representing the "disorder" of the system. For a given substance, $S_{solid} < S_{liquid} \ll S_{gas}$ in a given physical state at a given temperature, entropy is typically greater for heavier atoms or more complex molecules. Entropy increases when a system is heated and when solutions form. Using these guidelines, the sign of entropy changes for some chemical reactions may be reliably predicted.

Key Equations

- $\Delta S = \dfrac{q_{\text{rev}}}{T}$
- $S = k \ln W$
- $\Delta S = k \ln \dfrac{W_{\text{f}}}{W_{\text{i}}}$

Glossary

entropy (S)

state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates often described as a measure of the disorder of the system

microstate (W)

possible configuration or arrangement of matter and energy within a system

reversible process

process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes removed

Contributors and Attributions

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7: Extension 5 - Temperature

7.1: The Molecular Basis for Understanding Simple Entropy Change

Quantization of the motional energy of molecules

Early in their discussion of kinetic-molecular theory, most general chemistry texts have a Figure of the greatly increased distribution of molecular speeds at higher temperatures in gases than at moderate temperatures.
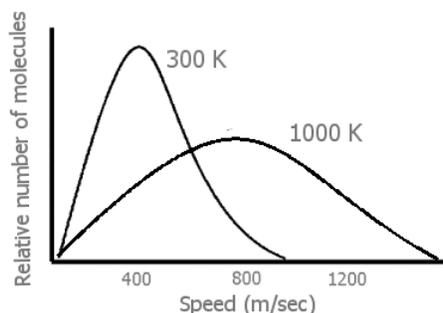

Figure $7.1.1$: Generalized plot of molecules at 300 K vs. 1000K (100m/sec = 224mph) Heavier molecules have broader peaks at both temperatures.

When the temperature of a gas is raised (by transfer of energy from the surroundings of the system), there is a great increase in the velocity, v, of many of the gas molecules (Figure $7.1.1$). From 1/2mv^2, this means that there has also been a great increase in the translational *energies* of those faster moving molecules. Finally, we can see that an input of energy not only causes the gas molecules in the system to move faster — but also to move at very many *different* fast speeds. (Thus, the energy in a heated system is more dispersed, spread out in being in many separate speeds rather than more localized in fewer moderate speeds.)

A symbolic indication of the different distributions of the translational energy of each molecule of a gas on low to high energy levels in a 36-molecule system is in Figure $7.1.2$, with the lower temperature gas as Figure $7.1.2A$ and the higher temperature gas as Figure $7.1.2B$.
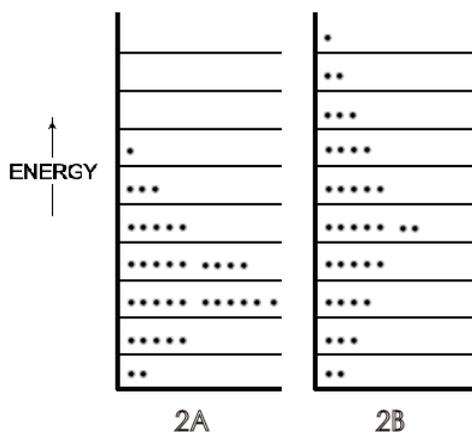
Figure $7.1.2$: [2A] is a distribution of gas molecules on specific energy levels at 300 K and [2B] is the same group of gas molecules on energy levels at 1000 K.

These and later Figures in this section are symbolic because, in actuality, this small number of molecules is not enough to exhibit thermodynamic temperature. For further simplification, rotational energies that range from zero in monatomic molecules to about half the total translational energy of di- and tri-atomic molecules (and more for most polyatomic) at 300 K are not shown in the Figures. If those rotational energies were included, they would constitute a set of energy levels (corresponding to a spacing of ~10^{-23} J) each with translational energy distributions of the 36 molecules (corresponding to a spacing of ~10^{-37} J). These numbers show why translational levels, though quantized, are considered virtually continuous compared to the separation of rotational energies. The details of vibrational energy levels — two at moderate temperatures (on the ground state of which would be almost all the rotational and translational levels populated by the molecules of a symbolic or real system) — can also be postponed until physical chemistry. At this point in the first year course, depending on the instructor's preference, only a verbal description of rotational and vibrational motions and energy level spacing need be introduced.

By the time in the beginning course that students reach thermodynamics, five to fifteen chapters later than kinetic theory, they can accept the concept that the total motional energies of molecules includes not just translational but also rotational and vibrational movements (that can be sketched simply below).
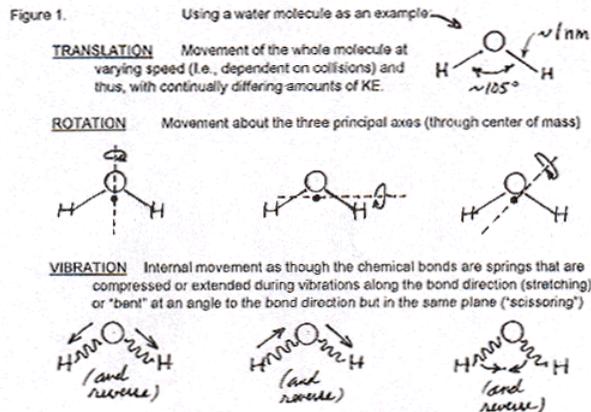

Figure 7.1.2A and 7.1.2B can be viewed as prototypes of more complex diagrams of molecular energies on specific levels, with additional higher energy levels populated (as well as prior higher energy levels more populated) when the temperature of a system is raised. Further, students can sense that, at the same temperature as in gases, molecules in liquids move, and rotate, and vibrate internally with the same total energy, but just do not travel as far before colliding.

A microstate is one of many arrangements of the molecular energies (i.e., 'the molecules on each particular energy level') for the total energy of a system. Thus, Figure 7.1.2A is one microstate for a system with a given energy and Figure 7.1.1B is a microstate of the same system but with a greater total energy. Figure 7.1.3A (just a repeat of Figure 7.1.2A, for convenience) is a different microstate than the microstate for the same system shown in Figure 7.1.3B; the total energy is the same in 7.1.3A and 7.1.3B, but in Figure 7.1.3B the arrangement of energies has been changed because two molecules have changed their energy levels, as indicated by the arrows.
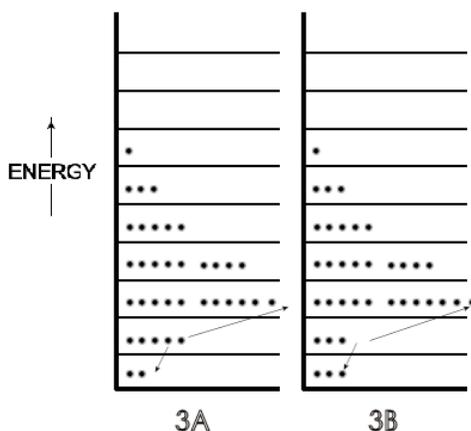
Figure 7.1.3: [3A] is the same as [2A], one microstate of molecules at 300 K. [3B] is a different microstate than [3A] of the same system of 300 K molecules — the same total energy but two molecules in [3B] having different energies than they had in the arrangement of [3A], as indicated by the arrows.

A possible scenario for that different microstate in Figure 7.1.3 is that these two molecules on the second energy level collided at a glancing angle such that one gained enough energy to be on the third energy level, while the other molecule lost the same amount of energy and dropped down to the lowest energy level. In the light of that result of a single collision and the billions of collisions of molecules per second in any system at room temperature, there can be a very large number of microstates even for this system of just 36 molecules in Figures 7.1.2 and 7.1.3. (This is true despite the fact that not every collision would change the energy of the two molecules involved, and thus not change the numbers on a given energy level. Glancing collisions could occur with no change in the energy of either participant.) For any real system involving 6 x 10^{23} molecules, however, the number of microstates becomes humanly incomprehensible for any system, even though we can express it in numbers, as will now be developed.

The quantitative entropy change in a reversible process is given by

$$\Delta S = \frac{q_{rev}}{T} \tag{7.1.1}$$

(Irreversible processes involving temperature or volume change or mixing can be treated by calculations from incremental steps that are reversible.) According to the Boltzmann entropy relationship,

$$\Delta S = k \ln \frac{W_{Final}}{W_{Initial}} \tag{7.1.2}$$

where k is Boltzmann's constant and W_{Final} or $W_{Initial}$ is the count of how many microstates correspond to the Final or Initial macrostates, respectively.

The number of microstates for a system determines the number of ways in any one of which that the total energy of a macrostate can be at one instant. Thus, an increase in entropy means a greater number of microstates for the Final state than for the Initial. In turn, this means that there are more choices for the arrangement of a system's total energy at any one instant, far less possibility of localization (such as cycling back and forth between just 2 microstates), i.e., greater dispersal of the total energy of a system because of so many possibilities.

> *An increase in entropy means a greater number of microstates for the Final state than for the Initial. In turn, this means that there are more choices for the arrangement of a system's total energy at any one instant.*

Delocalization vs. Dispersal

Some instructors may prefer "delocalization" to describe the status of the total energy of a system when there are a greater number of microstates rather than fewer, as an exact synonym for "dispersal" of energy as used here in this article for other situations in chemical thermodynamics. The advantage of uniform use of 'dispersal' is its correct common-meaning applicability to examples ranging from motional energy becoming literally spread out in a larger volume to the cases of thermal energy transfer from hot surroundings to a cooler system, as well as to distributions of molecular energies on energy levels for either of those general cases. Students of lesser ability should be able to grasp what 'dispersal' means in three dimensions, even though the next steps of abstraction to what it means in energy levels and numbers of microstates may result in more of a 'feeling' than a preparation for physical chemistry that it can be for the more able.

Of course, dispersal of the energy of a system in terms of microstates does **not** mean that the energy is smeared or spread out over microstates like peanut butter on bread! All the energy of the macrostate is always in only *one* microstate at one instant. It is the possibility that the total energy of the macrostate can be in *any one* of so many more different arrangements of that energy at the next instant — an increased probability that it could not be localized by returning to the same microstate — that amounts to a greater dispersal or spreading out of energy when there are a larger number of microstates

(The numbers of microstates for chemical systems above 0 K are astounding. For any substance at a temperature about 1-4 K, there are $10^{26,000,000,000,000,000,000}$ microstates (*5*). For a mole of water at 273.15 K, there are $10^{2,000,000,000,000,000,000,000}$ microstates and when it is heated to be just one degree warmer, that number is increased 10^{22} *times* to $10^{2,010,000,000,000,000,000,000}$ microstates. For comparison, an estimate of the number of atoms in the entire universe is 'only' about 10^{70}, while a googol, considered a large number in mathematics, is `only' 10^{100}.)

Summarizing, when a substance is heated, its entropy increases because the energy acquired and that previously within it can be far more dispersed on the previous higher energy levels and on those additional high energy levels that now can be occupied. This in turn means that there are many many more possible *arrangements* of the molecular energies on their energy levels than before and thus, there is a great increase in accessible *microstates* for the system at higher temperatures. A concise statement would be that when a system is heated, there are many more microstates accessible and this amounts to greater delocalization or dispersal of its total energy. (The common comment "heating causes or favors molecular disorder" is an anthropomorphic labeling of molecular behavior that has more flaws than utility. There is virtual chaos, so far as the distribution of energy for a system (its number of microstates) is concerned, *before* as well as after heating at any temperature above 0 K and energy distribution is at the heart of the meaning of entropy and entropy change.) (*5*).

Contributors

- Frank L. Lambert, Professor Emeritus, Occidental College

8: Fundamental 6 - Work

8.1: Work

> ## Learning Objectives
>
> - To know the relationship between energy, work, and heat.

One definition of energy is the capacity to do work. There are many kinds of work, including mechanical work, electrical work, and work against a gravitational or a magnetic field. Here we will consider only mechanical work and focus on the work done during changes in the pressure or the volume of a gas.

Mechanical Work

The easiest form of work to visualize is mechanical work (Figure 8.1.1), which is the energy required to move an object a distance d when opposed by a force F, such as gravity:

$$w = F\,d \tag{8.1.1}$$

with

- w is work
- F is opposing force
- d is distance
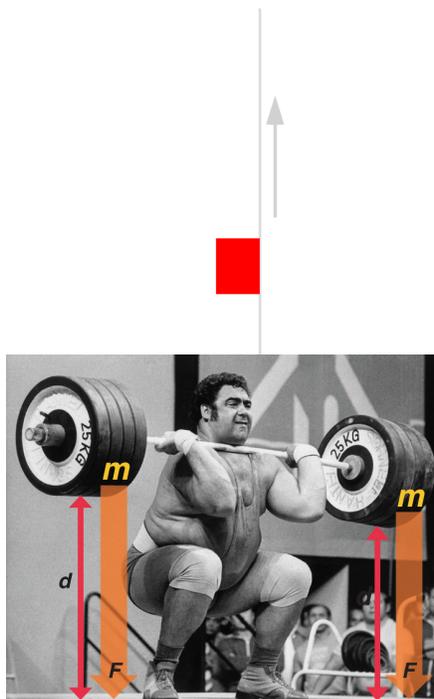
Figure 7.4.1: One form of energy is mechanical work, the energy required to move an object of mass m a distance d when opposed by a force F, such as gravity.

Because the force (F) that opposes the action is equal to the mass (m) of the object times its acceleration (a), Equation 8.1.1 can be rewritten to:

$$w = m\,a\,d \tag{8.1.2}$$

with

- w is work
- m is mass
- a is a acceleration, and
- d is distance

Recall from that weight is a force caused by the gravitational attraction between two masses, such as you and Earth. Hence for works against gravity (on Earth), a can be set to $g = 9.8 \ m/s^2$). Consider the mechanical work required for you to travel from the first floor of a building to the second. Whether you take an elevator or an escalator, trudge upstairs, or leap up the stairs two at a time, energy is expended to overcome the opposing force of gravity. The amount of work done (w) and thus the energy required depends on three things:

1. the height of the second floor (the distance \(d\));
2. your mass, which must be raised that distance against the downward acceleration due to gravity; and
3. your path.

Pressure-Volume (PV) Work

To describe this pressure–volume work (PV work), we will use such imaginary oddities as frictionless pistons, which involve no component of resistance, and ideal gases, which have no attractive or repulsive interactions. Imagine, for example, an ideal gas, confined by a frictionless piston, with internal pressure (P_{int}) and initial volume V_i (Figure 7.4.2). If $P_{ext} = P_{int}$, the system is at equilibrium; the piston does not move, and no work is done. If the external pressure on the piston (P_{ext}) is less than P_{int}, however, then the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings; that is, the final volume (V_f) will be greater than V_i. If $P_{ext} > P_{int}$, then the gas will be compressed, and the surroundings will perform work on the system.
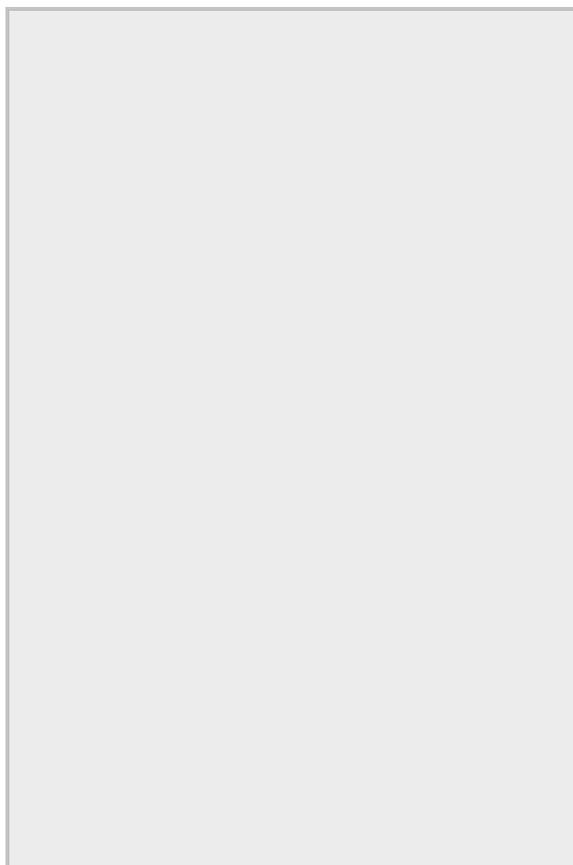
Figure 7.4.2: PV Work. Using a frictionless piston, if the external pressure is less than P_{int} (a), the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings. The final volume (V_f) will be greater than V_i. Alternatively, if the external pressure is greater than P_{int} (b), the gas will be compressed, and the surroundings will perform work on the system.

If the piston has cross-sectional area A, the external pressure exerted by the piston is, by definition, the force per unit area:

$$P_{ext} = \frac{F}{A} \tag{8.1.3}$$

The volume of any three-dimensional object with parallel sides (such as a cylinder) is the cross-sectional area times the height ($V = Ah$). Rearranging to give $F = P_{ext}A$ and defining the distance the piston moves (d) as Δh, we can calculate the magnitude of the work performed by the piston by substituting into Equation 7.4.1:

$$w = Fd = P_{ext}A\Delta h \tag{8.1.4}$$

The change in the volume of the cylinder (ΔV) as the piston moves a distance d is $\Delta V = A\Delta h$, as shown in Figure 7.4.3. The work performed is thus

$$w = P_{ext}\Delta V \tag{8.1.5}$$

The units of work obtained using this definition are correct for energy: pressure is force per unit area (newton/m^2) and volume has units of cubic meters, so

$$w = \left(\frac{F}{A}\right)_{ext}(\Delta V) = \frac{\text{newton}}{\text{m}^2} \times \text{m}^3 = \text{newton} \cdot \text{m} = \text{joule} \tag{8.1.6}$$
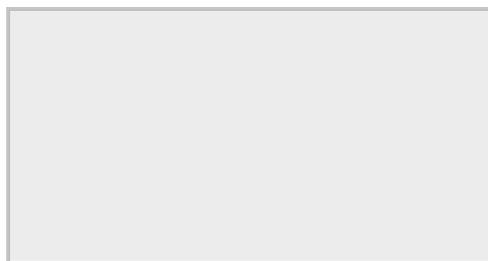
Figure 7.4.3: Work Performed with a change in volume. The change in the volume (ΔV) of the cylinder housing a piston is $\Delta V = A\Delta h$ as the piston moves. The work performed by the surroundings on the system as the piston moves inward is given by w = $P_{ext}\Delta V$.

If we use atmospheres for P and liters for V, we obtain units of L·atm for work. These units correspond to units of energy, as shown in the different values of the ideal gas constant R:

$$R = \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = \frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} \tag{8.1.7}$$

Thus 0.08206 L·atm = 8.314 J and 1 L·atm = 101.3 J.

Whether work is defined as having a positive sign or a negative sign is a matter of convention. Heat flow is defined from a system to its surroundings as negative; using that same sign convention, we define work done by a system on its surroundings as having a negative sign because it results in a transfer of energy from a system to its surroundings. This is an arbitrary convention and one that is not universally used. Some engineering disciplines are more interested in the work done on the surroundings than in the work done by the system and therefore use the opposite convention. Because $\Delta V > 0$ for an expansion, Equation 7.4.4 must be written with a negative sign to describe PV work done by the system as negative:

$$w = -P_{ext}\Delta V \tag{8.1.8}$$

The work done by a gas expanding against an external pressure is therefore negative, corresponding to work done by a system on its surroundings. Conversely, when a gas is compressed by an external pressure, $\Delta V < 0$ and the work is positive because work is being done on a system by its surroundings.

> ### Note: A Matter of Convention
> - Heat flow is defined from the system to its surroundings as **negative**
> - Work is defined as by the system on its surroundings as **negative**

Outside Links

- Gasparro, Frances P. "Remembering the sign conventions for q and w in deltaU = q - w." J. Chem. Educ. 1976: 53, 389.
- Koubek, E. "PV work demonstration (TD)." J. Chem. Educ. 1980: 57, 374. '

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8.2: Gas Expansion

In Gas Expansion, we assume Ideal behavior for the two types of expansions:

Isothermal Expansion
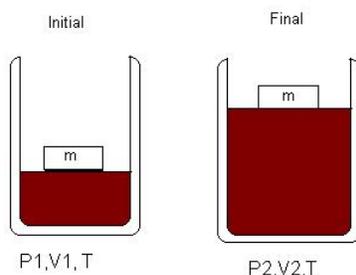
This shows the expansion of gas at constant temperature against weight of an object's mass (m) on the piston. Temperature is held constant, therefore the change in energy is zero (U=0). So, the heat absorbed by the gas equals the work done by the ideal gas on its surroundings. Enthalpy change is also equal to zero because the change in energy zero and the pressure and volume is constant.

Isothermal Irreversible/Reversible process
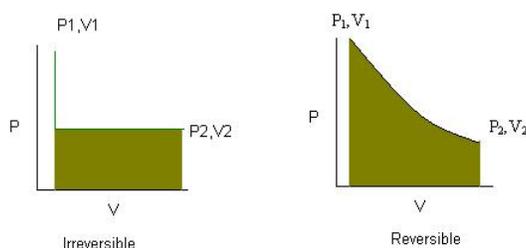
The graphs clearly show work done (area under the curve) is greater in a reversible process.

Adiabatic Expansions

Adiabatic means when no heat exchange occurs during expansion between system and surrounding and the temperature is no longer held constant.

Reversible Adiabatic Expansion

This equation shows the relationship between PV and is useful only when it applies to ideal gas and reversible adiabatic change. The equation is very similar to Boyle's law except it has exponent (gamma) due to change in temperature. The work done by an adiabatic reversible process is given by the following equation:

where T_2 is less than T_1. The internal energy of the system decreases as the gas expands. The work can be calculated in two ways because the Internal energy (U) does not depend on path. The graph shows that less work is done in an adiabatic reversible process than an Isothermal reversible process.
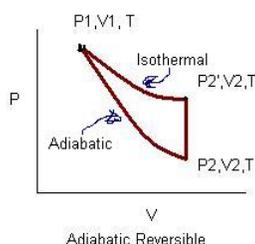
References

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

CHAPTER OVERVIEW

9: Fundamental 7 - Variable Changes

9.1: Partial Differentiation

The development of thermodynamics would have been unthinkable without calculus in more than one dimension (multivariate calculus) and partial differentiation is essential to the theory.

'Active' Variables

When applying partial differentiation it is very important to keep in mind, which symbol is the variable and which ones are the constants. Mathematicians usually write the variable as x or y and the constants as a, b or c but in Physical Chemistry the symbols are different. It sometimes helps to replace the symbols in your mind.

For example the van der Waals equation can be written as:

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2} \tag{9.1.1}$$

Suppose we must compute the partial differential

$$\left(\frac{\partial P}{\partial \overline{V}} \right)_T \tag{9.1.2}$$

In this case molar volume is the variable 'x' and the pressure is the function $f(x)$, the rest is just constants, so Equation 9.1.1 can be rewritten in the form

$$f(x) = \frac{c}{x - b} - \frac{a}{x^2} \tag{9.1.3}$$

When calculating

$$\left(\frac{\partial P}{\partial T} \right)_{\overline{V}} \tag{9.1.4}$$

should look at Equation 9.1.1 as:

$$f(x) = cx - d \tag{9.1.5}$$

The active variable 'x' is now the temperature T and all the rest is just constants. It is useful to train your eye to pick out the one active one from all the inactive ones. Use highlighters, underline, rewrite, do whatever helps you best.

9.2: Functions of Two Independent Variables

A (real) function of one variable, $y = f(x)$, defines a curve in the plane. The first derivative of a function of one variable can be interpreted graphically as the slope of a tangent line, and dynamically as the rate of change of the function with respect to the variable Figure 9.2.1.
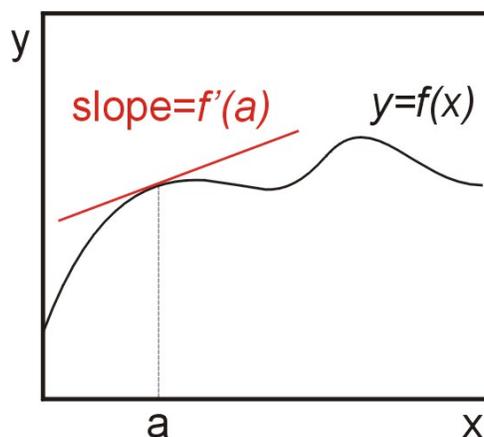
Figure 9.2.1: Geometric interpretation of a derivative. (CC BY-NC-SA; Marcia Levitus)

A function of two independent variables, $z = f(x, y)$, defines a surface in three-dimensional space. For a function of two or more variables, there are as many independent first derivatives as there are independent variables. For example, we can differentiate the function $z = f(x, y)$ with respect to x keeping y constant. This derivative represents the slope of the tangent line shown in Figure 9.2.2A. We can also take the derivative with respect to y keeping x constant, as shown in Figure 9.2.2B.
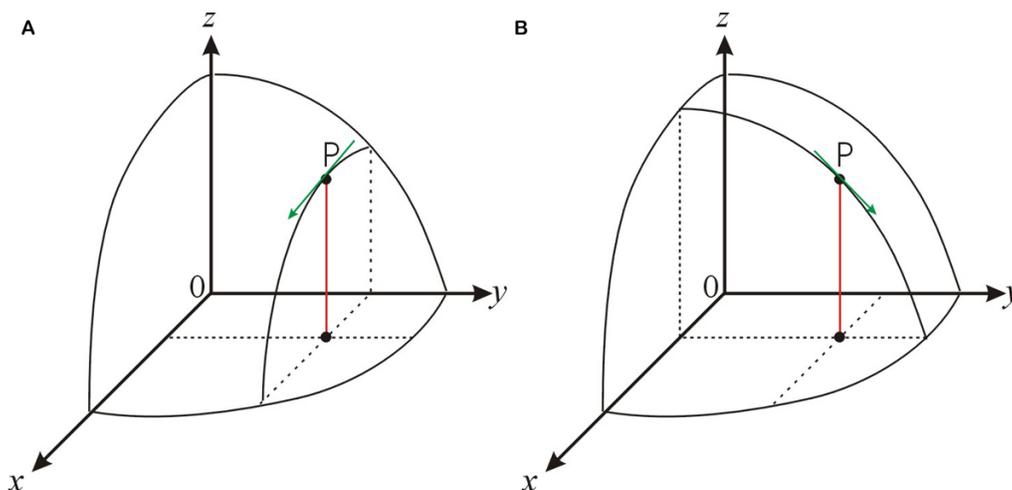
Figure 9.2.2: Geometric interpretation of a partial derivative. (CC BY-NC-SA; Marcia Levitus)

For example, let's consider the function $z = 3x^2 - y^2 + 2xy$. We can take the derivative of this function with respect to x treating y as a constant. The result is $6x + 2y$. This is the partial derivative of the function with respect to x, and it is written:

$$\left(\frac{\partial z}{\partial x} \right)_y = 6x + 2y$$

where the small subscripts indicate which variables are held constant. Analogously, the partial derivate of z with respect to y is:

$$\left(\frac{\partial z}{\partial y} \right)_x = 2x - 2y$$

We can extend these ideas to functions of more than two variables. For example, consider the function $f(x, y, z) = x^2 y / z$. We can differentiate the function with respect to x keeping y and z constant to obtain:

$$\left(\frac{\partial f}{\partial x} \right)_{y,z} = 2x\frac{y}{z}$$

We can also differentiate the function with respect to z keeping x and y constant:

$$\left(\frac{\partial f}{\partial z} \right)_{x,y} = -x^2 y/z^2$$

and differentiate the function with respect to y keeping x and z constant:

$$\left(\frac{\partial f}{\partial y} \right)_{x,z} = \frac{x^2}{z}$$

Functions of two or more variables can be differentiated partially more than once with respect to either variable while holding the other constant to yield second and higher derivatives. For example, the function $z = 3x^2 - y^2 + 2xy$ can be differentiated with respect to x two times to obtain:

$$\left(\frac{\partial}{\partial x} \left(\frac{\partial z}{\partial x} \right)_y \right)_y = \left(\frac{\partial^2 z}{\partial x^2} \right)_y = 6$$

We can also differentiate with respect to x first and y second:

$$\left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right)_y \right)_x = \left(\frac{\partial^2 f}{\partial y \partial x} \right) = 2$$

> Check the videos below if you are learning this for the first time, or if you feel you need to refresh the concept of partial derivatives.
>
> - Partial derivatives: http://patrickjmt.com/derivatives-finding-partial-derivatives (don't get confused by the different notation!)
> - Partial derivatives: http://www.youtube.com/watch?v=vxJR5graUfI
> - Higher order partial derivatives: http://www.youtube.com/watch?v=3itjTS2Y9oE

If a function of two or more variables and its derivatives are single-valued and continuous, a property normally attributed to physical variables, then the mixed partial second derivatives are equal (Euler reciprocity):

$$\left(\frac{\partial^2 f}{\partial x \partial y} \right) = \left(\frac{\partial^2 f}{\partial y \partial x} \right) \tag{9.2.1}$$

For example, for $z = 3x^2 - y^2 + 2xy$:

$$\left(\frac{\partial^2 f}{\partial y \partial x} \right) = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right)_y \right)_x = \left(\frac{\partial}{\partial y} (6x + 2y) \right)_x = 2$$

$$\left(\frac{\partial^2 f}{\partial x \partial y} \right) = \left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right)_x \right)_y = \left(\frac{\partial}{\partial x} (-2y + 2x) \right)_y = 2$$

Another useful property of the partial derivatives is the so-called reciprocal identity, which holds when the same variables are held constant in the two derivatives:

$$\left(\frac{\partial y}{\partial x} \right) = \frac{1}{\left(\frac{\partial x}{\partial y} \right)} \tag{9.2.2}$$

For example, for $z = x^2 y$:

$$\left(\frac{\partial z}{\partial x} \right)_y = \left(\frac{\partial}{\partial x} x^2 y \right)_y = 2xy$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial}{\partial z}\sqrt{z/y}\right)_y = \frac{1}{2y}(z/y)^{-1/2} = \frac{1}{2xy} = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

Finally, let's mention the cycle rule. For a function $z(x,y)$:

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1 \tag{9.2.3}$$

We can construct other versions as follows:

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

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

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

Figure 9.2.3: The chain rule: Start with any partial derivative, and follow the pattern to construct the rest (CC BY-NC-SA; Marcia Levitus)

For example, for $z = x^2 y$:

$$\left(\frac{\partial y}{\partial x}\right)_z = \left(\frac{\partial}{\partial x}(z/x^2)\right)_z = -2z/x^3$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial}{\partial z}\sqrt{z/y}\right)_y = \frac{1}{2y}(z/y)^{-1/2}$$

$$\left(\frac{\partial z}{\partial y}\right)_x = \left(\frac{\partial}{\partial y}x^2 y\right)_x = x^2$$

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -\frac{2z}{x^3}\frac{1}{2y}\left(\frac{y}{z}\right)^{1/2}x^2 = -\left(\frac{z}{y}\right)^{1/2}\frac{1}{x} = -\left(\frac{x^2y}{y}\right)^{1/2}\frac{1}{x} = -1$$

Before discussing partial derivatives any further, let's introduce a few physicochemical concepts to put our discussion in context.

9.3: The Total Differential

In Chapter 8 we learned that partial derivatives indicate how the dependent variable changes with one particular independent variable keeping the others fixed. In the context of an equation of state $P = P(T, V, n)$, the partial derivative of P with respect to V at constant T and n is:

$$\left(\frac{\partial P}{\partial V} \right)_{T,n}$$

and physically represents how the pressure varies as we change the volume at constant temperature and constant n.

The partial derivative of P with respect to T at constant V and n is:

$$\left(\frac{\partial P}{\partial T} \right)_{V,n}$$

and physically represents how the pressure varies as we change the temperature at constant volume and constant n.

What happens with the dependent variable (in this case P) if we change two or more independent variables simultaneously? For an infinitesimal change in volume and temperature, we can write the change in pressure as:

$$dP = \left(\frac{\partial P}{\partial V} \right)_{T,n} dV + \left(\frac{\partial P}{\partial T} \right)_{V,n} dT \tag{9.3.1}$$

Equation 9.3.1 is called the *total differential of P*, and it simply states that the change in P is the sum of the individual contributions due to the change in V at constant T and the change in T at constant V. This equation is true for infinitesimal changes. If the changes are not infinitesimal we will integrate this expression to calculate the change in P.[differentials_position1]

Let's now consider the volume of a fluid, which is a function of pressure, temperature and the number of moles: $V = V(n, T, P)$. The total differential of V, by definition, is:

$$dV = \left(\frac{\partial V}{\partial T} \right)_{P,n} dT + \left(\frac{\partial V}{\partial P} \right)_{T,n} dP + \left(\frac{\partial V}{\partial n} \right)_{T,V} dn \tag{9.3.2}$$

If we want to calculate the change in volume in a fluid upon small changes in P, T and n, we could use:

$$\Delta V \approx \left(\frac{\partial V}{\partial T} \right)_{P,n} \Delta T + \left(\frac{\partial V}{\partial P} \right)_{T,n} \Delta P + \left(\frac{\partial V}{\partial n} \right)_{T,V} \Delta n \tag{9.3.3}$$

Of course, if we know the function $V = V(n, T, P)$, we could also calculate ΔV as $V_f - F_i$, where the final and initial volumes are calculated using the final and initial values of P, T and n. This seems easy, so why do we need to bother with Equation 9.3.3? The reason is that sometimes we can measure the partial derivatives experimentally, but we do not have an equation of the type $V = V(n, T, P)$ to use. For example, the following quantities are accessible experimentally and tabulated for different fluids and materials (Fig. [fig:diff_tables]):

- $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,n}$ (coefficient of thermal expansion)
- $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{V,n}$ (isothermal compressibility)[differentials:compressibility]
- $V_m = \left(\frac{\partial V}{\partial n} \right)_{P,T}$ (molar volume)

Using these definitions, Equation 9.3.2 becomes:

$$dV = \alpha V dT - \kappa V dP + V_m dn \tag{9.3.4}$$

You can find tables with experimentally determined values of α and κ under different conditions, which you can use to calculate the changes in V. Again, as we will see later in this chapter, this equation will need to be integrated if the changes are not small. In any case, the point is that you may have access to information about the derivatives of the function, but not to the function itself (in this case V as a function of T, P, n).

In general, for a function $u = u(x_1, x_2 \ldots x_n)$, we define the total differential of u as:

$$du = \left(\frac{\partial u}{\partial x_1}\right)_{x_2...x_n} dx_1 + \left(\frac{\partial u}{\partial x_2}\right)_{x_1,x_3...x_n} dx_2 + ... + \left(\frac{\partial u}{\partial x_n}\right)_{x_1...x_{n-1}} dx_n \qquad (9.3.5)$$

✔ **Example 9.3.1**

Calculate the total differential of the function $z = 3x^3 + 3yx^2 + xy^2$.

Solution

By definition, the total differential is:

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

For the function given in the problem,

$$\left(\frac{\partial z}{\partial x}\right)_y = 9x^2 + 6xy + y^2$$

and

$$\left(\frac{\partial z}{\partial y}\right)_x = 3x^2 + 2xy$$

and therefore,

$$dz = (9x^2 + 6xy + y^2)dx + (3x^2 + 2xy)dy$$

COMPRESSIBILITY AND EXPANSION COEFFICIENTS OF LIQUIDS

This table gives data on the variation of the density of some common liquids with pressure and temperature. The pressure dependence is described to first order by the isothermal compressibility coefficient κ defined as

→ $\kappa_T = -(1/V)(\partial V/\partial P)_T$

where V is the volume, and the temperature dependence by the cubic expansion coefficient α,

→ $\alpha_V = (1/V)(\partial V/\partial T)_P$

Substances are listed by molecular formula in the Hill order. More precise data on the variation of density with temperature over a wide temperature range can be found in Reference 1.

References

1. Lide, D. R., and Kehiaian, H. V., *CRC Handbook of Thermophysical and Thermochemical Data*, CRC Press, Boca Raton, FL, 1994.
2. Le Neindre, B., *Effets des Hautes et Très Hautes Pressions, in Techniques de l'Ingénieur*, Paris, 1991.
3. *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology*, New Series, IV/4, High-Pressure Properties of Matter, Springer-Verlag, Heidelberg, 1980.
4. Riddick, J.A., Bunger, W.B., and Sakano, T.K., *Organic Solvents, Fourth Edition*, John Wiley & Sons, New York, 1986.
5. Isaacs, N. S., *Liquid Phase High Pressure Chemistry*, John Wiley, New York, 1981.

Molecular formula	Name	Isothermal compressibility $t/°C$	$\kappa_T \times 10^3/\text{MPa}^{-1}$	Cubic expansion coefficient $t/°C$	$\alpha_V \times 10^3/°C^{-1}$
Cl₃P	Phosphorus trichloride	20	9.45	20	1.9
H₂O	Water	20	4.591	20	0.206
		25	4.524	25	0.256
		30	4.475	30	0.302
Hg	Mercury	20	0.401	20	0.1811
CCl₄	Tetrachloromethane	20	10.50	20	1.14
		40	12.20	40	1.21
		70	15.6	70	1.33
CHBr₃	Tribromomethane	50	8.76	25	0.91
CHCl₃	Trichloromethane	20	9.96	20	1.21
		50	12.9	50	1.33
CH₂Br₂	Dibromomethane	27	6.85		
CH₂Cl₂	Dichloromethane	25	10.3	25	1.39
CH₃I	Iodomethane	27	10.3	25	1.26
CH₄O	Methanol	20	12.14	20	1.49
		40	13.83	40	1.59
CS₂	Carbon disulfide	20	9.38	20	1.12
		40	10.6	35	1.16
C₂Cl₄	Tetrachloroethylene	25	7.56	25	1.02
C₂HCl₃	Trichloroethylene	25	8.57	25	1.17
C₂H₂Cl₂	trans-1,2-Dichloroethylene	25	11.2	25	1.36
C₂H₄Cl₂	1,1-Dichloroethane	20	7.97	25	0.93
C₂H₄Cl₂	1,2-Dichloroethane	30	8.46	20	1.14
C₂H₄O₂	Acetic acid	20	9.08	20	1.08
		80	13.7	80	1.38
C₂H₅Br	Bromoethane	20	11.53	20	1.31
C₂H₅I	Iodoethane	20	9.82	25	1.17
C₂H₆O	Ethanol	20	11.19	20	1.40
		70	15.93	70	1.67
C₂H₆O₂	Ethylene glycol	20	3.64	20	0.626
C₃H₆O	Acetone	20	12.62	20	1.46
		40	15.6	40	1.57
C₃H₇Br	1-Bromopropane	0	10.22	25	1.2
C₃H₇Cl	1-Chloropropane	0	12.09	20	1.4
C₃H₇I	1-Iodopropane	0	10.22	25	1.09
C₃H₈O	1-Propanol	0	8.43	0	1.22
C₃H₈O	2-Propanol	40	13.32	40	1.55
C₃H₈O₂	1,2-Propanediol	0	4.45	20	0.695
C₃H₈O₂	1,3-Propanediol	0	4.09	20	0.61
C₃H₈O₃	Glycerol	0	2.54	20	0.520

VOLUMETRIC PROPERTIES OF AQUEOUS SODIUM CHLORIDE SOLUTIONS

This table gives the following properties of aqueous solutions of NaCl as a function of temperature and concentration:

Specific volume v (reciprocal of density) in cm³/g
Isothermal compressibility $\kappa_T = -(1/v)(\partial v/\partial P)_T$ in GPa⁻¹
Cubic expansion coefficient $\alpha_v = (1/v)(\partial v/\partial T)_P$ in kK⁻¹

All data refer to a pressure of 100 kPa (1 bar). The reference gives properties over a wider range of temperature and pressure.

Reference

Rogers, P. S. Z., and Pitzer, K. S., *J. Phys. Chem. Ref. Data*, 11, 15, 1982.

t/°C	0.100	0.250	0.500	0.750	1.000	2.000	3.000	4.000	5.000
Specific volume v in cm³/g									
0	0.995732	0.989259	0.978889	0.968991	0.959525	0.925426	0.896292	0.870996	0.848646
10	0.995998	0.989781	0.979804	0.970256	0.961101	0.927905	0.899262	0.874201	0.851958
20	0.997620	0.991564	0.981833	0.972505	0.963544	0.930909	0.902565	0.877643	0.855469
25	0.998834	0.992832	0.983185	0.973932	0.965038	0.932590	0.904339	0.879457	0.857301
30	1.000279	0.994319	0.984735	0.975539	0.966694	0.934382	0.906194	0.881334	0.859185
40	1.003796	0.997883	0.988374	0.979243	0.970455	0.938287	0.910145	0.885276	0.863108
50	1.008064	1.002161	0.992668	0.983551	0.974772	0.942603	0.914411	0.889473	0.867241
60	1.0130	1.0071	0.9976	0.9885	0.9797	0.9474	0.9191	0.8940	0.8716
70	1.0186	1.0127	1.0031	0.9939	0.9851	0.9526	0.9240	0.8987	0.8762
80	1.0249	1.0188	1.0092	0.9999	0.9909	0.9581	0.9293	0.9037	0.8809
90	1.0317	1.0256	1.0157	1.0063	0.9972	0.9640	0.9348	0.9089	0.8858
100	1.0391	1.0329	1.0228	1.0133	1.0040	0.9703	0.9406	0.9144	0.8910
Isothermal Compressibility κ_T in GPa⁻¹									
0	0.503	0.492	0.475	0.459	0.443	0.389	0.346	0.315	0.294
10	0.472	0.463	0.449	0.436	0.423	0.377	0.341	0.313	0.294
20	0.453	0.446	0.433	0.422	0.411	0.371	0.338	0.313	0.294
25	0.447	0.440	0.428	0.417	0.407	0.369	0.337	0.313	0.294
30	0.443	0.436	0.425	0.414	0.404	0.367	0.337	0.313	0.294
40	0.438	0.432	0.421	0.411	0.401	0.367	0.338	0.315	0.296
50	0.438	0.431	0.421	0.411	0.402	0.369	0.340	0.317	0.299
60	0.44	0.44	0.43	0.42	0.41	0.38	0.35	0.32	0.30
70	0.45	0.44	0.43	0.42	0.42	0.38	0.36	0.33	0.31
80	0.46	0.45	0.44	0.43	0.43	0.39	0.37	0.34	0.32
90	0.47	0.47	0.46	0.45	0.44	0.41	0.38	0.35	0.33
100	0.49	0.48	0.47	0.46	0.45	0.42	0.39	0.37	0.34
Cubic expansion coefficient α_v in kK⁻¹									
0	−0.058	−0.026	0.024	0.069	0.110	0.237	0.313	0.355	
10	0.102	0.123	0.156	0.186	0.213	0.297	0.349	0.380	
20	0.218	0.232	0.254	0.274	0.292	0.349	0.384	0.406	
25	0.267	0.278	0.296	0.312	0.327	0.373	0.401	0.420	
30	0.311	0.320	0.334	0.347	0.359	0.395	0.418	0.433	
40	0.389	0.394	0.402	0.410	0.417	0.438	0.451	0.460	
50	0.458	0.460	0.464	0.467	0.470	0.479	0.484	0.486	
60	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	
70	0.58	0.58	0.58	0.57	0.57	0.56	0.55	0.54	
80	0.64	0.63	0.63	0.62	0.61	0.60	0.58	0.56	
90	0.69	0.68	0.67	0.67	0.66	0.63	0.61	0.59	
100	0.74	0.73	0.72	0.71	0.70	0.66	0.64	0.61	

Figure 9.3.1: Tables of isothermal compressibilities and expansion coefficients of different fluids (top) and sodium chloride solutions (bottom). Source: CRC Handbook of Physics and Chemistry (CC BY-NC-SA; Marcia Levitus)

> **Want to see more examples?**
>
> - Example 1: http://www.youtube.com/watch?v=z0TxZ0EHzIg Notice that she calls it 'the differential', but I prefer 'the total differential'.

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10: Extension 7 - Path Dependence

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10.1: Exact Differentials

In general, if a differential can be expressed as

$$df(x, y) = X\,dx + Y\,dy \tag{10.1.1}$$

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

$$\left(\frac{\partial X}{\partial y}\right)_x = \left(\frac{\partial Y}{\partial x}\right)_y \tag{10.1.2}$$

In order to illustrate this concept, consider $P(\overline{V}, T)$ using the ideal gas law.

$$P = \frac{RT}{\overline{V}} \tag{10.1.3}$$

The total differential of P can be written

$$dP = \left(-\frac{RT}{\overline{V}^2}\right) dV + \left(\frac{R}{\overline{V}}\right) dT \tag{10.1.4}$$

Example 10.1.1: Euler Relation

Does Equation 10.1.4 follow the Euler relation (Equation 10.1.2)?

Solution

Let's confirm!

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

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

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, which are **path functions**, are not exact differential and dw and dq are called *inexact* differentials instead.

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CHAPTER OVERVIEW

11: Fundamental 8 - Energy Transformations

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11.1: Internal Energy

The internal energy of a system is identified with the random, disordered motion of molecules; the total (internal) energy in a system includes potential and kinetic energy. This is contrast to external energy which is a function of the sample with respect to the outside environment (e.g. kinetic energy if the sample is moving or potential energy if the sample is at a height from the ground etc). The symbol for Internal Energy Change is ΔU.

Energy on a smaller scale

- Internal energy includes energy on a microscopic scale
- It is the sum of all the microscopic energies such as:

    1. translational kinetic energy
    2. vibrational and rotational kinetic energy
    3. potential energy from intermolecular forces

Example

One gram of water at zero °Celsius compared with one gram of copper at zero °Celsius do NOT have the same internal energy because even though their kinetic energies are equal, water has a much higher potential energy causing its internal energy to be much greater than the copper's internal energy.

Internal Energy Change Equations

The first law of thermodynamics states:

$$dU = dq + dw \tag{11.1.1}$$

where dq is heat and dw is work.

An isolated system cannot exchange heat or work with its surroundings making the change in internal energy equal to zero:

$$dU_{\text{isolated system}} = 0 \tag{11.1.2}$$

Therefore, in an isolated system:

$$dq = -dw \tag{11.1.3}$$

Energy is Conserved

ΔUsystem = -ΔUsurroundings
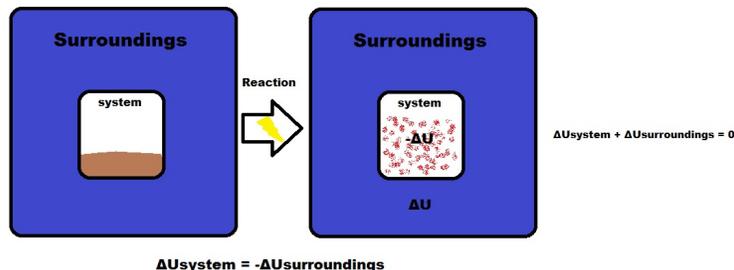
$$dU_{\text{isolated system}} = dU_{\text{system}} + dU_{\text{surroundings}} \tag{11.1.4}$$

$$dU_{\text{system}} = -dU_{\text{surroundings}} \tag{11.1.5}$$

The signs of internal energy

- Energy *entering* the system is **POSITIVE (+)**, meaning heat is *absorbed*, **q>0**. Work is thus done *on* the system, **w>0**
- Energy *leaving* the system is **NEGATIVE (-)**, meaning heat is *given off* by the system, **q<0** and work is done *by* the system, **w<0**

Quick Notes

- A system *contains* ONLY Internal Energy
- A system does NOT *contain* energy in the form of heat or work
- Heat and work only exist during a change in the system; they are path functions
- Internal energy is a state function

Outside Links

- Levine, Ira N. "Thermodynamic internal energy of an ideal gas of rigid rotors." J. Chem. Educ. **1985**: 62, 53.

Contributors

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11.2: Total Differential of the Internal Energy

One Component, Closed Systems

Consider a closed system of one chemical component (e.g., a pure substance) in a single homogeneous phase. The only kind of work is expansion work, with V as the work variable. This kind of system has *two* independent variables. During a *reversible* process in this system, the heat is $dq = T dS$, the work is $dw = -P dV$, and an infinitesimal internal energy change is given by

$$dU = T dS - P dV \tag{11.2.1}$$

The appearance of the intensive variables T and P in 11.2.1 implies, of course, that the temperature and pressure are uniform throughout the system during the process. If they were not uniform, the phase would not be homogeneous and there would be more than two independent variables. The temperature and pressure are strictly uniform only if the process is reversible; it is not necessary to include "reversible" as one of the conditions of validity.

A real process approaches a reversible process in the limit of infinite slowness. For all practical purposes, therefore, we may apply 11.2.1 to a process obeying the conditions of validity and taking place so slowly that the temperature and pressure remain essentially uniform—that is, for a process in which the system stays very close to thermal and mechanical equilibrium.

Because the system under consideration has two independent variables, 11.2.1 is an expression for the total differential of U with S and V as the independent variables. In general, an expression for the differential dX of a state function X is a total differential if

1. it is a valid expression for dX consistent with the physical nature of the system and any conditions and constraints;
2. it is a sum with the same number of terms as the number of independent variables;
3. each term of the sum is a function of state functions multiplied by the differential of one of the independent variables.

Note that the work coordinate of any kind of dissipative work—work without a reversible limit—cannot appear in the expression for a total differential, because it is not a state function.

We may identify the coefficient of each term in an expression for the total differential of a state function as a partial derivative of the function. We identify the coefficients on the right side of 11.2.1 as follows:

$$T = \left(\frac{\partial U}{\partial S} \right)_V \tag{11.2.2}$$

$$-P = \left(\frac{\partial U}{\partial V} \right)_S \tag{11.2.3}$$

One Component, Open Systems

Now let us consider some of the ways a system might have more than two independent variables. Suppose the system has one phase and one substance, with expansion work only, and is *open* so that the amount N of the substance can vary. Such a system has three independent variables. Let us write the formal expression for the total differential of U with S, V, and N as the three independent variables:

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V,n} dS + \left(\frac{\partial U}{\partial V} \right)_{S,n} dV + \left(\frac{\partial U}{\partial n} \right)_{S,V} dn \tag{11.2.4}$$

We have seen above that if the system is *closed*, the partial derivatives are $(\partial U/\partial S)_V = T$ and $(\partial U/\partial V)_S = -P$. Since both of these partial derivatives are for a closed system in which N is constant, they are the same as the first two partial derivatives on the right side of 11.2.4.

The quantity given by the third partial derivative, $(\partial U/\partial N)_{S,V}$, is represented by the symbol μ (mu). This quantity is an intensive state function called the **chemical potential**.

With these substitutions, 11.2.4 becomes

$$dU = T dS - P dV + \mu dN \tag{11.2.5}$$

and this is a valid expression for the total differential of U under the given conditions.

Multiple Component, Open Systems

If a system contains a mixture of M different substances in a single phase, and the system is open so that the amount of each substance can vary independently, there are $2 + M$ independent variables and the total differential of U can be written

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_{i=1}^{M} \mu_i \mathrm{d}N_i \tag{11.2.6}$$

The coefficient μ_i is the chemical potential of substance i. We identify it as the partial derivative $(\partial U/\partial N_i)_{S,V,N_{j \neq i}}$.

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12: Fundamental 10 - Processes

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12.1: 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_{ex}) can be replaced by a single value (P) which represents both the internal pressure of the gas and the external pressure.

$$dw = -PdV \tag{12.1.1}$$

or

$$w = -\int PdV \tag{12.1.2}$$

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

$$w = -\int PdV - \int \left(\frac{nRT}{V}\right)dV \tag{12.1.3}$$

Constant Temperature (Isothermal) Pathways

If the temperature is held constant (so that the expansion follows an **isothermal** pathway) the nRT term can be extracted from the integral.

$$w = -nRT\int_{V_1}^{V_2}\frac{dV}{V} = -nRT\ln\left(\frac{V_1}{V_2}\right) \tag{12.1.4}$$

Equation 12.1.4 is derived for ideal gases only; a van der Waal gas would result in a different version.

> ### Example 12.1.1: 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 12.1.4 to calculate this
>
> $$w = -(1.00 \; \cancel{mol})\left(8.314 \; \frac{J}{\cancel{mol} \; \cancel{K}}\right)(273 \; \cancel{K})\ln\left(\frac{44.8 \; L}{22.4 \; L}\right)$$
>
> $$= -1570 \; J = 1.57 \; kJ$$
>
> *Note*: A reversible expansion will **always** require more work than an irreversible expansion (such as an expansion against a constant external pressure) when the final states of the two expansions are the same!

The work of expansion can be depicted graphically as the area under the P-V curve depicting the expansion. Comparing examples 12.1.1 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.
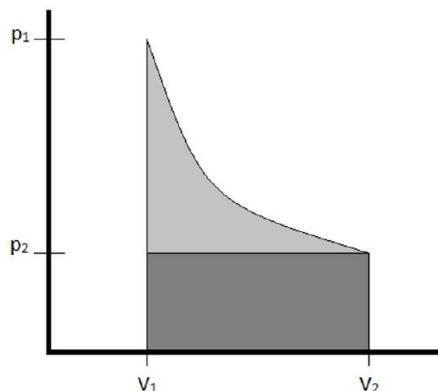
The work is depicted as the shaded portion of the graph. It is clear to see that the reversible expansion (the work for which is shaded in both light and dark gray) exceeds that of the irreversible expansion (shaded in dark gray only) due to the changing pressure of the reversible expansion. In general, 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 (Isochoric) 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:

$$dU = dq + dw = dq - PdV \qquad (12.1.5)$$

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

$$dU = dq_v \qquad (12.1.6)$$

Recall that dq can be found by

$$dq = \frac{dq}{\partial T} dT = C \, dt \qquad (12.1.7)$$

This suggests an important definition for the **constant volume heat capacity** (C_V) which is

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V \qquad (12.1.8)$$

When Equation 12.1.7 is integrated the

$$q = \int_{T_1}^{T_2} nC_V dt \tag{12.1.9}$$

Example 12.1.2: 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 12.1.9 is applicable for an isochoric process,

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

Assuming C_V is independent of temperature:

$$q = nC_V \int_{T_1}^{T_2} dt$$
$$= nC_V(T_2 - T_1)$$
$$= (1.00\, mol)\left(\frac{3}{2}8.314\,\frac{J}{mol\,K}\right)(255\,K - 125\,K)$$
$$= 1620\,J = 1.62\,kJ$$

Since this a constant volume pathway,

$$\Delta U = q + \cancel{w}$$
$$= 1.62\,kJ$$

Constant Pressure (Isobaric) 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

$$dH \equiv dU + d(pV)$$
$$= dU + pdV + Vdp$$

For reversible changes at constant pressure ($dp = 0$) for which only P-V work is done

$$dH = dq + dw + pdV + Vdp \tag{12.1.10}$$
$$= dq - \cancel{pdV} + \cancel{pdV} + \cancel{Vdp}^{\,0} \tag{12.1.11}$$
$$= dq \tag{12.1.12}$$

And just as in the case of constant volume changes, this implies an important definition for the **constant pressure heat capacity**

$$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p \tag{12.1.13}$$

Example 12.1.3: 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 12.1.12 (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 12.1.4: Isothermal Gas Expansion

Calculate q, w, ΔU, and ΔH for 1.00 mol of an ideal gas expanding reversibly and isothermally at 273 K from a volume of 22.4 L and a pressure of 1.00 atm to a volume of 44.8 L and a pressure of 0.500 atm.

Solution

Since this is an isothermal expansion, Equation 12.1.4 is applicable

$$
\begin{aligned}
w &= -nRT\ln\frac{V_2}{V_1} \\
&= (1.00\,mol)\left(8.314\,\frac{J}{mol\,K}\right)(255\,K)\ln\left(\frac{44.8\,L}{22.4\,L}\right) \\
&= 1572\,J = 1.57\,kJ
\end{aligned}
$$

$$
\begin{aligned}
\Delta U &= q + w \\
&= q + 1.57\,KJ \\
&= 0 \\
q &= -1.57\,kJ
\end{aligned}
$$

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,

$$dw = -PdV \tag{12.1.14}$$

and

$$dw = dU = nC_v dT \tag{12.1.15}$$

Equating these two terms yields

$$-PdV = nC_v dT \tag{12.1.16}$$

Using the ideal gas law for an expression for P ($P = nRT/V$)

$$-\frac{nRT}{V}dV = nC_v dT \tag{12.1.17}$$

And rearranging to gather the temperature terms on the right and volume terms on the left yields

$$\frac{dV}{V} = -\frac{C_V}{R}\frac{dT}{T} \tag{12.1.18}$$

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.

$$\int_{V_1}^{V_2}\frac{dV}{V} = -\frac{C_V}{R}\int_{T_1}^{T_2}\frac{dT}{T} \tag{12.1.19}$$

The result is

$$\ln\left(\frac{V_2}{V_1}\right) = -\frac{C_V}{R}\ln\left(\frac{T_2}{T_1}\right) \tag{12.1.20}$$

or

$$\left(\frac{V_2}{V_1}\right) = \left(\frac{T_2}{T_1}\right)^{-\frac{C_V}{R}} \tag{12.1.21}$$

or

$$V_1 T_1^{\frac{C_V}{R}} = V_2 T_2^{\frac{C_V}{R}} \tag{12.1.22}$$

or

$$T_1\left(\frac{V_1}{V_2}\right)^{-\frac{R}{C_V}} = T_2 \tag{12.1.23}$$

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

Example 12.1.5:

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 12.1.23

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

$$= (273 \, K) \left(\frac{22.4 \, L}{44.8 \, L} \right)^{2/3}$$

$$= 172 \, K$$

So

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

For calculating work, we integrate Equation 12.1.15 to get

$$w = \Delta U = nC_v\Delta T$$

$$= (1.00 \, mol) \left(\frac{3}{2} 8.314 \, \frac{J}{mol \, K} \right) (-101 \, K)$$

$$= 1.260 \, kJ$$

$$\Delta H = \Delta U + nR\Delta T$$

$$= -1260 \, J + (1.00 \, mol) \left(\frac{3}{2} 8.314 \, \frac{J}{mol \, K} \right) (-101 \, K)$$

$$= -2100 \, J$$

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	$C_V\Delta T$	$C_V\Delta T$	$C_p\Delta T$

Contributors and Attributions

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CHAPTER OVERVIEW

13: Extension 10 - Cycles

13.1: Carnot Cycle

In the early 19th century, steam engines came to play an increasingly important role in industry and transportation. However, a systematic set of theories of the conversion of thermal energy to motive power by steam engines had not yet been developed. Nicolas Léonard Sadi Carnot (1796-1832), a French military engineer, published *Reflections on the Motive Power of Fire* in 1824. The book proposed a generalized theory of heat engines, as well as an idealized model of a thermodynamic system for a heat engine that is now known as the Carnot cycle. Carnot developed the foundation of the second law of thermodynamics, and is often described as the "Father of thermodynamics."

The Carnot Cycle

The Carnot cycle consists of the following four processes:

 I. A reversible isothermal gas expansion process. In this process, the ideal gas in the system absorbs q_{in} amount heat from a heat source at a high temperature T_{high}, expands and does work on surroundings.
 II. A reversible adiabatic gas expansion process. In this process, the system is thermally insulated. The gas continues to expand and do work on surroundings, which causes the system to cool to a lower temperature, T_{low}.
 III. A reversible isothermal gas compression process. In this process, surroundings do work to the gas at T_{low}, and causes a loss of heat, q_{out}.
 IV. A reversible adiabatic gas compression process. In this process, the system is thermally insulated. Surroundings continue to do work to the gas, which causes the temperature to rise back to T_{high}.
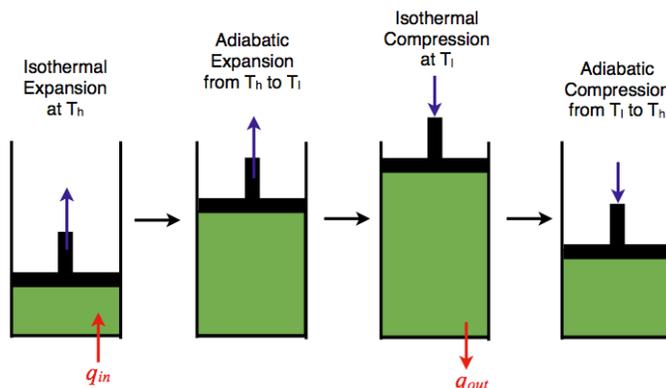
Figure 13.1.1: An ideal gas-piston model of the Carnot cycle. (CC BY 4.0; XiSen Hou via Hope College)

P-V Diagram

The P-V diagram of the Carnot cycle is shown in Figure 13.1.2. In isothermal processes I and III, ΔU=0 because ΔT=0. In adiabatic processes II and IV, q=0. Work, heat, ΔU, and ΔH of each process in the Carnot cycle are summarized in Table 13.1.1.
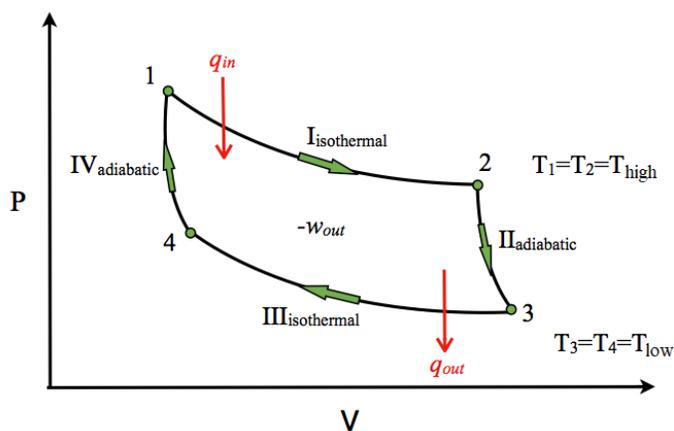
Figure 13.1.2: A P-V diagram of the Carnot Cycle.

Table 13.1.1: Work, heat, ΔU, and ΔH in the P-V diagram of the Carnot Cycle.

Process	w	q	ΔU	ΔH
I	$-nRT_{high}\ln\left(\frac{V_2}{V_1}\right)$	$nRT_{high}\ln\left(\frac{V_2}{V_1}\right)$	0	0
II	$n\bar{C}_v(T_{low}-T_{high})$	0	$n\bar{C}_v(T_{low}-T_{high})$	$n\bar{C}_p(T_{low}-T_{high})$
III	$-nRT_{low}\ln\left(\frac{V_4}{V_3}\right)$	$nRT_{low}\ln\left(\frac{V_4}{V_3}\right)$	0	0
IV	$n\bar{C}_v(T_{high}-T_{low})$	0	$n\bar{C}_v(T_{hight}-T_{low})$	$n\bar{C}_p(T_{high}-T_{low})$
Full Cycle	$-nRT_{high}\ln\left(\frac{V_2}{V_1}\right)-nRT_{low}\ln\left(\frac{V_4}{V_3}\right)$	$nRT_{high}\ln\left(\frac{V_4}{V_3}\right)\left(\frac{V_2}{V_1}\right)+nRT_{low}\ln\left(\frac{V_4}{V_3}\right)$	0	0

T-S Diagram

The T-S diagram of the Carnot cycle is shown in Figure $13.1.3$. In isothermal processes I and III, ΔT=0. In adiabatic processes II and IV, ΔS=0 because dq=0. ΔT and ΔS of each process in the Carnot cycle are shown in Table $13.1.2$
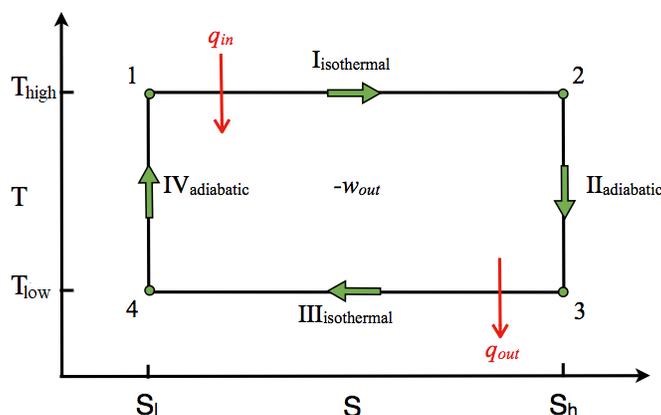
Figure 13.1.3: A T-S diagram of the Carnot Cycle. (CC BY 4.0; XiSen Hou via Hope College)

Table 13.1.1: Work, heat, and ΔU in the T-S diagram of the Carnot Cycle.

Process	ΔT	ΔS
I	0	$-nR\ln\left(\frac{V_2}{V_1}\right)$
II	$T_{low}-T_{high}$	0
III	0	$-nR\ln\left(\frac{V_4}{V_3}\right)$
IV	$T_{high}-T_{low}$	0
Full Cycle	0	0

Efficiency

The Carnot cycle is the most efficient engine possible based on the assumption of the absence of incidental wasteful processes such as friction, and the assumption of no conduction of heat between different parts of the engine at different temperatures. The efficiency of the carnot engine is defined as the ratio of the energy output to the energy input.

$$\text{efficiency} = \frac{\text{net work done by heat engine}}{\text{heat absorbed by heat engine}}$$

$$= \frac{-w_{sys}}{q_{high}}$$

$$= \frac{nRT_{high}\ln\left(\dfrac{V_2}{V_1}\right) + nRT_{low}\ln\left(\dfrac{V_4}{V_3}\right)}{nRT_{high}\ln\left(\dfrac{V_2}{V_1}\right)}$$

Since processes II (2-3) and IV (4-1) are adiabatic,

$$\left(\frac{T_2}{T_3}\right)^{C_V/R} = \frac{V_3}{V_2}$$

and

$$\left(\frac{T_1}{T_4}\right)^{C_V/R} = \frac{V_4}{V_1}$$

And since $T_1 = T_2$ and $T_3 = T_4$,

$$\frac{V_3}{V_4} = \frac{V_2}{V_1}$$

Therefore,

$$\text{efficiency} = \frac{nRT_{high}\ln\left(\dfrac{V_2}{V_1}\right) - nRT_{low}\ln\left(\dfrac{V_2}{V_1}\right)}{nRT_{high}\ln\left(\dfrac{V_2}{V_1}\right)}$$

$$\boxed{\text{efficiency} = \frac{T_{high} - T_{low}}{T_{high}}}$$

Summary

The Carnot cycle has the greatest efficiency possible of an engine (although other cycles have the same efficiency) based on the assumption of the absence of incidental wasteful processes such as friction, and the assumption of no conduction of heat between different parts of the engine at different temperatures.

Problems

1. You are now operating a Carnot engine at 40% efficiency, which exhausts heat into a heat sink at 298 K. If you want to increase the efficiency of the engine to 65%, to what temperature would you have to raise the heat reservoir?
2. A Carnot engine absorbed 1.0 kJ of heat at 300 K, and exhausted 400 J of heat at the end of the cycle. What is the temperature at the end of the cycle?
3. An indoor heater operating on the Carnot cycle is warming the house up at a rate of 30 kJ/s to maintain the indoor temperature at 72 ºF. What is the power operating the heater if the outdoor temperature is 30 ºF?

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13.2: 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

$$q_{tot} = nRT_h \ln\left(\frac{V_4}{V_3}\right) - nRT_l \ln\left(\frac{V_4}{V_3}\right) \tag{13.2.1}$$

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:

$$\sum \frac{q}{T} = \frac{nR\, T_h \ln\left(\frac{V_4}{V_3}\right)}{T_h} - \frac{nR\, T_l \ln\left(\frac{V_4}{V_3}\right)}{T_l}$$

$$= nR\ln\left(\frac{V_4}{V_3}\right) - nR\ln\left(\frac{V_4}{V_3}\right)$$

$$= 0$$

This is the behavior expected for a state function! It leads to the definition of entropy in differential form,

$$dS \equiv \frac{dq_{rev}}{T} \tag{13.2.2}$$

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 ΔS 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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14: Fundamental 11 - Boundary Changes

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14.1: Helmholtz Energy

We have answered the question: what is entropy, but we still do not have a general criterion for spontaneity, just one that works in an isolated system. We will consider what happens when we hold volume and temperature constant. As discussed previously, the expression for the change in internal energy:

$$dU = TdS - PdV$$

is only valid for *reversible* changes. Let us consider a spontaneous change. If we assume constant volume, the $-PdV$ work term drops out. From the *Clausius inequality* $dS > \dfrac{\delta q}{T}$ we get:

$$\underset{\text{constant V}}{dU \leq TdS}$$

$$\underset{\text{constant V}}{dU - TdS \leq 0}$$

Consider a new state function, **Helmholtz energy**, **A**:

$$A \equiv U - TS$$

$$dA = dU - TdS - SdT \tag{14.1.1}$$

If we also set T constant, we see that Equation 14.1.1 becomes

$$\underset{\text{constant V and T}}{dA = dU - TdS \leq 0}$$

This means that the Helmholtz energy, A, is a ***decreasing quantity*** for spontaneous processes (regardless of isolation!) when T and V are held constant. A becomes constant once a reversible equilibrium is reached.

> ### ✔ Example 22.1.1 : What A stands for
>
> A good example is the case of the mixing of two gases. Let's assume isothermal conditions and keep the total volume constant. For this process, ΔU is zero (isothermal, ideal) but the
>
> $$\Delta S_{molar} = -y_1 R \ln y_1 - y_2 R \ln y_2$$
>
> This means that
>
> $$\Delta A_{molar} = RT(y_1 \ln y_1 + y_2 \ln y_2).$$
>
> This is a negative quantity because the mole ratios are smaller than unity. So yes this spontaneous process has a negative ΔA. If we look at $\Delta A = \Delta U - T\Delta S$ we should see that the latter term is the same thing as $-q_{rev}$ So we have :
>
> $$\Delta A = \Delta U - q_{rev} = w_{rev}$$
>
> This is however the *maximal work that a system is able to produce* and so the Helmholtz energy is a direct measure of how much work one can get out of a system. A is therefore often called the Helmholtz *free* energy. Interestingly this work **cannot** be volume work as volume is constant. so it stands for the maximal *other* work (e.g. electrical work) that can be obtained under the unlikely condition that volume is constant.

Natural variables of A

Because $A \equiv U - TS$ we can write

$$
\begin{aligned}
dA &= dU - TdS - SdT \\
&= TdS - PdV - TdS - SdT \\
&= -PdV - SdT
\end{aligned}
$$

The natural variables of A are volume V and temperature T.

15: Extension 11 - Legendre Transforms

15.1: Differential Forms of Fundamental Equations

The fundamental thermodynamic equations follow from five primary thermodynamic definitions and describe internal energy, enthalpy, Helmholtz energy, and Gibbs energy in terms of their natural variables. Here they will be presented in their differential forms.

Introduction

The fundamental thermodynamic equations describe the thermodynamic quantities U, H, G, and A in terms of their natural variables. The term "natural variable" simply denotes a variable that is one of the convenient variables to describe U, H, G, or A. When considered as a whole, the four fundamental equations demonstrate how four important thermodynamic quantities depend on variables that can be controlled and measured experimentally. Thus, they are essentially equations of state, and using the fundamental equations, experimental data can be used to determine sought-after quantities like G or H.

First Law of Thermodynamics

The first law of thermodynamics is represented below in its differential form

$$dU = dq + dw \tag{15.1.1}$$

where

- U is the internal energy of the system,
- q is heat flow of the system, and
- w is the work of the system.

Recall that U is a state function, while q and w are path functions. The first law states that internal energy changes occur only as a result of heat flow and work done.

It is assumed that w refers only to PV work, where

$$w = -\int P dV \tag{15.1.2}$$

The Principle of Clausius

The *Principle of Clausius* states that the entropy change of a system is equal to the ratio of heat flow in a reversible process to the temperature at which the process occurs. Mathematically this is written as

$$dS = \frac{dq_{rev}}{T} \tag{15.1.3}$$

where

- S is the entropy of the system,
- q_{rev} is the heat flow of a reversible process, and
- T is the temperature in Kelvin.

Internal Energy

The fundamental thermodynamic equation for internal energy follows directly from the first law and the principle of Clausius:

$$dU = dq + dw \tag{15.1.4}$$

$$dS = \frac{dq_{rev}}{T} \tag{15.1.5}$$

we have

$$dU = TdS + dw \tag{15.1.6}$$

Since only PV work is performed,

$$dU = TdS - PdV \tag{15.1.7}$$

The above equation is the fundamental equation for U with natural variables of entropy S and volume V.

Enthalpy

Mathematically, enthalpy is defined as

$$H = U + PV \tag{15.1.8}$$

where H is enthalpy of the system, p is pressure, and V is volume. The fundamental thermodynamic equation for enthalpy follows directly from it definition (Equation 15.1.8) and the fundamental equation for internal energy (Equation 15.1.7) :

$$dH = dU + d(PV) \tag{15.1.9}$$

$$dH = dU + PdV + VdP \tag{15.1.10}$$

Because $dU = TdS - PdV$, the enthalpy equation becomes:

$$dH = TdS - PdV + PdV + VdP \tag{15.1.11}$$

$$dH = TdS + VdP \tag{15.1.12}$$

The above equation is the fundamental equation for H. The natural variables of enthalpy are S and P, entropy and pressure.

Gibbs Energy

The mathematical description of Gibbs energy is as follows

$$G = U + PV - TS = H - TS \tag{15.1.13}$$

where G is the Gibbs energy of the system. The fundamental thermodynamic equation for Gibbs Energy follows directly from its definition 15.1.13 and the fundamental equation for enthalpy 15.1.8:

$$dG = dH - d(TS) \tag{15.1.14}$$

$$dG = dH - TdS - SdT \tag{15.1.15}$$

Since $dH = TdS + VdP$,

$$dG = TdS + VdP - TdS - SdT \tag{15.1.16}$$

$$dG = VdP - SdT \tag{15.1.17}$$

The above equation is the fundamental equation for G. The natural variables of Gibbs energy are P and T, pressure and temperature.

Helmholtz Energy

Mathematically, Helmholtz energy is defined as

$$A = U - TS \tag{15.1.18}$$

where A is the Helmholtz energy of the system, which sometimes also written as the symbol F. The fundamental thermodynamic equation for Helmholtz energy follows directly from its definition (Equation 15.1.18) and the fundamental equation for internal energy (Equation 15.1.7):

$$dA = dU - d(TS) \tag{15.1.19}$$

$$dA = dU - TdS - SdT \tag{15.1.20}$$

Since $dU = TdS - PdV$,

$$dA = TdS - PdV - TdS - SdT \tag{15.1.21}$$

$$dA = -PdV - SdT \tag{15.1.22}$$

The above equation is the fundamental equation for A with natural variables of V and T.

Importance/Relevance of Fundamental Equations

The differential fundamental equations describe U, H, G, and A in terms of their natural variables. The natural variables become useful in understanding not only how thermodynamic quantities are related to each other, but also in analyzing relationships between measurable quantities (i.e. P, V, T) in order to learn about the thermodynamics of a system. Below is a table summarizing the natural variables for U, H, G, and A:

Thermodynamic Quantity	Natural Variables
U (internal energy)	S, V
H (enthalpy)	S, P
G (Gibbs energy)	T, P
A (Helmholtz energy)	T, V

For these definitions to hold, it is assumed that **only** PV work is done and that **only reversible** processes are used. These assumptions are required for the first law and the principle of Clausius to remain valid. Also, these equations do not account include n, the number of moles, as a variable. When n is included, the equations appear different, but the essence of their meaning is captured without including the n-dependence.

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Problems

1. If the assumptions made in the derivations above were not made, what would effect would that have? Try to think of examples were these assumptions would be violated. Could the definitions, principles, and laws used to derive the fundamental equations still be used? Why or why not?
2. For what kind of system does the number of moles not change? This said, do the fundamental equations without n-dependence apply to a wide range of processes and systems?
3. Derive the Maxwell Relations.
4. Derive the expression

$$\left(\frac{\partial H}{\partial P}\right)_{T,n} = -T\left(\frac{\partial V}{\partial T}\right)_{P,n} + V \tag{15.1.23}$$

Then apply this equation to an ideal gas. Does the result seem reasonable?
5. Using the definition of Gibbs energy and the conditions observed at phase equilibria, derive the Clapeyron equation.

Answers

1. If it was not assumed that PV-work was the only work done, then the work term in the second law of thermodynamics equation would include other terms (e.g. for electrical work, mechanical work). If reversible processes were not assumed, the Principle of Clausius could not be used. One example of such situations could the movement of charged particles towards a region of like charge (electrical work) or an irreversible process like combustion of hydrocarbons or friction.
2. In general, a closed system of non-reacting components would fit this description. For example, the number of moles would not change for a closed system in which a gas is sealed (to prevent leaks) in a container and allowed to expand/is contracted.
3. See the Maxwell Relations section.
4. $(\frac{\partial H}{\partial P})_{T,n} = 0$ for an ideal gas. Since there are no interactions between ideal gas molecules, changing the pressure will not involve the formation or breaking of any intermolecular interactions or bonds.

5. See the third outside link.

Contributors

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CHAPTER OVERVIEW

16: Fundamental 12 - Laboratory Conditions

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16.1: Expressions for Heat Capacity

The heat capacity of a closed system is defined as the ratio of an infinitesimal quantity of heat transferred across the boundary under specified conditions and the resulting infinitesimal temperature change: $\text{heat capacity} \overset{\text{def}}{=} \mathrm{d}q/\mathrm{d}T$. The heat capacities of isochoric (constant volume) and isobaric (constant pressure) processes are of particular interest.

The **heat capacity at constant volume**, C_V, is the ratio $\mathrm{d}q/\mathrm{d}T$ for a process in a closed constant-volume system with no nonexpansion work—that is, no work at all. The first law shows that under these conditions the internal energy change equals the heat: $\mathrm{d}U = \mathrm{d}q$. We can replace $\mathrm{d}q$ by $\mathrm{d}U$ and write C_V as a partial derivative:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \tag{16.1.1}$$

> If the closed system has more than two independent variables, additional conditions are needed to define C_V unambiguously. For instance, if the system is a gas mixture in which reaction can occur, we might specify that the system remains in reaction equilibrium as T changes at constant V.
>
> 16.1.1 does not require the condition $\mathrm{d}w' = 0$ (no nonexpansion work), because all quantities appearing in the equation are *state* functions whose relations to one another are fixed by the nature of the system and not by the path. Thus, if heat transfer into the system at constant V causes U to increase at a certain rate with respect to T, and this rate is defined as C_V, the performance of electrical work on the system at constant V will cause the same rate of increase of U with respect to T and can equally well be used to evaluate C_V.

Note that C_V is a state function whose value depends on the state of the system—that is, on T, V, and any additional independent variables. C_V is an *extensive* property: the combination of two identical phases has twice the value of C_V that one of the phases has by itself.

For a phase containing a pure substance, the **molar heat capacity at constant volume** is defined by $\overline{C_V} \overset{\text{def}}{=} C_V/n$. $\overline{C_V}$ is an *intensive* property.

If the system is an ideal gas, its internal energy depends only on T, regardless of whether V is constant, and 16.1.1 can be simplified to

$$C_V = \frac{\mathrm{d}U}{\mathrm{d}T} \tag{16.1.2}$$

Thus the internal energy change of an ideal gas is given by $\mathrm{d}U = C_V \mathrm{d}T$, as mentioned earlier.

The **heat capacity at constant pressure**, C_P, is the ratio $\mathrm{d}q/\mathrm{d}T$ for a process in a closed system with a constant, uniform pressure and with expansion work only. Under these conditions, the heat $\mathrm{d}q$ is equal to the enthalpy change $\mathrm{d}H$, and we obtain a relation analogous to 16.1.1:

$$C_P = \left(\frac{\partial H}{\partial T} \right)_p \tag{16.1.3}$$

C_P is an extensive state function. For a phase containing a pure substance, the **molar heat capacity at constant pressure** is $\overline{C_P} \overset{\text{def}}{=} C_P/n$, an intensive property.

Since the enthalpy of a fixed amount of an ideal gas depends only on T, we can write a relation analogous to 16.1.2:

$$C_p = \frac{\mathrm{d}H}{\mathrm{d}T} \tag{16.1.4}$$

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16.2: The Third Law of Thermodynamics

Learning Objectives

- The ***absolute entropy*** of a pure substance at a given temperature is the sum of all the entropy it would acquire on warming from absolute zero (where $S = 0$) to the particular temperature.
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure 16.2.1). The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy. A perfectly ordered system with only a single microstate available to it would have an entropy of zero. The only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), in which each component atom, molecule, or ion is fixed in place within a crystal lattice and exhibits no motion (ignoring quantum *zero point motion*).
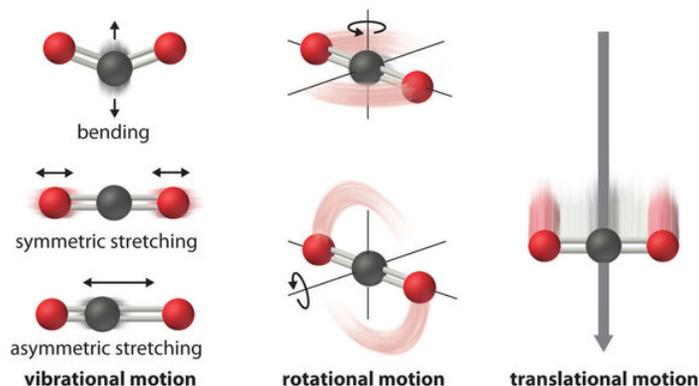
Figure 16.2.1: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion (classically; there will always be motion quantum mechanically) and have zero entropy. In practice, this is an unattainable ideal. (CC BY-SA-NC; Anonymous by request)

This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion (at least classically, quantum mechanics argues for constant motion) means there is but one possible location for each identical atom or molecule comprising the crystal ($W = 1$). According to the Boltzmann equation, the entropy of this system is zero.

$$S = k \ln W$$
$$= k \ln(1)$$
$$= 0$$

In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved. Nonetheless, the combination of these two ideals constitutes the basis for the third law of thermodynamics: the entropy of any perfectly ordered, crystalline substance at absolute zero is zero.

Definition: Third Law of Thermodynamics

The entropy of a pure, perfect crystalline substance at 0 K is zero.

The third law of thermodynamics has two important consequences: it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature. In this section, we examine two different ways to calculate ΔS for a reaction or a physical change. The first, based on the definition of absolute entropy provided by the third law of thermodynamics, uses tabulated values of absolute entropies of substances. The second, based on the fact that entropy is a state function, uses a thermodynamic cycle similar to those discussed previously.

Standard-State Entropies

One way of calculating ΔS for a reaction is to use tabulated values of the standard molar entropy ($\overline{S}^o$), which is the entropy of 1 mol of a substance under standard pressure (1 bar). Often the standard molar entropy is given at 298 K and is often demarked as $\Delta \overline{S}^o_{298}$. The units of $\overline{S}^o$ are J/(mol•K). Unlike enthalpy or internal energy, it is possible to obtain absolute entropy values by measuring the entropy change that occurs between the reference point of 0 K (corresponding to $\overline{S} = 0$) and 298 K (Tables T1 and T2).

As shown in Table 16.2.1, for substances with approximately the same molar mass and number of atoms, $\overline{S}^o$ values fall in the order

$$\overline{S}^o(\text{gas}) \gg \overline{S}^o(\text{liquid}) > \overline{S}^o(\text{solid}). \tag{16.2.1}$$

For instance, $\overline{S}^o$ for liquid water is 70.0 J/(mol•K), whereas $\overline{S}^o$ for water vapor is 188.8 J/(mol•K). Likewise, $\overline{S}^o$ is 260.7 J/(mol•K) for gaseous I_2 and 116.1 J/(mol•K) for solid I_2. This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases (Figure 16.2.1). The correlation between physical state and absolute entropy is illustrated in Figure 16.2.2, which is a generalized plot of the entropy of a substance versus temperature.
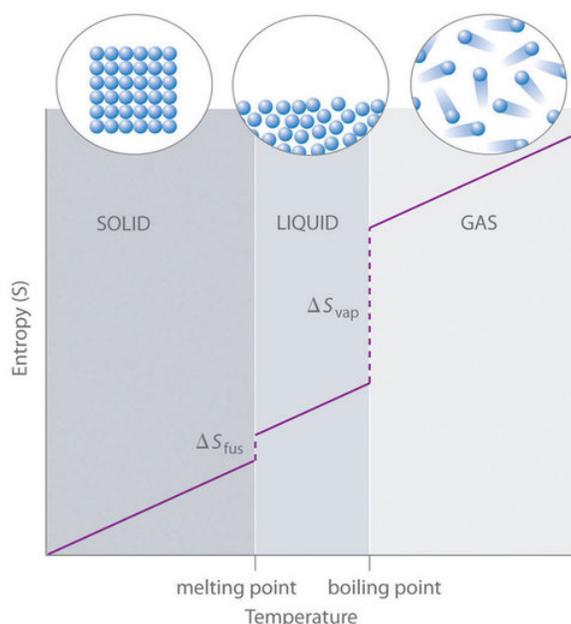
Figure 16.2.2: A Generalized Plot of Entropy versus Temperature for a Single Substance. Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (ΔS_{fus}). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas (ΔS_{vap}). (CC BY-SA-NC; anonymous).

The Third Law Lets us Calculate Absolute Entropies

The *absolute entropy* of a substance at any temperature above 0 K must be determined by calculating the increments of heat q required to bring the substance from 0 K to the temperature of interest, and then summing the ratios q/T. Two kinds of experimental measurements are needed:

1. The enthalpies associated with any **phase changes** the substance may undergo within the temperature range of interest. Melting of a solid and vaporization of a liquid correspond to sizeable increases in the number of microstates available to accept thermal energy, so as these processes occur, energy will flow into a system, filling these new microstates to the extent required to maintain a constant temperature (the freezing or boiling point); these inflows of thermal energy correspond to the heats of fusion and vaporization. The entropy increase associated with transition at temperature T is

$$\frac{\Delta H_{fusion}}{T}. \tag{16.2.2}$$

2. The **heat capacity** C of a phase expresses the quantity of heat required to change the temperature by a small amount ΔT, or more precisely, by an infinitesimal amount dT. Thus the entropy increase brought about by warming a substance over a range of temperatures that does not encompass a phase transition is given by the sum of the quantities $C\frac{dT}{T}$ for each increment of temperature dT. This is of course just the integral

$$S_{0 \to T} = \int_0^T \frac{C_p}{T}\, dt \tag{16.2.3}$$

Because the heat capacity is itself slightly temperature dependent, the most precise determinations of absolute entropies require that the functional dependence of C on T be used in the integral in Equation 16.2.3, i.e.,:

$$S_{0 \to T} = \int_0^T \frac{C_p(T)}{T}\, dt. \tag{16.2.4}$$

When this is not known, one can take a series of heat capacity measurements over narrow temperature increments ΔT and measure the area under each section of the curve. The area under each section of the plot represents the entropy change associated with heating the substance through an interval ΔT. To this must be added the enthalpies of melting, vaporization, and of any solid-solid phase changes.
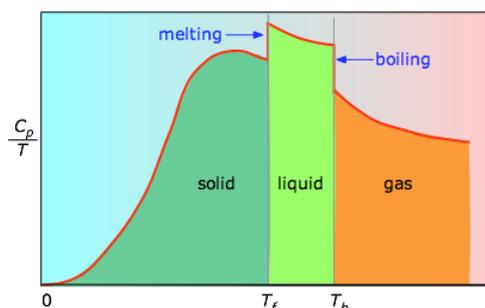
Figure 16.2.3: Heat capacity/temperature as a function of temperature. (CC BY; Stephan Lower)

Values of C_p for temperatures near zero are not measured directly, but can be estimated from quantum theory. The cumulative areas from 0 K to any given temperature (Figure 16.2.3) are then plotted as a function of T, and any phase-change entropies such as

$$S_{vap} = \frac{H_{vap}}{T_b} \tag{16.2.5}$$

are added to obtain the absolute entropy at temperature T. As shown in Figure 16.2.2 above, the entropy of a substance increases with temperature, and it does so for two reasons:

- As the temperature rises, more microstates become accessible, allowing thermal energy to be more widely dispersed. This is reflected in the gradual increase of entropy with temperature.
- The molecules of solids, liquids, and gases have increasingly greater freedom to move around, facilitating the spreading and sharing of thermal energy. Phase changes are therefore accompanied by massive and discontinuous increase in the entropy.

Calculating ΔS_{sys}

We can make careful calorimetric measurements to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. Standard molar entropies are given the label $\overline{S}^o_{298}$ for values determined for one mole of substance at a pressure of 1 bar and a temperature of 298 K. The standard entropy change (ΔS^o) for any process may be computed from the standard molar entropies of its reactant and product species like the following:

$$\Delta S^o = \sum \nu \overline{S}^o_{298}(\text{products}) - \sum \nu \overline{S}^o_{298}(\text{reactants}) \tag{16.2.6}$$

Here, ν represents stoichiometric coefficients in the balanced equation representing the process. For example, ΔS^o for the following reaction at room temperature

$$m\text{A} + n\text{B} \longrightarrow x\text{C} + y\text{D} \tag{16.2.7}$$

is computed as the following:

$$\Delta S^o = [x\overline{S}^{o}_{298}(C) + y\overline{S}^{o}_{298}(D)] - [m\overline{S}^{o}_{298}(A) + n\overline{S}^{o}_{298}(B)] \qquad (16.2.8)$$

Table 16.2.1 lists some standard molar entropies at 298.15 K. You can find additional standard molar entropies in Tables T1 and T2

Table 16.2.1: Standard Molar Entropy Values of Selected Substances at 25°C

Gases		Liquids		Solids	
Substance	$\overline{S}^{o}$ [J/(mol•K)]	Substance	$\overline{S}^{o}$ [J/(mol•K)]	Substance	$\overline{S}^{o}$ [J/(mol•K)]
He	126.2	H_2O	70.0	C (diamond)	2.4
H_2	130.7	CH_3OH	126.8	C (graphite)	5.7
Ne	146.3	Br_2	152.2	LiF	35.7
Ar	154.8	CH_3CH_2OH	160.7	SiO_2 (quartz)	41.5
Kr	164.1	C_6H_6	173.4	Ca	41.6
Xe	169.7	CH_3COCl	200.8	Na	51.3
H_2O	188.8	C_6H_{12} (cyclohexane)	204.4	MgF_2	57.2
N_2	191.6	C_8H_{18} (isooctane)	329.3	K	64.7
O_2	205.2			NaCl	72.1
CO_2	213.8			KCl	82.6
I_2	260.7			I_2	116.1

A closer examination of Table 16.2.1 also reveals that substances with similar molecular structures tend to have similar $\overline{S}^{o}$ values. Among crystalline materials, those with the lowest entropies tend to be rigid crystals composed of small atoms linked by strong, highly directional bonds, such as diamond ($\overline{S}^{o} = 2.4\,J/(mol \bullet K)$). In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher $\overline{S}^{o}$ (5.7 J/(mol•K)) due to more ~~disorder~~ (microstates) in the crystal. Soft crystalline substances and those with larger atoms tend to have higher entropies because of increased molecular motion and disorder. Similarly, the absolute entropy of a substance tends to increase with increasing molecular complexity because the number of available microstates increases with molecular complexity. For example, compare the $\overline{S}^{o}$ values for CH_3OH(l) and CH_3CH_2OH(l). Finally, substances with strong hydrogen bonds have lower values of $\overline{S}^{o}$, which reflects a more ordered structure.

> *Entropy increases with softer, less rigid solids, solids that contain larger atoms, and solids with complex molecular structures.*

To calculate ΔS^o for a chemical reaction from standard molar entropies, we use the familiar "products minus reactants" rule, in which the absolute molar entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example 16.2.1 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

Example 16.2.1

Use the data in Table 16.2.1 to calculate ΔS^o for the reaction of liquid isooctane with $O_2(g)$ to give $CO_2(g)$ and $H_2O(g)$ at 298 K.

Given: standard molar entropies, reactants, and products

Asked for: ΔS°

Strategy:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table 16.2.1. Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their

appropriate stoichiometric coefficients, to obtain ΔS^o for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:

$$C_8H_{18}(l) + \frac{25}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(g)$$
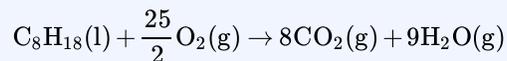
We calculate ΔS^o for the reaction using the "products minus reactants" rule, where m and n are the stoichiometric coefficients of each product and each reactant:

$$
\begin{aligned}
\Delta S^o_{\text{rxn}} &= \sum m\overline{S}^o(\text{products}) - \sum n\overline{S}^o(\text{reactants}) \\
&= [8\overline{S}^o(CO_2) + 9\overline{S}^o(H_2O)] - [\overline{S}^o(C_8H_{18}) + \frac{25}{2}\overline{S}^o(O_2)] \\
&= \{[8 \text{ mol } CO_2 \times 213.8 \text{ J/(mol} \cdot \text{K)}] + [9 \text{ mol } H_2O \times 188.8 \text{ J/(mol} \cdot \text{K)}]\} \\
&\quad - \left\{[1 \text{ mol } C_8H_{18} \times 329.3 \text{ J/(mol} \cdot \text{K)}] + \left[\frac{25}{2} \text{ mol } O_2 \times 205.2 \text{ J/(mol} \cdot \text{K)}\right]\right\} \\
&= 515.3 \text{ J/K}
\end{aligned}
$$

ΔS^o is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

Exercise 16.2.1

Use the data in Table 16.2.1 to calculate ΔS^o for the reaction of $H_2(g)$ with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}) at 298 K.

Answer:

361.1 J/K

Example 16.2.2: Determination of ΔS°

Calculate the standard entropy change for the following process at 298 K:

$$H_2O(g) \longrightarrow H_2O(l)$$

Solution

The value of the standard entropy change at room temperature, ΔS^o_{298}, is the difference between the standard entropy of the product, $H_2O(l)$, and the standard entropy of the reactant, $H_2O(g)$.

$$
\begin{aligned}
\Delta S^o_{298} &= \overline{S}^o_{298}(H_2O(l)) - \overline{S}^o_{298}(H_2O(g)) \\
&= (70.0 \; J\,mol^{-1}K^{-1}) - (188.8 \; Jmol^{-1}K^{-1}) \\
&= -118.8 \; J\,mol^{-1}K^{-1}
\end{aligned}
$$

The value for ΔS^o_{298} is negative, as expected for this phase transition (condensation), which the previous section discussed.

Exercise 16.2.2

Calculate the standard entropy change for the following process at 298 K:

$$H_2(g) + C_2H_4(g) \longrightarrow C_2H_6(g)$$
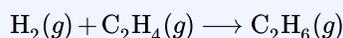
Answer

-120.6 J mol^{-1} K^{-1}

Example 16.2.3: Determination of ΔS°

Example 16.2.3: Determination of ΔS

Calculate the standard entropy change for the combustion of methanol, CH_3OH at 298 K:

$$2\,CH_3OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 4\,H_2O(l)$$
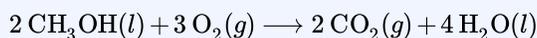
Solution

The value of the standard entropy change is equal to the difference between the standard entropies of the products and the entropies of the reactants scaled by their stoichiometric coefficients. The standard entropy of formations are found in Table 16.2.1.

$$\Delta S^o = \Delta S^o_{298}$$
$$= \sum \nu \overline{S}^o_{298}(\text{products}) - \sum \nu \overline{S}^o_{298}(\text{reactants})$$
$$= 2\overline{S}^o_{298}(CO_2(g)) + 4\overline{S}^o_{298}(H_2O(l))] - [2\overline{S}^o_{298}(CH_3OH(l)) + 3\overline{S}^o_{298}(O_2(g))]$$
$$= [(2 \times 213.8) + (4 \times 70.0)] - [(2 \times 126.8) + (3 \times 205.03)]$$
$$= -161.6\ J/mol \cdot K$$

Exercise 16.2.3

Calculate the standard entropy change for the following reaction at 298 K:

$$Ca(OH)_2(s) \longrightarrow CaO(s) + H_2O(l)$$
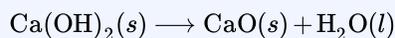
Answer

24.7 J/mol•K

Summary

Energy values, as you know, are all relative, and must be defined on a scale that is completely arbitrary; there is no such thing as the absolute energy of a substance, so we can arbitrarily define the enthalpy or internal energy of an element in its most stable form at 298 K and 1 atm pressure as zero. The same is *not* true of the entropy; since entropy is a measure of the "dilution" of thermal energy, it follows that the less thermal energy available to spread through a system (that is, the lower the temperature), the smaller will be its entropy. In other words, as the absolute temperature of a substance approaches zero, so does its entropy. This principle is the basis of the *Third law of thermodynamics*, which states that the entropy of a perfectly-ordered solid at 0 K is zero.

In practice, chemists determine the absolute entropy of a substance by measuring the molar heat capacity (C_p) as a function of temperature and then plotting the quantity C_p/T versus T. The area under the curve between 0 K and any temperature T is the absolute entropy of the substance at T. In contrast, other thermodynamic properties, such as internal energy and enthalpy, can be evaluated in only relative terms, not absolute terms.

The second law of thermodynamics states that a spontaneous process increases the entropy of the universe, $\Delta S_{univ} > 0$. If $\Delta S_{univ} < 0$, the process is nonspontaneous, and if $\Delta S_{univ} = 0$, the system is at equilibrium. The third law of thermodynamics establishes the zero for entropy as that of a perfect, pure crystalline solid at 0 K. With only one possible microstate, the entropy is zero. We may compute the standard entropy change for a process by using standard entropy values for the reactants and products involved in the process.

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- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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CHAPTER OVERVIEW

17: Extension 12 - Working Equations

17.1: The Maxwell Relations

Modeling the dependence of the Gibbs and Helmholtz functions behave with varying temperature, pressure, and volume is fundamentally useful. But in order to do that, a little bit more development is necessary. To see the power and utility of these functions, it is useful to combine the First and Second Laws into a single mathematical statement. In order to do that, one notes that since

$$dS = \frac{dq}{T} \tag{17.1.1}$$

for a reversible change, it follows that

$$dq = TdS \tag{17.1.2}$$

And since

$$dw = -PdV \tag{17.1.3}$$

for a reversible expansion in which only P-V works is done, it also follows that (since $dU = dq + dw$):

$$dU = TdS - PdV \tag{17.1.4}$$

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) can be expressed:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{17.1.5}$$

Also, by inspection (comparing the two expressions for dU) it is apparent that:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{17.1.6}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \tag{17.1.7}$$

But the value doesn't stop there! Since dU is an exact differential, the Euler relation must hold that

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V \tag{17.1.8}$$

By substituting Equations 17.1.6 and 17.1.7, we see that

$$\left[\frac{\partial}{\partial V}(T)_V\right]_S = \left[\frac{\partial}{\partial S}(-P)_S\right]_V \tag{17.1.9}$$

or

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{17.1.10}$$

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.

$$H \equiv U + PV \tag{17.1.11}$$

Differentiating (and using the chain rule on $d(PV)$) yields

$$dH = dU + PdV + VdP \tag{17.1.12}$$

Making the substitution using the combined first and second laws ($dU = TdS - PdV$) for a reversible change involving on expansion (P-V) work

$$dH = TdS - \cancel{PdV} + \cancel{PdV} + VdP \tag{17.1.13}$$

This expression can be simplified by canceling the PdV terms.

$$dH = TdS + VdP \tag{17.1.14}$$

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

$$dH = \left(\frac{\partial H}{\partial S} \right)_P dS + \left(\frac{\partial H}{\partial P} \right)_S dV \tag{17.1.15}$$

Comparing Equations 17.1.14 and 17.1.15 show that

$$\left(\frac{\partial H}{\partial S} \right)_P = T \tag{17.1.16}$$

and

$$\left(\frac{\partial H}{\partial P} \right)_S = V \tag{17.1.17}$$

It is worth noting at this point that both (Equation 17.1.6)

$$\left(\frac{\partial U}{\partial S} \right)_V \tag{17.1.18}$$

and (Equation 17.1.16)

$$\left(\frac{\partial H}{\partial S} \right)_P \tag{17.1.19}$$

are equation to T. So they are equation to each other

$$\left(\frac{\partial U}{\partial S} \right)_V = \left(\frac{\partial H}{\partial S} \right)_P \tag{17.1.20}$$

Moreover, the Euler Relation must also hold

$$\left[\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial S} \right)_P \right]_S = \left[\frac{\partial}{\partial S} \left(\frac{\partial H}{\partial P} \right)_S \right]_P \tag{17.1.21}$$

so

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P \tag{17.1.22}$$

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	$\left(\frac{\partial T}{\partial V} \right)_S = -\left(\frac{\partial P}{\partial S} \right)_V$
H	$dH = TdS + VdP$	S, P	$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$

Function	Differential	Natural Variables	Maxwell Relation
A	$dA = -PdV - SdT$	V, T	$\left(\dfrac{\partial P}{\partial T}\right)_V = \left(\dfrac{\partial S}{\partial V}\right)_T$
G	$dG = VdP - SdT$	P, T	$\left(\dfrac{\partial V}{\partial T}\right)_P = -\left(\dfrac{\partial S}{\partial P}\right)_T$

The Maxwell relations are extraordinarily useful in deriving the dependence of thermodynamic variables on the state variables of P, T, and V.

Example 17.1.1

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:

$$\left.\frac{dU}{dV}\right|_T = \left.\frac{TdS}{dV}\right|_T - \left.P\frac{dV}{dV}\right|_T$$

Noting that

$$\left.\frac{dU}{dV}\right|_T = \left(\frac{\partial U}{\partial V}\right)_T \tag{17.1.23}$$

$$\left.\frac{TdS}{dV}\right|_T = \left(\frac{\partial S}{\partial V}\right)_T \tag{17.1.24}$$

$$\left.\frac{dV}{dV}\right|_T = 1 \tag{17.1.25}$$

The result is

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

Now, employ the Maxwell relation on A (Table 6.2.1)

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

to get

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

and since

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

It is apparent that

$$\left(\frac{\partial V}{\partial T}\right)_P = T\frac{\alpha}{\kappa_T} - P$$

> *Note*: How cool is that? This result was given without proof in Chapter 4, but can now be proven analytically using the Maxwell Relations!

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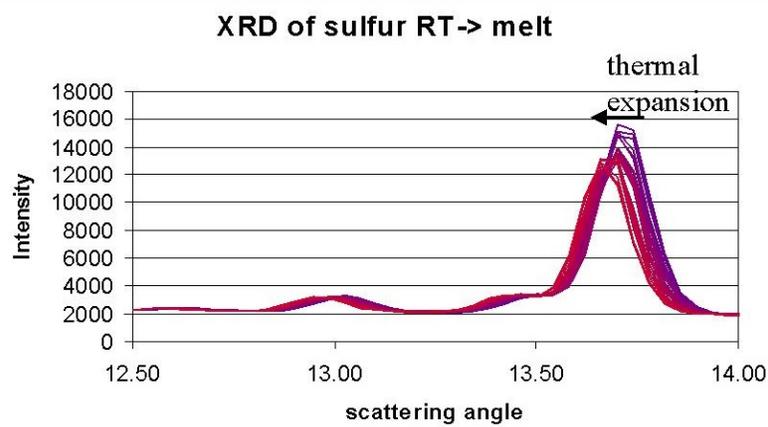
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CHAPTER OVERVIEW

18: Fundamental 13 - Composition Changes

18.1: Partial Molar Quantities

Because they are easy to control in typical laboratory experiments, pressure, temperature, and the number of moles of each component are the independent variables that we find useful most often. Partial derivatives of thermodynamic quantities, taken with respect to the number of moles of a component, **at constant pressure and temperature,** are given a special designation; they are called **partial molar quantities**. That is,

$$\left(\frac{\partial U}{\partial n_i}\right)_{P,T,n_{j\neq i}} \tag{18.1.1}$$

is the partial molar energy of component i,

$$\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}} \tag{18.1.2}$$

is the partial molar Gibbs free energy, etc. All partial molar quantities are intensive variables.

Because partial molar quantities are particularly useful, it is helpful to have a distinctive symbol to represent them. We use a horizontal bar over a thermodynamic variable to represent a partial molar quantity. (We have been using the horizontal over-bar to mean simply per mole. When we use it to designate a partial molar quantity, it means per mole of a specific component.) Thus, we write

$$\left(\frac{\partial U}{\partial n_i}\right)_{P,T,n_{j\neq i}} = \overline{U}_i \tag{18.1.3}$$

$$\left(\frac{\partial V}{\partial n_i}\right)_{P,T,n_{j\neq i}} = \overline{V}_i \tag{18.1.4}$$

$$\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}} = \overline{G}_i \tag{18.1.5}$$

etc.

In Sections 14.1 and 14.2, we introduce the chemical potential for substance i, μ_i, and find that the chemical potential of substance i is equivalently expressed by several partial derivatives. In particular, we have

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}} = \overline{G}_i \tag{18.1.6}$$

that is, **the chemical potential is also the partial molar Gibbs free energy**.

It is important to recognize that the other partial derivatives that we can use to calculate the chemical potential are not partial molar quantities. Thus,

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} \neq \left(\frac{\partial U}{\partial n_i}\right)_{P,T,n_{j\neq i}} \tag{18.1.7}$$

That is, $\mu_i \neq \overline{U}_i$. Similarly, $\mu_i \neq \overline{H}_i$, $\mu_i \neq \overline{A}_i$, and $\mu_i \neq -T\overline{S}_i$.

We can think of a thermodynamic variable as a manifold—a "surface" in a multidimensional space. If there are two independent variables, the dependent thermodynamic variable is a surface in a three-dimensional space. Then we can visualize the partial derivative of the dependent thermodynamic variable with respect to an independent variable as the slope of a line tangent to the surface. This tangent lies in a plane in which the other independent variable is constant. If the independent variables are pressure, temperature, and compositions, the slope of the tangent line at $(P, T, , n_1, n_2, \ldots, n_\omega)$ is the value of a partial molar quantity at that point.

A more concrete way to think of a partial molar quantity for component i is to view it as the change in that quantity when we add one mole of i to a very large system having the specified pressure, temperature, and composition. When we add one mole of i to this system, the relative change in any of the system's properties is very small; for example, the ratio of the final volume to the initial volume is essentially unity. Nevertheless, the volume of the system changes by a finite amount. This amount approximates

the partial molar volume of substance i. This approximation becomes better as the size of the system becomes larger. We expect the change in the volume of the system to be approximately equal to the volume of one mole of pure i, but we know that in general it will be somewhat different because of the effects of attractive and repulsive forces between the additional i molecules and the molecules comprising the original system.

Partial molar quantities can be expressed as functions of other thermodynamic variables. Because pressure and temperature are conveniently controlled variables, functions involving partial molar quantities are particularly useful for describing chemical change in systems that conform to the assumptions that we introduce in §1. Because the chemical potential is the same thing as the partial molar Gibbs free energy, it plays a prominent role in these equations.

To use these equations to describe a real system, we must develop empirical models that relate the partial molar quantities to the composition of the system. In general, these empirical models are non-linear functions of the system composition. However, simple approximations are sometimes adequate. The simplest approximation is a case we have already considered. If we can ignore the attractive and repulsive interactions among the molecules comprising the system, the effect of increasing n_i by a small amount, dn_i, is simply the effect of adding dn_i moles of pure component i to the system. If we let $\overline{U}_i^*$ be the energy per mole of pure component i, the contribution to the energy of the system, at constant temperature and pressure, is

$$\left(\frac{\partial U}{\partial n_i} \right)_{P,T,n_{j \neq i}} dn_i = \overline{U}_i^* \, dn_i \tag{18.1.8}$$

In Chapter 12, we apply the thermodynamic criteria for change to the equilibria between phases of a pure substance. To do so, we use the Gibbs free energies of the pure phases. In Chapter 13, we apply these criteria to chemical reactions of ideal gases, using the Gibbs free energies of the pure gases. In these cases, the properties of a phase of a pure substance are independent of the amounts of any other substances that are present. That is, we use the approximation

$$\left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_{j \neq i}} dn_i = \overline{G}_i^* \, dn_i \tag{18.1.9}$$

albeit without using the over-bar or the bullet superscript to indicate that we are using the partial molar Gibbs free energy of the pure substance. In Section 14.1, we develop the principle that $\sum_{i=1}^{N} \mu_i dn_i \leq 0$ are general criteria for change that are applicable not only to closed systems but also to open systems composed of homogeneous phases.

Thus far in this chapter, we have written each partial derivative with a complete list of the variables that are held constant. This is typographically awkward. Clarity seldom requires that we include the work-related variables and composition variables, n_i, in this list. From here on, we usually omit them.

18.2: 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:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j \neq i} \tag{18.2.1}$$

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

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,n_j \neq i} dn_i \tag{18.2.2}$$

Or, by substituting the definition for the chemical potential, and evaluating the pressure and temperature derivatives as was done in [Chapter 6](#):

$$dG = VdP - SdT + \sum_i \mu_i dn_i \tag{18.2.3}$$

But as it turns out, the chemical potential can be defined as the partial molar derivative of any of the four major thermodynamic functions U, H, A, or G:

Table **18.2.1***: Chemical potential can be defined as the partial molar derivative any of the four major thermodynamic functions*

$dU = TdS - PdV + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j \neq i}$
$dH = TdS + VdP + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j \neq i}$
$dA = -SdT - PdV + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_j \neq i}$
$dG = -SdT + VdP + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j \neq i}$

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 18.2.1). As the partial molar Gibbs function, it is easy to show that

$$d\mu = -\overline{S}dT + \overline{V}dP \tag{18.2.4}$$

where $\overline{V}$ is the molar volume, and $\overline{S}$ is the molar entropy. Using this expression, it is easy to show that

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \overline{V} \tag{18.2.5}$$

and so at constant temperature

$$\int_{\mu^o}^{\mu} d\mu = \int_{P^o}^{P} \overline{V}\, dP \tag{18.2.6}$$

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, as in a solid or liquid), therefore Equation 18.2.6 becomes

$$\int_{\mu^o}^{\mu} d\mu = \overline{V} \int_{P^o}^{P} dP \tag{18.2.7}$$

$$\mu - \mu^o = \overline{V}(P - P^o) \tag{18.2.8}$$

or

$$\mu = \mu^o + \overline{V}(P - P^o) \tag{18.2.9}$$

Where P^o is a reference pressure (generally the standard pressure of 1 bar) and μ^o is the chemical potential at the standard pressure. If the substance is highly compressible (such as a gas) the pressure dependence of the molar volume is needed to complete the integral. If the substance is an ideal gas

$$\overline{V} = \frac{RT}{P} \tag{18.2.10}$$

So at constant temperature, Equation 18.2.6 then becomes

$$\int_{\mu^o}^{\mu} d\mu = RT \int_{P^o}^{P} \frac{dP}{P} \tag{18.2.11}$$

or

$$\mu = \mu^o + RT \ln\left(\frac{P}{P^o}\right) \tag{18.2.12}$$

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18.3: ΔrG is the rate at which the Gibbs Free Energy Changes with The Extent of Reaction

For the reaction $a\,A + b\,B \rightleftharpoons c\,C + d\,D$, let us call the consumption of a moles of A one "unit of reaction." $\Delta_r G$ corresponds to the actual Gibbs free energy change for one unit of reaction only in the limiting case where the reaction occurs in an arbitrarily large system. For a closed system of specified initial composition, n_A^o, n_B^o, n_C^o, and n_D^o, whose composition at any time is specified by n_A, n_B, n_C, and n_D, the extent of reaction, ξ, is

$$\xi = -\left(\frac{n_A - n_A^o}{a}\right) = -\left(\frac{n_B - n_B^o}{b}\right) = \frac{n_C - n_C^o}{c} = \frac{n_D - n_D^o}{d}$$

At constant pressure and temperature, every possible state of this system is represented by a point on a plot of $\Delta_r G$ *versus* ξ. Every such state is also represented by a point on a plot of G_{system} *versus* ξ.

From the general result that $(dG_{system})_{PT} = 0$ if and only if the system is at equilibrium, it follows that $\Delta_r G\left(\xi_{eq}\right) = 0$ if and only if ξ_{eq} specifies the equilibrium state. (We can arrive at the same conclusion by considering the heat exchanged for one unit of reaction in an infinitely large system at equilibrium. This process is reversible, and it occurs at constant pressure and temperature, so we have $\Delta_r H = q_P^{rev}$, $\Delta_r S = q_P^{rev}/T$, and $\Delta_r G = q_P^{rev} + T\left(q_P^{rev}/T\right) = 0$.)

Below, we show that

$$\Delta_r G\left(\xi\right) = \left(\frac{\partial G_{system}}{\partial \xi}\right)_{PT}$$

for any value of ξ. (In Section 15.9, we use essentially the same argument to show that this conclusion is valid for any reaction among any substances.) Given this result, we see that the equilibrium composition corresponds to the extent of reaction, ξ_{eq}, for which the Gibbs free energy change for one unit of the reaction is zero

$$\Delta_r G\left(\xi_{eq}\right) = 0$$

and

$$\left(\frac{\partial G_{system}}{\partial \xi}\right)_{PT} = 0$$

So that the Gibbs free energy of the system is a minimum.

In the next section, we show that the condition $\Delta_r G\left(\xi_{eq}\right) = 0$ makes it easy to calculate the equilibrium extent of reaction, ξ_{eq}. Given the stoichiometry and initial composition, the equation for $\Delta_r G\left(\xi_{eq}\right)$ specifies the equilibrium composition and the partial pressures P_A, P_B, P_C, and P_D. This is the usual application of these results. Setting $\Delta_r G = 0$ enables us to answer the question: If we initiate reaction at a given composition, what will be the equilibrium composition of the system? Usually this is what we want to know. The amount by which the Gibbs free energy changes as the reaction goes to equilibrium is seldom of interest.

To show that $\Delta_r G = (\partial G/\partial \xi)_{PT}$ for any reaction, it is helpful to introduce modified stoichiometric coefficients, ν_j, defined such that $\nu_j > 0$ if the j-th species is a product and $\nu_j < 0$ if the j-th species is a reactant. That is, for the reaction $a\,A + b\,B \rightleftharpoons c\,C + d\,D$, we define $\nu_A = -a$, $\nu_B = -b$, $\nu_C = c$, and $\nu_D = d$. Associating successive integers with the reactants and products, we represent the j-th chemical species as X_j and an arbitrary reaction as

$$|\nu_1|\,X_1 + |\nu_2|\,X_2 + \cdots + |\nu_i|\,X_i \rightleftharpoons \nu_j X_j + \cdots + \nu_\omega X_\omega$$
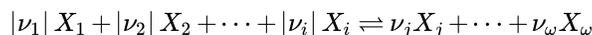
Let the initial number of moles of ideal gas X_j be n_j^o; then $n_j = n_j^o + \nu_j \xi$. (For species that are present but do not participate in the reaction, we have $\nu_j = 0$.)

We have shown that the Gibbs free energy of a mixture of ideal gases is equal to the sum of the Gibbs free energies of the components. In calculating $\Delta_r G$, we assume that this is as true for a mixture undergoing a spontaneous reaction as it is for a mixture at equilibrium. In doing so, we assume that the reacting system is homogeneous and that its temperature and pressure are well defined. In short, we assume that the Gibbs free energy of the system is the same continuous function of temperature, pressure, and composition, $G = G\left(T, P, n_1, n_2, \ldots\right)$, whether the system is at equilibrium or undergoing a spontaneous reaction. For the

equilibrium system, we have $(\partial G/\partial T)_{P,n_j} = -S$ and $(\partial G/\partial P)_{T,n_j} = V$. When we assume that these functions are the same for a spontaneously changing system as they are for a reversible system, it follows that

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_j} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_j} dP + \sum_j \left(\frac{\partial G}{\partial n_j}\right)_{P,T,n_{i\neq j}} dn_j = -SdT + VdP + \sum_j \left(\frac{\partial G}{\partial n_j}\right)_{P,T,n_{i\neq j}} dn_j$$

whether the system is at equilibrium or undergoing spontaneous change. At constant temperature and pressure, when pressure–volume work is the only work, the thermodynamic criteria for change, $dG_{TP} \leq 0$ become

$$\sum_j \left(\frac{\partial G}{\partial n_j}\right)_{P,T,n_{i\neq j}} dn_j \leq 0$$

When a reaction occurs in the system, the composition is a continuous function of the extent of reaction. We have $G = G\left(T, P, n_1^o + \nu_1\xi, n_2^o + \nu_2\xi, \dots\right)$. At constant temperature and pressure, the dependence of the Gibbs free energy on the extent of reaction is

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T,n_m} = \sum_j \left(\frac{\partial G}{\partial \left(n_J^o + \nu_j\xi\right)}\right)_{P,T,n_{m\neq j}} \left(\frac{\partial \left(n_J^o + \nu_j\xi\right)}{\partial \xi}\right)_{P,T,n_{m\neq j}}$$

Since

$$\left(\frac{\partial G}{\partial \left(n_J^o + \nu_j\xi\right)}\right)_{P,T,n_{m\neq j}} = \left(\frac{\partial G}{\partial n_j}\right)_{P,T,n_{m\neq j}} = \overline{G}_j$$

and

$$\left(\frac{\partial \left(n_J^o + \nu_j\xi\right)}{\partial \xi}\right)_{P,T,n_{m\neq j}} = \nu_j$$

it follows that

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T,n_m} = \sum_j \nu_j\overline{G}_j = \Delta_r G$$

Moreover, we have

$$(dG)_{PT} = \left(\frac{\partial G}{\partial \xi}\right)_{P,T,n_m} d\xi$$

The criteria for change, $(dG)_{PT} \leq 0$, become

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T,n_m} d\xi \leq 0$$

From our definition of ξ, we have $d\xi > 0$ for a process that proceeds spontaneously from left to right, so the criteria become

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T,n_m} \leq 0$$

or, equivalently,

$$\sum_j \nu_j\overline{G}_j = \Delta_r G \leq 0$$

- **13.5: ΔrG is the rate at which the Gibbs Free Energy Changes with The Extent of Reaction** by Paul Ellgen is licensed CC BY-SA 4.0.
  Original source: https://www.amazon.com/Thermodynamics-Chemical-Equilibrium-Paul-Ellgen/dp/1492114278.

18.4: Molar Reaction Enthalpy

Recall that $\Delta\overline{H}_{\text{rxn}}$ is a molar integral reaction enthalpy equal to $\Delta H_{\text{rxn}}/\Delta\xi$, and that $\Delta_r H$ is a molar differential reaction enthalpy defined by $\sum_i \nu_i \overline{H}_i$ and equal to $(\partial H/\partial\xi)_{T,P}$.

Molar reaction enthalpy and heat

During a process in a closed system at constant pressure with expansion work only, the enthalpy change equals the energy transferred across the boundary in the form of heat: $dH = dq$. Thus for the molar reaction enthalpy $\Delta_r H = (\partial H/\partial\xi)_{T,P}$, which refers to a process not just at constant pressure but also at constant temperature, we can write

$$\Delta_r H = \left(\frac{dq}{d\xi}\right)_{T,P,w'} \tag{18.4.1}$$

Note that when there is nonexpansion work (w'), such as electrical work, the enthalpy change is not equal to the heat. For example, if we compare a reaction taking place in a galvanic cell with the same reaction in a reaction vessel, the heats at constant T and P for a given change of ξ are different, and may even have opposite signs. The value of $\Delta_r H$ is the same in both systems, but the ratio of heat to extent of reaction, $dq/d\xi$, is different.

An **exothermic** reaction is one for which $\Delta_r H$ is negative, and an **endothermic** reaction is one for which $\Delta_r H$ is positive. Thus in a reaction at constant temperature and pressure with expansion work only, heat is transferred out of the system during an exothermic process and into the system during an endothermic process. If the process takes place at constant pressure in a system with thermally-insulated walls, the temperature increases during an exothermic process and decreases during an endothermic process.

These comments apply not just to chemical reactions, but to the other chemical processes at constant temperature and pressure discussed in this chapter.

Standard molar enthalpies of reaction and formation

A **standard molar reaction enthalpy**, $\Delta_r H^\circ$, is the same as the molar integral reaction enthalpy $\Delta\overline{H}_{\text{rxn}}$ for the reaction taking place under standard state conditions (each reactant and product at unit activity) at constant temperature.

At constant temperature, partial molar enthalpies depend only mildly on pressure. It is therefore usually safe to assume that unless the experimental pressure is much greater than P°, the reaction is exothermic if $\Delta_r H^\circ$ is negative and endothermic if $\Delta_r H^\circ$ is positive.

The **formation reaction** of a substance is the reaction in which the substance, at a given temperature and in a given physical state, is formed from the constituent elements in their reference states at the same temperature. The *reference state of an element* is usually chosen to be the standard state of the element in the allotropic form and physical state that is stable at the given temperature and the standard pressure. For instance, at 298.15 K and 1 bar the stable allotrope of carbon is crystalline graphite rather than diamond.

Phosphorus is an exception to the rule regarding reference states of elements. Although red phosphorus is the stable allotrope at 298.15 K, it is not well characterized. Instead, the reference state is white phosphorus (crystalline P_4) at 1 bar.

At 298.15 K, the reference states of the elements are the following:

- For H_2, N_2, O_2, F_2, Cl_2, and the noble gases, the reference state is the ideal gas at 1 bar.
- For Br_2 and Hg, the reference state is the liquid at 1 bar.
- For P, as mentioned above, the reference state is crystalline white phosphorus at 1 bar.
- For all other elements, the reference state is the stable crystalline allotrope at 1 bar.

The **standard molar enthalpy of formation** (or standard molar heat of formation), $\Delta_f H^\circ$, of a substance is the enthalpy change per amount of substance produced in the formation reaction of the substance in its standard state. Thus, the standard molar enthalpy of formation of gaseous methyl bromide at 298.15 K is the molar reaction enthalpy of the reaction

$$C\,(s,\text{ graphite},P^\circ)+\frac{3}{2}H_2\,(\text{ ideal gas, }P^\circ)+\frac{1}{2}Br_2\,(1,P^\circ)\rightarrow CH_3Br\,(\text{ ideal gas, }P^\circ)$$
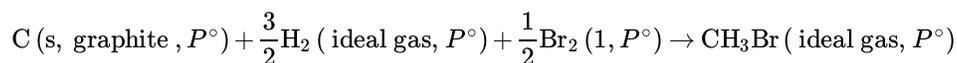
The value of $\Delta_f H^\circ$ for a given substance depends only on T. By definition, $\Delta_f H^\circ$ for the reference state of an element is zero.

A principle called **Hess's law** can be used to calculate the standard molar enthalpy of formation of a substance at a given temperature from standard molar reaction enthalpies at the same temperature, and to calculate a standard molar reaction enthalpy from tabulated values of standard molar enthalpies of formation. The principle is an application of the fact that enthalpy is a state function. Therefore, ΔH for a given change of the state of the system is independent of the path and is equal to the sum of ΔH values for any sequence of changes whose net result is the given change. (We may apply the same principle to a change of *any* state function.)

For example, the following combustion reactions can be carried out experimentally in a bomb calorimeter, yielding the values shown below of standard molar reaction enthalpies (at $T = 298.15$ K, $P = P^\circ = 1$ bar):

$$\mathrm{C(s,\ graphite\,)} + \mathrm{O_2(g)} \to \mathrm{CO_2(g)} \qquad \Delta_\mathrm{r} H^\circ = -393.51\ \mathrm{kJ\ mol^{-1}}$$
$$\mathrm{CO(g)} + \frac{1}{2}\mathrm{O_2(g)} \to \mathrm{CO_2(g)} \qquad \Delta_\mathrm{r} H^\circ = -282.98\ \mathrm{kJ\ mol^{-1}}$$
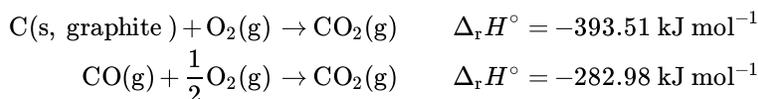
(Note that the first reaction, in addition to being the combustion reaction of graphite, is also the formation reaction of carbon dioxide.) The change resulting from the first reaction followed by the reverse of the second reaction is the formation reaction of carbon monoxide:

$$\mathrm{C(s,\ graphite\,)} + \frac{1}{2}\mathrm{O_2(g)} \to \mathrm{CO(g)}$$
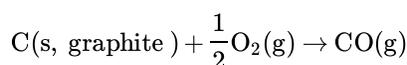
It would not be practical to measure the molar enthalpy of this last reaction by allowing graphite to react with oxygen in a calorimeter, because it would be difficult to prevent the formation of some CO_2. From Hess's law, the standard molar enthalpy of formation of CO is the sum of the standard molar enthalpies of the reactions that have the formation reaction as the net result:

$$\Delta_\mathrm{f} H^\circ(\mathrm{CO, g}, 298.15\ \mathrm{K}) = (-393.51 + 282.98)\ \mathrm{kJ\ mol^{-1}}$$
$$= -110.53\ \mathrm{kJ\ mol^{-1}}$$

This value is one of the many standard molar enthalpies of formation to be found in compilations of thermodynamic properties of individual substances. We may use the tabulated values to evaluate the standard molar reaction enthalpy $\Delta_\mathrm{r} H^\circ$ of a reaction using a formula based on Hess's law. Imagine the reaction to take place in two steps: First each reactant in its standard state changes to the constituent elements in their reference states (the reverse of a formation reaction), and then these elements form the products in their standard states. The resulting formula is:

$$\Delta_\mathrm{r} H^\circ = \sum_i \nu_i \Delta_\mathrm{f} H_i^\circ \tag{18.4.2}$$

where $\Delta_\mathrm{f} H_i^\circ$ is the standard molar enthalpy of formation of substance i. Recall that the stoichiometric number ν_i of each reactant is negative and that of each product is positive, so according to Hess's law the standard molar reaction enthalpy is the sum of the standard molar enthalpies of formation of the products minus the sum of the standard molar enthalpies of formation of the reactants. Each term is multiplied by the appropriate stoichiometric coefficient from the reaction equation.

A standard molar enthalpy of formation can be defined for a *solute in solution* to use in 18.4.2. For instance, the formation reaction of aqueous sucrose is:

$$12\mathrm{C(s,\ graphite\,)} + 11\mathrm{H_2(g)} + \frac{11}{2}\mathrm{O_2(g)} \to \mathrm{C_{12}H_{22}O_{11}(aq)}$$
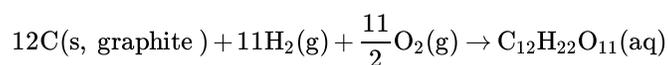
and $\Delta_\mathrm{f} H_i^\circ$ for $\mathrm{C_{12}H_{22}O_{11}(aq)}$ is the enthalpy change per amount of sucrose formed when the reactants and product are in their standard states. Note that this formation reaction does *not* include the formation of the solvent H_2O from H_2 and O_2. Instead, the solute once formed combines with the amount of pure liquid water needed to form the solution. If the aqueous solute is formed in its standard state, the amount of water needed is very large so as to have the solute exhibit infinite-dilution behavior.

There is no ordinary reaction that would produce an individual *ion in solution* from its element or elements without producing other species as well. We can, however, prepare a consistent set of standard molar enthalpies of formation of ions by assigning a value to a single reference ion. We can use these values for ions in 18.4.2 just like values of $\Delta_\mathrm{f} H_i^\circ$ for substances and nonionic solutes. Aqueous hydrogen ion is the usual reference ion, to which is assigned the arbitrary value

$$\Delta_\mathrm{f} H^\circ\left(\mathrm{H^+, aq}\right) = 0 \quad (\text{at all temperatures})$$

To see how we can use this reference value, consider the reaction for the formation of aqueous HCl (hydrochloric acid):

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq)$$
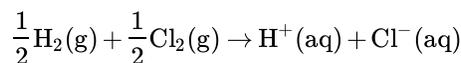
The standard molar reaction enthalpy at 298.15 K for this reaction is known, from reaction calorimetry, to have the value $\Delta_r H^\circ = -167.08 \text{ kJ mol}^{-1}$. The standard states of the gaseous H_2 and Cl_2 are, of course, the pure gases acting ideally at pressure P°, and the standard state of each of the aqueous ions is the ion at the standard molality and standard pressure, acting as if its activity coefficient on a molality basis were 1. From $ref1$, we equate the value of $\Delta_r H^\circ t$ to the sum

$$-\frac{1}{2}\Delta_f H^\circ(H_2, g) - \frac{1}{2}\Delta_f H^\circ(Cl_2, g) + \Delta_f H^\circ(H^+, aq) + \Delta_f H^\circ(Cl^-, aq) \tag{18.4.3}$$

But the first three terms of this sum are zero. Therefore, the value of $\Delta_f H^\circ(Cl^-, aq)$ is $-167.08 \text{ kJ mol}^{-1}$.

Next we can combine this value of $\Delta_f H^\circ(Cl^-, aq)$ with the measured standard molar enthalpy of formation of aqueous sodium chloride

$$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow Na^+(aq) + Cl^-(aq)$$
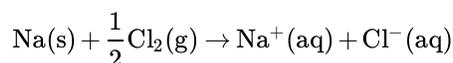
to evaluate the standard molar enthalpy of formation of aqueous sodium ion. By continuing this procedure with other reactions, we can build up a consistent set of $\Delta_f H^\circ$ values of various ions in aqueous solution.

Molar reaction heat capacity

The molar reaction enthalpy $\Delta_r \overline{H}$ is in general a function of T, P, and ξ. Using the relations $\Delta_r H = \sum_i \nu_i H_i$ and $C_{P,i} = (\partial H_i/\partial T)_{P,\xi}$, we can write

$$\left(\frac{\partial \Delta_r H}{\partial T}\right)_{p,\xi} = \left(\frac{\partial \sum_i \nu_i H_i}{\partial T}\right)_{p,\xi} = \sum_i \nu_i C_{p,i} = \Delta_r C_p \tag{18.4.4}$$

where $\Delta_r C_P$ is the molar reaction heat capacity at constant pressure, equal to the rate at which the heat capacity C_P changes with ξ at constant T and P.

Under standard state conditions, 18.4.4 becomes

$$d\Delta_r H^\circ / dT = \Delta_r C_p^\circ \tag{18.4.5}$$

Effect of temperature on reaction enthalpy

Consider a reaction occurring with a certain finite change of the extent of reaction in a closed system at temperature T' and at constant pressure. The reaction is characterized by a change of the extent of reaction from ξ_1 to ξ_2, and the integral reaction enthalpy at this temperature is denoted $\Delta H_{rxn}(T')$. We wish to find an expression for the reaction enthalpy $\Delta H_{rxn}(T'')$ for the same values of ξ_1 and ξ_2 at the same pressure but at a different temperature, T''.

The heat capacity of the system at constant pressure is related to the enthalpy: $C_P = (\partial H/\partial T)_{P,\xi}$. We integrate $dH = C_p dT$ from T' to T'' at constant P and ξ, for both the final and initial values of the extent of reaction:

$$H(\xi_2, T'') = H(\xi_2, T') + \int_{T'}^{T''} C_p(\xi_2) dT \tag{18.4.6}$$

$$H(\xi_1, T'') = H(\xi_1, T') + \int_{T'}^{T''} C_p(\xi_1) dT \tag{18.4.7}$$

Subtracting 18.4.7 from 18.4.6, we obtain

$$\Delta H_{rxn}(T'') = \Delta H_{rxn}(T') + \int_{T'}^{T''} \Delta C_p dT \tag{18.4.8}$$

where ΔC_P is the difference between the heat capacities of the system at the final and initial values of ξ, a function of T: $\Delta C_p = C_p(\xi_2) - C_p(\xi_1)$. 18.4.8 is the **Kirchhoff equation**.

When ΔC_P is essentially constant in the temperature range from T' to T'', the Kirchhoff equation becomes

$$\Delta H_{rxn}(T'') = \Delta H_{rxn}(T') + \Delta C_p(T'' - T') \tag{18.4.9}$$
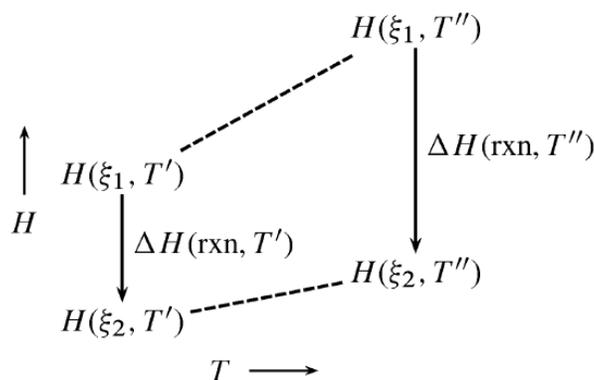
Figure 18.4.1: Dependence of reaction enthalpy on temperature at constant pressure.

Figure 18.4.1 illustrates the principle of the Kirchhoff equation as expressed by 18.4.9. ΔC_P equals the difference in the slopes of the two dashed lines in the figure, and the product of ΔC_P and the temperature difference $T'' - T'$ equals the change in the value of ΔH_{rxn}. The figure illustrates an exothermic reaction with negative ΔC_P, resulting in a more negative value of ΔH_{rxn} at the higher temperature.

We can also find the effect of temperature on the molar differential reaction enthalpy $\Delta_{\text{r}} H$. From 18.4.4, we have $C_P = (\partial H / \partial T)_{P,\xi}$. Integration from temperature T' to temperature T'' yields the relation

$$\Delta_{\text{r}} H\left(T'', \xi\right) = \Delta_{\text{r}} H\left(T', \xi\right) + \int_{T'}^{T''} \Delta_{\text{r}} C_p(T, \xi) \mathrm{d}T \qquad (18.4.10)$$

This relation is analogous to 18.4.8, using molar differential reaction quantities in place of integral reaction quantities.

Contributors

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CHAPTER OVERVIEW

19: Extension 13 - More Cycles

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19.1: How The Enthalpy Change for a Reaction Depends on Temperature

Previously, we saw how to use tabulated enthalpies of formation to calculate the enthalpy change for a particular chemical reaction. Such tables typically give enthalpies of formation at a number of different temperatures, so that the enthalpy change for a given reaction can also be calculated at these different temperatures; it is just a matter of repeating the same calculation at each temperature.

We often need to find the enthalpy change associated with increasing the temperature of a substance at constant pressure. This enthalpy change is readily calculated by integrating the heat capacity over the temperature change. We may want to know, for example, the enthalpy change for increasing the temperature of one mole of methane from 300 K to 400 K, with the pressure held constant at one bar. From the table, we find

$$\Delta_f H^o \left(CH_4, g, 300\ K \right) = -74.656\ \text{kJ mol}^{-1} \tag{19.1.1}$$

$$\Delta_f H^o \left(CH_4, g, 400\ \text{K} \right) = -77.703\ \text{kJ mol}^{-1} \tag{19.1.2}$$

We might be tempted to think that the difference represents the enthalpy change associated with heating the methane. This is not so! The reason becomes immediately apparent if we consider a cycle in which we go from the elements to a compound at two different temperatures. For methane, this cycle is shown in Figure 19.1.1.
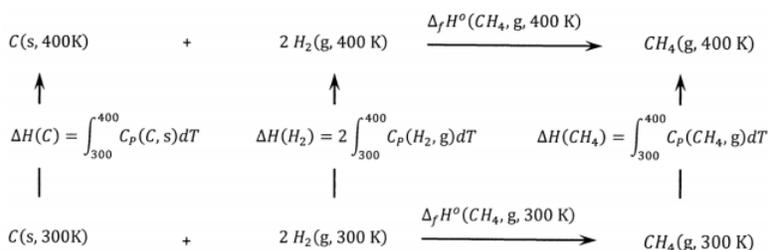
Figure 19.1.1: A thermochemical cycle relating $\Delta_f H^o (CH_4)$ at two temperatures.

The difference between the standard enthalpies of formation of methane at 300 K and 400 K reflects the enthalpy change for increasing the temperatures of all of the reactants and products from 300 K to 400 K. That is,

$$\Delta_f H^o \left(CH_4, g, 400\ \text{K} \right) - \Delta_f H^o \left(CH_4, g, 300\ \text{K} \right) \tag{19.1.3}$$

$$= \int_{300}^{400} C_P \left(CH_4, g \right) dT - \int_{300}^{400} C_P \left(C, s \right) dT - 2 \int_{300}^{400} C_P \left(H_2, g \right) dT \tag{19.1.4}$$

Over the temperature range from 300 K to 400 K, the heat capacities of carbon, hydrogen, and methane are approximated by $C_P = a + bT$, with values of a and b given in Table 1. From this information, we calculate the enthalpy change for increasing the temperature of one mole of each substance from 300 K to 400 K at 1 bar: $\Delta H \left(C \right) = 1,029\ \text{J mol}^{-1}$, $\Delta H \left(H_2 \right) = 2,902\ \text{J mol}^{-1}$, and $\Delta H \left(CH_4 \right) = 3,819\ \text{J mol}^{-1}$. Thus, from the cycle, we calculate:

$$\Delta_f H^o \left(CH_4, g, 400\ \text{K} \right) = -74,656 + 3,819 - 1,029 - 2 \left(2,902 \right)\ \text{J mol}^{-1} = -77,670\ \text{J mol}^{-1} \tag{19.1.5}$$

The tabulated value is $-77,703\ \text{J mol}^{-1}$. The two values differ by $33\ \text{J mol}^{-1}$, or about 0.04%. This difference arises from the limitations of the two-parameter heat-capacity equations.

As another example of a thermochemical cycle, let us consider the selective oxidation of methane to methanol at 300 K and 400 K. From the enthalpies of formation in Table 1, we calculate the enthalpies for the reaction to be $\Delta_r H^o \left(300\ \text{K} \right) = -126.412\ \text{kJ mol}^{-1}$ and $\Delta_r H^o \left(400\ \text{K} \right) = -126.919\ \text{kJ mol}^{-1}$. As in the previous example, we use the tabulated heat-capacity parameters to calculate the enthalpy change for increasing the temperature of one mole of each of these gases from 300 K to 400 K at 1 bar. We find: $\Delta H \left(CH_3OH \right) = 4,797\ \text{J mol}^{-1}$, $\Delta H \left(CH_4 \right) = 3,819\ \text{J mol}^{-1}$, and $\Delta H \left(O_2 \right) = 2,975\ \text{J mol}^{-1}$.

$$\Delta_r H^o(400\ K)$$

$$CH_4(g, 400K) \quad + \quad \tfrac{1}{2}O_2(g, 400\ K) \xrightarrow{\hspace{3cm}} CH_3OH(g, 400\ K)$$

$$\Delta H(CH_4) = \int_{300}^{400} C_P(CH_4, g)\,dT \quad \Delta H(O_2) = \tfrac{1}{2}\int_{300}^{400} C_P(O_2, g)\,dT \quad \Delta H(CH_3OH) = \int_{300}^{400} C_P(CH_3OH, g)\,dT$$

$$\Delta_r H^o(300\ K)$$

$$CH_4(g, 300K) \quad + \quad \tfrac{1}{2}O_2(g, 300\ K) \xrightarrow{\hspace{3cm}} CH_3OH(g, 300\ K)$$
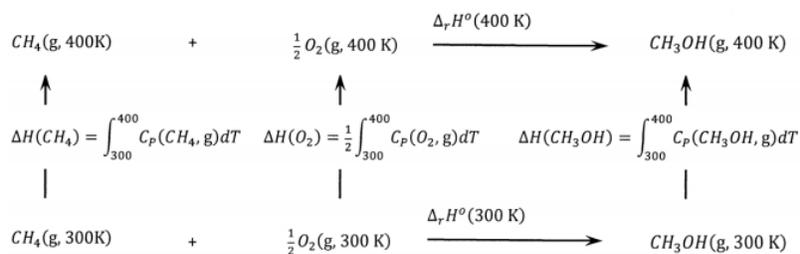
Figure 19.1.2: A thermochemical cycle relating $\Delta_r H^o$ at two temperatures.

The cycle is shown in 19.1.2. Inspecting this cycle, we see that we can calculate the enthalpy change for warming one mole of methanol from 300 K to 400 K by summing the enthalpy changes around the bottom, left side, and top of the cycle; that is,

$$\Delta H\left(CH_3OH\right) = 126,412 + 3,819 + \left(\frac{1}{2}\right)2,975 - 126,919\ \text{J mol}^{-1} = 4,800\ \text{J mol}^{-1} \tag{19.1.6}$$

This is 3 J or about 0.06 % larger than the value obtained $(4,797\ \text{J})$ by integrating the heat capacity for methanol.

20: Fundamental 14 - Reaction Equilibrium

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20.1: 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.

Reaction coordinate ξ
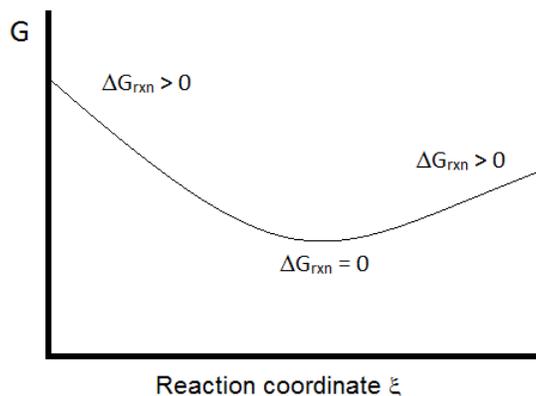
From the diagram above, it should be clear that the direction of spontaneous change is determined by minimizing

$$\left(\frac{\partial G}{\partial \xi} \right)_{P,T}. \tag{20.1.1}$$

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.

Contributors

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)

20.2: 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

$$A(g) \rightleftharpoons B(g) \tag{20.2.1}$$

The criterion for equilibrium will be

$$\mu_A = \mu_B \tag{20.2.2}$$

If the gases behave ideally, the chemical potentials can be described in terms of the mole fractions of A and B

$$\mu_A^o + RT \ln \left(\frac{P_A}{P_{tot}} \right) = \mu_B^o + RT \ln \left(\frac{P_B}{P_{tot}} \right) \tag{20.2.3}$$

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

$$\chi_i = \frac{P_i}{P_{tot}} \tag{20.2.4}$$

Equation 20.2.3 can be simplified by collecting all chemical potentials terms on the left

$$\mu_A^o - \mu_B^o = RT \ln \left(\frac{P_B}{P_{tot}} \right) - RT \ln \left(\frac{P_A}{P_{tot}} \right) \tag{20.2.5}$$

Combining the logarithms terms and recognizing that

$$\mu_A^o - \mu_B^o = -\Delta G^o \tag{20.2.6}$$

for the reaction, one obtains

$$-\Delta G^o = RT \ln \left(\frac{P_B}{P_A} \right) \tag{20.2.7}$$

And since the equilibrium constant is $P_A/P_B = K_P$ for this reaction (assuming perfectly ideal behavior), one can write

$$\Delta G^o = RT \ln K_P \tag{20.2.8}$$

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

$$Q_P = \frac{\prod_i P_i^{\nu_i}}{\prod_j P_j^{\nu_j}} \tag{20.2.9}$$

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

$$0 = \sum_i \nu_i X_i \tag{20.2.10}$$

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

$$Q_P = \prod_i P_i^{\nu_i} \tag{20.2.11}$$

Using this expression, the Gibbs function change for the system can be calculated from

$$\Delta G = \Delta G^o + RT \ln Q_P \tag{20.2.12}$$

And since at equilibrium

$$\Delta G = 0 \tag{20.2.13}$$

and

$$Q_P = K_P \tag{20.2.14}$$

It is evident that

$$\Delta G^o_{rxn} = -RT \ln K_P \tag{20.2.15}$$

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 20.2.1:

Based on the data below at 298 K, calculate the value of the equilibrium constant (K_P) for the reaction

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \tag{20.2.16}$$
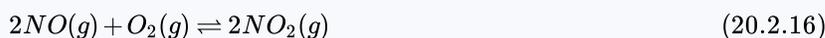
$NO(g)$	$NO_2(g)$
G_f^o (kJ/mol)	51.53

Solution:

First calculate the value of ΔG^o_{rxn} from the ΔG^o_f data.

$$\Delta G^o_{rxn} = 2 \times (51.53\,kJ/mol) - 2 \times (86.55\,kJ/mol) = -70.04\,kJ/mol \tag{20.2.17}$$

And now use the value to calculate K_p using Equation 20.2.15

$$-70040\,J/mol = -(8.314 J/(mol\,K))(298\,K)\ln K_p \tag{20.2.18}$$

$$K_p = 1.89 \times 10^{12} \tag{20.2.19}$$

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.

Contributors

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CHAPTER OVERVIEW

21: Extension 14 - Temperature Dependence of Equilibrium

21.1: 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_{rxm}^o 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

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

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.

$$\ln\left(\frac{K_2}{K_1} \right) = -\frac{\Delta H^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{21.1.1}$$

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 21.1.1
>
> A certain reaction has a value of $K_p = 0.0260$ at 25 °C and $\Delta H_{rxm}^o = 32.4\,kJ/mol$. 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
> - $\Delta H_{rxm}^o = 32.4\,kJ/mol$
> - K_1 = 0.0260
> - K_2 = ?
>
> So Equation 21.1.1 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 21.1.2
>
> 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.

22: Fundamental 15 - Phase Equilibrium

22.1: Fundamentals of Phase Transitions

Phase transition is when a substance changes from a solid, liquid, or gas state to a different state. Every element and substance can transition from one phase to another at a specific combination of temperature and pressure.

Phase Changes

Each substance has three phases it can change into; solid, liquid, or gas[1]. Every substance is in one of these three phases at certain temperatures. The temperature and pressure at which the substance will change is very dependent on the intermolecular forces that are acting on the molecules and atoms of the substance[2]. There can be two phases coexisting in a single container at the same time. This typically happens when the substance is transitioning from one phase to another. This is called a two-phase state[4]. In the example of ice melting, while the ice is melting, there is both solid water and liquid water in the cup.

There are six ways a substance can change between these three phases; melting, freezing, evaporating, condensing, sublimination, and deposition[2]. These processes are reversible and each transfers between phases differently:

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

How Phase Transition works

There are two variables to consider when looking at phase transition, pressure (P) and temperature (T). For the gas state, The relationship between temperature and pressure is defined by the equations below:

Ideal Gas Law:

$$PV = nRT \qquad (22.1.1)$$

van der Waals Equation of State:

$$\left(P + a * \frac{n^2}{V^2} \right) (V - nb) = nRT \qquad (22.1.2)$$

Where V is volume, R is the gas constant, and n is the number of moles of gas.

The ideal gas law assumes that no intermolecular forces are affecting the gas in any way, while the van der Waals equation includes two constants, a and b, that account for any intermolecular forces acting on the molecules of the gas.

Temperature

Temperature can change the phase of a substance. One common example is putting water in a freezer to change it into ice. In the picture above, we have a solid substance in a container. When we put it on a heat source, like a burner, heat is transferred to the substance increasing the kinetic energy of the molecules in the substance. The temperature increases until the substance reaches its melting point[2]. As more and more heat is transferred beyond the melting point, the substance begins to melt and become a liquid[3]. This type of phase change is called an isobaric process because the pressure of the system stays at a constant level.

Solid   Add heat   Liquid
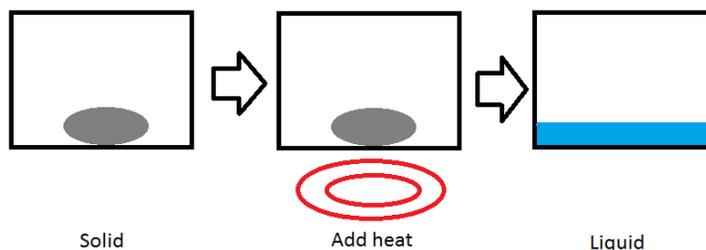
Melting point (T$_f$)

Each substance has a melting point. The melting point is the temperature that a solid will become a liquid. At different pressures, different temperatures are required to melt a substance. Each pure element on the periodic table has a normal melting point, the temperature that the element will become liquid when the pressure is 1 atmosphere[2].

Boiling Point (T$_b$)

Each substance also has a boiling point. The boiling point is the temperature that a liquid will evaporate into a gas. The boiling point will change based on the temperature and pressure. Just like the melting point, each pure element has a normal boiling point at 1 atmosphere[2].

Pressure

Pressure can also be used to change the phase of the substance. In the picture above, we have a container fitted with a piston that seals in a gas. As the piston compresses the gas, the pressure increases. Once the boiling point has been reached, the gas will condense into a liquid. As the piston continues to compress the liquid, the pressure will increase until the melting point has been reached. The liquid will then freeze into a solid. This example is for an isothermal process where the temperature is constant and only the pressure is changing.
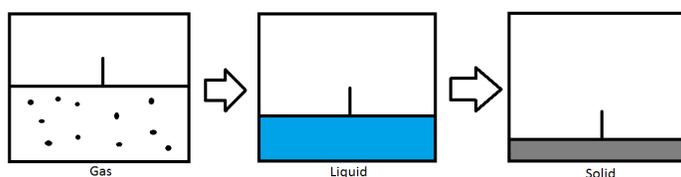
A Brief Explanation of a Phase Diagram

Phase transition can be represented with a phase diagram. A phase diagram is a visual representation of how a substance changes phases.
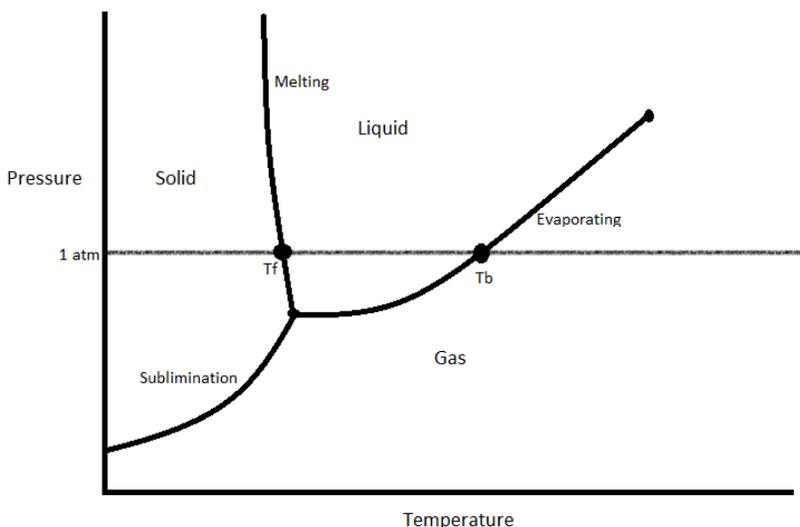
This is an example of a phase diagram. Often, when you are asked about a phase transition, you will need to refer to a phase diagram to answer it. These diagrams usually have the normal boiling point and normal melting point marked on them, and have the pressures on the y-axis and temperatures on the x-axis. The bottom curve marks the temperature and pressure combinations in which the substance will subliminate [1]. The left left marks the temperature and pressure combinations in which the substance will melt [1]. Finally, the right line marks the conditions under which the substance will evaporate [1].

References

1. Olander, Donald R. *General Thermodynamics*. Boca Raton: CRC, 2008.

2. Oxtoby, David W., H. P. Gillis, and Alan Campion. "Phase Transition." *Principles of Modern Chemistry*. 6th ed. Singapore: Thomson/Brooks/Cole, 2008. 428-30.
3. Schmidt, Philip S. *Thermodynamics: an Integrated Learning System*. Hoboken, NJ: Wiley, 2006.
4. Sherwin, Keith. *Introduction to Thermodynamics*. London: Chapman & Hall, 1994.

Problems

1. Using the phase diagram for carbon dioxide below, explain what phase carbon dioxide is normally in at standard temperature and pressure, 1 atm and 273.15 K.
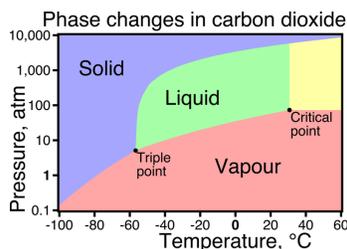
Phase diagram for CO2.from Wikipedia.

2: Looking at the same diagram, we see that carbon dioxide does not have a normal melting point or a normal boiling point. Explain what kind of a change carbon dioxide makes at 1 atm and estimate the temperature of this point.

Solutions

1: Before we can completely answer the question, we need to convert the given information to match the units in the diagram. First we convert 25 degrees Kelvin into Celsius: $K = 273.15 + C$

$$298.15 - 273.25C \tag{22.1.3}$$

Now we can look at the diagram and determine its phase. At 25 degrees Celsius and 1 atm carbon dioxide is in the gas phase.

2: Carbon dioxide sublimes at 1 atm because it transitions from the solid phase directly to the gas phase. The temperature of sublimation at 1 atm is about -80 degrees Celsius.

Contributors and Attributions

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22.2: Phase Diagrams

Phase diagram is a graphical representation of the physical states of a substance under different conditions of temperature and pressure. A typical phase diagram has pressure on the y-axis and temperature on the x-axis. As we cross the lines or curves on the phase diagram, a phase change occurs. In addition, two states of the substance coexist in equilibrium on the lines or curves.

Introduction

A phase transition is the transition from one state of matter to another. There are three states of matter: **liquid, solid, and gas**.

- **Liquid:** A state of matter that consists of loose, free moving particles which form the shape set by the boundaries of the container in which the liquid is in. This happens because the motion of the individual particles within a liquid is much less restricted than in a solid. One may notice that some liquids flow readily whereas some liquids flow slowly. A liquid's relative resistance to flow is **viscosity**.
- **Solid:** A state of matter with tightly packed particles which do not change the shape or volume of the container that it is in. However, this does not mean that the volume of a solid is a constant. Solids can expand and contract when temperatures change. This is why when you look up the density of a solid, it will indicate the temperature at which the value for density is listed. Solids have strong intermolecular forces that keep particles in close proximity to one another. Another interesting thing to think about is that all true solids have crystalline structures. This means that their particles are arranged in a three-dimensional, orderly pattern. Solids will undergo phase changes when they come across energy changes.
- **Gas:** A state of matter where particles are spread out with no definite shape or volume. The particles of a gas will take the shape and fill the volume of the container that it is placed in. In a gas, there are no intermolecular forces holding the particles of a gas together since each particle travels at its own speed in its own direction. The particles of a gas are often separated by great distances.

Phase diagrams illustrate the variations between the states of matter of elements or compounds as they relate to pressure and temperatures. The following is an example of a phase diagram for a generic single-component system:
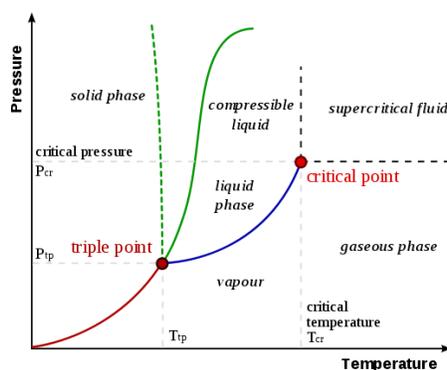
Figure 1. General Phase diagram

- **Triple point** – the point on a phase diagram at which the three states of matter: gas, liquid, and solid coexist
- **Critical point** – the point on a phase diagram at which the substance is indistinguishable between liquid and gaseous states
- **Fusion(melting) (or freezing) curve** – the curve on a phase diagram which represents the transition between liquid and solid states
- **Vaporization (or condensation) curve** – the curve on a phase diagram which represents the transition between gaseous and liquid states
- **Sublimation (or deposition) curve** – the curve on a phase diagram which represents the transition between gaseous and solid states

Phase diagrams plot pressure (typically in atmospheres) versus temperature (typically in degrees Celsius or Kelvin). The labels on the graph represent the stable states of a system in equilibrium. The lines represent the combinations of pressures and temperatures at which two phases can exist in equilibrium. In other words, these lines define phase change points. The red line divides the solid and gas phases, represents sublimation (solid to gas) and deposition (gas to solid). The green line divides the solid and liquid phases and represents melting (solid to liquid) and freezing (liquid to solid). The blue divides the liquid and gas phases, represents vaporization (liquid to gas) and condensation (gas to liquid). There are also two important points on the diagram, the triple point

and the critical point. The triple point represents the combination of pressure and temperature that facilitates all phases of matter at equilibrium. The critical point terminates the liquid/gas phase line and relates to the critical pressure, the pressure above which a supercritical fluid forms.

With most substances, the temperature and pressure related to the triple point lie below standard temperature and pressure and the pressure for the critical point lies above standard pressure. Therefore at standard pressure as temperature increases, most substances change from solid to liquid to gas, and at standard temperature as pressure increases, most substances change from gas to liquid to solid.

Exception: Water

Normally the solid/liquid phase line slopes positively to the right (as in the diagram for carbon dioxide below). However for other substances, notably water, the line slopes to the left as the diagram for water shows. This indicates that the liquid phase is more dense than the solid phase. This phenomenon is caused by the crystal structure of the solid phase. In the solid forms of water and some other substances, the molecules crystalize in a lattice with greater average space between molecules, thus resulting in a solid with a lower density than the liquid. Because of this phenomenon, one is able to melt ice simply by applying pressure and not by adding heat.
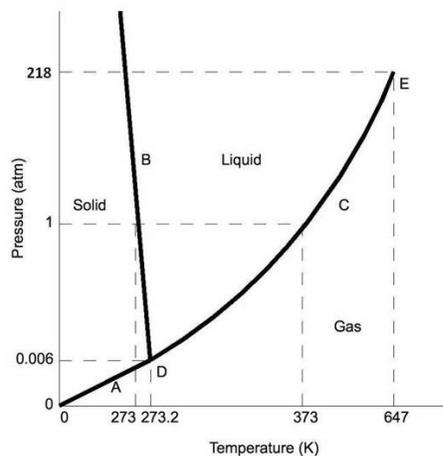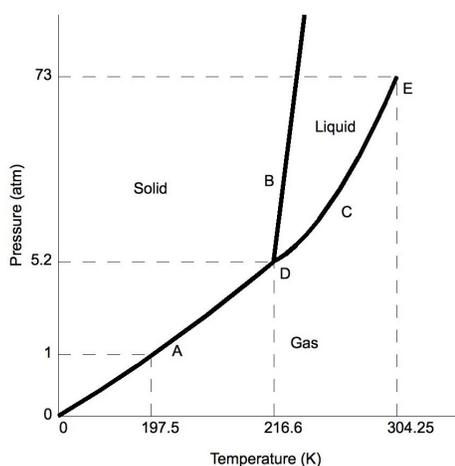
Figure 22.2.2a: Phase diagrams for CO_2

Figure 22.2.2b:Phase diagrams for H_2O

Moving About the Diagram

Moving about the phase diagram reveals information about the phases of matter. Moving along a constant temperature line reveals relative densities of the phases. When moving from the bottom of the diagram to the top, the relative density increases. Moving along a constant pressure line reveals relative energies of the phases. When moving from the left of the diagram to the right, the relative energies increases.

Important Definitions

- **Sublimation** is when the substance goes directly from solid to the gas state.
- **Deposition** occurs when a substance goes from a gas state to a solid state; it is the reverse process of sublimation.
- **Melting** occurs when a substance goes from a solid to a liquid state.
- **Fusion** is when a substance goes from a liquid to a solid state, the reverse of melting.
- **Vaporization** (or **evaporation**) is when a substance goes from a liquid to a gaseous state.
- **Condensation** occurs when a substance goes from a gaseous to a liquid state, the reverse of vaporization.
- **Critical Point** – the point in temperature and pressure on a phase diagram where the liquid and gaseous phases of a substance merge together into a single phase. Beyond the temperature of the critical point, the merged single phase is known as a **supercritical fluid**.
- **Triple Point** occurs when both the temperature and pressure of the three phases of the substance coexist in equilibrium.

References

1. Kotz, John C., and Paul Jr. Treichel. <u>Chemistry & Chemical Reactivity</u>. N.p.: Saunders College Publishing, 1999.
2. Oxtoby, David W., H. P. Gillis, and Alan Campion. <u>Principles of Modern Chemistry</u>. Belmont, CA: Thomson Brooks/?Cole, 2008.
3. Petrucci, Ralph, and William Harwood. F. Geoffrey Herring. Jeffry Madura. General Chemistry: Principles and Modern Applications. 9th ed. Upper Saddle River, NJ: Pearson, 2007.
4. Vollmer, John J. "Out of "Thin Air": Exploring Phase Changes.' J. Chem. Educ. **2000**: 77, 488A.

Problems

Imagine a substance with the following points on the phase diagram: a triple point at .5 atm and -5°C; a normal melting point at 20°C; a normal boiling point at 150°C; and a critical point at 5 atm and 1000°C. The solid liquid line is "normal" (meaning positive sloping). For this, complete the following:

1. Roughly sketch the phase diagram, using units of atmosphere and Kelvin.

Answer

1-solid, 2-liquid, 3-gas, 4-supercritical fluid, point O-triple point, C-critical point -78.5 °C (The phase of dry ice changes from solid to gas at -78.5 °C)

2. Rank the states with respect to increasing density and increasing energy.

3. Describe what one would see at pressures and temperatures above 5 atm and 1000°C.

Answer

One would see a super-critical fluid, when approaching the point, one would see the meniscus between the liquid and gas disappear.

4. Describe what will happen to the substance when it begins in a vaccum at -15°C and is slowly pressurized.

Answer

The substance would begin as a gas and as the pressure increases, it would compress and eventually solidify without liquefying as the temperature is below the triple point temperature.

5. Describe the phase changes from -80°C to 500°C at 2 atm.

Answer

The substance would melt at somewhere around, but above 20°C and then boil at somewhere around, but above 150°C. It would not form a super-critical fluid as the neither the pressure nor temperature reach the critical pressure or temperature.

6. What exists in a system that is at 1 atm and 150°?

Answer

Depending on how much energy is in the system, there will be different amounts of liquid and gas at equilibrium. If just enough energy was added to raise the temperature of the liquid to 150°C, there will just be liquid. If more was added, there will be some liquid and some gas. If just enough energy was added to change the state of all of the liquid without raising the temperature of the gas, there will just be gas.

7. Label the area 1, 2, 3, and 4 and points O and C on the diagram.

8. A sample of dry ice (solid CO_2) is cooled to -100 °C, and is set on a table at room temperature (25 °C). At what temperature is the rate of sublimation and deposition the same? (Assume pressure is held constant at 1 atm).

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23: Extension 15 - Phase Rule

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23.1: 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:

$$\mu_\alpha = \mu_\beta \qquad\qquad (23.1.1)$$

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

$$\sum_i \chi_i = 1 \qquad\qquad (23.1.2)$$

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.

$$
\begin{aligned}
F\ &= 2 + p(c-1) - c(p-1) \\
&= 2 + pc - p - pc + c \\
&= 2 + c - p \qquad\qquad (23.1.3)
\end{aligned}
$$

Equation 23.1.3 is the Gibbs phase rule.

Example 23.1.1:

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.

$$0 = 2 + 1 - p$$
$$p = 3$$

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.

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CHAPTER OVERVIEW

24: Fundamental 16 - Solution Equilibrium

24.1: Ideal Solutions - Raoult's Law

When two substances whose molecules are very similar form a liquid solution, the vapor pressure of the mixture is very simply related to the vapor pressures of the pure substances. Suppose, for example, we mix 1 mol benzene with 1 mol toluene as shown in the figure below.
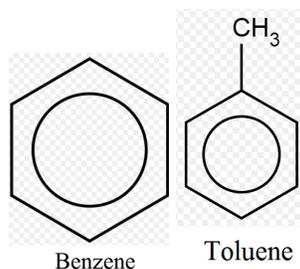
The mole fraction of benzene, X_b, and the mole fraction of toluene, X_t, are both equal to 0.5. At 79.6°C the measured vapor pressure of this mixture is 516 mmHg, slightly less than 517 mmHg, the average of the vapor pressures of pure benzene (744 mmHg) and of pure toluene (290 mmHg) at the same temperature.

It is easy to explain this behavior if we assume that because benzene and toluene molecules are so nearly alike, they behave the same way in solution as they do in the pure liquids. Since there are only half as many benzene molecules in the mixture as in pure benzene, the rate at which benzene molecules escape from the surface of the solution will be half the rate at which they would escape from the pure liquid. In consequence the partial vapor pressure of benzene above the mixture will be one-half the vapor pressure of pure benzene. By a similar argument the partial vapor pressure of the toluene above the solution is also one-half that of pure toluene. Accordingly, we can write

$$P_b = \frac{1}{2} P_b^* \tag{24.1.1}$$

and

$$P_t = \frac{1}{2} P_t^* \tag{24.1.2}$$

where P_b and P_t are the partial pressures of benzene and toluene vapors, respectively, and P_b^* and P_y^* are the vapor pressures of the pure liquids. The total vapor pressure of the solution is

$$P = P_b + P_t = \frac{1}{2} P_b^* + \frac{1}{2} P_t^* = \frac{P_b^* + P_t^*}{2} \tag{24.1.3}$$
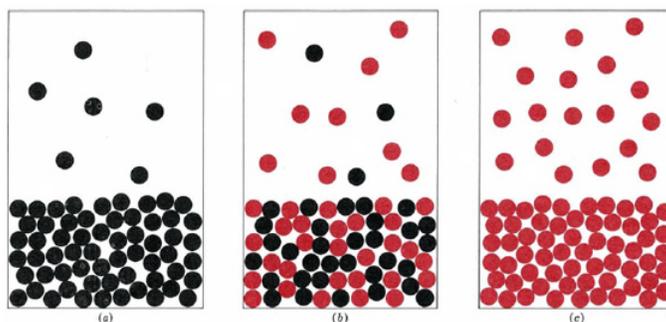
Figure 24.1.1: Vapor-liquid equilibria for (a) pure toluene; (b) a mixture of equal amounts of toluene and benzene: and (c) pure benzene. In the solution (b) only half the molecules are benzene molecules, and so the concentration of benzene molecules in the vapor phase is only half as great as above pure benzene. Note also that although the initial amounts of benzene and toluene in the solution were equal, more benzene than toluene escapes to the gas phase because of benzene's higher vapor pressure.

The vapor pressure of the mixture is equal to the mean of the vapor pressures of the two pure liquids.

We can generalize the above argument to apply to a liquid solution of any composition involving any two substances A and B whose molecules are very similar. The partial vapor pressure of A above the liquid mixture, P_A, will then be the vapor pressure of

pure A, P_A^*, multiplied by the fraction of the molecules in the liquid which are of type A, that is, the mole fraction of A, X_A. In equation form

$$P_A = X_A P_A^* \tag{24.1.4}$$

Similarly for component B

$$P_B = X_B P_B^* \tag{24.1.5}$$

Adding these two partial pressures, we obtain the total vapor pressure

$$P = P_A + P_B = X_A P_A^* + X_B P_B^* \tag{24.1.6}$$

Liquid solutions which conform to Eqs. 24.1.4 and 24.1.6 are said to obey **Raoult's law** and to be **ideal mixtures** or **ideal solutions**.

In addition to its use in predicting the vapor pressure of a solution, Raoult's law may be applied to the solubility of a gas in a liquid. Dividing both sides of Equation 24.1.4 by P_A^* gives

$$X_A = \frac{1}{P_A^*} \times P_A = k_A \times P_A \tag{24.1.7}$$

Since the vapor pressure of any substance has a specific value at a given temperature, Equation 24.1.7 tells us that the mole fraction X_A of a gaseous solute is proportional to the partial pressure P_A of that gas above the solution.

For an ideal solution the proportionality constant k_A is the reciprocal of the vapor pressure of the pure solute at the temperature in question. Since vapor pressure increases as temperature increases, k_A, which is $1/P_A^*$, must decrease. Thus we expect the solubility of a gas in a liquid to increase as the partial pressure of gas above the solution increases, but to decrease as temperature increases. Equation 24.1.7 is known as **Henry's law**. It also applies to gaseous solutes which do not form ideal solutions, but in such cases the Henry's-law constant k_A does not equal the reciprocal of the vapor pressure.

The video below shows the effect of varied pressure on the amount of CO_2 dissolved in soda. The amount of dissolved CO_2 is monitored by a pH indicator. The more dissolved CO_2, the lower the pH (the more red the solution). Watch the video to find out how the solubility of CO_2 is related to the pressure, paying particular attention to the color of the solution.
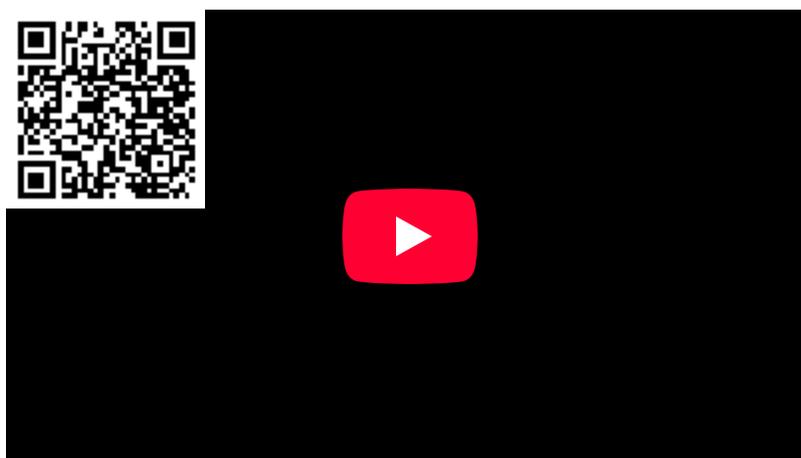
In actual fact very few liquid mixtures obey Raoult's law exactly. Even for molecules as similar as benzene and toluene, we noted a deviation of 517 mmHg – 516 mmHg, or 1 mmHg at 79.6°C. Much larger deviations occur if the molecules are not very similar. These deviations are of two kinds. As can be seen from Figure $24.1.2$, a plot of the vapor pressure against the mole fraction of one component yields a straight line for an ideal solution. For non-ideal mixtures the actual vapor pressure can be larger than the ideal value (positive deviation from Raoult's law) or smaller (negative deviation). Negative deviations correspond to cases where attractions between unlike molecules are greater than those between like molecules.
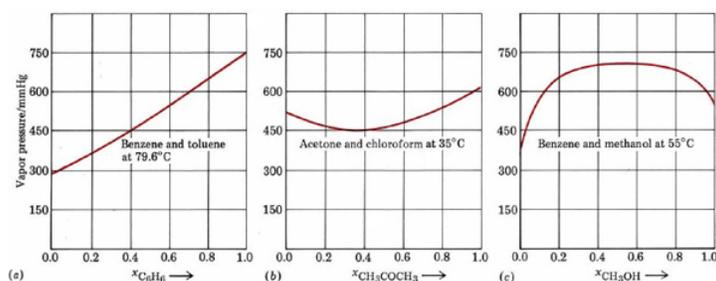
Figure 24.1.2: Deviations from Raoult's law. (a) When Raoult's law is obeyed, a plot of vapor pressure against mole fraction yields a straight line. This is nearly true for the benzene and toluene mixture at 79.6°C. (b) A mixture of acetone and chloroform shows negative deviations from Raoult's law at 35°C, indicating that the two different molecules prefer each other's company to their own. (c) The opposite behavior is shown at 55°C by a benzene-methanol mixture where the polar and nonpolar molecules prefer the company of their own kind.

In the case illustrated below, acetone (CH_3COCH_3) and chloroform ($CHCl_3$) can form a weak hydrogen bond:
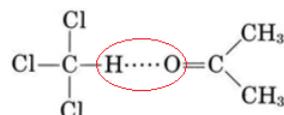
Because of this extra intermolecular attraction, molecules have more difficulty escaping the solution and the vapor pressure is lower. The opposite is true of a mixture of benzene and methanol. When C_6H_6 molecules are randomly distributed among CH_3OH molecules, the latter cannot hydrogen bond effectively. Molecules can escape more readily from the solution, and the vapor pressure is higher than Raoult's law would predict.

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24.2: Thermodynamics of Mixing

When solids, liquids or gases are combined, the thermodynamic quantities of the system experience a change as a result of the mixing. This module will discuss the effect that mixing has on a solution's Gibbs energy, enthalpy, and entropy, with a specific focus on the mixing of two gases.

Introduction

A solution is created when two or more components mix homogeneously to form a single phase. Studying solutions is important because most chemical and biological life processes occur in systems with multiple components. Understanding the thermodynamic behavior of mixtures is integral to the study of any system involving either ideal or non-ideal solutions because it provides valuable information on the molecular properties of the system.

Most real gases behave like ideal gases at standard temperature and pressure. This allows us to combine our knowledge of ideal systems and solutions with standard state thermodynamics in order to derive a set of equations that quantitatively describe the effect that mixing has on a given gas-phase solution's thermodynamic quantities.

Gibbs Free Energy of Mixing

Unlike the extensive properties of a one-component system, which rely only on the amount of the system present, the extensive properties of a solution depend on its temperature, pressure and composition. This means that a mixture must be described in terms of the partial molar quantities of its components. The total Gibbs free energy of a two-component solution is given by the expression

$$G = n_A \overline{G}_A + n_B \overline{G}_B \tag{24.2.1}$$

where

- G is the total Gibbs energy of the system,
- n_i is the number of moles of component i, and
- $\overline{G}_i$ is the partial molar Gibbs energy of component i.

The molar Gibbs energy of an ideal gas can be found using the equation

$$\overline{G} = \overline{G}^\circ + RT \ln \frac{P}{1\,\text{bar}} \tag{24.2.2}$$

where $\overline{G}^\circ$ is the standard molar Gibbs energy of the gas at 1 bar, and P is the pressure of the system. In a mixture of ideal gases, we find that the system's partial molar Gibbs energy is equivalent to its chemical potential, or that

$$\overline{G}_i = \mu_i \tag{24.2.3}$$

This means that for a solution of ideal gases, Equation 24.2.2 can become

$$\overline{G}_i = \mu_i = \mu_i^\circ + RT \ln \frac{P_i}{1\,\text{bar}} \tag{24.2.4}$$

where

- μ_i is the chemical potential of the ith component,
- μ_i° is the standard chemical potential of component i at 1 bar, and
- P_i is the partial pressure of component i.

Now pretend we have two gases at the same temperature and pressure, gas A and gas B. The Gibbs energy of the system before the gases are mixed is given by Equation 24.2.1, which can be combined with Equation 24.2.4 to give the expression

$$G_{initial} = n_A(\mu_A^\circ + RT \ln P) + n_B(\mu_B^\circ + RT \ln P) \tag{24.2.5}$$

If gas A and gas B are then mixed together, they will each exert a partial pressure on the total system, P_A and P_B, so that $P_A + P_B = P$. This means that the final Gibbs energy of the final solution can be found using the equation

$$G_{final} = n_A(\mu_A^\circ + RT \ln P_A) + n_B(\mu_B^\circ + RT \ln P_B) \tag{24.2.6}$$

The Gibbs energy of mixing, $\Delta_{mix}G$, can then be found by subtracting $G_{initial}$ from G_{final}.

$$\Delta_{mix}G = G_{final} - G_{initial} \tag{24.2.7}$$

$$= n_A RT \ln \frac{P_A}{P} + n_B RT \ln \frac{P_B}{P} \tag{24.2.8}$$

$$= n_A RT \ln X_A + n_B RT \ln X_B \tag{24.2.9}$$

where

$$P_i = X_i P \tag{24.2.10}$$

and X_i is the mole fraction of gas i. This equation can be simplified further by knowing that the mole fraction of a component is equal to the number of moles of that component over the total moles of the system, or

$$X_i = \frac{n_i}{n}. \tag{24.2.11}$$

Equation 24.2.9 then becomes

$$\Delta_{mix}G = nRT(X_A \ln X_A + X_B \ln X_B) \tag{24.2.12}$$

This expression gives us the effect that mixing has on the Gibbs free energy of a solution. Since X_A and X_B are mole fractions that range from 0 to 1, we can conclude that $\Delta_{mix}G$ will be a negative number. This is consistent with the idea that gases mix spontaneously at constant pressure and temperature.

Entropy of mixing

Figure 24.2.1 shows that when two gases mix, it can really be seen as two gases expanding into twice their original volume. This greatly increases the number of available microstates, and so we would therefore expect the entropy of the system to increase as well.
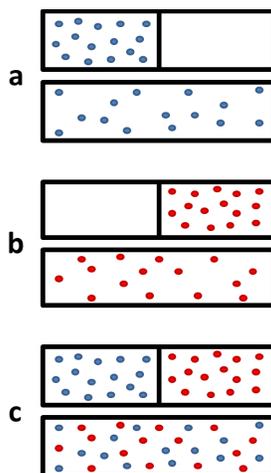
Figure 24.2.1: The mixing of two gases can be seen as two expansions. (a) Expansion of gas A alone when the barrier is removed. The molecules have twice as many microstates in the open box. (b) Expansion of gas B along. (c) the simultaneous expansion of gases A and B is equivalent to mixing

Thermodynamic studies of an ideal gas's dependence of Gibbs free energy of temperature have shown that

$$\left(\frac{dG}{dT}\right)_P = -S \tag{24.2.13}$$

This means that differentiating Equation 24.2.12 at constant pressure with respect to temperature will give an expression for the effect that mixing has on the entropy of a solution. We see that

$$\left(\frac{dG_{mix}}{dT}\right)_P = nR(X_A \ln X_A + X_B \ln X_B) \tag{24.2.14}$$

$$= -\Delta_{mix}S \tag{24.2.15}$$

$$\Delta_{mix}S = -nR(X_A \ln X_A + X_2 \ln X_2) \qquad (24.2.16)$$

Since the mole fractions again lead to negative values for $\ln X_A$ and $\ln X_B$, the negative sign in front of the equation makes $\Delta_{mix}S$ positive, as expected. This agrees with the idea that mixing is a spontaneous process.

Enthalpy of mixing

We know that in an ideal system $\Delta G = \Delta H - T\Delta S$, but this equation can also be applied to the thermodynamics of mixing and solved for the enthalpy of mixing so that it reads

$$\Delta_{mix}H = \Delta_{mix}G + T\Delta_{mix}S \qquad (24.2.17)$$

Plugging in our expressions for $\Delta_{mix}G$ (Equation 24.2.12) and $\Delta_{mix}S$ (Equation 24.2.16) , we get

$$\Delta_{mix}H = nRT(X_A \ln X_A + X_B \ln X_B) + T\left[-nR(X_A \ln X_A + X_B \ln X_B)\right] = 0 \qquad (24.2.18)$$

This result makes sense when considering the system. The molecules of ideal gas are spread out enough that they do not interact with one another when mixed, which implies that no heat is absorbed or produced and results in a $\Delta_{mix}H$ of zero. Figure 24.2.2 illustrates how $T\Delta_{mix}S$ and $\Delta_{mix}G$ change as a function of the mole fraction so that $\Delta_{mix}H$ of a solution will always be equal to zero (this is for the mixing of two ideal gasses).
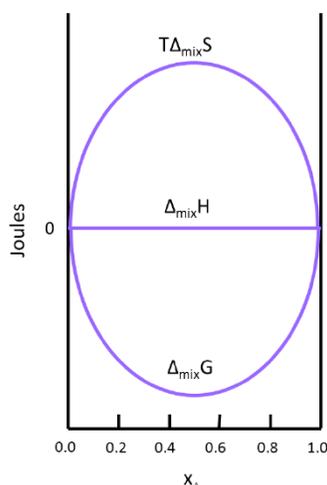
Figure 24.2.2: A graph of $T\Delta_{mix}S$, $T\Delta_{mix}H$, and $T\Delta_{mix}G$ as a function of X_A for the mixing of two ideal gases.

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1. Chang, R. Physical Chemistry for the Biosciences, 1st Herdon, VA: University Science Books, 132-133. Print.
2. Meyer, E.F. (1987). Theromodynamics of "Mixing" of Ideal Gases. J. Chem. Educ. 64, 676-677.

Outside Links

- Satter, S. (2000). Thermodynamics of Mixing Real Gases. J. Chem. Educ. 77, 1361-1365.
- Brandani, V., Evangelista, F. (1987). Correlation and prediction of enthalpies of mixing for systems containing alcohols with UNIQUAC associated-solution theory. Ind. Eng. Chem. Res. 26 (12), 2423–2430.

Problems

1. Use Figure 2 to find the x_1 that has the largest impact on the thermodynamic quantities of the final solution. Explain why this is true.
2. Calculate the effect that mixing 2 moles of nitrogen and 3 moles of oxygen has on the entropy of the final solution.
3. Another way to find the entropy of a system is using the equation $\Delta S = nR\ln(V_2/V_1)$. Use this equation and the fact that volume is directly proportional to the number of moles of gas at constant temperature and pressure to derive the final expression for $T\Delta_{mix}S$. (Hint: Use the derivation of $T\Delta_{mix}G$ as a guide).

Answers

1. $x_1 = 0.5$
2. Increases the entropy of the system by 27.98 J/molK

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CHAPTER OVERVIEW

25: Extension 16 - Vapor-Solution Phase Diagrams

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25.1: Raoult's Law and Ideal Mixtures of Liquids

This page deals with Raoult's Law and how it applies to mixtures of two volatile liquids. It covers cases where the two liquids are entirely miscible in all proportions to give a single liquid - NOT those where one liquid floats on top of the other (immiscible liquids). The page explains what is meant by an ideal mixture and looks at how the phase diagram for such a mixture is built up and used.

Ideal Mixtures

An ideal mixture is one which obeys Raoult's Law, but I want to look at the characteristics of an ideal mixture before actually stating Raoult's Law. The page will flow better if I do it this way around. There is actually no such thing as an ideal mixture! However, some liquid mixtures get fairly close to being ideal. These are mixtures of two very closely similar substances. Commonly quoted examples include:

- hexane and heptane
- benzene and methylbenzene
- propan-1-ol and propan-2-ol

In a pure liquid, some of the more energetic molecules have enough energy to overcome the intermolecular attractions and escape from the surface to form a vapor. The smaller the intermolecular forces, the more molecules will be able to escape at any particular temperature.
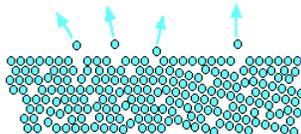
If you have a second liquid, the same thing is true. At any particular temperature a certain proportion of the molecules will have enough energy to leave the surface.
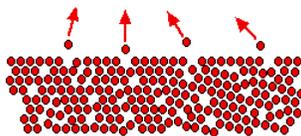
In an ideal mixture of these two liquids, the tendency of the two different sorts of molecules to escape is unchanged.
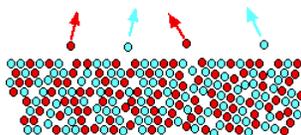
You might think that the diagram shows only half as many of each molecule escaping - but the proportion of each escaping is still the same. The diagram is for a 50/50 mixture of the two liquids. That means that there are only half as many of each sort of molecule on the surface as in the pure liquids. If the proportion of each escaping stays the same, obviously only half as many will escape in any given time. If the red molecules still have the same tendency to escape as before, that must mean that the intermolecular forces between two red molecules must be exactly the same as the intermolecular forces between a red and a blue molecule.

If the forces were any different, the tendency to escape would change. Exactly the same thing is true of the forces between two blue molecules and the forces between a blue and a red. They must also be the same otherwise the blue ones would have a different tendency to escape than before. If you follow the logic of this through, the intermolecular attractions between two red molecules, two blue molecules or a red and a blue molecule must all be exactly the same if the mixture is to be ideal.

This is why mixtures like hexane and heptane get close to ideal behavior. They are similarly sized molecules and so have similarly sized van der Waals attractions between them. However, they obviously are not identical - and so although they get close to being ideal, they are not actually ideal. For the purposes of this topic, getting close to ideal is good enough!

Ideal Mixtures and the Enthalpy of Mixing

When you make any mixture of liquids, you have to break the existing intermolecular attractions (which needs energy), and then remake new ones (which releases energy). If all these attractions are the same, there won't be any heat either evolved or absorbed. That means that an ideal mixture of two liquids will have zero enthalpy change of mixing. If the temperature rises or falls when you mix the two liquids, then the mixture is not ideal. You may have come cross a slightly simplified version of Raoult's Law if you have studied the effect of a non-volatile solute like salt on the vapor pressure of solvents like water. The definition below is the one to use if you are talking about mixtures of two volatile liquids.

Definition: Raoult's Law

The partial vapor pressure of a component in a mixture is equal to the vapor pressure of the pure component at that temperature multiplied by its mole fraction in the mixture.

Raoult's Law only works for ideal mixtures. In equation form, for a mixture of liquids A and B, this reads:

$$P_A = X_A P_A^* \tag{25.1.1}$$

$$P_B = X_B P_B^* \tag{25.1.2}$$

In this equation, P_A and P_B are the **partial vapor pressures** of the components A and B. In any mixture of gases, each gas exerts its own pressure. This is called its partial pressure and is independent of the other gases present. Even if you took all the other gases away, the remaining gas would still be exerting its own partial pressure. The total vapor pressure of the mixture is equal to the sum of the individual partial pressures:

$$P_{\text{total}} = P_A + P_B \tag{25.1.3}$$

The P^* values are the vapor pressures of A and B if they were on their own as pure liquids. X_A and X_B are the mole fractions of A and B. That is exactly what it says it is - the fraction of the total number of moles present which is A or B. You calculate mole fraction using, for example:

$$X_A = \frac{\text{moles of A}}{\text{total number of moles}} \tag{25.1.4}$$

Example 25.1.1

Suppose you had a mixture of 2 moles of methanol and 1 mole of ethanol at a particular temperature. The vapor pressure of pure methanol at this temperature is 81 kPa, and the vapor pressure of pure ethanol is 45 kPa. What is total vapor pressure of this solution?

Solution

There are 3 moles in the mixture in total.

- 2 of these are methanol. The mole fraction of methanol is 2/3.
- Similarly, the mole fraction of ethanol is 1/3.

You can easily find the partial vapor pressures using Raoult's Law - assuming that a mixture of methanol and ethanol is ideal.

First for methanol:

$$P_{methanol} = \frac{2}{3} \times 81 \ kPa \tag{25.1.5}$$

$$= 54 \ kPa \tag{25.1.6}$$

Then for ethanol:

$$P_{ethanol} = \frac{1}{3} \times 45 \ kPa \tag{25.1.7}$$

$$= 15 \ kPa \tag{25.1.8}$$

You get the total vapor pressure of the liquid mixture by adding these together.

$$P_{total} = 54 \ kPa + 15 \ kPa = 69 kPa \qquad (25.1.9)$$

In practice, this is all a lot easier than it looks when you first meet the definition of Raoult's Law and the equations!

Vapor Pressure and Composition Diagrams

Suppose you have an ideal mixture of two liquids A and B. Each of A and B is making its own contribution to the overall vapor pressure of the mixture - as we've seen above. Let's focus on one of these liquids - A, for example. Suppose you double the mole fraction of A in the mixture (keeping the temperature constant). According to Raoult's Law, you will double its partial vapor pressure. If you triple the mole fraction, its partial vapor pressure will triple - and so on. In other words, the partial vapor pressure of A at a particular temperature is proportional to its mole fraction. If you plot a graph of the partial vapor pressure of A against its mole fraction, you will get a straight line.
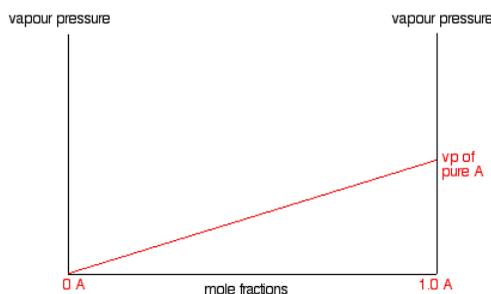
Now we'll do the same thing for B - except that we will plot it on the same set of axes. The mole fraction of B falls as A increases so the line will slope down rather than up. As the mole fraction of B falls, its vapor pressure will fall at the same rate.
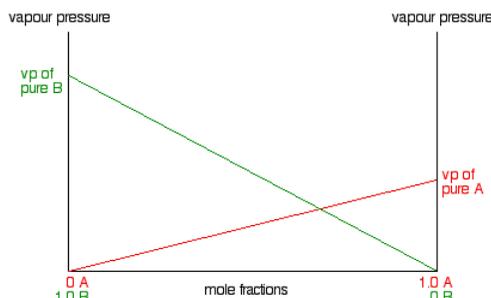
Notice that the vapor pressure of pure B is higher than that of pure A. That means that molecules must break away more easily from the surface of B than of A. B is the more volatile liquid. To get the total vapor pressure of the mixture, you need to add the values for A and B together at each composition. The net effect of that is to give you a straight line as shown in the next diagram.
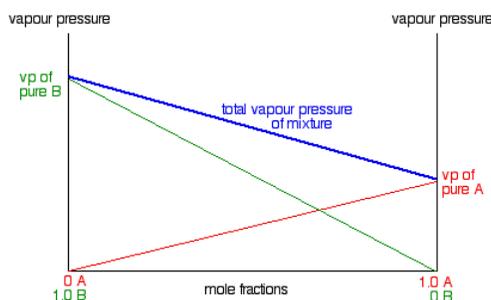
Boiling point and Composition Diagrams

The relationship between boiling point and vapor pressure

- If a liquid has a high vapor pressure at a particular temperature, it means that its molecules are escaping easily from the surface.
- If, at the same temperature, a second liquid has a low vapor pressure, it means that its molecules are not escaping so easily.

What do these two aspects imply about the boiling points of the two liquids? There are two ways of looking at the above question:

Either:

- If the molecules are escaping easily from the surface, it must mean that the intermolecular forces are relatively weak. That means that you won't have to supply so much heat to break them completely and boil the liquid. **Therefore, the liquid with the higher vapor pressure at a particular temperature is the one with the lower boiling point.**

Or:

- Liquids boil when their vapor pressure becomes equal to the external pressure. If a liquid has a high vapor pressure at some temperature, you won't have to increase the temperature very much until the vapor pressure reaches the external pressure. On the other hand if the vapor pressure is low, you will have to heat it up a lot more to reach the external pressure. **Therefore, the liquid with the higher vapor pressure at a particular temperature is the one with the lower boiling point.**

> *For two liquids at the same temperature, the liquid with the higher vapor pressure is the one with the lower boiling point.*

Constructing a boiling point / composition diagram

To remind you - we've just ended up with this vapor pressure / composition diagram:
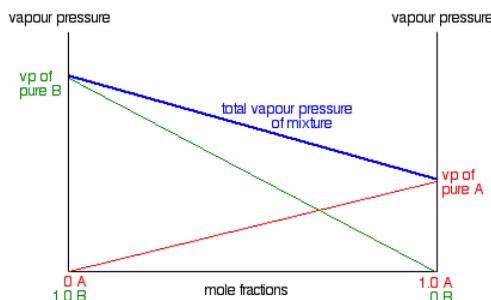
We're going to convert this into a boiling point / composition diagram. We'll start with the boiling points of pure A and B. Since B has the higher vapor pressure, it will have the lower boiling point. If that is not obvious to you, go back and read the last section again!
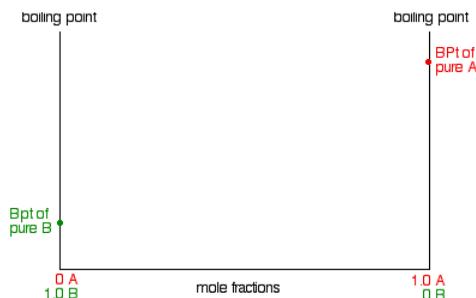
For mixtures of A and B, you might perhaps have expected that their boiling points would form a straight line joining the two points we've already got. Not so! In fact, it turns out to be a curve.
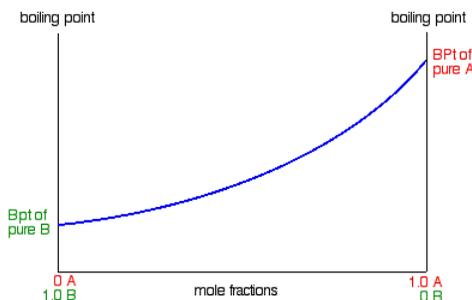
To make this diagram really useful (and finally get to the phase diagram we've been heading towards), we are going to add another line. This second line will show the composition of the vapor over the top of any particular boiling liquid.

If you boil a liquid mixture, you would expect to find that the more volatile substance escapes to form a vapor more easily than the less volatile one. That means that in the case we've been talking about, you would expect to find a higher proportion of B (the more volatile component) in the vapor than in the liquid. You can discover this composition by condensing the vapor and analyzing it. That would give you a point on the diagram.
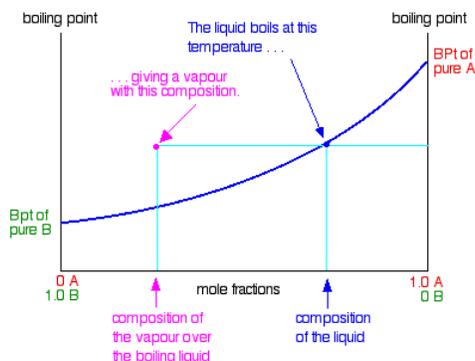
The diagram just shows what happens if you boil a particular mixture of A and B. Notice that the vapor over the top of the boiling liquid has a composition which is much richer in B - the more volatile component. If you repeat this exercise with liquid mixtures of lots of different compositions, you can plot a second curve - a vapor composition line.
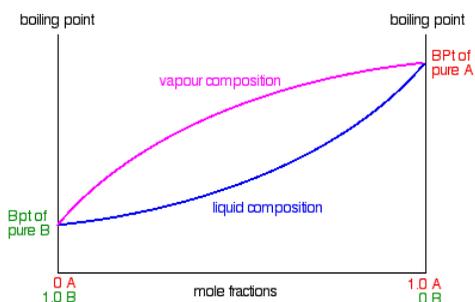
This is now our final phase diagram.

Using the phase diagram

The diagram is used in exactly the same way as it was built up. If you boil a liquid mixture, you can find out the temperature it boils at, and the composition of the vapor over the boiling liquid. For example, in the next diagram, if you boil a liquid mixture C_1, it will boil at a temperature T_1 and the vapor over the top of the boiling liquid will have the composition C_2.
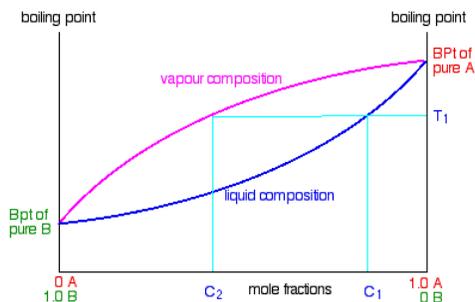
All you have to do is to use the liquid composition curve to find the boiling point of the liquid, and then look at what the vapor composition would be at that temperature. Notice again that the vapor is much richer in the more volatile component B than the original liquid mixture was.

The beginnings of fractional distillation

Suppose that you collected and condensed the vapor over the top of the boiling liquid and reboiled it. You would now be boiling a new liquid which had a composition C_2. That would boil at a new temperature T_2, and the vapor over the top of it would have a composition C_3.
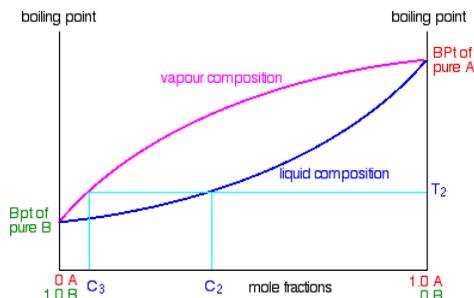
You can see that we now have a vapor which is getting quite close to being pure B. If you keep on doing this (condensing the vapor, and then reboiling the liquid produced) you will eventually get pure B. This is obvious the basis for fractional distillation. However, doing it like this would be incredibly tedious, and unless you could arrange to produce and condense huge amounts of vapor over the top of the boiling liquid, the amount of B which you would get at the end would be very small. Real fractionating columns (whether in the lab or in industry) automate this condensing and reboiling process. How these work will be explored on another page.

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25.2: 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.
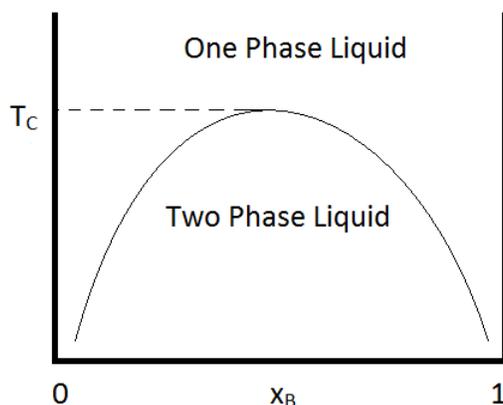
Figure 25.2.1 :

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 25.2.1. 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.
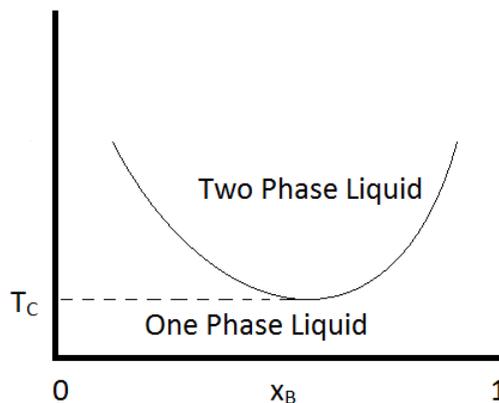
Figure 25.2.2 :

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 25.2.2 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.
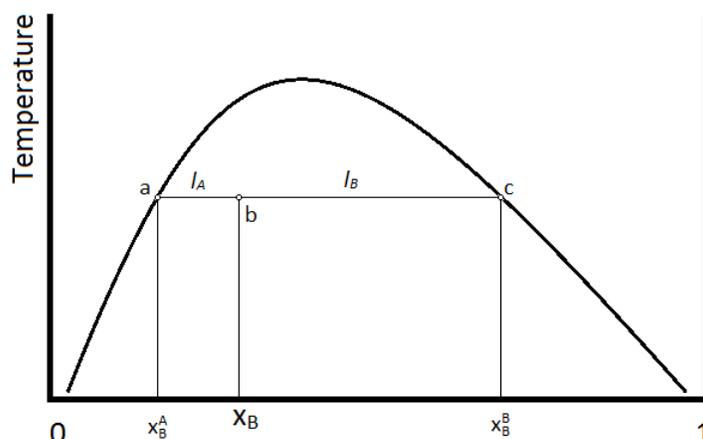
Figure 25.2.3 :

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 (X_B^A) in the layer that is predominantly A, whereas the point c indicates the composition (X_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,

$$l_A = X_B - X_B^A \tag{25.2.1}$$

and

$$l_B = X_B^B - X_B \tag{25.2.2}$$

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.

$$n_A l_A = n_B l_B \tag{25.2.3}$$

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.

$$\frac{n_A}{n_B} = \frac{l_B}{l_A} = \frac{X_B^B - X_B}{X_B - X_B^A} \tag{25.2.4}$$

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25.3: 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 $P_A^* = 450\, Torr$ and the other having a pure vapor pressure of $P_B^* = 350\, Torr$. In Figure 25.3.1, the liquid phase is represented at the top of the graph where the pressure is higher.
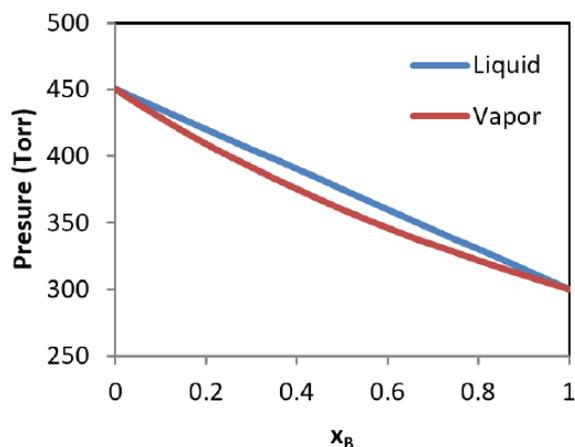
Figure 25.3.1: *The liquid phase is represented at the top of the graph where the pressure is higher*

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 25.3.2 for an ideal mixture of two volatile liquids.
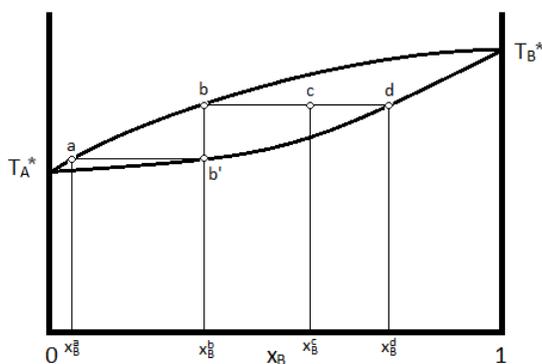
Figure 25.3.2: *A typical temperature vs. composition diagram.*

In this diagram, T_A^* and T_B^* represent the boiling points of pure compounds A and B. If a system having the composition indicated by X_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 X_B^d and a vapor phase indicated with a composition indicated by X_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 X_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 X_B^a. This demonstrates how the more volatile liquid (the one with the lower boiling temperature, which is A in the case of the above diagram) can be purified from the mixture by collecting and re-

evaporating fractions of the vapor. If the liquid was the desired product, one would collect fractions of the residual liquid to achieve the desired result. This process is known as distillation.

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26: Fundamental 17 - Colligative Properties

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26.1: 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 (aerosols are examples of gas-phase solutions) 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

$$\mu_{solid} \leq \mu_{liquid} \tag{26.1.1}$$

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

$$\mu_A = \mu_A^o + RT \ln X_A \tag{26.1.2}$$

And because X_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

$$\mu_{A,solid} = \mu_{A,liquid} \tag{26.1.3}$$

where the chemical potential of the liquid is given by Equation 26.1.2, which rearrangement to

$$\frac{\mu_A - \mu_A^o}{RT} = \ln X_A \tag{26.1.4}$$

To evaluate the temperature dependence of the chemical potential, it is useful to consider the temperature derivative at constant pressure.

$$\left[\frac{\partial}{\partial T} \left(\frac{\mu_A - \mu_A^o}{RT} \right) \right]_P = \left(\frac{\partial \ln X_A}{\partial T} \right)_P \tag{26.1.5}$$

$$-\frac{\mu_A - \mu_A^o}{RT^2} + \frac{1}{RT} \left[\left(\frac{\partial \mu_A}{\partial T} \right)_P - \left(\frac{\partial \mu_A^o}{\partial T} \right)_P \right] = \left(\frac{\partial \ln X_A}{\partial T} \right)_P \tag{26.1.6}$$

Recalling that

$$\mu = \overline{H} - T\overline{S} \tag{26.1.7}$$

and

$$\left(\frac{\partial \mu}{\partial T} \right)_P = -\overline{S} \tag{26.1.8}$$

Equation 26.1.6 becomes

$$-\frac{(\overline{H}_A - T\overline{S}_A - \overline{H}_A^o + T\overline{S}_A^o)}{RT^2} + \frac{1}{RT} \left[-\overline{S}_A + \overline{S}_A^o \right] = \left(\frac{\partial \ln X_A}{\partial T} \right)_P \tag{26.1.9}$$

And noting that in the case of the solvent freezing, $\overline{H}_A^o$ is the enthalpy of the pure solvent in solid form, and $\overline{H}_A$ is the enthalpy of the solvent in the liquid solution. So

$$\overline{H}_A^o - \overline{H}_A = \Delta \overline{H}_{fus} \tag{26.1.10}$$

Equation 26.1.9 then becomes

$$\frac{\Delta \overline{H}_{fus}}{RT^2} - \frac{-\overline{S}_A + \overline{S}_A^o}{RT} + \frac{-\overline{S}_A + \overline{S}_A^o}{RT} = \left(\frac{\partial \ln X_A}{\partial T} \right)_P \tag{26.1.11}$$

or

$$\frac{\Delta \overline{H}_{fus}}{RT^2} = \left(\frac{\partial \ln X_A}{\partial T} \right)_P \tag{26.1.12}$$

Separating the variables puts the equation into an integrable form.

$$\int_{T^o}^{T} \frac{\Delta \overline{H}_{fus}}{RT^2} dT = \int d \ln X_A \tag{26.1.13}$$

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 26.1.13

$$-\frac{\Delta \overline{H}_{fus}}{R} \left(\frac{1}{T} - \frac{1}{T^o} \right) = \ln X_A \tag{26.1.14}$$

This can be simplified further by noting that

$$\frac{1}{T} - \frac{1}{T^o} = \frac{T^o - T}{TT^o} = \frac{\Delta T}{TT^o} \tag{26.1.15}$$

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 26.1.14 becomes

$$-\frac{\Delta \overline{H}_{fus}}{R(T^o)^2} \Delta T = \ln X_A \tag{26.1.16}$$

Further, for dilute solutions, for which X_A, the mole fraction of the solvent is very nearly 1, then

$$\ln X_A \approx -(1 - X_A) = -X_B \tag{26.1.17}$$

where X_B is the mole fraction of the solute. After a small bit of rearrangement, this results in an expression for freezing point depression of

$$\Delta T = \left(\frac{R(T^o)^2}{\Delta \overline{H}_{fus}} \right) X_B \tag{26.1.18}$$

The first factor can be replaced by K_f:

$$\frac{R(T^o)^2}{\Delta \overline{H}_{fus}} = K_f \tag{26.1.19}$$

which is the **cryoscopic constant** for the solvent.

ΔT gives the magnitude of the reduction of freezing point for the solution. Since $\Delta \overline{H}_{fus}$ 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 X_B was introduced as $(1 - X_A)$, 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 such, 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

$$\Delta T = K_b X_B \tag{26.1.20}$$

where

$$\frac{R(T^o)^2}{\Delta \overline{H}_{vap}} = K_b \tag{26.1.21}$$

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

$$\Delta T = K_f m \tag{26.1.22}$$

or

$$\Delta T = K_b m \tag{26.1.23}$$

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 26.1.1:

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:

$$(85.5\,^\circ C - 76.8\,^\circ C) = (5.02\,^\circ C\,kg/mol)\,m \tag{26.1.24}$$

$$m = 0.936\,mol/kg \tag{26.1.25}$$

Using the number of kg of solvent, one finds the number for moles of solute:

$$\left(0.936\,mol/\,\cancel{kg}\right)(0.02\,\cancel{kg}) = 0.0234\,mol \tag{26.1.26}$$

The ratio of mass to moles yields the final answer:

$$\frac{3.00\,g}{0.0234} = 128 g/mol \tag{26.1.27}$$

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.

$$\mu_{vapor} = \mu_{solvent} \tag{26.1.28}$$

If the solute is not volatile, the vapor will be pure, so (assuming ideal behavior)

$$\mu_{vap}^o + RT \ln \frac{P'}{P^o} = \mu_A^o + RT \ln X_A \tag{26.1.29}$$

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

$$\mu_A^o = \mu_{vap}^o + RT \ln \frac{P_A}{P^o} \tag{26.1.30}$$

where P^o is the standard pressure of 1 bar, and P_A is the vapor pressure of the pure solvent. Substituting Equation 26.1.30 into Equation 26.1.29 yields

$$\mu_{vap}^o + RT \ln \frac{P'}{P^o} = \left(\mu_{vap}^o + RT \ln \frac{P_A}{P^o} \right) + RT \ln X_A \tag{26.1.31}$$

The terms for μ_{vap}^o cancel, leaving

$$RT \ln \frac{P'}{P^o} = RT \ln \frac{P_A}{P^o} + RT \ln X_A \tag{26.1.32}$$

Subtracting $RT \ln(P_A/P^o)$ from both side produces

$$RT \ln \frac{P'}{P^o} - RT \ln \frac{P_A}{P^o} = RT \ln X_A \tag{26.1.33}$$

which rearranges to

$$RT \ln \frac{P'}{P_A} = RT \ln X_A \tag{26.1.34}$$

Dividing both sides by RT and then exponentiating yields

$$\frac{P'}{P_A} = X_A \tag{26.1.35}$$

or

$$P' = X_A P_A \tag{26.1.36}$$

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 26.1.2:

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 26.1.36)

$$P_A = (0.400)(150\,Torr) = 60.0\,Torr \tag{26.1.37}$$

$$P_B = (0.600)(300\,Torr) = 180.0\,Torr \tag{26.1.38}$$

$$P_{\text{total}} = P_A + P_B = 240\,Torr \tag{26.1.39}$$

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

$$X_A = \frac{P_A}{P_{tot}} = \frac{60.0\,Torr}{240\,Torr} = 0.250 \tag{26.1.40}$$

$$X_B = \frac{P_B}{P_{tot}} = \frac{180.0\,Torr}{240\,Torr} = 0.750 \tag{26.1.41}$$

And, of course, it is also useful to note that the sum of the mole fractions is 1 (as it must be!)

$$X_A + X_B = 1 \tag{26.1.42}$$

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, Π,** is the pressure that when exerted on the region of high solute concentration will halt the process of osmosis.
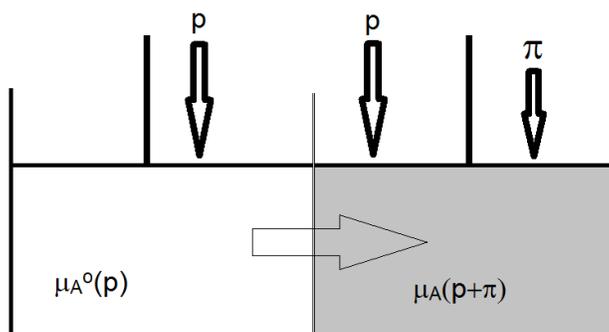
The nature of osmosis and the magnitude of the osmotic pressure can be understood by examining the chemical potential of a pure solvent and that of the solvent in a solution. The chemical potential of the solvent in the solution (before any extra pressure is applied) is given by

$$\mu_A = \mu_A^o + RT \ln X_A \tag{26.1.43}$$

And since $X_A < 1$, the chemical potential 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

$$\mu_A^o(P) = \mu_A(P + \Pi) \tag{26.1.44}$$

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

$$\mu_A^o - \mu_A = RT \ln X_A \tag{26.1.45}$$

And the increase in chemical potential due to the application of excess pressure is given by

$$\mu(P + \Pi) = \mu(P) + \int_P^{P+\Pi} \left(\frac{\partial \mu}{\partial P} \right)_T dP \tag{26.1.46}$$

The integrals on the right can be evaluated by recognizing

$$\left(\frac{\partial \mu}{\partial P} \right)_T = \overline{V} \tag{26.1.47}$$

where $\overline{V}$ is the molar volume of the substance. Combining these expressions results in

$$-RT \ln X_A = \int_P^{P+\Pi} \overline{V} \, dP \tag{26.1.48}$$

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.

$$\int_P^{P+\Pi} \overline{V} \, dP = \overline{V} P \Big|_P^{P+\Pi} = \overline{V} \pi \tag{26.1.49}$$

Also, for values of X_A very close to 1

$$\ln X_A \approx -(1 - X_A) = -X_B \tag{26.1.50}$$

So, for dilute solutions

$$X_B RT = \overline{V} \Pi \tag{26.1.51}$$

Or after rearrangement

$$\Pi = \frac{X_B RT}{\overline{V}} \tag{26.1.52}$$

again, where $\overline{V}$ is the molar volume of the solvent. And finally, since $X_B / \overline{V}$ 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

$$\Pi = [B]RT \tag{26.1.53}$$

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.

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CHAPTER OVERVIEW

27: Extension 17 - Solid-Solution Phase Diagrams

27.1: 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 27.1.1. 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)
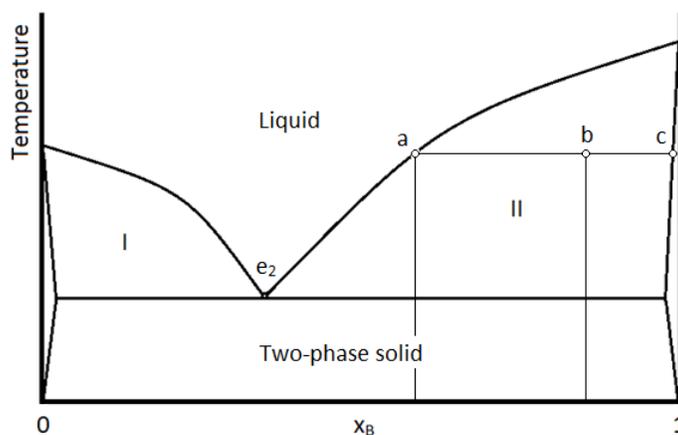
Figure 27.1.1: Phase diagram of a two-component system that exhibits an eutectic point.

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 27.1.2 can be used. In this case, it is assumed that the solids never form a single phase! The tin-lead system exhibits such behavior.
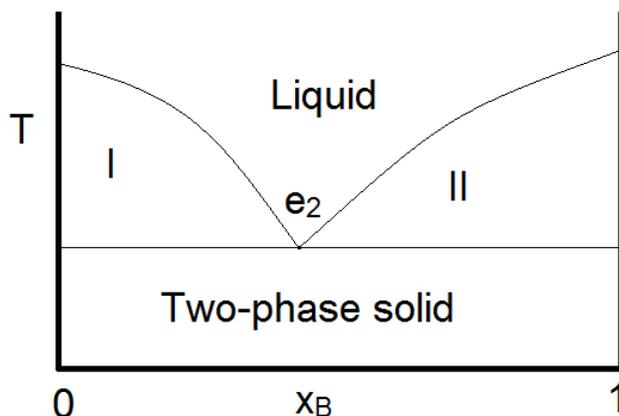
Figure 27.1.2: A simplified phase diagram of a two-component system that exhibits an eutectic point.

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 27.1.3.
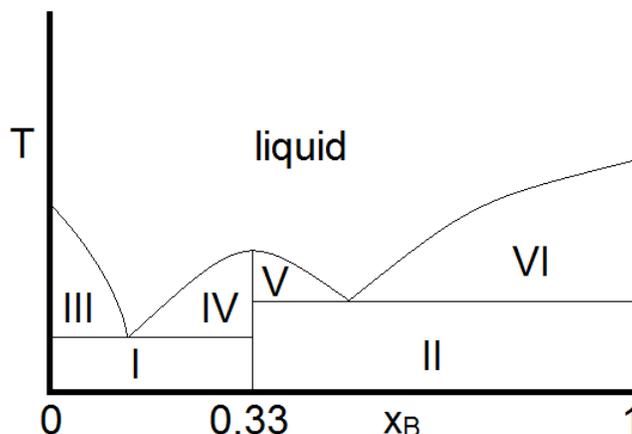
Figure 27.1.3: A simplified phase diagram of a two-component system that exhibits an eutectic point.

In this diagram, the vertical boundary at $X_B = 0.33$ 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

$$2A + B \rightarrow C \tag{27.1.1}$$

Thus, at overall compositions where $X_B < 0.33$, there is excess compound A (B is the limiting reagent) and for X_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 $27.1.4$
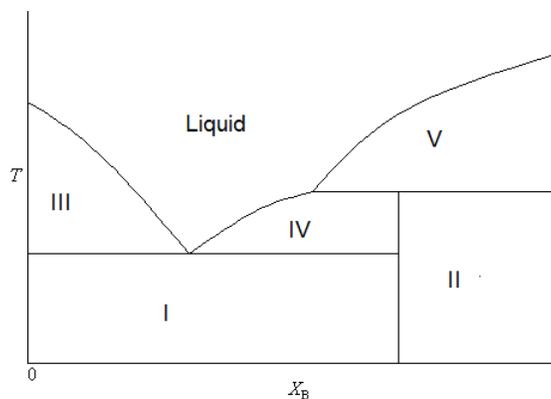
Figure 27.1.4: A phase diagram of a two-component system that exhibits incongruent melting.

In this diagram, the formula of the stable compound is AB_3 (consistent with $X_B < 0.75$). 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).

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27.2: 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 $27.2.1A$. A cooling curve for a sample that begins at the temperature and composition given by point a is shown in Figure $27.2.1B$.
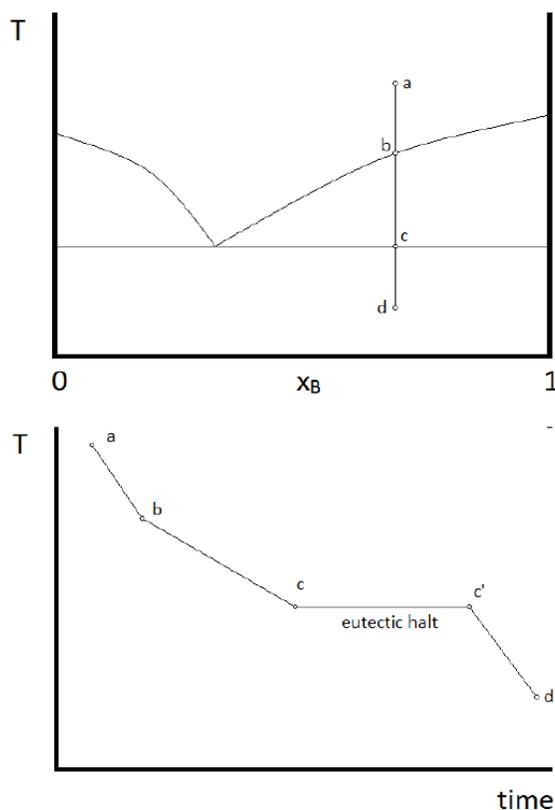
Figure 27.2.1: (A) cooling of a two-component system from liquid to solid. (B) Cooresponding cooling curve for this process.

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.

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