

# Chemical Energetics and Change

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# Preface

## First Edition

This is a collection of lecture notes for chem 20B at UCLA, from when I taught during the Winter quarter of 2018 and Spring quarter of 2017, as well as chem 20BH (honors version) Winter quarter of 2015. Chem 20B (“Energetics and Change”) is the second quarter of general chemistry for physical sciences students. Chem 20B mainly follows the second half of the textbook by Oxtoby, Gillis and Campion, “Principles of Modern Chemistry” [1]. The lecture notes were originally based on certain chapters of the book (hence the similar structure and organization), but evolved over time to provide more in-depth coverage of selected topics. This document is in the form of “lecture notes” rather than a textbook; the former being less wordy than the latter. The word *energetics* here refers to all aspects of energy, as it relates to chemical transformations and more generally speaking, physical interactions and the conversion of energy between thermodynamical systems.

The pre-requisites are calculus (differential and integral) as well as high-school or freshman physics. For example I assume you know introductory concepts in classical mechanics and electromagnetism, such as forces, Newton’s laws, Coulomb’s law, etc. I did include exercises to review and/or perfect these skills. Other concepts such as probability and partial differentiation, which will likely be new concepts to most freshman students, are introduced as needed, either in the various chapters or in the “Appendix” chapter. Practice may be found by working through end-of-chapter problems, whose solutions are provided for self-study. Some students may find it helpful to supplement these class-notes with an introductory textbook on

general chemistry. The latter typically contain more extensive discussions, worked examples, as well as end-of-chapter practice problems.

I have assembled the notes into a single PDF file during the summer of 2018, with the help of some UCLA students that offered to draw and redraw some of the figures. Many thanks go to Ellee Vikram and Emily Hays (two former chem 20B students) for drawing the illustrations. Ellee has also kindly proofread the entire book for typos and overall logical flow and organization. Any remaining errors are mine. These notes are made available on the internet as a downloadable PDF file, so they can remain accessible to anyone anywhere, free of charge.

For those wishing to pursue more in-depth studies, more advanced textbooks exist. To learn more about intermolecular forces, see “Intermolecular and surface forces” by Israelachvili [2] or “The molecular theory of gases and liquids” by Hirschfelder [3]. For statistical mechanics, McQuarrie has authored an excellent textbook (“Statistical mechanics”) [4]. McQuarrie and Simon’s “Molecular thermodynamics” [5] provides excellent coverage of both equilibrium and non-equilibrium thermodynamics. Kjelstrup and Bedeaux (“Non-equilibrium thermodynamics for engineers”) [6] as well as De Groot and Mazur (“Non-equilibrium thermodynamics”) [7] are also recommended. To learn more about probability, the book by A.N. Shiryaev (“Probability”) [8] is outstanding. For chemical kinetics, see Ancheyta’s “Chemical reaction kinetics” [9] as well as Chorkendorff and Niemantsverdriet (“Concepts of modern catalysis and kinetics”) [10].

Finally, a few words about notation. For work, the unusual notation  $\Delta W$  is used rather than  $w$ , to emphasize that it is obtained from infinitesimal quantities, i.e.  $\Delta W = \int \delta W$  (along some path). Same for heat transfer, the notation  $\Delta Q$  is used instead of  $q$  because  $\Delta Q = \int \delta Q$  (along some path). The “Capital Delta” notation is used to emphasize that those quantities are obtained by integrating a differential 1-form along a given path. I use bold-face and arrows to denote vectors ( $\mathbf{E}$  and  $\vec{E}$ ); both notations mean the same thing. Instead of  $\ln$  the natural log is written  $\log$  to avoid confusion with  $\ln$ . Integration volume is often written  $vol$  to avoid confusion with  $V$ , the thermodynamic system volume, when the two are different. The shorthand notation  $\partial_x$  is sometimes used for the partial derivative  $\frac{\partial}{\partial x}$ . Finally,  $\nabla f$  denotes the gradient of a function  $f$ , i.e. the vector  $\nabla f = (\partial_x f, \partial_y f, \partial_z f)$ .

Louis Bouchard  
Los Angeles, CA  
September 23, 2018

# Gases

## 1.1. The Ideal Gas

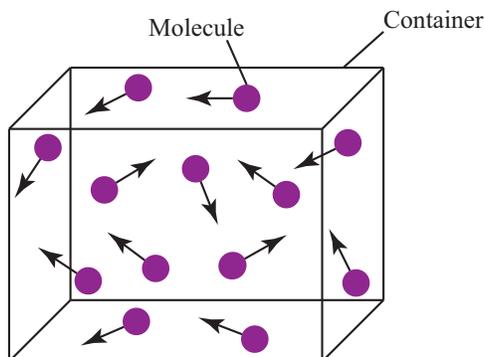
The famous ideal gas law,  $PV = nRT$  ( $P$ , pressure;  $V$ , volume;  $n$ , number of moles;  $R$ , gas constant;  $T$ , temperature), originated in 18th research by Boyle, Avogadro, and Charles. The ideal gas consists of an ensemble of  $N$  classical molecules which are moving randomly (due to thermal motion at positive temperature,  $T > 0$ ) and *do not interact with each other*.  $N$  and  $n$  are related by the Avogadro's constant,  $N_A$ , which counts the number of atoms in 12 grams of  $^{12}\text{C}$  isotope:

$$N \equiv n \cdot N_A \approx N \cdot (6.022 \times 10^{23} \text{ molecules/mol}).$$

The statement that the particles do not interact with each other implies that the gas density is low enough, so that intermolecular forces are not important. No interactions means no collisions. No collisions implies that the cross-sectional area of the particles is very small. In Fig. 1.1 the molecules should be thought of as as point particles. At low densities, the average distance,  $\langle r_{12} \rangle$ , between nearest neighbor molecules (labelled “1” and “2” here)

$$\langle r_{12} \rangle \sim \sqrt[3]{\frac{V}{N}},$$

is large, much larger than the molecular diameter.  $N/V$  is called the *number density*. At higher densities, the assumption of non-interacting particles is no longer valid and we must invoke principles of kinetic molecular theory to describe the behavior of the gas. At very low temperatures ( $\ll 1$  K), quantum effects become important and the ideal gas law breaks down [11].



**Figure 1.1.** Ideal gases are modeled as classical particles in a box, in the limit of low density. At low densities, interactions are not important. The particles have infinitesimally small radius (no collisions). At higher densities, deviations from the ideal gas law are observed, kinetic theory is used to describe collisions and intermolecular interactions become important.

While the properties of liquids and solids can be quite different among different substances, the properties of different types of gases are very similar to each other, especially in the low density limit, where the ideal gas law applies. The ideal gas law reflects the view that the properties of a gas ( $P, V, n, T$ ) do not depend on the type of gas. This implies, for example, that 1 mole of ideal gas at 300 K and 1 atm occupies exactly the same volume regardless of the type of gas (e.g., oxygen, nitrogen, xenon, etc.). It also implies that the total pressure in a mixture of different types of non-reacting gases is the sum of the partial pressures of each constituent gas (Dalton's law, see Section 1.2.2).

**1.1.1. Equation of State.** A thermodynamic system is described by an *equation of state*, which describes a relationship between the variables that describe the state of matter. It is a relation of the form:

$$f(n, P, T, V) = 0,$$

where  $n$  is the number of moles of a substance,  $P$  is the pressure of the gas,  $T$  is its temperature and  $V$  is the volume occupied by the substance. For a given set of physical conditions (e.g. pressure, volume, temperature, etc.) a state function is useful for analyzing the behavior of the system (gases, liquids and solids).

The function  $f$  is not necessarily smooth<sup>1</sup> and may contain discontinuities, especially at the boundaries between different phases of matter. Phase transitions that are “abrupt” will give rise to discontinuities in  $f$ . The ideal gas law ( $PV = nRT$ ), which can be put in this form as  $f(n, P, T, V) = PV - nRT = 0$ , appears to be a smooth function of its variables. However, this is only because this analytical expression describes a gas state only; it does not describe the transition to the liquid or solid phases. This can be seen by plotting the function (we do this in Section 1.4.4). In Section 1.4.2 we discuss the equation of state for a Van Der Waals (VDW) gas, which can describe a transition from gas to liquid phase.

Real substances will undergo phase transitions and in principle,  $f$ , is defined over all possible states of the substance, and may include discontinuities at the boundaries of phase transitions. We note that the equation of state is often obtained numerically from a discrete set of experimental data points and may not always exist in the form of a mathematical formula (analytical expression).

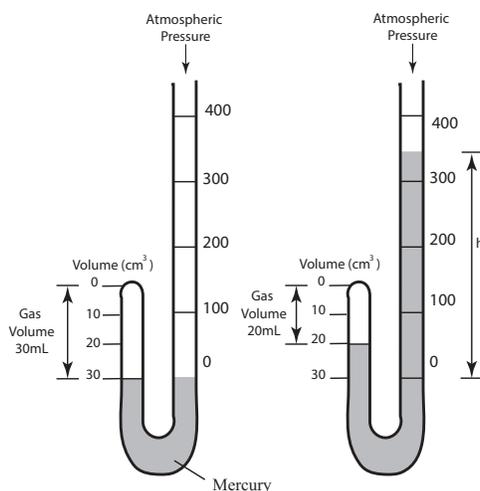
**1.1.2. Description of the Ideal Gas.** In the context of the ideal gas law, it is sufficient to define the ideal gas as a set of noninteracting classical molecules. The state of the gas is described by its macroscopic properties:  $T, n, P, V$ . Particles have zero size (no collisions, no intermolecular interactions); collisions will be discussed later, in the context of kinetic theory. The substance (gas) is characterized by macroscopic variables such as  $T$  (temperature),  $P$  (pressure),  $N$  (number of particles) and  $V$  (volume of container). The mass of the particles plays no role in the description of the gas. The equation of state for the ideal gas can be derived using three important concepts: Boyle’s law, Charles’ law and Avogadro’s law. If we think of the  $n, P, T, V$  space as 4-dimensional, the equation of state adds a constraint which reduces the dimensionality of the space to 3. The ideal gas molecule is required to “live” in that 3-dimensional space. For fixed  $n$ , we can take  $n/V$  (density) to be a single variable. In that case,  $n/V, P, T$  is a 3-dimensional space and the ideal gas law constraint reduces it to a 2-dimensional space (surface), as you will see in Section 1.4.4.

**1.1.3. Boyle’s Law (Robert William Boyle, 1627-1691).** In the 17th century Robert Boyle trapped a gas within a glass tube with one end sealed. Mercury was added to the tube to trap the gas. Any changes in the gas volume could be measured as changes in the mercury level. The glass tube was J-shaped, with a long end and a short end. The difference in mercury levels on both ends of the tube enabled him to determine the gas pressure

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<sup>1</sup>A smooth function is a function that can be differentiated with respect to its variables as many times as desired, and all of its derivatives are continuous.

(assuming that the ambient pressure to which the other end of the tube was in contact which remained constant). Boyle's 1662 J-tube experiment is illustrated in Fig. 1.2.



**Figure 1.2.** Boyle's law describes the inverse proportionality between pressure and volume ( $P \propto 1/V$ ). Left: When the heights of mercury on the two sides of the tube are the same, the pressure of the confined gas must equal that of the atmosphere, 1 atm or 760 mm Hg. Right: Boyle then added mercury to the J-tube. This caused the pressure of the gas to be increased by the number of millimeters of mercury in the height difference  $h$ . The compression of the gas causes it to occupy a smaller volume.

**Boyle's law:** In his experiments, Boyle noted that the gas volume varied inversely with pressure

$$P \propto \frac{1}{V}. \quad \text{at constant } T, n$$

$P$ : pressure of the gas (force/area)

$V$ : volume of the gas within the container

This relationship is independent of the gas type. In the case of the J-tube, the gas of interest is trapped at the sealed end by mercury.

An equivalent way to express this law is:

$$PV = \text{constant}.$$

This *constant* does not change as long as the temperature and number of gas and mercury molecules are held constant. This means that:

$$P_1V_1 = \text{constant} = P_2V_2$$

where  $P_1, V_1$  denote the pressure and volume (respectively) of the system in state 1 (i.e. at time 1), whereas  $P_2, V_2$  are pressure and volume of the system in state 2 (i.e. at time 2). For this to hold, everything else must be held constant. This constant is also independent of the type of gas.

Example: Consider a rigid sphere filled with air. At time 1 its volume is 50 L and the internal air has pressure 1 bar. The number of molecules is 2 mol, which remains constant because the sphere does not leak. At time 2, we manage to compress the size of the rigid sphere by half so that its volume is now 25 L. What is the pressure inside? (Temperature and number of molecules are held constant.) *Answer:* It will be 2 bars because  $P_1V_1 = P_2V_2$  or  $P_2 = P_1V_1/V_2 = (1 \text{ bar})(50 \text{ L}/25 \text{ L}) = 2 \text{ bars}$ .

#### 1.1.4. Charles' Law (Jacques Alexandre César Charles, 1746-1823).

Charles' law, also known as the law of Charles and Gay-Lussac, involves the concept of temperature. Charles (and later, Gay-Lussac, in similar experiments) found experimentally that different gases expand to the same extent over the same temperature interval. This established a linear relationship between volume and temperature:

**Charles' law:** The gas volume varies in proportion with temperature

$$V \propto T \quad \text{at constant } P, n$$

$T$ : temperature of the gas

$V$ : volume of the gas within the container

The constant of proportionality depends on the pressure and number of molecules of gas present, but not on the type of gas.

Figure 1.3 illustrates the experimental finding that the volume of a gas confined at constant pressure increases as the temperature increases. Since  $V \propto T$  we can write  $V/T = \text{constant}$ . The constant is *independent of gas type*. It does not change as long as the pressure and number of molecules are kept fixed. From this, we can then write

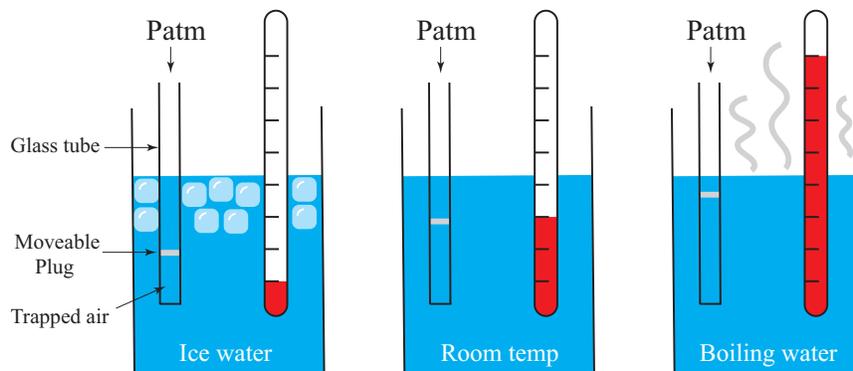
$$\frac{V_1}{V_2} = \frac{T_1}{T_2}.$$

#### 1.1.5. Avogadro's Law (Lorenzo Romano Avogadro, 1776-1856).

Avogadro's law states that the volume is proportional to the number of molecules  $N$  provided that temperature and pressure are held constant:

$$V \propto N.$$

You can imagine inflating a balloon by blowing two identical puffs of air consecutively. The first puff ( $N$  molecules) will inflate the balloon from volume 0 to volume  $V_1$ . This volume  $V_1$  corresponds to  $N$  molecules. The



**Figure 1.3.** Charles' law describes the proportionality between volume and temperature ( $V \propto T$ ).

second puff, because it is identical to the first one, adds  $N$  more molecules so that  $N_{final} = N + N = 2N$ . Its volume will have doubled,  $V_2 = 2V_1$ . If the balloon is spherical, doubling the volume corresponds to a radius or diameter increase of  $(2)^{1/3} \approx 1.26$  (26% higher), since  $V = \frac{4}{3}\pi r^3$ .

Avogadro's law is also known as the *extensive property of  $V$* . An extensive property is often defined as one which scales with the size of the system, i.e.  $V$  doubles if  $N$  doubles (and vice-versa).

**1.1.6. Some Definitions.** We will make frequent use of the following terminology, especially in the context of thermodynamics:

- **Macroscopic property:** properties which involve many molecules.
- **Microscopic property:** properties which involve one or few molecules.
- **Extensive property:** properties which depend on the size of the system (e.g. total mass, volume, number of moles of substance).
- **Intensive property:** properties which are not extensive (e.g., temperature, pressure, density, molar volume, molar mass).

**1.1.7. Combining All Three Laws to Get Ideal Gas Law.** We summarize the above laws:

- $P \propto \frac{1}{V}$  at constant  $T, N$  (Boyle's law)
- $V \propto T$  at constant  $P, N$  (Charles' law)
- $V \propto N$  at constant  $T, P$  (extensive property of  $V$ )

If we combine these laws together we get:

$$V \propto \frac{NT}{P}$$

The proportionality constant is known as Boltzmann's constant,  $k_B$ . We get the ideal gas law:

**Ideal gas law:** Equation of state for the ideal gas:

$$PV = Nk_B T$$

$P$ : Pressure of the gas (force/area)

$T$ : temperature of the gas (Kelvin scale:  $0^\circ\text{C} = 273.15\text{ K}$ )

$N$ : number of particles in the container

$V$ : volume of the container

$k_B = R/N_A$ : Boltzmann's constant ( $k_B = 1.38 \times 10^{-23}\text{ J/K}$ )

We can also express the ideal gas law in terms of the number of moles ( $n$ : number of moles) by using the relationship (1 mole =  $N_A = 6.022 \times 10^{23}$  molecules)

$$nR = Nk_B$$

where  $R = 8.31\text{ J/mol}\cdot\text{K}$  (ideal gas constant). Note: since  $k_B = nR/N$ , plugging  $n = 1\text{ mol}$  and  $N = N_A$  molecules gives  $k_B = 8.31/(6.022 \times 10^{23}) = 1.38 \times 10^{-23}\text{ J/K}$ .

**Ideal gas law (if working in moles):** The alternative form is:

$$PV = nRT.$$

**1.1.8. Units of Pressure.** It is very important to know the units of pressure and how they are related to each other. The unit of pressure in the SI system is the pascal (Pa), defined as a force of one Newton per square meter. The conversion between atm, Pa, and torr is as follows:  $1\text{ atm} = 101,325\text{ Pa} = 760\text{ torr}$ . Another common unit of pressure is the psi (pounds per square inch):  $1\text{ atm} = 14.69595\text{ psi}$ . Another unit is bar:  $1\text{ bar} = 100\text{ kPa}$  (not to be confused with atm, where  $1\text{ atm} = 101.325\text{ kPa}$ ).

**1.1.9. Gases at Standard Conditions.** Chemists define standard conditions as *standard temperature and pressure* (STP):

$$\text{STP: } 0^\circ\text{C (273.15 K)} \quad \text{and} \quad 1\text{ atm (760 torr)}.$$

Under these conditions, the volume of 1 mol of ideal gas is called the *standard molar volume*:

$$\text{standard molar volume} = 22.414\text{ L, or } 22.4\text{ L (to 3 significant figures)}.$$

Indeed, this follows from the ideal gas law,

$$V = \frac{nRT}{P} = \frac{(1\text{ mol})(0.082057\text{ L}\cdot\text{atm/mol}\cdot\text{K})(273.15\text{ K})}{(1\text{ atm})} = 22.414\text{ L}.$$

This particular value of  $R$  and its units ( $0.082057\text{ L}\cdot\text{atm/mol}\cdot\text{K}$ ) are explained at the end of Section 1.4.2.

**1.1.10. Ideal Gas Law Does Not Depend on Gas Type.** You may ask, Why don't these properties depend on the type of molecule/atom in the gas? For example, why isn't pressure (at fixed  $n, V, T$ ), which is force per unit area, higher for a heavy atom than a light one? This has to do with the velocity of molecules at a given temperature, which is lower for heavy atoms.

The force exerted by a molecule colliding against a wall is related to the transfer of momentum  $\Delta p$ , via  $F = \Delta p / \Delta t$ , where  $\Delta t$  is a time interval. The change in momentum is  $2mv$ , where  $m$  is the molecular mass and  $v$  is the molecule's velocity. Let's take  $v$  to be an average velocity. In a cubic container of side length  $L$ ,  $\Delta t$  is equal to  $\Delta t = 2L/v$ , so that  $P = F/L^2 \propto mv^2$ .

The independence of  $P$  on molecular mass means, for example, that  $m_{\text{O}_2}v_{\text{O}_2}^2 = m_{\text{H}_e}v_{\text{H}_e}^2$ , where  $m_{\text{H}_e} = 4$  amu and  $m_{\text{O}_2} = 32$  amu. Thus, if the mass is 8 times larger, the velocity must be  $\sqrt{8}$  times slower.

Oxygen molecules at room temperature have an average speed of about 480 m/s. This means that helium molecules at room temperature must have an average speed of approximately  $\sqrt{8}$  times  $480 \approx 1,360$  m/s. This is the only way that the ideal gas law can hold.

We will see later (in Section 1.3.9) that the kinetic theory of gases tells us that the speed of gas molecules is inversely proportional to the square root of the molecular mass, e.g.

$$v_p = \sqrt{\frac{2k_B T}{m}}, \quad \bar{v} = \sqrt{\frac{8k_B T}{\pi m}}, \quad v_{rms} = \sqrt{\frac{3k_B T}{m}}.$$

where  $v_p$  is the most probable speed,  $\bar{v}$  is the average speed and  $v_{rms}$  is the root-mean-square speed.

**1.1.11. Ideal Gas Example: Heating Gas at Constant Volume.**

Suppose that we trap a gas inside a container of fixed volume  $V$ . The temperature is  $T_1 = 293$  K and the pressure  $P_1$  is 1 atm. There is a pressure gauge attached to the volume. Now we place the container in boiling water ( $T_2 = 393$  K). What is the pressure gauge showing?

*Answer:* We can invoke the ideal gas law before and after, and use the fact that the ideal gas constant  $R$  is the same both before and after, i.e.  $PV = nRT$  is written as  $R = PV/nT$ . Then:  $P_1V_1/n_1T_1 = P_2V_2/n_2T_2$ . Since the number of moles doesn't change (container is leak-proof) and the volume remains fixed, we can cancel out the  $n$ 's and the  $V$ 's:  $P_1/T_1 = P_2/T_2$ . Solving for  $P_2$  gives  $P_2 = P_1(T_2/T_1)$ . Inserting the numbers we get:

$$P_2 = (1 \text{ atm}) \left( \frac{393}{293} \right) \approx (1 \text{ atm})(1.34) = 1.34 \text{ atm}.$$

Note: we used an equation of state (namely, the ideal gas law). An equation of state means that the state of the gas only depends on the current values of its thermodynamic variables (e.g.,  $P, T, V, n$ ), and not on their histories. Fortunately, the solution of this problem does not depend on how fast or slow the heating takes place.

**1.1.12. Phase Diagrams.** A phase diagram is a plot which shows the different phases of a given substance as function of the conditions (macroscopic variables, such as  $T, P, V$ ). The substance is in thermal equilibrium. On the phase diagram you will find regions corresponding to the different phases (e.g. solid, liquid, gas), as well as “phase boundary” lines between the different phases. These lines mark conditions under which multiple phases can coexist at equilibrium. Phase transitions occur along lines of equilibrium.

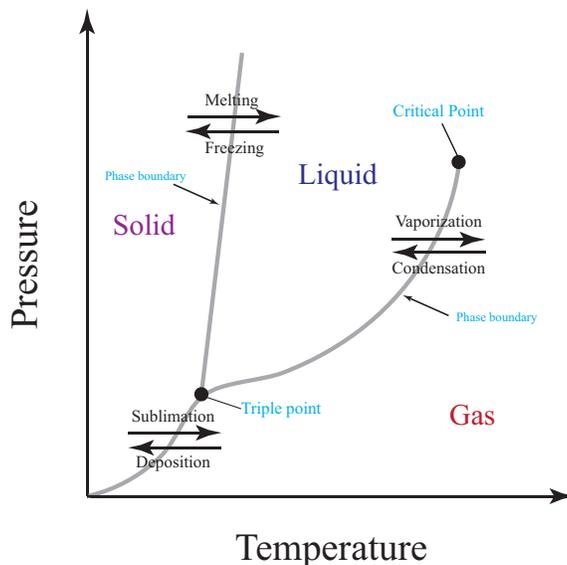
The triple point marks the condition where the substance coexists as a solid, liquid and a gas simultaneously. Different substances have different triple points. The critical point is the point where the substance may transition to the supercritical fluid state. To be in the supercritical state, the temperature and pressure must be at or above the critical temperature and pressure, respectively. Different substances have different critical points. *Each substance has a different phase diagram*, the characteristics of which are determined by *intermolecular forces*. Intermolecular forces are discussed in Chapter 2.

A phase diagram should describe real substances. Typically, phase diagrams are obtained from experimental measurements. For any substance, there exists an “equation of state” describing a constraint between  $P, T$  and  $N/V$ . This equation of state can be obtained from experimental data<sup>2</sup>. A hypothetical phase diagram is shown in Fig. 1.4.

Do not confuse Fig. 1.4 with the ideal gas law, as the ideal gas law does not describe solids or liquids. The ideal gas law applies only to gases in the low-density limit (e.g., the bottom-right region of  $P - T$  diagrams such as Fig. 1.4. For example, take a fixed value of the temperature  $T$ . Consider the compression of a gas inside a cylinder by a piston. Isothermal compression means that we move along a vertical line ( $T$  fixed) from bottom to the top on the diagram of Fig. 1.4. At low gas densities,  $PV = \text{constant}$  (Boyle’s law), and the gas pressure  $P$  increases as  $V$  decreases. As  $P$  increases, the gas eventually undergoes a phase transition from gas to liquid or gas to solid (depending on the value of  $T$ ). The ideal gas law does not describe the transition to the liquid, nor does it describe the state of the liquid itself.

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<sup>2</sup>Some equations of state, such as the Van Der Waals equation of state, are obtained from theoretical arguments.



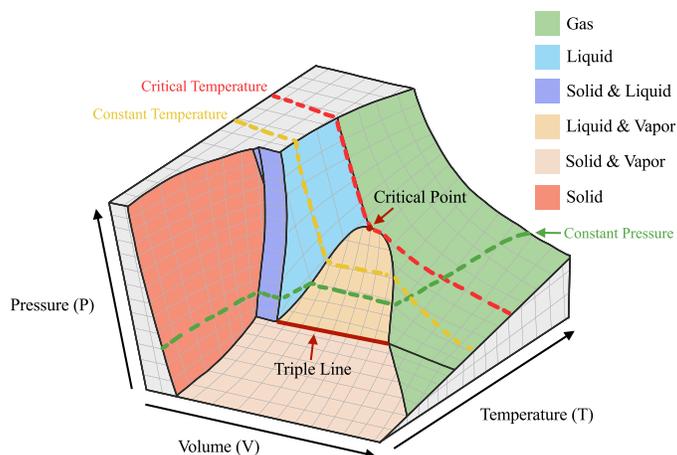
**Figure 1.4.** Pressure-temperature ( $V, n$  fixed) diagram representation of the phase diagram of some (unspecified) substance. The exact position of the phase boundaries depends on the substance.

For fixed  $N$ , an equation of state  $f(P, T, N/V) = 0$  (such as  $PV = Nk_B T$ , i.e.  $P - k_B T N/V = 0$ ) is a constraint that defines a 2D surface in the 3D space of  $T$ ,  $P$  and  $N/V$  ( $N/V = \text{number density}$ ). Thus, phase diagrams can also be represented as surfaces, such as the one shown in Fig. 1.5. In these diagrams, “volume” refers to the specific volume (ratio of a substance’s volume to its mass). Specific volume is the inverse of mass density.

**1.1.13. Example: Pressurized CO<sub>2</sub> in Tank.** Suppose that we have a gas cylinder (40 cm high, 15 cm diameter) at ambient temperature filled with CO<sub>2</sub>. The cylinder contains 10 lbs of CO<sub>2</sub>. The questions we ask is whether the tank is filled with liquid CO<sub>2</sub> or gaseous CO<sub>2</sub>. And if so, what is the pressure?

*Answer:* The tank is a cylinder whose volume is  $V = (40 \text{ cm})(\pi r^2) = (0.4 \text{ m})(\pi (0.075 \text{ m})^2) \approx 7.1 \times 10^{-3} \text{ m}^3$ . How many moles do we have in the tank? The mass of CO<sub>2</sub> is  $m = 10 \text{ lbs} = 4,500 \text{ g}$ . (1 lb is 450 g.) The molecular mass of CO<sub>2</sub> is  $12 + 32 = 44 \text{ g/mol}$ . Thus,  $n = 4,500 \text{ g} / (44 \text{ g} \cdot \text{mol}^{-1}) \approx 10^2 \text{ mol}$ .

Ambient temperature is 293 K. If this were a gas, we would have  $P = nRT/V \approx 3 \cdot 10^7 \text{ Pa} \approx 300 \text{ atm} \approx 300 \text{ bar}$ . This is a very high pressure. We suspect that there is probably no gas inside the tank because at that high pressure, the CO<sub>2</sub> probably becomes a liquid.



**Figure 1.5.** Surface plot representation of the phase diagram of some substance. The equation of state,  $f(P, T, N/V) = 0$ , defines a 2D surface in the 3D space of  $P, T$  and  $N/V$ . Some lines of constant pressure (isobar), temperature (isotherm) and volume (isochoric) are indicated on the graph.

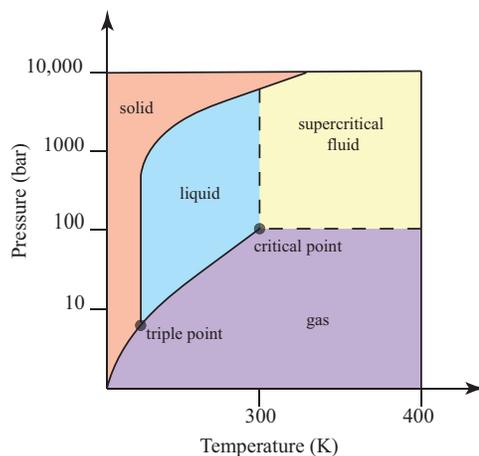
The phase diagram for  $\text{CO}_2$  is shown in Fig. 1.6. This graph shows that we cannot have a pure gas in the tank. At 293 K, increasing the pressure leads to a liquid. We have either a liquid or a supercritical fluid, depending on the exact position of the vertical dashed line. (Although I looked up the critical point of  $\text{CO}_2$ , and found it to be 73 atm and  $31^\circ\text{C}$ , which suggests we have a liquid since our temperature is not high enough.)  $P$  inside the tank is most definitely *not* equal to 300 atm because the gas eventually turns into a liquid (phase transition).

## 1.2. Mixtures of Gases (ideal)

**1.2.1. Partial Pressures.** A consequence of the ideal gas law is that the total pressure of a gas mixture,  $P_{tot}$ , is a sum of the partial pressures of each individual gas components, i.e.,

$$\begin{aligned} P_{tot} &= n_{tot} \frac{RT}{V} = (n_1 + n_2 + \cdots + n_N) \frac{RT}{V} = P_1 + \cdots + P_N \\ &= X_1 P_{tot} + \cdots + X_N P_{tot}, \end{aligned}$$

where  $n_i$  is the number of moles of species  $i$ ,  $n_{tot} = n_1 + \cdots + n_N$  is the total number of moles in the mixture,  $X_i = n_i/n_{tot}$  is the mole fraction of species  $i$  and  $P_i = n_i RT/V = X_i P_{tot}$  is the partial pressure of species  $i$ . This result follows because the ideal gas law only cares about the number of moles (at fixed  $T, P$ ), not the nature of the molecules.



**Figure 1.6.** Phase diagram for CO<sub>2</sub>.

Let's look at an example. Suppose that a gas mixture consists of  $n_{\text{N}_2}$  moles of N<sub>2</sub> and  $n_{\text{O}_2}$  moles of O<sub>2</sub>. The **mole fraction**  $X_{\text{N}_2}$  of N<sub>2</sub> is defined as:

$$X_{\text{N}_2} = \frac{n_{\text{N}_2}}{n_{\text{N}_2} + n_{\text{O}_2}} = \frac{n_{\text{N}_2}}{n_{\text{tot}}}.$$

Similarly, the mole fraction  $X_{\text{O}_2}$  of O<sub>2</sub> is defined as:

$$X_{\text{O}_2} = \frac{n_{\text{O}_2}}{n_{\text{N}_2} + n_{\text{O}_2}} = \frac{n_{\text{O}_2}}{n_{\text{tot}}}.$$

In particular, the **partial pressure** of N<sub>2</sub> within the gas container is given by:

$$P_{\text{N}_2} = n_{\text{N}_2} \frac{RT}{V} = X_{\text{N}_2} P_{\text{tot}},$$

where  $P_{\text{tot}} = P_{\text{N}_2} + P_{\text{O}_2}$  is the total pressure in the container. The second equality follows from:

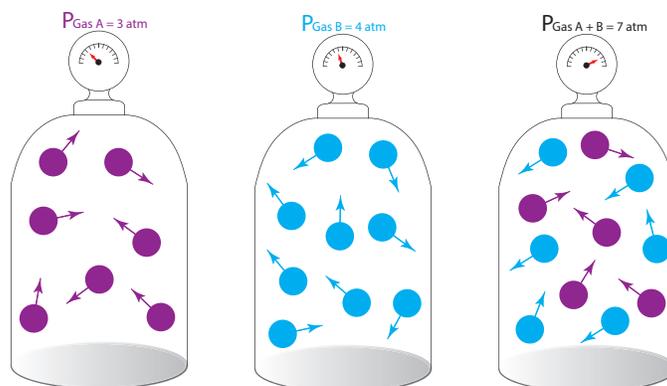
$$X_{\text{N}_2} P_{\text{tot}} = \left( \frac{n_{\text{N}_2}}{n_{\text{tot}}} \right) \left( n_{\text{tot}} \frac{RT}{V} \right) = n_{\text{N}_2} \frac{RT}{V}.$$

Similarly, the partial pressure of O<sub>2</sub> within the gas container is:

$$P_{\text{O}_2} = n_{\text{O}_2} \frac{RT}{V} = X_{\text{O}_2} P_{\text{tot}}.$$

**1.2.2. Dalton's Law For Gas Mixtures.** The result from the previous section is known as Dalton's law. Dalton's law says that the total pressure of a gas mixture is the sum of the pressures exerted by the individual gases. This is illustrated in Fig. 1.7 for the case of two gases mixed together into one tank. Note that the total volume is the same in all three containers.

The total pressure is the sum of the partial pressures:



**Figure 1.7.** Dalton's law: the total pressure in a mixture of gases equals the sum of the partial pressures of each gas. Here, 7 atm = 3 atm + 4 atm.

**Dalton's law:** Consider a gas mixture with  $N$  species and total number of moles  $n_{tot} = n_1 + n_2 + \dots + n_N$ , where  $n_i$  is the number of moles of species  $i$ . Then, the total pressure  $P_{tot}$  in the mixture

$$P_{tot} = P_1 + \dots + P_N = (n_1 + \dots + n_N) \frac{RT}{V}$$

$$= (X_1 + \dots + X_N) P_{tot} = n_{tot} \frac{RT}{V}$$

where  $n_{tot}$  is the total number of moles in the gas mixture,  $P_i$  is the partial pressure of species  $i$  and  $X_i$  is its mole fraction.

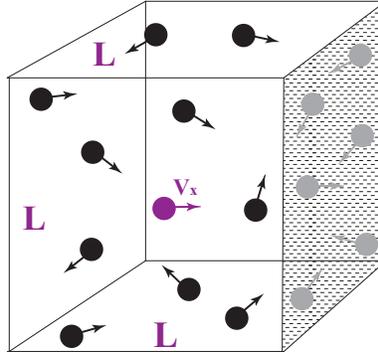
Dalton's law is valid in the absence of significant interactions. It is a consequence of the ideal gas law.

### 1.3. Translational Molecular Motion

**1.3.1. Estimating Pressure in Terms of Wall Collisions.** Pressure arises from collisions of gas molecules against a wall (Fig. 1.8). An ensemble of  $N$  gas molecules is held in a container of volume  $V = L^3$  at temperature  $T$ . Consider *elastic* collisions of gas molecules against the shaded wall whose area is  $A = L^2$  as shown below. Only the  $v_x$  component of the molecule's velocity matters, as orthogonal components ( $v_y, v_z$ ) do not lead to collisions against the shaded wall.

When a gas molecule collides with the wall in an *elastic* collision, its  $x$  velocity component  $v_x$  is reversed  $\rightarrow -v_x$ . Consider a molecule which is initially near the left wall, moves to the right, collides with the shaded wall, then bounces back to the left wall. Its momentum change is:

$$\Delta p_x = p_{x,before} - p_{x,after} = p_{x,before} - (-p_{x,before}) = 2p_{x,before} = 2mv_x.$$



**Figure 1.8.** Pressure on the wall is force per unit area exerted by the molecules colliding on the wall and abruptly changing their momentum upon collision.

( $m$ : mass of molecule) The transit time for this trajectory is

$$\Delta t = \frac{2L}{v_x}.$$

Force exerted on the shaded wall is obtained from Newton's second law

$$F_x = \frac{dp_x}{dt} \approx \frac{\Delta p_x}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}.$$

The total force on the wall arising from  $N$  molecules is

$$F_{x,tot} = \sum_{i=1}^N F_{x,i} = \sum_i \frac{m}{L} v_{x,i}^2 = \frac{Nm}{L} \underbrace{\left( \frac{1}{N} \sum_i v_{x,i}^2 \right)}_{\equiv \overline{v_x^2}} = \frac{Nm\overline{v_x^2}}{L}.$$

The bar denotes the average over  $N$  molecules. If there is no preference for the velocity direction (isotropic motion) we have that

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}$$

where  $\vec{v} = (v_x, v_y, v_z)$ . Therefore,  $\overline{v_x^2} = \frac{1}{3}\overline{v^2}$ .

**Pressure and Kinetic Energy:** The pressure  $P$  on the shaded wall is force,  $F = F_{x,tot}$ , divided by the wall area ( $L^2$ ):

$$P = \frac{F_{x,tot}}{L^2} = \frac{Nm\overline{v^2}}{3L^3}.$$

Since  $V = L^3$ , this can be written in the form of an ideal gas law:

$$PV = \frac{1}{3}Nm\overline{v^2}.$$

If we denote the average kinetic energy per molecule as

$$K_{av} = \frac{1}{2}m\overline{v^2}$$

we see that the pressure, a *macroscopic* property, is related to the average translational kinetic energy per molecule, which is a *microscopic* property.

$$(1.1) \quad P = \frac{2}{3} \frac{NK_{av}}{L^3} = \frac{2}{3} \frac{NK_{av}}{V} \quad \text{or} \quad PV = \frac{2}{3} NK_{av}.$$

**1.3.2. Temperature and Kinetic Energy of Molecules.** Molecular motions can be related to temperature of the gas if we invoke the ideal gas law:

$$(1.2) \quad PV = Nk_B T.$$

**Temperature and Kinetic Energy:** Comparison of (1.1) and (1.2) yields the important result that the average molecular kinetic energy is proportional to the absolute temperature:

$$T = \frac{m\overline{v^2}}{3k_B} = \frac{2}{3} \frac{K_{av}}{k_B}.$$

Thus, temperature is a measure of the average kinetic energy of the atoms in a monatomic gas. (This is valid only for a monatomic gas because the kinetic energy,  $K$ , would be different than  $\frac{1}{2}mv^2$  in the case of molecules, which possess internal rotational and translational motions.)

**1.3.3. Derivation of Ideal Gas Law.** To “prove” or derive the ideal gas law from kinetic theory<sup>3</sup> we need to show that  $\overline{v^2}$  is proportional to temperature:

$$\overline{v^2} = \int_0^\infty v^2 f(v) dv \propto T,$$

where  $f(v)dv$  is the probability that a molecule chosen at random in the gas will have speed in the range  $[v, v + dv]$ . Ludwig Boltzmann derived the result

$$f(v) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} 4\pi v^2 \exp\left( -\frac{mv^2}{2k_B T} \right) \quad \left\{ \begin{array}{l} \text{Maxwell-Boltzmann} \\ \text{speed distribution} \end{array} \right\}$$

<sup>3</sup>The combination of the results  $T = \frac{2}{3} \frac{K_{av}}{k_B}$  and  $P = \frac{2}{3} \frac{NK_{av}}{V}$  does not lead to the ideal gas law,  $PV = Nk_B T$ , because we’ve had to invoke the ideal gas law in order to obtain the relationship between temperature and kinetic energy,  $T = \frac{2}{3} \frac{K_{av}}{k_B}$ .

for the speed of a particle of mass  $m$ , where the speed  $v$  is  $\sqrt{v_x^2 + v_y^2 + v_z^2}$  and the velocity is  $\vec{v} = (v_x, v_y, v_z)$ . Then<sup>4</sup>

$$K_{av} = \frac{1}{2} \overline{mv^2} = \frac{m}{2} \overline{v^2} = \frac{m}{2} \int_0^\infty v^2 f(v) dv = \frac{3}{2} k_B T.$$

This equality is called the equipartition theorem. This theorem states that at thermal equilibrium, every particle has exactly the same average kinetic energy,  $(3/2)k_B T$ . Boltzmann thus established a definition of temperature (macroscopic quantity) in terms of the kinetic energy of the gas particles (microscopic quantities),  $T = (2/3)K_{av}/k_B$ .

**1.3.4. Root-Mean-Square Speed.** In the previous section we found that  $\frac{1}{2}mv^2 = \frac{3}{2}k_B T$ . Cancelling out the  $1/2$ , solving for  $\overline{v^2}$  and taking the square root gives the root-mean-square speed:

$$v_{rms} \equiv \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{\mathcal{M}}}.$$

where  $\mathcal{M}$  is the molar mass.

**1.3.5. Interpretation of Maxwellian Density.** The velocity of the center-of-mass of a molecule can be denoted by  $\vec{V} = (V_x, V_y, V_z)$  (capital  $V$ ). We view this velocity as a random variable, in the sense that the act of picking a molecule at random within an ensemble is a random experiment. When a molecule is selected, we then have a deterministic quantity, which we denoted by a lowercase  $\vec{v} = (v_x, v_y, v_z)$ . The probability that the random variable  $\vec{V}$  will take on values in the range  $V_x \in [v_x^1, v_x^2]$ ,  $V_y \in [v_y^1, v_y^2]$ ,  $V_z \in [v_z^1, v_z^2]$  is given by the integral:

$$\mathbb{P}\left(V_x \in [v_x^1, v_x^2], V_y \in [v_y^1, v_y^2], V_z \in [v_z^1, v_z^2]\right) = \int_{v_x^1}^{v_x^2} dv_x \int_{v_y^1}^{v_y^2} dv_y \int_{v_z^1}^{v_z^2} dv_z f_{\vec{V}}(\vec{v}),$$

where  $f_{\vec{V}}(\vec{v}) = f_{\vec{V}}(v_x, v_y, v_z)$  if the probability density function for  $\vec{V}$ .

<sup>4</sup>Let  $a = m/2k_B T$ . From integral tables,  $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\pi/a}$ , differentiating both sides twice with respect to  $a$  gives:  $\frac{d^2}{da^2} \int_{-\infty}^{\infty} e^{-ax^2} dx = \int_{-\infty}^{\infty} x^4 e^{-ax^2} dx = \sqrt{\pi}(-1/2)(-3/2)a^{-5/2} = (3/4)\sqrt{\pi}a^{-5/2}$ . Changing the limits of integration to  $\int_0^\infty$  leads to a factor of  $1/2$  and we have:  $\int_0^\infty x^4 e^{-ax^2} dx = (3/8)\sqrt{\pi}a^{-5/2}$ . Now we can easily integrate:

$$\begin{aligned} \overline{v^2} &= \int_0^\infty v^2 f(v) dv = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} 4\pi \int_0^\infty v^4 \exp(-av^2) dv \\ &= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} 4\pi \left\{ \frac{3\sqrt{\pi}}{8} \left(\frac{m}{2k_B T}\right)^{-\frac{5}{2}} \right\} = \frac{3k_B T}{m}. \end{aligned}$$

Learn more about Gaussian integrals: [https://en.wikipedia.org/wiki/Gaussian\\_integral](https://en.wikipedia.org/wiki/Gaussian_integral)

The left hand side denotes a *joint probability*, which is the probability of the *simultaneous occurrence* of all three events  $V_x \in [v_x^1, v_x^2]$ ,  $V_y \in [v_y^1, v_y^2]$ , and  $V_z \in [v_z^1, v_z^2]$ . If we take the intervals to be infinitesimally small, i.e.  $V_x \in [v_x, v_x + dv_x]$ ,  $V_y \in [v_y, v_y + dv_y]$ ,  $V_z \in [v_z, v_z + dv_z]$ , then the integrals reduce to the following<sup>5</sup>

$$\begin{aligned} \mathbb{P}(V_x \in [v_x, v_x + dv_x], V_y \in [v_y, v_y + dv_y], V_z \in [v_z, v_z + dv_z]) \\ = f_{\vec{V}}(\vec{v})dv_x dv_y dv_z. \end{aligned}$$

This quantity is the probability of finding a molecule whose  $x$  component of velocity,  $V_x$ , lies in the range  $[v_x, v_x + dv_x]$  (centered near  $v_x$ , with width  $dv_x$ ), and similarly for  $V_y$  and  $V_z$ . This can be written in terms of the volume element  $dV$  (the symbol  $\times$  denotes Cartesian product):

$$dV = [v_x, v_x + dv_x] \times [v_y, v_y + dv_y] \times [v_z, v_z + dv_z].$$

Thus,

$$f_{\vec{V}}(\vec{v})dv_x dv_y dv_z = \mathbb{P}(\vec{V} \in dV).$$

In 1D the situation is even simpler. The quantity

$$\mathbb{P}(V_x \in [v_1, v_2]) = \int_{v_1}^{v_2} f_{V_x}(v_x)dv_x$$

denotes the probability that the  $x$  component of the velocity of a molecule chosen at random will be in the interval  $[v_1, v_2]$ . The *probability density function* can be obtained from this probability by taking the interval  $[v_1, v_2]$  to be an infinitesimally small interval, e.g.  $[v_x, v_x + dv_x]$ , in which case we have:

$$\mathbb{P}(V_x \in [v_x, v_x + dv_x]) = \int_{v_x}^{v_x + dv_x} f_{V_x}(v_x)dv_x = f_{V_x}(v_x)dv_x.$$

**1.3.6. Derivation of Maxwellian Distribution.** We will show how the speed distribution is obtained from the velocity distribution. Boltzmann has shown that the velocity distribution is

$$(1.3) \quad f_{\vec{V}}(\vec{v}) = f_{V_x}(v_x)f_{V_y}(v_y)f_{V_z}(v_z) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right),$$

He did this by assuming that the kinetic energies  $\epsilon = \frac{1}{2}mv^2$  of a gas molecule are distributed according to the Gibbs distribution (Boltzmann factor):

$$p(x) = Ae^{-\epsilon(x)/k_B T},$$

where  $x$  denotes the state of the system (in our case,  $x$  is the velocity  $v$ ),  $\epsilon(x)$  is the energy of the state  $x$ ,  $A$  is a normalization constant such that  $\int p(x)dx = 1$ . (We will derive this Gibbs distribution later in the course,

<sup>5</sup>In other words, we made use of  $\int_y^{y+dy} f(x)dx = f(y)dy$ . To prove this, simply write the integrals as Riemannian sums. There is only 1 term in the summation.

using the first law of thermodynamics.) For  $\epsilon(v) = \frac{1}{2}mv^2$ , we shall denote this distribution as  $f_{\vec{v}}(\vec{v})$ :

**Maxwell velocity distribution:** The Maxwell velocity distribution

$$f_{\vec{v}}(\vec{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right),$$

describes the probability distribution of the velocities of gas molecules in an ideal gas. The quantity  $f_{\vec{v}}(\vec{v})d^3\vec{v} = f_{\vec{v}}(\vec{v})dv_x dv_y dv_z$  is the probability that you will find a molecule whose velocity lies within the volume element  $d^3\vec{v}$  centered at  $\vec{v}$ , i.e. where the  $x$  component of velocity is in the interval  $[v_x, v_x + dv_x]$ , its  $y$  component is in the interval  $[v_y, v_y + dv_y]$  and its  $z$  component, in  $[v_z, v_z + dv_z]$ .

**1.3.7. Maxwellian is a Product of Gaussians.** In the previous section we wrote that the velocity distribution factors into a product,  $f_{\vec{v}}(\vec{v}) = f_{V_x}(v_x)f_{V_y}(v_y)f_{V_z}(v_z)$ . This is due to the independence of the directions  $x$ ,  $y$  and  $z$ . The velocity of a gas molecule is described with a vector  $\vec{v} = (v_x, v_y, v_z)$ . In a gas the velocity components  $v_i$  ( $i = x, y, z$ ) average to zero,  $\bar{v}_i = 0$ , since negative values are equally likely to occur as positive values in an isotropic gas. To say that the gas is “isotropic” means that  $f_{\vec{v}}(\vec{v})$  is only a function of the magnitude  $|\vec{v}|$ , or equivalently,  $v^2 = v_x^2 + v_y^2 + v_z^2$ . Thus, we can write  $f_{\vec{v}}(\vec{v})$  as  $f_{\vec{v}}(|\vec{v}|)$ . I prefer to use  $f_{\vec{v}}(v^2) = f_{\vec{v}}(v_x^2 + v_y^2 + v_z^2)$  instead, since  $v^2$  also depends only on the magnitude of  $\vec{v}$ .

Also, the  $x, y, z$  components of the velocity are statistically independent of each other. Thus,  $f_{\vec{v}}(v^2) = f_{\vec{v}}(v_x^2 + v_y^2 + v_z^2)$  can be factored into a product of three independent functions, one for each coordinate:

$$f_{\vec{v}}(v^2) = f_{\vec{v}}(v_x^2 + v_y^2 + v_z^2) = f_{V_x}(v_x^2)f_{V_y}(v_y^2)f_{V_z}(v_z^2).$$

where  $f_{V_x}$ ,  $f_{V_y}$  and  $f_{V_z}$  are the same function because motion along  $x$  follows the same behavior as motion along  $y$  or  $z$ .

The only mathematical function which fulfills this condition is the exponential, since  $\exp(-av^2) = \exp(-av_x^2)\exp(-av_y^2)\exp(-av_z^2)$ , where  $a > 0$  is a constant. We need  $a > 0$  so that the  $f_{V_i}$  ( $i = x, y, z$ ) integrate to 1. (If  $a < 0$  the function  $f_{V_i}$  would blow up at infinity and is not integrable.) Thus these probability density functions are all Gaussian. If  $f_{\vec{v}}$  is to be a probability distribution it must be nonnegative ( $f_{\vec{v}} \geq 0$ ) and normalized:  $\int f_{\vec{v}}(v^2)d^3\vec{v} = 1$ .

A normalization constant  $c$  can be determined from the normalization condition  $1 = \int_{-\infty}^{\infty} f_{V_i}(v_i)dv_i = c \int_{-\infty}^{\infty} \exp(-av_i^2)dv_i$  ( $i = x, y, z$ ), leading to  $c = \sqrt{a/\pi}$ . By assuming that the molecular kinetic energies are distributed according to the Gibbs distribution (Boltzmann factor), Ludwig Boltzmann

found that  $a$  is related to the average kinetic energy per particle,  $K_{av} = \frac{3}{2}k_B T = \frac{1}{2}m\overline{v^2}$ . Namely,  $a = m/2k_B T$ .

**1.3.8. Maxwell-Boltzmann Speed Distribution.** In the previous section, we saw that each  $f_{V_i}(v_i)$  ( $i = x, y, z$ ) has the form of a Gaussian distribution centered at 0. However, the speed  $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$  does not average to zero at finite temperatures because each component is squared, turning negative values into positive ones.

Let's now find the probability of observing a molecule with speed in the range  $[v, v + dv]$ . We must “add” the probability  $f_{\vec{v}}(\vec{v})$  over all velocities in a spherical shell of radius  $v$  and thickness  $dv$ , as illustrated in Fig. 1.9.

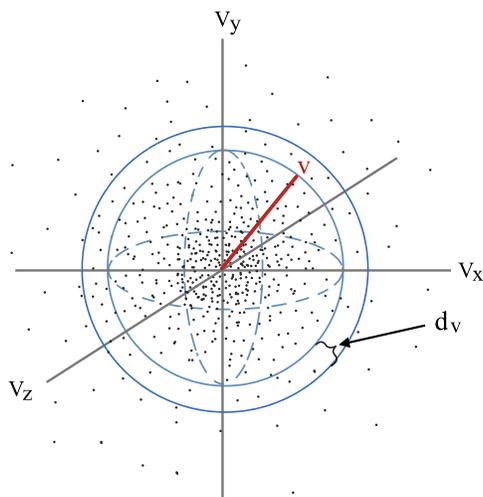


Figure 1.9. Velocity space.

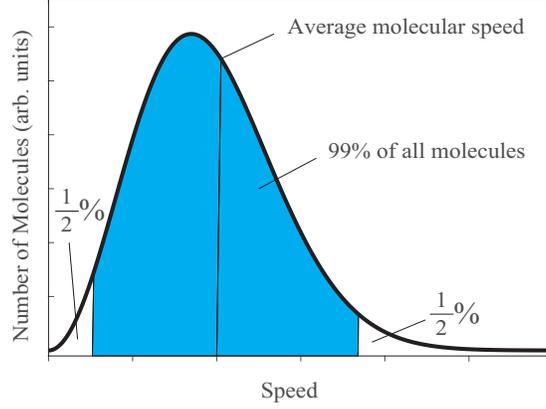
This shell has volume  $4\pi v^2 dv$ , and  $f_{\vec{v}}(\vec{v})$  has the same “constant” value over this entire shell. The result is obtained trivially by multiplying  $f(\vec{v})$  by  $4\pi v^2$ .

**Maxwell speed distribution:** The Maxwell speed distribution is:

$$(1.4) \quad f(v) = f_{\vec{v}}(\vec{v})4\pi v^2 = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 e^{-\frac{mv^2}{2k_B T}}.$$

The product  $f(v)dv$  gives the probability of finding a molecule with speed in the range  $[v, v + dv]$ . We note that the units of  $f(v)$  are  $s/m$  because the integral  $\int_0^\infty f(v)dv = 1$ . Thus, since  $dv$  has units  $m/s$ ,  $f(v)$  must have the inverse units,  $s/m$ .

This distribution is no longer Gaussian, but is skewed toward nonnegative values, as seen in Fig. 1.10.



**Figure 1.10.** Shape of the Maxwell-Boltzmann speed distribution (equation 1.4).

Another way to derive this is to transform to spherical coordinates in velocity space,  $(v, \theta, \phi)$ . Denoting,  $V = |\vec{V}| = \sqrt{V_x^2 + V_y^2 + V_z^2}$  ( $V$  is also a random variable, since it is constructed from the components  $V_x$ ,  $V_y$  and  $V_z$ , which are themselves random variables), the probability  $\mathbb{P}(V \in [v_1, v_2])$  is

$$\begin{aligned} \mathbb{P}(V \in [v_1, v_2]) &= \int_{\{\vec{v} | v_1 \leq v \leq v_2\}} dv_x dv_y dv_z f_{\vec{v}}(\vec{v}) \\ &= \int_{v_1}^{v_2} v^2 dv \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta f_{\vec{v}}(\vec{v}) = (4\pi) \int_{v_1}^{v_2} v^2 dv f_{\vec{v}}(\vec{v}) \end{aligned}$$

since  $f_{\vec{v}}(\vec{v})$  is independent of  $\theta, \phi$  (*by definition*, it only depends on the magnitude  $|\vec{v}|$ ). In particular, if we choose the interval  $[v_1, v_2]$  to be  $[v, v+dv]$ , then

$$(1.5) \quad \mathbb{P}(V \in [v, v+dv]) = 4\pi v^2 f_{\vec{v}}(\vec{v}) dv = \underbrace{\left(\frac{m}{2\pi k_B T}\right)^{3/2}}_{\text{Maxwell speed dist.}} 4\pi v^2 e^{-\frac{mv^2}{2k_B T}} dv.$$

**1.3.9. How Fast do Molecules Travel?** There are three different types of average speeds we may be interested in, depending on the context. The *most probable speed* is obtained by setting  $df(v)/dv = 0$  and solving for  $v$ , i.e.  $df/dv \propto (2v - v^2 m/2k_B T) = 0$ . The result is:

$$(1.6) \quad v_p = \sqrt{\frac{2k_B T}{m}}.$$

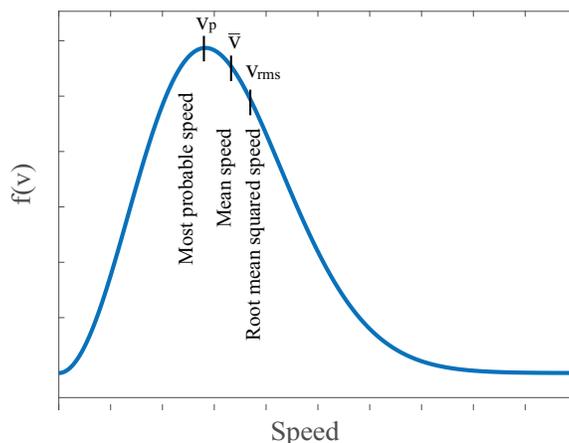
The mean value of the speed is

$$(1.7) \quad \bar{v} = \sqrt{\frac{8k_B T}{\pi m}}.$$

The root-mean-square speed is (derived in Section 1.3.4):

$$(1.8) \quad v_{rms} = \sqrt{\frac{3k_B T}{m}}.$$

We see that:  $v_p < \bar{v} < v_{rms}$ . These formulae can be expressed in terms of molar mass  $\mathcal{M}$  instead by simply replacing  $k_B/m$  by  $R/\mathcal{M}$ . These quantities are illustrated in Fig. 1.11 relative to the probability distribution (Eq. 1.5). Geometrically, the most probable speed corresponds to the peak of this distribution whereas the mean speed is the velocity at which the areas to its left and to its right are equal. And you will recall from the previous lecture that the RMS speed is related to temperature and average kinetic energy of a molecule.



**Figure 1.11.** Maxwell-Boltzmann speed distribution (equation 1.4). Most probable speed ( $v_p$ ), mean speed ( $\bar{v}$ ) and rms speed ( $v_{rms}$ ) are shown on the plot (see also equations 1.6, 1.7 and 1.8).

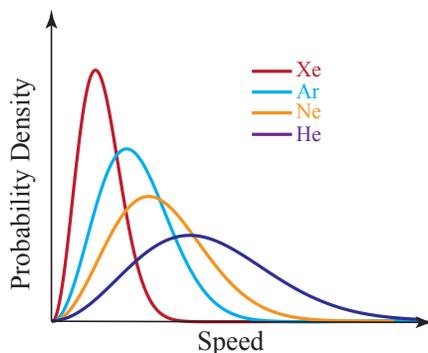
1.3.9.1. *Sample Calculation.* Calculate the most probable speed,  $v_p$ , for  $\text{H}_2$  gas at room temperature ( $T=300$  K).

*Strategy:* Invoke the formula in molar units,  $v_p = (2RT/\mathcal{M})^{1/2}$  and plug in  $\mathcal{M}=2$  g/mol.

*Solution:*

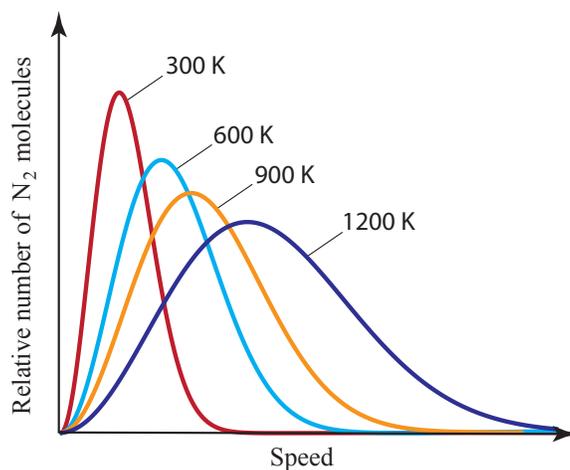
$$v_p = \sqrt{\frac{2(8.31 \text{ J/mol.K})(300 \text{ K})}{(2 \text{ g/mol})} \frac{1000 \text{ g}}{1 \text{ kg}}} \sim 1580 \text{ m/s}.$$

**1.3.10. Dependence of Speed Distribution on  $T$  and  $m$ .** For a fixed temperature  $T$  the Maxwell speed distribution (Eq. 1.4) for heavy gases (e.g.  $^{132}\text{Xe}$ ) is shifted to the left because of the low velocities, whereas the distribution for light gases (e.g.  $^4\text{He}$ ) is shifted to the right because of higher velocities. This is illustrated in Fig. 1.12.



**Figure 1.12.** Dependence of the Maxwell-Boltzmann speed distribution (Eq. 1.4) on molecular mass. For heavier molecules, it is shifted to the left. The total area equals 1 regardless of mass.

The area under the curve, however, remains constant, which explains the flattening of the curves with light gases. If we fix the gas type (e.g.  $\text{N}_2$ ) the distribution is skewed to the left for cold gases and to the right for warmer gases. This is illustrated in Fig. 1.13.

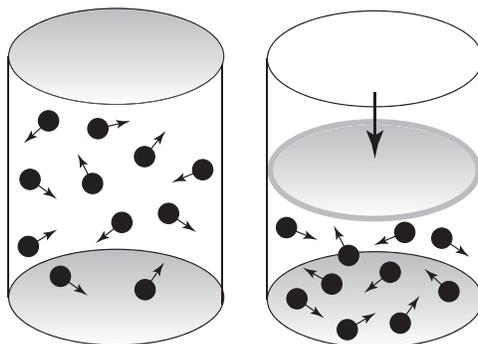


**Figure 1.13.** Dependence of the Maxwell-Boltzmann speed distribution (Eq. 1.4) on temperature. For higher temperatures, the distribution is shifted towards larger speeds. The total area equals 1 regardless of temperature.

## 1.4. Real Gases

In this section we look at the case where the ideal gas law is inadequate.

**1.4.1. Deviations From the Ideal Gas Law.** If we compress a gas, its density increases and deviations from the ideal gas law are expected (Fig. 1.14).



**Figure 1.14.** Compression of a gas leads to higher density, where intermolecular interactions become more important.

The ideal gas law becomes less accurate when intermolecular interactions are important. Such a situation occurs at high pressures and low temperatures. At high pressures, the molecules are closer to each other and interact more. At low temperatures their velocities are reduced and intermolecular collisions last longer.

Consider two different gases, He and HF. In both cases, we have 0.1 mol of each gas, and each gas is placed in a cubic container of volume 2 L. The temperature of both containers is held at 500 K. Experimentally, we measure the pressures to be  $P_{\text{He}} = 2.05$  atm and  $P_{\text{HF}} = 2.03$  atm. The ideal gas law predicts that the pressure will be (recall that 1 atm = 101.325 Pa)

$$P_{\text{ideal}} = \frac{nRT}{V} = \frac{(0.1 \text{ mol})(8.31 \text{ J/mol.K})(500 \text{ K})}{(2 \text{ L})(0.001 \text{ m}^3/\text{L})} = 207.750 \text{ kPa} = 2.05 \text{ atm},$$

or<sup>6</sup>

$$P_{\text{ideal}} = \frac{nRT}{V} = \frac{(0.1 \text{ mol})(0.08206 \text{ L.atm/K.mol})(500 \text{ K})}{2 \text{ L}} = 2.05 \text{ atm}.$$

Comparing this to the experimentally measured pressure values we conclude that He gas behaves like an ideal gas under those conditions whereas HF deviates from an ideal gas. This is due to the nature of the intermolecular

<sup>6</sup>You can find values of the gas constant  $R$  expressed in many different convenient units at the URL [https://en.wikipedia.org/wiki/Gas\\_constant](https://en.wikipedia.org/wiki/Gas_constant)

interactions. In He, such interactions are small, limited to VDW forces, where as HF is a polar molecule and dipole-dipole interactions are significant. This experiment can be repeated for numerous additional gases and we obtain the results:

Molecule	$P_{real}(\text{atm})$
CO <sub>2</sub>	2.06
Ar	2.05
H <sub>2</sub> O	2.02
SF <sub>6</sub>	2.08
CH <sub>2</sub> Cl <sub>2</sub>	2.04

Repulsive forces increase the pressure compared to the ideal gas law. Repulsive forces can arise when the molecules are ions. They also arise because of the finite volume of the molecules. Indeed, molecules take up space, leading to a “reduced volume” in which gas molecules can diffuse. These molecules also hit the walls harder due to their finite-size, compared to ideal gas molecules which have size zero. Thus,  $P$  is larger.

Attractive forces exist when molecules have opposite charges, or dipole moments (permanent or induced), or VDW interactions. This has the effect of reducing the pressure of the gas.

**1.4.2. Van Der Waals Gas.** A simple model for a non-ideal gas is the VDW gas. It accounts for the volume occupied by the particles and for the attractive forces between pairs of particles. Although it performs slightly better than the ideal gas law, its range of applicability is limited, making it mainly a pedagogical tool.

The starting point is the ideal gas law,  $PV = nRT$ , where  $P$  is the “ideal gas pressure” and  $V$  is the “ideal gas volume”. The volume is set equal to the container volume  $\tilde{V}$  less the volume occupied by the gas molecules,  $nb$ :

$$V = \tilde{V} - nb,$$

where  $b$  is the particle volume occupied by one mole of gas. The ideal gas pressure,  $P$ , is equal to the measured pressure  $\tilde{P}$  plus a correction term,  $an^2/V^2$ :

$$P = \tilde{P} + a \frac{n^2}{V^2}$$

where  $a > 0$  for attractive intermolecular forces and  $a < 0$  for repulsive forces. The result is (dropping the tilde notation):

**Van Der Waals equation of state:** The VDW equation of state is

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

where  $a > 0$  for attractive intermolecular interactions and  $a < 0$  for repulsive forces.  $b$  is always positive because it represents volume. Rearranging this equation

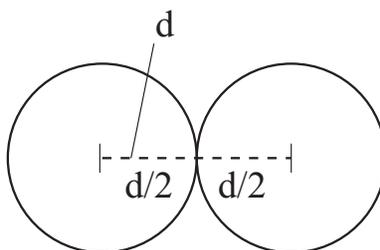
$$P_{vdw} = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2}$$

makes it obvious that the effect of the term  $\frac{n^2 a}{V^2}$  is to *reduce* the pressure in the system (when forces are attractive,  $a > 0$ ). In general, both  $a$  and  $b$  depend on temperature.

The excluded volume for one mole of particles is:

$$b = N_A \cdot 4 \times \left(\frac{4\pi r^3}{3}\right),$$

where  $r$  is the particle radius and  $N_A$  is Avogadro's number. The factor of 4 arises because the radius of the sphere is taken to be  $2r$  (instead of  $r$ ), which is the distance of closest approach between two spheres' centers (Fig. 1.15).



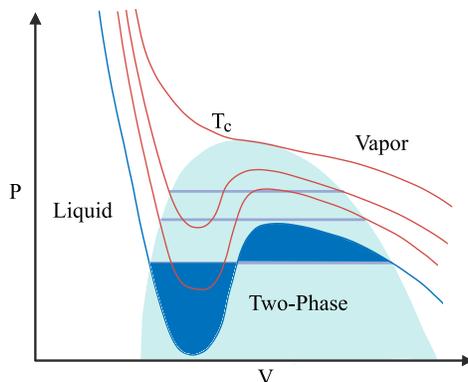
**Figure 1.15.** Molecules as hard spheres. The distance of closest approach is  $d$  (as measured from center to center).

This gives a factor of  $2^3 = 8$ , but we then divide by 2 to avoid over-counting (adding up excluded volumes for each sphere would over-count this total excluded volume by a factor of two).

The quantity  $(n/V)^2$  is proportional to  $\rho^2$ , the square of the gas density. This reflects the fact that pressure drops occur because of *pairwise* encounters between molecules.

The VDW equation of state describes a first order phase transition from liquid to vapor. Several isotherms are shown in Fig. 1.16.

$T_c$  is the critical temperature. At  $T_c$ , the local maximum and minimum coalesce into a single inflection point where  $(\partial^2 P / \partial V^2)_T = 0$ , in addition



**Figure 1.16.** VDW equation of state illustrated in the form of isotherms in the  $P, V$  plane. The critical temperature ( $T_c$ ) is indicated on this graph; see Section 1.4.3. The Maxwell construction is shown in dark blue.

to  $(\partial P/\partial V)_T = 0$ . The critical point is the maximum temperature and pressure at which distinct liquid and gas phases exist. In Section 1.4.3 we show how to express the critical point in terms of the substance ( $a, b$ ).

The quantity

$$\kappa = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T \approx -\frac{1}{V} \frac{\Delta V}{\Delta P} \text{ at constant } T$$

is called *isothermal compressibility*. For a normal substance, pressure should drop with increasing volume (think Boyle's law,  $P \propto 1/V$ ), leading to  $\kappa > 0$ . However, for the VDW gas we see that  $\kappa < 0$  in the oscillatory region of Fig. 1.16. Such behavior is not physical. The Maxwell construction was invented to avoid non-physical behavior where  $P$  increases with  $V$ . This construction is shown in the blue isotherm of Fig. 1.16: the oscillatory region of the VDW isotherm is deleted and replaced by a horizontal straight line. The vertical position of the horizontal straight line is such that the two blue areas are equal. The horizontal line indicates the phase transition from liquid to gas and is characterized by infinite isothermal compressibility,  $\kappa = -(1/V)(\partial V/\partial P) \rightarrow \infty$ . Experimentally measured values of the isothermal compressibility for different substances are shown in Table 1.1.

The VDW constants  $a$  and  $b$  depend on the gas type.  $a$  is a measure of the attractive forces between the molecules.  $b$  is due to the finite volume of the molecules and to their general incompressibility. Table 1.2 provides examples for several gases.

Substance	Compressibility ( $\text{Pa}^{-1}$ )		
	$T/^\circ\text{C}$	1 atm	1000 atm
Acetic acid	20	9.08	—

Acetone	20	12.75	—
	25	12.39	6.02
Benzene	20	9.44	—
	25	9.67	5.07
Chloroform	20	10.15	—
	25	9.74	5.34
Cyclohexane	25	11.20	—
Ethyl alcohol	20	10.98	—
Mercury	20	0.40	0.39
Methanol	20	12.11	—
Water	20	4.58	—
	25	4.57	3.48

**Table 1.1.** Isothermal compressibility,  $\kappa$ , of selected compounds.  $\kappa$  depends on temperature and pressure. Source: CRC Handbook of chemistry and physics [12].

Substance	Formula	a	b
		$\frac{\text{L}^2 \times \text{atm}}{(\text{mole})^2}$	$\frac{\text{L}}{\text{mole}}$
Acetic acid	CH <sub>3</sub> COOH	17.59	0.1068
Acetone	(CH <sub>3</sub> ) <sub>2</sub> CO	13.91	0.0994
Ammonia	NH <sub>3</sub>	4.170	0.03707
Argon	Ar	1.345	0.03219
Benzene	C <sub>6</sub> H <sub>6</sub>	18.00	0.1154
Carbon dioxide	CO <sub>2</sub>	3.592	0.04267
Carbon monoxide	CO	1.485	0.03985
Chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	25.43	0.1453
Cyclohexane	C <sub>6</sub> H <sub>12</sub>	22.81	0.1424
Ethane	C <sub>2</sub> H <sub>6</sub>	5.489	0.06380
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	12.02	0.08407
Helium	He	0.03412	0.02370
Hydrogen	H <sub>2</sub>	0.2444	0.02661
Methane	CH <sub>4</sub>	2.253	0.04278
Nitrogen	N <sub>2</sub>	1.390	0.03913
Nitrous oxide	N <sub>2</sub> O	3.782	0.04415
Oxygen	O <sub>2</sub>	1.360	0.03183
Phosphine	PH <sub>3</sub>	4.631	0.05156

**Table 1.2.** VDW constants  $a$  and  $b$  for different substances.  $a$  and  $b$  are known to vary with temperature. Source: CRC Handbook of chemistry and physics [12].

Note: to use the values from Table 1.2, the pressure must be in atmospheres, temperature should be in Kelvin and volume must be in liters. To use the VDW formula with these constants,  $R$  must be 0.08206 L.atm/mol/K. The value of  $R$  that is appropriate depends on the units you are working with. Here are some commonly used values of  $R$  you may encounter in the literature:

$$0.082057 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$62.364 \text{ L Torr mol}^{-1} \text{ K}^{-1}$$

$$8.3145 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$$

$$8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$$

These values of  $R$  are all equal to each other. They are obtained by converting units. For example,  $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$  is equal to  $8.3145 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$  because  $1 \text{ J} = 1 \text{ m}^3 \text{ Pa}$ . Likewise, if we multiply  $8.3145 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$  by  $(1 \text{ atm}/101,325 \text{ Pa})$  and by  $(1 \text{ L}/0.001 \text{ m}^3)$ , we obtain  $0.082057 \text{ L atm mol}^{-1} \text{ K}^{-1}$ .

**1.4.3. Critical Point.** Differentiating the VDW pressure

$$P = \frac{nRT}{(V - nb)} - \frac{n^2a}{V^2}$$

with respect to  $V$ , we get

$$-nRT(V - nb)^{-2} + 2n^2aV^{-3}.$$

Differentiating again gives

$$2nRT(V - nb)^{-3} - 6n^2aV^{-4}.$$

Setting these two expressions equal to zero and solving for  $T$  and  $V$  gives the critical temperature and volume, respectively. Multiply

$$-nRT(V - nb)^{-2} + 2n^2aV^{-3} = 0$$

by  $2/(V - nb)$  to get

$$-2nRT(V - nb)^{-3} + 4n^2aV^{-3}(V - nb)^{-1} = 0.$$

Then add the second equation

$$2nRT(V - nb)^{-3} - 6n^2aV^{-4} = 0$$

to get (cancelling terms with  $T$ ),

$$-6an^2V^{-4} + 4an^2V^{-3}(V - nb)^{-1}.$$

Then multiply by  $V^3/(2an^2)$  to get,  $2(V - nb)^{-1} = 3V^{-1}$ , which is solved to get  $V_c = 3nb$ .

To get  $T_c$  we substitute  $V_c$  into any of the two equations (say the first one), which gives

$$-nRT(3nb - nb)^{-2} + 2an^2(3nb)^{-3} = 0,$$

or  $RT/4 = 2a/(27b)$ , from which  $T_c = 8a/(27bR)$ .

To get  $P_c$  we substitute  $V_c$  and  $T_c$  into the VDW equation and solve for  $P$ ,

$$P_c = \frac{nRT_c}{V_c - nb} - a\frac{n^2}{V_c^2} = \frac{nR(8a/(27bR))}{3nb - nb - an^2/(3nb)^2},$$

which simplifies to  $P_c = a/(27b^2)$ . In Section 1.4.4, we show how the critical point can be used to express the VDW equation of state in dimensionless form.

**1.4.4. Dimensionless VDW Eq. of State.** In the previous section we have found the critical point:

$$P_c = a/(27b^2), \quad T_c = 8a/(27bR), \quad V_c = 3nb.$$

We can define the reduced parameters:

$$P' = \frac{P}{P_c}, \quad T' = \frac{T}{T_c}, \quad V' = \frac{V}{V_c}.$$

Solve for  $P$ ,  $T$  and  $V$  and substitute into

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

to get:

$$\left(P' \frac{a}{27b^2} + \frac{an^2}{(V'3nb)^2}\right)(V'3nb - nb) = nR \frac{8aT'}{27bR}.$$

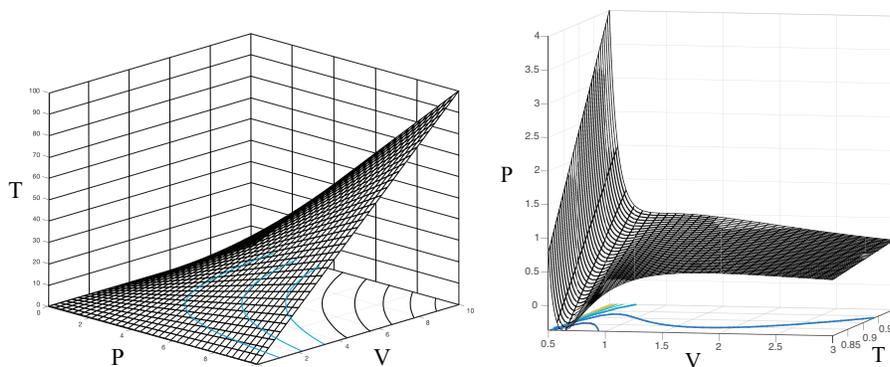
This simplifies to:

$$\left(P' + \frac{3}{V'^2}\right)\left(V' - \frac{1}{3}\right) = \frac{8}{3}T'.$$

This dimensionless form is useful for graphing the VDW equation. As a function of  $V', T', P'$ , it is independent of the type of gas (the dependence on gas type has been absorbed in the definitions of  $V', T', P'$ ).

**1.4.5. P-V-T Diagrams for VDW Gas.** For fixed number of moles, the equation of state is a function of three variables ( $P, V, T$ ). In 3D space, this relation between these variables represents a constraint, i.e. a 2D surface. The equation of state plotted as a 2D surface is called P-V-T diagram. Figure 1.17 compares surface plots of the equation of state for ideal vs VDW gas.

In Fig. 1.17 the “isothermals” ( $T = \text{constant}$ ) are shown in the horizontal plane for the ideal gas. For the VDW gas, “isobars” ( $P = \text{constant}$ ) are shown in the horizontal plane. For the ideal gas law, the isothermals are  $P \propto 1/V$  whereas for the VDW gas the relationship between  $T$  and  $V$  is more complicated.



**Figure 1.17.** P-V-T surface for an ideal gas (left) and a VDW gas (right). Note: The axes are rotated ( $TPV$  vs  $PVT$ ) to show the best view of each surface.

**1.4.6. Virial Expansion.** The virial expansion of the pressure of a many-particle system in powers of the density provides systematic corrections to the ideal gas law. Denoting the gas density as  $\rho = N/V$  the ideal gas law reads:

$$PV = Nk_B T \quad \rightarrow \quad \frac{P}{k_B T} = \frac{N}{V} \equiv \rho. \quad (\text{ideal gas law})$$

We know that the ideal gas law holds at low pressures, or equivalently (for fixed  $T$ ), at low densities. As the gas density is increased, we expect some deviations from the ideal gas law behavior. These deviations can be described by replacing the right hand side by a Taylor series in the gas density.

**Virial expansion:**

$$\frac{P}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots$$

The ideal gas law is then viewed as the low density limit ( $\rho \rightarrow 0$ ) of the virial expansion. The virial coefficients  $B_i(T)$  depend on temperature and describe the interactions between the particles. The calculation of virial coefficients from knowledge of the intermolecular potentials is done using methods of *statistical mechanics*.

The first correction term,  $B_2(T)\rho^2$ , describes pairwise collisions between molecules. It is proportional to  $\rho^2$  because two-body collisions depend on the product of the probability of finding molecule 1 in some volume element times the probability of finding molecule 2 in the same volume element. For a uniform gas, each probability is proportional to the gas density; their product is  $\rho^2$ . The second correction term,  $B_3(T)\rho^3$  describes three-body collisions. The probability of a three-body encounter is proportional to  $\rho^3$ .

The latter are extremely rare events and this term is typically much smaller than the previous term,  $B_2(T)\rho^2$ .

#### 1.4.7. VDW eq. of State vs Virial Expansion, Boyle Temperature.

Comparison of the virial expansion:

$$(1.9) \quad \frac{P}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots$$

where  $\rho = N/V$ , with the VDW equation of state:

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

This leads to the virial coefficients of the VDW gas:

$$B_2(T) = \frac{b}{N_A} - \frac{a}{N_A^2 k_B T}, \quad B_3(T) = \frac{b^2}{N_A^3}, \quad \text{etc.}$$

This is left to the reader as an exercise.<sup>7</sup> The point at which  $B_2(T) = 0$  is called the *Boyle temperature*:

$$T_B = \frac{a}{bk_B N_A} = \frac{a}{bR}.$$

It is at the Boyle temperature that the attractive and repulsive forces acting on the gas particles balance out. At that temperature, the non-ideal gas behaves like an ideal gas over some range of pressures.

## 1.5. Diffusion

Molecular diffusion, often simply called diffusion, is the thermal motion of all (liquid or gas) particles at temperatures above absolute zero. The rate of this movement is a function of temperature, viscosity of the fluid and the size (mass) of the particles. Diffusion explains the net flux of molecules from a region of higher concentration to one of lower concentration. Once the concentrations are equal the molecules continue to move, but since there is no concentration gradient the process of molecular diffusion has ceased and is instead governed by the process of self-diffusion, originating from the random motion of the molecules. The result of diffusion is a gradual mixing of material such that the distribution of molecules is uniform. Since the molecules are still in motion, but an equilibrium has been established, the end result of molecular diffusion is called a “dynamic equilibrium”. In a phase with uniform temperature, absent external net forces acting on the particles, the diffusion process will eventually result in complete mixing.

<sup>7</sup>Hint: 1) expand the VDW eq. into powers of  $\rho$ ; 2) identify the coefficients of like powers of  $\rho$ .

**1.5.1. Einstein's Theory of Brownian Motion (1905).** A translation of Einstein's paper from German to English can be found here:

[http://www.relatividad.org/einstein\\_brownian05.pdf](http://www.relatividad.org/einstein_brownian05.pdf)

Suppose that we have a probability density function<sup>8</sup>  $\phi(\Delta)$  which describes the probability that a molecule will undergo a displacement  $\Delta$  during a short time interval  $\tau$ . The medium contains  $n$  particles and during this time interval the number of particles,  $dn$ , which experience a shift between  $\Delta$  and  $\Delta + d\Delta$  is:

$$\frac{dn}{n} = \phi(\Delta)d\Delta = \left\{ \begin{array}{l} \text{probability that a particle at } x \text{ at time } t \text{ will be} \\ \text{in the range } [x + \Delta, x + \Delta + d\Delta] \text{ at time } t + \tau \end{array} \right\}$$

We assume that  $\phi$  is normalized,  $\int \phi(\Delta)d\Delta = 1$ , and symmetric (probability of a displacement to the left equals the probability of a displacement to the right):

$$\phi(\Delta) = \phi(-\Delta).$$

Let  $c(x, t)$  be the number of particles per unit volume at position  $x$  and time  $t$ . When going from time  $t$  to time  $t + \tau$  the particle density at  $x$  is a result of particles which undergo a displacement  $\Delta$  from another location:

$$c(x, t + \tau) = \int_{-\infty}^{\infty} c(x + \Delta, t)\phi(\Delta)d\Delta. \quad (*)$$

Next we assume that  $\phi$  extends over short distances only and that beyond  $\Delta$  its value is small. Thus, we can Taylor expand  $c$  in both space and time:

$$c(x, t + \tau) = c(x, t) + \tau \frac{\partial c}{\partial t} + \dots$$

$$c(x + \Delta, t) = c(x, t) + \Delta \frac{\partial c(x, t)}{\partial x} + \frac{\Delta^2}{2!} \frac{\partial^2 c(x, t)}{\partial x^2} + \dots$$

Substituting into (\*) we get (all limits of integration are over all space):

$$c + \tau \frac{\partial c}{\partial t} = c \int_{\mathbb{R}} \phi(\Delta)d\Delta + \frac{\partial c}{\partial x} \int_{\mathbb{R}} \Delta \phi(\Delta)d\Delta + \frac{\partial^2 c}{\partial x^2} \int_{\mathbb{R}} \frac{\Delta^2}{2} \phi(\Delta)d\Delta.$$

Because  $\phi(\Delta) = \phi(-\Delta)$  (even function), the second, fourth, etc. terms on the right hand side vanish. This is because those terms feature an odd function ( $\Delta, \Delta^3, \Delta^5$ , etc.) times an even function ( $\phi(\Delta)$ ), which is odd.

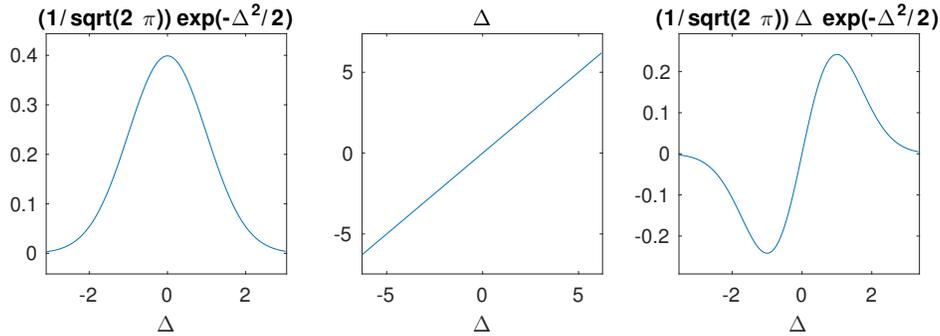
<sup>8</sup>A probability density function is one which is nonnegative ( $\phi \geq 0$ ) and normalized  $\int_{-\infty}^{\infty} \phi(\Delta)d\Delta = 1$ .

The integral of an odd function over all space is zero:<sup>9</sup>

$$\int_{\mathbb{R}} \text{odd} \times \text{even} = \int_{\mathbb{R}} \text{odd} = 0.$$

This is illustrated in Fig. 1.18 for the special case of

$$\phi(\Delta) = (1/\sqrt{2\pi}) \exp(-\Delta^2/2).$$



**Figure 1.18.** An even function (left) times an odd function (middle) yields an odd function (right), whose area under the curve is zero.

Using  $\int \phi(\Delta) d\Delta = 1$  for the first term and setting

$$\frac{1}{\tau} \int_{\mathbb{R}} \frac{\Delta^2}{2} \phi(\Delta) d\Delta \equiv D, \quad (\text{diffusion coefficient})$$

we get that  $c(x, t)$  must satisfy:

$$(1.10) \quad \boxed{\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}}.$$

$c(x, t)$  is a solution to this equation for given initial and boundary conditions. For initial condition  $c(x, 0) = n\delta(x)$  (all particles are at the origin at time  $t = 0$ ) and no physical boundaries (the case of unrestricted diffusion), the solution to the 1D diffusion equation is

$$c(x, t) = \frac{n}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}$$

where  $\sqrt{x^2} = \sqrt{2Dt}$  is the root-mean-square displacement. You can check that this is indeed a solution by direct substitution into equation 1.10.

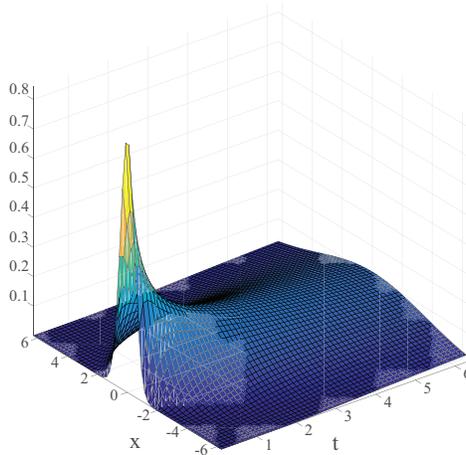
<sup>9</sup>If you don't like  $\Delta$ , use  $x$ :

$$\int_{\mathbb{R}} x\phi(x)dx = 0, \quad \int_{\mathbb{R}} x^3\phi(x)dx = 0, \quad \int_{\mathbb{R}} x^5\phi(x)dx = 0, \quad \text{etc.}$$

Calculation of the value of  $D$  requires knowledge of  $\phi$  which the above analysis does not provide. For a gas, we can obtain an estimate for  $D$  using simple arguments about molecular collisions.

The solution  $c(x, t)$  is a function of two variables,  $x$  and  $t$ . For fixed  $t$ , this can be thought as the concentration profile as function of space ( $x$ ). The time dependence means that the concentration profile evolves over time. For the case where all the particles are found at  $x = 0$  at time  $t = 0$ , the time-evolution simply describes the diffusional spreading of particles over space until the concentration is uniform. If there are no boundaries (i.e. space extends to infinity), the limit  $t \rightarrow \infty$  results in a spatially uniform concentration (of zero)

One way to represent the solution  $c(x, t)$  is a two-dimensional surface in 3D space (see Fig. 1.19). For fixed  $t$ , the function of  $x$  always describes a Gaussian (bell-shaped) profile. At time  $t = 0$ , it is sharply peaked near the origin ( $x = 0$ ); however, its width increases over time ( $t > 0$ ).



**Figure 1.19.** Concentration of particles as function of time ( $t$ ) and space ( $x$ ), then all particles are at the origin ( $x = 0$ ) at time  $t = 0$ .

**1.5.2. Diffusion Coefficient: Estimating the Value of  $D$ .** The Einstein model for diffusion does include a prescription to calculate the diffusion coefficient,

$$D = \frac{\overline{\Delta^2}}{2\tau},$$

where  $\Delta$  is the particle displacement along some direction and  $\overline{\Delta^2}$  is the *mean square displacement*. To calculate it, we require knowledge of the PDF  $\phi(\Delta)$ . But  $\phi(\Delta)$  may not necessarily be known to us.

Kinetic theory can be used to estimate  $D$ : First we note that from the formula,  $D = \overline{\Delta^2}/2\tau$ ,  $D$  has units of  $\text{m}^2/\text{s}$ . The collision rate  $Z_1$  among molecules in a gas should be proportional to gas density  $N/V$ , molecular cross-sectional area  $\pi d^2$  (where  $d = 2r$  instead of  $r$  as the hard spheres cannot overlap) and mean speed  $\bar{v}$ :

$$Z_1 = \sqrt{2} \frac{N}{V} \pi d^2 \bar{v}.$$

The factor  $\sqrt{2}$  comes from a more detailed calculation. We can express  $\bar{v}$  in terms of the temperature using

$$\bar{v} = \sqrt{\frac{8k_B T}{\pi m}}$$

to get:

$$Z_1 = 4 \frac{N}{V} d^2 \sqrt{\frac{\pi k_B T}{m}}.$$

Then the mean free path  $\lambda$  (average distance travelled between collisions)

$$\lambda = \bar{v} Z_1^{-1} = \frac{\bar{v}}{\sqrt{2}(N/V)\pi d^2 \bar{v}} = \frac{1}{\sqrt{2}\pi d^2 N/V}.$$

We then have for the diffusion coefficient

**Diffusion coefficient:** is proportional to the mean free path and the mean molecular speed

$$(1.11) \quad D = \frac{3\pi}{16} \lambda \bar{v} = \frac{3\pi}{16} \frac{1}{\sqrt{2}\pi d^2 N/V} \cdot \sqrt{\frac{8k_B T}{\pi m}} = \frac{3}{8} \sqrt{\frac{k_B T}{\pi m}} \cdot \frac{1}{d^2 N/V}.$$

The numerical constants shown arise from a more detailed theoretical analysis. The main trends are that if  $T$  increases the diffusion is faster whereas if  $m, d$  or  $N/V$  increase diffusion is slower. We note that  $D \sim \sqrt{T}$  here, whereas  $D \sim T$  for the Stokes-Einstein model:

$$(1.12) \quad D = 2\gamma k_B T/M,$$

where  $\gamma$  is a friction coefficient and  $M$  is the mass of the Brownian particle. The former is for a gas, whereas the latter is for a Brownian particle in a liquid. Example calculations:

1.5.2.1. *Example 1.* Calculate the collision frequency for a molecule of nitrogen gas at 1 atm and 300 K (room temperature). Take the diameter of  $\text{N}_2$  to be 370 picometers.

*Solution:* The density  $\frac{N}{V} = \frac{N_A P}{RT}$  (ideal gas law) is

$$\frac{(6.022 \times 10^{23} \text{ mol}^{-1})(1 \text{ atm})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(300 \text{ K})} = 2.46 \times 10^{22} \text{ L}^{-1} = 2.45 \times 10^{25} \text{ m}^{-3}.$$

To calculate the collision frequency, we need the mean speed:

$$\bar{v} = \sqrt{\frac{8RT}{\pi\mathcal{M}}} = \sqrt{\frac{8(8.3145 \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1})(300 \text{ K})}{\pi(28.00 \times 10^{-3} \text{ kg/mol})}} = 445 \text{ m}\cdot\text{s}^{-1},$$

where  $\mathcal{M}$  is the molar mass. Then,

$$Z_1 = \sqrt{2}\pi(2.45 \times 10^{25} \text{ m}^{-3})(3.70 \times 10^{-10} \text{ m})^2(445 \text{ m}\cdot\text{s}^{-1}) = 6.63 \times 10^9 \text{ s}^{-1}.$$

1.5.2.2. *Example 2.* Calculate the mean free path and the diffusion constant for the nitrogen molecules of the previous example.

*Solution:* The mean free path is

$$\lambda = \frac{1}{\sqrt{2}\pi(3.70 \times 10^{-10} \text{ m})^2(2.45 \times 10^{25} \text{ m}^{-3})} = 6.68 \times 10^{-8} \text{ m}.$$

The diffusion constant is

$$D = \frac{3\pi}{16}\lambda\bar{v} = \frac{3\pi}{16}(6.68 \times 10^{-8} \text{ m})(445 \text{ m}\cdot\text{s}^{-1}) = 1.75 \times 10^{-5} \text{ m}^2\text{s}^{-1}.$$

**1.5.3. Mean-Square Displacement.** If we denote the displacement along  $x$  by  $\Delta_x$  (and similarly for  $y$  and  $z$ ), we have seen that the root-mean-square (RMS) displacement along  $x$  is related to the diffusion coefficient  $D$  by:

$$D = \frac{\overline{\Delta_x^2}}{2\tau} \quad \text{or} \quad \overline{\Delta_x^2} = 2D\tau.$$

This relation is valid for displacement in one dimension. In three dimensions, the length of the displacement is  $\Delta_r = \sqrt{\Delta_x^2 + \Delta_y^2 + \Delta_z^2}$ , and by linearity of the averaging operator<sup>10</sup> we have

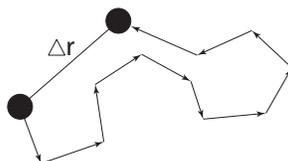
$$\overline{\Delta_r^2} = \overline{\Delta_x^2 + \Delta_y^2 + \Delta_z^2} = \overline{\Delta_x^2} + \overline{\Delta_y^2} + \overline{\Delta_z^2} = 6Dt.$$

The last equality follows from the assumption that the mean-square displacement along  $x$  is the same (on average) as the displacements along  $y$  and  $z$ , i.e.  $\overline{\Delta_x^2} = \overline{\Delta_y^2} = \overline{\Delta_z^2} = 2Dt$ . This is the assumption of isotropic diffusion, which is correct in the absence of external fields or physical barriers to diffusion. In  $d$ -dimensions, the mean-square displacement is  $2dDt$ .

In Section 1.5.1, we have seen that in the case where all diffusing particles are located at the origin  $x = 0$  at time  $t = 0$ , their distribution (concentration as function of  $x$ ) at some later time  $t > 0$  will be Gaussian centered at  $x = 0$  and width proportional to  $\sqrt{2Dt}$ . This distribution is a statistical concept: the Gaussian function describes the behavior of a very large number of particles.

<sup>10</sup>The average of a function,  $f(X)$  of a random variable  $X$ , is the integral  $\overline{f(X)} = \int f(x)p(x)dx$ , where  $p(x)$  is the probability density of  $X$  and the integral is over the range of allowed values of  $X$ . Thus, the averaging operation is a linear operation because the integral is a linear operator, i.e.  $\overline{af(X) + bg(X)} = a\overline{f(X)} + b\overline{g(X)}$ , where  $a$  and  $b$  are constants and  $f, g$  are functions.

The RMS displacement, which is proportional to  $\sqrt{t}$ , should be contrasted with ballistic motion, for which a projectile thrown at velocity  $v$  undergoes a displacement  $vt$ , i.e. displacement depends on  $t$  rather than  $\sqrt{t}$ . The  $\sqrt{t}$  dependence reflects the fact that random motion leads to much back-and-forth, in such a way that the RMS displacement increases over time but the growth is slower. An example path for a single particle<sup>11</sup> is shown in Fig. 1.20.



**Figure 1.20.** A particle undergoes random motion. A sample path is shown here. The displacement,  $\Delta\vec{r}$ , is the vector that connects the start and end points.

**1.5.4. Diffusion vs Self-Diffusion.** The theory of diffusion we have been discussing is called self-diffusion, i.e. the diffusion of gas molecules within the same gas type, i.e. oxygen molecules in a gas of oxygen. Diffusion is a more general concept: it generally refers to the diffusion of species 1 within species 2. For example, the diffusion of hydrogen atoms through copper, or the diffusion of oxygen impurity molecules through nitrogen gas.

## 1.6. Problems

**Problem 1.** Consider a monatomic gas with atoms whose diameter is  $d = 3.16 \times 10^{-10}$  m. At what pressure does the mean free path of the gas atoms become comparable with the diameter of an atom if  $T = 300$  K? Calculate the diffusion constant at this pressure and comment on its magnitude. Assume that the gas obeys the ideal gas law even at these high pressures.

**Solution.** The diameter of Kr atoms is  $d = 3.16 \times 10^{-10}$  m. When the mean free path  $\lambda = \frac{1}{\sqrt{2}\pi d^2 N/V}$  is comparable to the diameter of atom,  $N/V$

should be around  $7.12 \times 10^{27}/\text{m}^3$ . From the ideal gas law,  $N/V = \frac{P}{k_B T}$ ,

$P = 2.95 \times 10^7$  Pa. The diffusion constant is

$$D = \frac{3}{8} \sqrt{\frac{RT}{\pi M}} \frac{1}{d^2 N/V} = \frac{3}{8} \sqrt{\frac{8.314 \times 300}{\pi \times (83.789 \cdot 10^{-3})}} \frac{1}{(3.16 \cdot 10^{-10})^2 (7.12 \cdot 10^{27})}$$

<sup>11</sup>This picture shows a single trajectory (of a single molecule). The concept of RMS displacement is *statistical*, i.e. it is obtained from the random diffusion of many particles.

which evaluates to  $D = 5.1342 \times 10^{-8} \text{ m}^2/\text{s}$ . This value is comparable to diffusion in solids. Diffusion coefficients in solids are in the range  $10^{-8} - 10^{-30} \text{ m}^2/\text{s}$ . ■

**Problem 2.** Consider a VDW gas at the critical point. Obtain expressions for the critical pressure, molar volume, and temperature in terms of constants  $a$  and  $b$ . The critical point is defined as the point on the  $P - V_m$  curve where the first and second derivatives of the pressure with respect to molar volume vanish, i.e.  $\left. \frac{\partial P}{\partial V_m} \right|_c = 0$  and  $\left. \frac{\partial^2 P}{\partial V_m^2} \right|_c = 0$ .

**Solution.** This problem was solved in Section 1.4.3. Based on the VDW equation

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}.$$

The first derivative of pressure equals zero

$$\left. \frac{\partial P}{\partial V_m} \right|_c = -\frac{RT_c}{(V_m - b)^2} + \frac{2a}{V_m^3} \Big|_c = 0.$$

The second derivative of pressure equals zero

$$\left. \frac{\partial^2 P}{\partial V_m^2} \right|_c = \frac{2RT_c}{(V_m - b)^3} - \frac{6a}{V_m^4} \Big|_c = 0.$$

Solving the above equations then substituting  $V_c$  and  $T_c$  into the VDW equation to solve for  $p_c$  gives (see Section 1.4.3 for details):

$$V_c = 3b, \quad T_c = \frac{8a}{27bR}, \quad P_c = \frac{a}{27b^2}.$$

**Problem 3.** A 20 liter container is filled with 1 mol of Kr atoms at a temperature of 400 K. (a) Use the VDW equation of state to compute the pressure of the system. (b) Find the pressure once more but using the ideal gas law. (c) Calculate the percent error between the results. (d) Now calculate the VDW and ideal-gas pressures if the volume of the container was 4 liters. (e) Find the percent error between the results. (f) Compare the percent errors you have obtained and explain any differences. For Kr the VDW parameter are  $a = 2.325 \text{ L}^2 \text{ bar mol}^{-2}$  and  $b = 0.0396 \text{ L mol}^{-1}$ .

**Solution.** For (a), we use  $P = \frac{RT}{V_n - b} - \frac{a}{V_n^2}$ . This gives:

$$P = \frac{(0.082057 \text{ L atm K}^{-1} \text{ mol}^{-1})(400 \text{ K})}{20 \text{ L mol}^{-1} - 0.0396 \text{ L mol}^{-1}} - \frac{2.295 \text{ L}^2 \text{ atm mol}^{-2}}{(20 \text{ L mol}^{-1})^2} = 1.639 \text{ atm}$$

For (b) we use  $P = \frac{RT}{V_n}$ . This gives:

$$P = \frac{(0.082057 \text{ L atm K}^{-1} \text{ mol}^{-1})(400 \text{ K})}{20 \text{ L mol}^{-1}} = 1.641 \text{ atm}$$

For (c),

$$\% \text{ Error} = \left| \frac{1.639 - 1.641}{1.641} \right| \times 100 = 0.122\%$$

For (d),

$$P = \frac{(0.082057 \text{ L atm K}^{-1} \text{ mol}^{-1})(400 \text{ K})}{4 \text{ L mol}^{-1} - 0.0396 \text{ L mol}^{-1}} - \frac{2.295 \text{ L}^2 \text{ atm mol}^{-2}}{(4 \text{ L mol}^{-1})^2} = 8.144 \text{ atm}$$

For (e),

$$P = \frac{(0.082057 \text{ L atm K}^{-1} \text{ mol}^{-1})(400 \text{ K})}{20 \text{ L mol}^{-1}} = 8.206 \text{ atm}$$

■

**Problem 4.** There are 25 grams of He and 56 grams of Ar gas mixed in a 20 L container. The temperature of the mixture is 300 K. Find the partial pressure of each gas and total pressure inside the container. Assume the ideal-gas law is valid for both gases.

**Solution.**

$$n_{total} = \frac{25 \text{ g}}{4.0026 \text{ g mol}^{-1}} + \frac{56 \text{ g}}{39.948 \text{ g mol}^{-1}} = 7.65 \text{ mol}^{-1}$$

$$P = \frac{(7.65 \text{ mol}^{-1})(0.082057 \text{ L atm K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{20 \text{ L}} = 9.42 \text{ atm}$$

$$P_{He} = \frac{\frac{25 \text{ g}}{4.0026 \text{ g mol}^{-1}}}{7.65 \text{ mol}^{-1}} (9.42 \text{ atm}) = 7.69 \text{ atm}$$

$$P_{Ar} = 9.42 \text{ atm} - 7.69 \text{ atm} = 1.73 \text{ atm}$$

■

**Problem 5.** You have two ideal gases, M and N, in a container of fixed volume. The mole fraction of M is  $X_M = \frac{1}{3}$ . Initially the pressure was equal to  $P_i$ . Later a total of two moles of one of the gases are added to the container, while holding the temperature constant. The new pressure is equal to  $\frac{11}{9} P_i$ . Compute the number of moles of M and N that were initially present in the container.

**Solution.**

$$P_f = \frac{11}{9} P_i, \quad \frac{11}{9} \frac{(n_M + n_N)RT}{V} = \frac{(n_M + n_N + 2)RT}{V},$$

$$n_M + n_N + 2 = \frac{11}{9}(n_M + n_N), \quad \frac{1}{3} = \frac{n_M}{n_M + n_N} \rightarrow n_N = 2n_M,$$

$$3n_M + 2 = \frac{11}{9}(3n_M), \quad n_M = 3 \text{ mol}, \quad n_N = 6 \text{ mol}$$

■

**Problem 6.** Suppose that the diameter of a gas molecule is 0.4 nm. Next, draw a sphere around each molecule, whose diameter is approximately equal to the average distance between neighboring molecules (assuming a spatially uniform gas). What is the sphere diameter in units of molecular diameters at 0°C and 1 bar.

**Solution.**

$$PV = nRT$$

$$\frac{V}{n} = \frac{RT}{P} = \frac{(8.31)(273)}{100,000} \approx 0.023 \text{ m}^3/\text{mol}$$

$$V_{\text{molecule}} = \frac{V}{nN_A} = \frac{0.023}{6.022 \times 10^{23}} \approx 3.8 \times 10^{-26} \text{ m}^3 = 38 \text{ nm}^3$$

$$V_{\text{sphere}} = \frac{4\pi r^3}{3}$$

The answer is:

$$\frac{2\sqrt[3]{\frac{3V_{\text{molecule}}}{4\pi}}}{d} \approx \frac{2\sqrt[3]{9.07}}{0.4} \approx 10.4.$$

■

**Problem 7.** Calculate the RMS speed of oxygen molecules having a typical kinetic energy of 10 kJ mol<sup>-1</sup>. At what temperature would this be the RMS speed?

**Solution.**  $\bar{v}^{1/2} = \sqrt{\frac{3RT}{M}}$ ,  $\text{KE} = \frac{3}{2}RT$ ,  $\bar{v}^{1/2} = \sqrt{\frac{2\text{KE}}{M}} = 7.9 \times 10^2 \text{ ms}^{-1}$ ,  
 $T = \frac{2\text{KE}}{3R} = 802 \text{ K}$

■

**Problem 8.** An ideal gas A has a temperature  $T_A$  and molar mass  $\mathcal{M}_A$ . A second gas B has a molar mass  $\mathcal{M}_B$ . At what temperature  $T_B$  will the gases have the same average speed?

**Solution.**

$$\bar{v}_A = \sqrt{\frac{8RT_A}{\pi\mathcal{M}_A}}$$

$$\bar{v}_A = \bar{v}_B$$

$$\frac{T_A}{\mathcal{M}_A} = \frac{T_B}{\mathcal{M}_B} \rightarrow T_B = T_A \left( \frac{\mathcal{M}_B}{\mathcal{M}_A} \right)$$

■

**Problem 9.** The variance is useful because it measures how far data points are spread relative to their mean value. Let  $X$  be a random variable with discrete distribution  $\{P(x_i)\}$  ( $i = 1, \dots, N$ ). The variance is defined as  $\sigma^2 \equiv \overline{var(X)} = \overline{(X - \bar{X})^2} = \sum_{i=1}^N P(x_i)(x_i - \bar{x})^2$ . (a) Expanding the square in  $(X - \bar{X})^2$ , and invoking the linearity property of expectation value (i.e.  $\overline{aX + bY} = a\bar{X} + b\bar{Y}$ , where  $Y = X^2$  here), show that the variance is also equal to  $\overline{X^2} - (\bar{X})^2$ . (b) Instead of the variance, consider a slightly different quantity,  $\overline{X - \bar{X}}$ . Calculate the expectation value of  $X - \bar{X}$ . Explain why the latter is not a very useful quantity.

**Solution.**

$$\overline{X - \bar{X}} = \sum_{i=1}^N P(x_i)(x_i - \bar{X}) = \sum_{i=1}^N P(x_i)x_i - \sum_{i=1}^N P(x_i)\bar{X} = \bar{x} - \bar{X} = 0$$

$\overline{X - \bar{X}}$  is not a useful quantity because it is always zero. ■

**Problem 10.** Consider a volume  $V$  of an ideal gas inside a selectively permeable piston. What would the volume be if all of the other extensive properties of the gas double and all the intensive properties become a third of their initial values?

**Solution.** Extensive properties are  $V, n$ . Intensive properties are  $P, T$ .

$$V = \frac{nRT}{P}, \quad V_f = \frac{2nR\frac{1}{3}T}{\frac{1}{3}P}, \quad V_f = 2\frac{nRT}{P}, \quad V_f = 2V$$

■

**Problem 11.** The partial pressure of oxygen in a mixture of oxygen and hydrogen is 0.200 atm, and that of hydrogen is 0.800 atm.

- a) How many molecules of oxygen are in a 1.500-L container of this mixture at 40°C?  
 b) If a spark is introduced into the container, how many grams of water will be produced?

**Solution.** a) total pressure = 0.200 atm + 0.800 atm = 1.000 atm

$$n = \frac{PV}{RT}$$

$n = 0.05840$  mol of total gas

$$X_{O_2} = \frac{0.200 \text{ atm}}{1.000 \text{ atm}} = 0.200$$

$$n_{O_2} = X_{O_2}n = 0.0117 \text{ moles of } O_2$$

b)  $2 \text{ H}_2 + \text{O}_2 = 2 \text{ H}_2\text{O}$

$$X_{H_2} = \frac{0.800 \text{ atm}}{1.000 \text{ atm}} = 0.800$$

$n_{\text{H}_2} = X_{\text{H}_2}n = 0.0467$  moles of  $\text{H}_2$   
 $0.0467$  moles of  $\text{H}_2 / 2 = 0.0234$  moles  $> 0.0117$  moles  $\text{O}_2$   
 $\text{O}_2$  is thus the limiting reagent  
 $0.0117$  moles  $\times 2 = 0.0234$  moles  $\text{H}_2\text{O}$   
 $0.0234$  moles  $\times 18.0152$  g/mol  $= 0.422$  g  $\text{H}_2\text{O}$

■

**Problem 12.** Researchers recently reported the first optical atomic trap. In this device, tightly focused beams of laser light replace the physical walls of conventional containers, creating a type of trap where the motion of the atoms is substantially reduced. The laser beams briefly (0.5 s) exert enough pressure to confine 500 sodium atoms in a volume of  $1.0 \times 10^{-15}$  m<sup>3</sup>. The temperature of this gas can be cooled down to 0.00024 K (cooling means that the kinetic energy is lowered by the laser trap), a pretty low temperature. Compute the root-mean-square speed of atoms in this confinement.

**Solution.**  $M_{\text{Na}} = 22.9898$  g/mol  $= 0.0229898$  kg/mol

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \text{ J}/(\text{mol} \cdot \text{K}) \times 0.00024 \text{ K}}{0.02298 \text{ kg/mol}}} = 0.51 \text{ m/s}$$

■

**Problem 13.** Calculate the average (mean or expectation value) of the function  $\sin(X)$  over the interval  $[0, 1]$ , where  $X$  is a Gaussian-distributed random variable with mean 0 and variance 1, i.e. its pdf is  $p(x) = \frac{1}{\sqrt{2\pi}}e^{-x^2/2}$ .  
 (a) Write down an expression for the mean value of  $\sin(X)$ , namely  $\overline{\sin(X)}$ .  
 (b) Evaluate it numerically. (Hint: feel free to use a web site such as <https://www.wolframalpha.com> to get the result.)

**Solution.** (a) The integral we need to compute is:

$$\overline{\sin(X)} = \int_0^1 \frac{1}{\sqrt{2\pi}} e^{-x^2/2} \sin(x) dx$$

(b) In Wolfram Alpha, we can type

`Integrate (1/sqrt(2*Pi))*sin(x)*exp(-x^2/2) from 0 to 1`

in the box to get the result: 0.145352.

■

**Problem 14.** Show by direct calculation (integration) that the mean speed of an ideal gas molecule in 3D is  $\bar{v} = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$ . (Hint: consult tables of Gaussian integrals.)

**Solution.** We need to evaluate the integral  $\bar{v} = \int_0^\infty v f(v) dv$ , where  $f(v)$  is the Maxwell-Boltzmann speed distribution,

$$f(v) = (m/2\pi k_B T)^{3/2} 4\pi v^2 e^{-mv^2/2k_B T}.$$

From tables of Gaussian integrals, e.g.

[https://en.wikipedia.org/wiki/Gaussian\\_integral](https://en.wikipedia.org/wiki/Gaussian_integral), we invoke:

$$\int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}} = \frac{1}{2a^2} = \frac{1}{2} \left( \frac{2k_B T}{m} \right)^2$$

with  $n = 1$  and  $a = m/2k_B T$ . With this, we obtain  $\bar{v} = \sqrt{\frac{8k_B T}{\pi m}}$ . ■

For the problems below, you are asked to calculate probabilities. In all cases, this amounts to computing the integral of the PDF over the range of interest. (To get the result numerically, you can use Wolfram Alpha.) For example, let  $X$  be a random variable taking values in the range  $(-\infty, \infty)$ . By definition, the PDF is a non-negative function  $p(x) \geq 0$  that is normalized to 1, i.e.  $\int_{-\infty}^{\infty} p(x) dx = 1$ . Suppose you are asked what is the probability that  $X$  takes values in the range  $[-1, 1]$ , then you simply integrate over all  $x$  values in that range:

$$\mathbb{P}(-1 \leq X \leq 1) = \int_{-1}^1 p(x) dx$$

and knowing  $p(x)$ , you would integrate to get the result. If you are asked what is the probability that  $X$  takes values less than 10, this would be an integral of  $p(x)$  over the set  $(-\infty, 10]$ :

$$\mathbb{P}(-\infty < X \leq 10) = \int_{-\infty}^{10} p(x) dx$$

Likewise, the probability of  $X$  taking negative values is:

$$\mathbb{P}(X < 0) = \int_{-\infty}^0 p(x) dx$$

If you want to know the probability that  $X$  takes a value less than -1 but greater than -2, or greater than 3 and less than 4, i.e. in the range  $[-1, -2] \cup [3, 4]$ , then:

$$\mathbb{P}(-2 \leq X \leq -1 \text{ or } 3 \leq X \leq 4) = \int_{-2}^{-1} p(x) dx + \int_3^4 p(x) dx$$

You may also find the following page useful:

[https://en.wikipedia.org/wiki/Probability\\_density\\_function](https://en.wikipedia.org/wiki/Probability_density_function)

**Problem 15.** Show by direct integration that the Gaussian (normal) PDF

$$p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\mu)^2/2\sigma^2}$$

is normalized to 1. You can use analytical or numerical techniques, as long as you explain what you did. The Gaussian (bell-shaped distribution) random variables are frequently encountered in the physical sciences.

**Solution.** Shifting the origin to 0 (i.e. substitution of variable  $y = x - \mu$ ) and using the Gaussian integral:

$$\int_{-\infty}^{\infty} e^{-y^2/2\sigma^2} dy = \sqrt{\pi 2\sigma^2}$$

which cancels the prefactor  $\frac{1}{\sqrt{2\pi\sigma^2}}$  to give 1. ■

**Problem 16.** Use the Maxwell *velocity* distribution to calculate the probability of an oxygen ( $O_2$ ) molecule (a molecule chosen randomly) would have an  $x$  component of velocity between 10 and 20 m/s at room temperature and standard pressure (a). Does the pressure matter? Why? (b) At 20 K. (c) Calculate the probability of an oxygen ( $O_2$ ) molecule would have an  $x$  component of velocity between -20 and -10 m/s at room temperature and standard pressure. (d) Calculate the probability of an oxygen ( $O_2$ ) molecule would have an  $x$  component of velocity between -20 and 20 m/s at room temperature and standard pressure. (e) What is the probability of a molecule having an  $x$  velocity component exactly equal to 20 m/s? (Hint: you may use Wolfram Alpha to get the numerical result, but clearly explain what you did.)

**Solution.** The velocity distribution (PDF) for  $v_x$  is:

$$f_{v_x}(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_x^2/2k_B T} = \left(\frac{\mathcal{M}}{2\pi RT}\right)^{1/2} e^{-\mathcal{M}v_x^2/2RT}$$

where  $m$  is the molecular mass and  $\mathcal{M}$  is the molar mass ( $\mathcal{M}=0.032$  kg/mol for  $O_2$ ). Pressure does not matter because ideal gas assumes no intermolecular interactions. Plug in  $T=293$  K for (a); the factor  $\sqrt{\frac{\mathcal{M}}{2\pi k_B T}}$  evaluates numerically to  $\sqrt{0.032/(2\pi * 8.31 * 293)}=1.45 \times 10^{-3}$ . For  $T=20$  K it is  $\sqrt{0.032/(2\pi * 8.31 * 20)}=5.54 \times 10^{-3}$ . In Wolfram, type:

`integrate 1.45e-3*exp(-0.032*v^2/(2*8.31*293)) from 10 to 20`  
and get 0.014479. For (b) we use  $T=20$  K for (b), and integrate from 10 to 20 m/s:

`integrate 5.54e-3*exp(-0.032*v^2/(2*8.31*20)) from 10 to 20`  
and get 0.0541713. For (c) integrate from -20 to -10 at RT:

`integrate 1.45e-3*exp(-0.032*v^2/(2*8.31*293)) from -20 to -10`  
and get 0.0144778. For (d), from -20 to 20.

`integrate 1.45e-3*exp(-0.032*v^2/(2*8.31*293)) from -20 to 20`  
and get 0.0579492. For (e), the probability is zero, because the integral has no width (the length of the interval of integration is zero). ■

**Problem 17.** Use the Maxwell *speed* distribution to calculate the probability an oxygen ( $O_2$ ) molecule would have a speed between 10 and 20 m/s at room temperature and standard pressure (a). (b) What is the probability of the molecule having a speed between -20 and -10 m/s? (c) Probability of

speed between 0 and 1000 m/s? (d) What is the probability of a molecule having exactly the speed 20 m/s?

**Solution.** The Maxwell speed distribution is:

$$f_V(v) = \left( \frac{\mathcal{M}}{2\pi RT} \right)^{3/2} 4\pi v^2 e^{-\mathcal{M}v^2/2RT}.$$

The numerical factor is  $(4\pi)(0.032/(2\pi * 8.31 * 293))^{3/2} = 3.8 \times 10^{-8}$ . For (a), in Wolfram Alpha we type

`integrate 3.8e-8*v^2*exp(-0.032*v^2/(2*8.31*293)) from 10 to 20`

and get 0.000089. For (b) if we naively type

`integrate 3.8e-8*v^2*exp(-0.032*v^2/(2*8.31*293)) from -20 to -10`

we get 0.00496 (same as in (a)). However, negative speeds are not allowed, so the speed distribution is not defined for negative speeds. Thus, this probability is zero. For (c),

`integrate 3.8e-8*v^2*exp(-0.032*v^2/(2*8.31*293)) from 0 to 1000`

we get 0.995253. For (d), the probability is zero. ■

**Problem 18.** Consider molecules in thermal equilibrium that can diffuse only in 1 direction (say,  $x$ ). The Maxwellian distribution (PDF) for the velocity component  $v_x$  was given in class:

$$f_{v_x}(v_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-mv_x^2/2k_B T}$$

The meaning of this PDF is that the product

$$f_{v_x}(v_x)dv_x$$

gives the probability that a molecule chosen at random will have an  $x$  component of velocity between  $v_x$  and  $v_x + dv_x$ . Recall that in 3D the speed is  $v \equiv \|\vec{v}\| = \sqrt{v_x^2 + v_y^2 + v_z^2}$ . We computed the speed distribution by integrating the 3D velocity distribution over a spherical shell of volume  $4\pi v^2 dv$ . The speed distribution (PDF),  $f(v)$ , has the meaning that the product  $f(v)dv$  gives the probability that a molecule chosen at random will have a speed between  $v$  and  $v + dv$ . However, in 1 dimension, the *speed* is  $v \equiv \|\vec{v}\| = |v_x|$ . Calculate the *speed* distribution in the 1D case. Check that your result is normalized.

**Solution.** The velocity distribution integrated over the set of points  $v_x$  such that  $v \equiv \|\vec{v}\| = |v_x|$ . There are two such points:  $v_x = v$  and  $v_x = -v$ . Denoting  $V$  the *random variable* that corresponds to speed, the speed

distribution,  $f(v)dv = \mathbb{P}(v < V < v + dv)$ , is then the sum of two terms:

$$\begin{aligned}\mathbb{P}(v < V < v + dv) &= \int_{\{v_x: v < V < v + dv\}} f_{v_x}(v_x) dv_x \\ &= \left[ \sqrt{\frac{m}{2\pi k_B T}} e^{-m(-v)^2/2k_B T} + \sqrt{\frac{m}{2\pi k_B T}} e^{-mv^2/2k_B T} \right] dv \\ &= \sqrt{\frac{m}{2\pi k_B T}} 2e^{-mv^2/2k_B T} dv\end{aligned}$$

where the notation  $\{v_x : v < V < v + dv\}$  means we integrate over all points  $v_x \in (-\infty, \infty)$  such that the speed  $V$  is between  $v$  and  $v + dv$ . Normalization is easy to check by integrating from 0 to  $\infty$ ; you will see that the factor of 2 is essential. ■

**Problem 19.** Calculate the *speed distribution* in 2D,  $\mathbb{P}(v < V < v + dv) = f(v)dv$ . The 2D velocity distribution is:

$$f_{v_x}(v_x)f_{v_y}(v_y) = \left(\frac{m}{2\pi k_B T}\right) e^{-m(v_x^2 + v_y^2)/2k_B T}.$$

The meaning of this velocity distribution is that the product

$$f_{v_x}(v_x)f_{v_y}(v_y)dv_x dv_y$$

gives the probability that a molecule chosen randomly will have  $x$  velocity component in the range  $[v_x, v_x + dv_x]$  and  $y$  velocity component in the range  $[v_y, v_y + dv_y]$ . (Hint: integrate  $f_{v_x}(v_x)f_{v_y}(v_y)dv_x dv_y$  over the set of points  $(v_x, v_y)$  such that  $v < V < v + dv$ ; it is easiest to use polar coordinates.) Check that the resulting PDF is normalized.

**Solution.** In polar coordinates the area element is  $vdv d\theta$ . Then,  $v = \sqrt{v_x^2 + v_y^2}$  and

$$\begin{aligned}\mathbb{P}(v < V < v + dv) &= \int_{\{(v_x, v_y): v < V < v + dv\}} f_{v_x}(v_x)f_{v_y}(v_y)dv_x dv_y \\ &= \left(\frac{m}{2\pi k_B T}\right) \int_0^{2\pi} d\theta \int_v^{v+dv} v e^{-mv^2/2k_B T} dv \\ &= \left(\frac{m}{2\pi k_B T}\right) 2\pi v e^{-mv^2/2k_B T} dv.\end{aligned}$$

To check for normalization, we borrow the result  $\int_0^\infty x e^{-ax^2} dx = 1/(2a)$  from tables of integrals. Integrating  $f(v)dv$  from 0 to  $\infty$  gives:

$$\int_0^\infty f(v)dv = \left(\frac{m}{2\pi k_B T}\right) 2\pi \int_0^\infty v e^{-mv^2/2k_B T} dv = \left(\frac{m}{2\pi k_B T}\right) 2\pi \frac{2k_B T}{2m} = 1. \quad \blacksquare$$

**Problem 20.** Now that you have done the 1D and 2D cases, go back and study how the 3D case was done (see Section 1.3.8). What is the difference between 1D, 2D and 3D cases?

**Solution.**  $f(v)$  is proportional to  $v^n e^{-mv^2/2k_B T}$ , where  $n = 0, 1, 2$  (for 1D, 2D and 3D, respectively). The numerical coefficient also follows a pattern related to dimensionality. Namely, we have  $\left(\frac{m}{2\pi k_B T}\right)^{n/2}$ ,  $n = 1, 2, 3$  as well as the other numerical factor, which is either 2,  $2\pi$  or  $4\pi$ , depending on whether we have 1D, 2D or 3D, respectively. ■

**Problem 21.** Show that for an ideal gas, the most probable speed is  $u_p = \sqrt{\frac{2k_B T}{m}}$  and the average speed is  $\bar{u} = \sqrt{\frac{8k_B T}{\pi m}}$ . Recall the Maxwell-Boltzmann speed distribution is

$$f(u)du = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} 4\pi u^2 \exp\left(\frac{-mu^2}{2k_B T}\right) du.$$

Note: here we used  $u = \sqrt{v_x^2 + v_y^2 + v_z^2}$  for speed to avoid confusion with velocity ( $v$ ) which we use in the next problem.

**Solution.** The most probable speed the value of  $u$  at the point where the first derivative of the distribution is zero. Let  $a = \frac{m}{2k_B T}$ . Dropping the constants, since we are equating the derivative to zero,

$$\frac{df}{du} = \frac{d}{du} \left( u^2 \exp(-au^2) \right) = (2u - 2au^3) \exp(-au^2) = 0.$$

We denote this particular value of  $u$  as  $u_p$ . Therefore,

$$1 - au^2 = 0 \quad \text{or} \quad u_p = \sqrt{\frac{1}{a}} = \sqrt{\frac{2k_B T}{m}}.$$

To calculate  $\bar{u}$ , the integral that we need to solve is  $\int_0^\infty u^3 \exp(-au^2) du$  since the remaining terms are constants that we will multiply in later. We do a change of variables by setting  $w = u^2$  which also gives  $dw = 2u du$  and then do integration by parts.

$$\begin{aligned} \int_0^\infty u^3 \exp(-au^2) du &= \frac{1}{2} \int_0^\infty w \exp(-aw) dw \\ &= -\frac{1}{2a} e^{-aw} \Big|_0^\infty + \frac{1}{2a} \int_0^\infty e^{-aw} dw = \frac{1}{2a^2}. \end{aligned}$$

Now we restore the constants and substitute for  $a$ ,

$$\bar{u} = \sqrt{\frac{8k_B T}{\pi m}}. \quad \blacksquare$$

**Problem 22.** Show that  $\overline{v^2} = \overline{v_x^2 + v_y^2 + v_z^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$ .

**Solution.** By linearity of the integral

$$\begin{aligned}\overline{v^2} &= \overline{v_x^2 + v_y^2 + v_z^2} = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \int_{\mathbb{R}^3} (v_x^2 + v_y^2 + v_z^2) \exp\left(-\frac{mv^2}{2k_B T}\right) d^3\vec{v} \\ &= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \left[ \int_{\mathbb{R}^3} v_x^2 \exp\left(-\frac{mv^2}{2k_B T}\right) d^3\vec{v} + \int_{\mathbb{R}^3} v_y^2 \exp\left(-\frac{mv^2}{2k_B T}\right) d^3\vec{v} \right. \\ &\quad \left. + \int_{\mathbb{R}^3} v_z^2 \exp\left(-\frac{mv^2}{2k_B T}\right) d^3\vec{v} \right] \\ &= \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}\end{aligned}$$

where the averaging in the last line is done over  $\int_{\mathbb{R}^3}(\dots)d^3\vec{v}$ . This averaging can also be done along a single variable, as explained below.

For the  $\overline{v_x^2}$  term, integration with respect to  $y$  and  $z$  is immediate, since the PDFs are normalized, i.e. using  $\int_{\mathbb{R}} \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} \exp\left(-\frac{mv_y^2}{2k_B T}\right) dv_y = 1$  (and the analogous result for  $v_z$ ):

$$\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \int_{\mathbb{R}^3} v_x^2 \exp\left(-\frac{mv^2}{2k_B T}\right) d^3\vec{v} = \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} v_x^2 \exp\left(-\frac{mv_x^2}{2k_B T}\right) dv_x,$$

which equals  $\langle v_x^2 \rangle$ . The angle brackets in  $\langle v_x^2 \rangle$  denote averaging along a single variable  $\int_{\mathbb{R}}(\dots)dv_x$ . Thus,

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

■

**Problem 23.** Show that each degree of freedom of a gas particle adds  $\frac{1}{2}k_B T$  to the average kinetic energy of the gas,  $K_{av} = \frac{1}{2}m\overline{v^2}$ , where  $v^2 = v_x^2 + v_y^2 + v_z^2$ . In other words, show that

$$\langle K_x \rangle = \langle K_y \rangle = \langle K_z \rangle = \frac{1}{2}k_B T$$

where  $K_{av} = \langle K_x \rangle + \langle K_y \rangle + \langle K_z \rangle$  and  $K_x = \frac{1}{2}mv_x^2$ ,  $K_y = \frac{1}{2}mv_y^2$  and  $K_z = \frac{1}{2}mv_z^2$ . The angle brackets denote averaging along a single direction, e.g.  $\langle K_x \rangle = \int \frac{1}{2}mv_x^2 \cdot f_{V_x}(v_x)dv_x$ .

**Solution.**

$$\langle K_x \rangle = \frac{1}{2}m\langle v_x^2 \rangle$$

We have just shown that  $\overline{v^2} = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$  so the corresponding equality for kinetic energy is also true. We now just need to calculate  $\langle v_x^2 \rangle$ .

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

Let us switch to a more convenient notation:

$$\int_{-\infty}^{\infty} v_x^2 \exp\left(-\frac{mv_x^2}{2k_B T}\right) dv_x = \int_{-\infty}^{\infty} x^2 \exp(-ax^2) dx = -\frac{d}{da} \int_{-\infty}^{\infty} \exp(-ax^2) dx$$

which equals to  $-\frac{d}{da} \sqrt{\frac{\pi}{a}}$ , according to the well-known result for Gaussian integration. Then,

$$-\frac{d}{da} \sqrt{\frac{\pi}{a}} = \frac{1}{2} \sqrt{\frac{\pi}{a^3}} = \frac{\sqrt{\pi}}{2} \left(\frac{2k_B T}{m}\right)^{\frac{3}{2}}.$$

Finally,

$$\langle K_x \rangle = \frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} k_B T.$$

Same for  $K_y$  and  $K_z$ . Therefore, we see that  $K_{av}$ , which equals  $\frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T$ , is made up of 3 contributions, each equalling  $\frac{1}{2} k_B T$ . This is called the equipartition theorem. ■

**Problem 24.** In Section 1.4.6, we expressed the equation of state for a gas as a Taylor expansion in terms of gas density,  $\rho = \frac{N}{V}$ . That is,

$$\frac{P}{RT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots$$

This expansion is called the virial expansion.  $B_n(T)$  is the  $n^{\text{th}}$  virial coefficient. The virial expansion is a generalization of the ideal gas law ( $\frac{P}{RT} = \rho$ ) that includes higher powers of  $\rho$  to account for the gas behavior at higher densities. (The ideal gas law is only valid in the low density limit.)

(a) Show that for the VDW equation of state,

$$B_2(T) = \frac{b}{N_A} - \frac{a}{N_A^2 k_B T}.$$

(b) The temperature for which  $B_2(T) = 0$  is called Boyle's temperature,  $T_B$ . Find the expression for  $T_B$  for a VDW gas. Explain what is the Boyle temperature and discuss what are practical applications of the Boyle's temperature.

**Solution.** Let us compare the virial expansion:

$$(1.13) \quad \frac{P}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots$$

where  $\rho = N/V$ , with the VDW equation of state:

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

Expanding the product:

$$PV - Pnb + \frac{n^2 a}{V} - \frac{n^3 ab}{V^2} = nRT.$$

Dividing throughout by  $RT(V - nb)$ :

$$\frac{P}{RT} = \frac{n}{(V - nb)} + \frac{n^3 ab}{V^2 RT(V - nb)} - \frac{n^2 a}{VRT(V - nb)}.$$

Writing  $\tilde{\rho} = n/V$ :

$$\frac{P}{RT} = \frac{\tilde{\rho}}{(1 - b\tilde{\rho})} + \frac{\tilde{\rho}^3 ab}{RT(1 - b\tilde{\rho})} - \frac{\tilde{\rho}^2 a}{RT(1 - b\tilde{\rho})}.$$

Using the geometric series  $\frac{1}{1-r} = 1 + r + r^2 + r^3 + \dots$  with  $r = b\tilde{\rho}$  we get:

$$\frac{P}{RT} = \left\{ \tilde{\rho} + \frac{\tilde{\rho}^3 ab}{RT} - \frac{\tilde{\rho}^2 a}{RT} \right\} (1 + b\tilde{\rho} + b^2 \tilde{\rho}^2 + \dots).$$

Expanding,

$$\frac{P}{RT} = \tilde{\rho} + \tilde{\rho}^2 \left( b - \frac{a}{RT} \right) + \tilde{\rho}^3 (b^2) + \dots$$

Finally, we replace  $R = N_A k_B$  and  $\tilde{\rho} = n/V = N/(N_A V) = \rho/N_A$

$$(1.14) \quad \frac{P}{k_B T} = \rho + \rho^2 \left( \frac{b}{N_A} - \frac{a}{N_A^2 k_B T} \right) + \rho^3 \left( \frac{b^2}{N_A^3} \right) + \dots$$

Identifying the coefficients of like powers of  $\rho$  in (1.14) and (1.13), we find:

$$B_2(T) = \frac{b}{N_A} - \frac{a}{N_A^2 k_B T}, \quad B_3(T) = \frac{b^2}{N_A^3}, \quad \text{etc.}$$

The point at which  $B_2(T) = 0$  is called the *Boyle temperature*:

$$T_B = \frac{a}{b k_B N_A} = \frac{a}{b R}.$$

It is at the Boyle temperature that the attractive and repulsive forces acting on the gas particles balance out. At that temperature, the non-ideal gas behaves like an ideal gas over some range of pressures. (It's an ideal gas as far as the second virial coefficient is concerned; there are of course, higher-order terms that do not enforce the ideal-gas behavior, although these terms get progressively smaller in magnitude.)

Applications of Boyle temperature: gas cylinders and compression pumps are industrially important. If a gas in a mechanical cylinder liquefies it is a problem. The mechanical device needs to be above the Boyle temperature.

In thermodynamics, the Joule-Thomson (JT) effect describes the temperature change of real gases when forced through a valve or porous plug while being insulated from heat exchange with the environment. Whether the gas will cool or heat up depends on whether attractive or repulsive forces predominate at the temperature in which the forced expansion occurs. The

temperature at which this reversal occurs is known as the inversion temperature  $T_i$  which is defined as when the JT coefficient  $\mu_{JT}$  becomes zero.

$$\mu_{JT} = \left. \frac{\partial T}{\partial P} \right|_H = 0$$

Solving this expression for the VDW gas (undergoing an isenthalpic process) gives  $T_i = 2T_b$  and is used to determine whether an isenthalpic expansion of a real gas will cause it to cool or heat up. Thus, the concept of the Boyle temperature is not only important in refrigeration and air conditioning but also industrially for gas liquefaction. One such process of turning gases into liquids is the Hampson-Linde cycle which needs a positive  $\mu_{JT}$  to operate. In other words, a gas must be below its inversion temperature to be liquified by this process, which is true for all real gases at room temperature except for helium, hydrogen, and neon. If a gas undergoes a JT expansion at a temperature above its  $T_i$ , then it will actually heat up. ■

**Problem 25.** Derive expressions for the pressure, molar volume, and temperature of a VDW gas at its critical point in terms of VDW constants  $a$  and  $b$ . The critical point is defined as the point on the  $P - V_m$  curve where the first and second derivatives of the pressure with respect to molar volume vanish, i.e.  $\left. \frac{\partial P}{\partial V_m} \right|_c = 0$  and  $\left. \frac{\partial^2 P}{\partial V_m^2} \right|_c = 0$ .

**Solution.**

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\left. \frac{\partial P}{\partial V_m} \right|_c = -\frac{RT_c}{(V_m - b)^2} + \frac{2a}{V_m^3} \Big|_c = 0$$

$$\left. \frac{\partial^2 P}{\partial V_m^2} \right|_c = \frac{2RT_c}{(V_m - b)^3} - \frac{6a}{V_m^4} \Big|_c = 0$$

Solving the above expressions for  $V_c$  and  $T_c$  then substituting into the vdw equation of state to solve for  $P_c$  results in

$$V_c = 3b, \quad T_c = \frac{8a}{27bR}, \quad P_c = \frac{a}{27b^2}.$$

**Problem 26.** The diffusion coefficient of  $\text{CCl}_4$  in heptane at  $25.0^\circ\text{C}$  is  $3.89 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . How long will it take for a  $\text{CCl}_4$  molecule to undergo a mean-square displacement of 5.5 mm?

**Solution.** In 3D, the mean-square displacement is

$$\overline{\Delta r^2} = \overline{\Delta x^2} + \overline{\Delta y^2} + \overline{\Delta z^2} = 6Dt$$

Substituting values

$$t = \frac{(0.0055 \text{ m})^2}{6(3.89 \times 10^{-9} \text{ m}^2 \text{ s}^{-1})} = 1.30 \times 10^3 \text{ s}$$

■

**Problem 27.** Calculate the pressure necessary for the mean free path  $\lambda$  of argon at 25.0 °C to become comparable to the size of the 1.00 L vessel that contains it (in other words, when  $\lambda = V^{1/3}$ ). Take the radius of an Ar atom to be 188 pm. Assume argon behaves as an ideal gas.

**Solution.** The mean free path can be written as

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 N/V}$$

The number density of an ideal gas can be written as

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

Combining the above expressions, substituting values, and solving for  $P$

$$P = \frac{k_B T}{\sqrt{2}\pi d^2 \lambda} = \frac{(1.381 \times 10^{-23} \text{ J/K})(298.15 \text{ K})}{\sqrt{2}\pi(2 \times 188 \times 10^{-12} \text{ m})^2(0.100 \text{ m})} = 0.0656 \text{ Pa}$$

■

**Problem 28.** A tank is filled with 1000 g of nitrogen at 0.00°C and 16.0 atm pressure. The tank is then heated to 50.00°C and the valve is opened. What is the total mass (in grams) of the nitrogen that escapes if the external pressure is 1.00 atm. and the temperature is maintained at 50.00°C?

**Solution.** Using  $PV = nRT$  we can calculate the volume of the tank from the initial data.  $PV = nRT$ ,  $V = nRT/P$ ,  $n = ?$ .

$$n = (1000. \text{ g N}_2(g)) \left( \frac{1 \text{ mol N}_2(g)}{28.00 \text{ g N}_2(g)} \right) = 35.714 \text{ mol N}_2(g)$$

$$V = \frac{(35.714 \text{ mol})(0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(273.15 \text{ K})}{16.0 \text{ atm}} = 50.03 \text{ L} \rightarrow 50.0 \text{ L}$$

This gas will continue to escape until the internal pressure equals the external pressure of 1.00 atm. The amount of gas remaining in the tank:

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(50.03 \text{ L})}{(0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(323.15 \text{ K})} = 1.8867 \text{ mol N}_2(g)$$

$$(1.8867 \text{ mol N}_2(g)) \left( \frac{28.00 \text{ g N}_2(g)}{1 \text{ mol N}_2(g)} \right) = 52.827 \text{ g N}_2(g)$$

The amount of gas that escaped = 1000. g - 52.827 g = 947.172 g  $\rightarrow$  927 g N<sub>2</sub>(g). ■

**Problem 29.** For the given equation of states (a) and (b) below, find the 2<sup>nd</sup> virial coefficient,  $B_2(T)$ , by both methods (1) and (2) which are explained below. Recall that the virial expansion is a polynomial expansion of  $\frac{P}{k_B T}$  with respect to the number density  $\rho = N/V$ . To find  $B_2(T)$ , you will want to re-write the given equation of state in the proper form on the left hand side, and then do a polynomial expansion with respect to  $\rho$  on the remaining terms on the right hand side. Recall that a Taylor expansion of  $f(\rho)$  at  $\rho = 0$  will yield a polynomial expansion. Note: You may want to rationalize why it is a sound idea to Taylor expand  $\frac{P}{k_B T}$  at  $\rho = 0$ . Once you have the virial expansion, you can find  $B_2(T)$  by two methods.

(1) You can group terms by powers of  $\rho$  and then “select” the coefficient that goes with  $\rho^2$ .

(2) You can divide your virial expansion by  $\rho$ , subtract by one, divide by  $\rho$  again, then take the limit as  $\rho \rightarrow 0$  for the remaining terms. You may recognize the term  $Z = \frac{PV}{Nk_B T}$ .

$$(a) P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}V_m(V_m + b)}$$

$$(b) P = \frac{RT}{V_m - b} + \frac{RT}{V_m}(1 - \exp(b/V_m))$$

**Solution.** The general strategy is to write the given equation of state in the form of the virial expansion  $\frac{P}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots$  and then compare orders of  $\rho$  to determine the second virial coefficient,  $B_2(T)$ . Alternatively, we can manipulate the expression then take the limit as  $\rho \rightarrow 0$ . Both methods are demonstrated below.

(a) First we rewrite the expression to isolate constants and then do Taylor expansions with respect to  $\rho$  to write the equation of state in powers of  $\rho$ .

$$\begin{aligned} P &= \frac{Nk_B T}{V} \frac{1}{1 - \frac{Nb}{V}} - \frac{aN^2}{\sqrt{T}V^2 N_A^2} \frac{1}{1 - \frac{Nb}{VN_A}} \\ &= \rho k_B T \frac{1}{1 - b\rho} - \frac{a\rho^2}{\sqrt{T}N_A^2} \frac{1}{1 - \frac{b\rho}{N_A}} \end{aligned}$$

By Taylor expansion,

$$\begin{aligned} \frac{1}{1 - b\rho} &= 1 + b\rho + (b\rho)^2 + \dots \\ \frac{1}{1 - \frac{b\rho}{N_A}} &= 1 + \frac{b\rho}{N_A} + \left(\frac{b\rho}{N_A}\right)^2 + \dots \end{aligned}$$

Now utilizing the Taylor expansions and fitting to the form of the virial expansion,

$$\frac{P}{k_B T} = \rho + \rho^2 \left( b - \frac{a}{\sqrt{T}N_A^2} \right) + \mathcal{O}(\rho^3)$$

where  $\mathcal{O}(\rho^3)$  means terms of order equal to or higher than  $\rho^3$ . By method (1), clearly  $B_2(T) = \left(b - \frac{a}{\sqrt{T}N_A^2}\right)$ . Alternatively by method (2), we can manipulate the expression then take limit as  $\rho \rightarrow 0$ . Let  $Z = \frac{P}{k_B T \rho}$ .

$$Z = 1 + \rho \left( b - \frac{a}{\sqrt{T}N_A^2} \right) + \mathcal{O}(\rho^2)$$

$$\lim_{\rho \rightarrow 0} \frac{Z - 1}{\rho} = \lim_{\rho \rightarrow 0} \left( b - \frac{a}{\sqrt{T}N_A^2} + \mathcal{O}(\rho) \right) = b - \frac{a}{\sqrt{T}N_A^2} = B_2(T)$$

Since  $\mathcal{O}(\rho)$  depends on  $\rho$  or higher orders of  $\rho$ , it will vanish as  $\rho \rightarrow 0$ .

(b) We use the same strategy as in part (a)

$$P = k_B T \rho \left( \frac{1}{1 - b\rho} \right) - k_B T \rho (1 - \exp(b\rho/N_A))$$

By Taylor expansion,

$$\frac{1}{1 - b\rho} = 1 + b\rho + (b\rho)^2 + \dots$$

$$1 - \exp(b\rho/N_A) = \frac{b\rho}{N_A} + \frac{1}{2!} \left( \frac{b\rho}{N_A} \right)^2 + \dots$$

Now plugging in those Taylor expansions and fitting to the form of virial expansion,

$$\frac{P}{k_B T} = \rho + \rho^2 \left( b + \frac{b}{N_A} \right) + \mathcal{O}(\rho^3)$$

Since we have grouped terms by order of  $\rho$  it is clear that

$$B_2(T) = b + \frac{b}{N_A}$$

Alternatively,

$$Z = 1 + \rho \left( b + \frac{b}{N_A} \right) + \mathcal{O}(\rho^2)$$

$$\lim_{\rho \rightarrow 0} \frac{Z - 1}{\rho} = \lim_{\rho \rightarrow 0} \left( b + \frac{b}{N_A} + \mathcal{O}(\rho) \right) = b + \frac{b}{N_A} = B_2(T)$$

■

# Intermolecular Interactions

Intermolecular forces are very important in chemistry because they determine the properties of dense matter such as the nature of phase transitions. For example, the boiling point depends on the strength of intermolecular interactions: tightly bound solvent molecules typically have a higher boiling point. In a (dense) gas, intermolecular interactions may manifest themselves in deviations from the ideal gas law at higher pressures. In a liquid, they determine the spatial arrangement of solvent molecules or the interaction of solvent molecules with solutes. In a crystalline solid, these forces hold the crystal together.

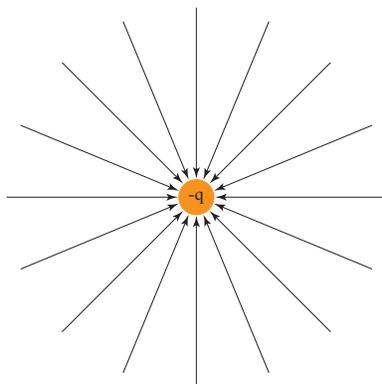
## 2.1. Electrostatics

The electric field  $\mathbf{E}$  is a vector field whose SI units are N/C (Newtons per Coulomb) or V/m (Volts per meter). It gives rise to the force exerted on a charged particle,  $q$  (units: Coulomb), according to the Lorentz force law:

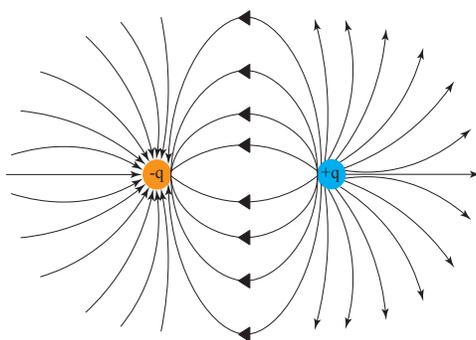
$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}).$$

( $\mathbf{v}$ : particle velocity;  $\mathbf{B}$ : magnetic field, assumed zero here.)

The electric field of a point charge falls off as  $1/R^2$ , where  $R$  is the distance to the charge, whereas the vector field  $\mathbf{E}$  points along the radial direction as shown in Fig. 2.1. The fact that the field falls off with distance is illustrated by the lower density of  $E$ -field lines away from the charge. For a charge of opposite sign, the direction of the arrows is reversed.



**Figure 2.1.** Electric field lines of a negatively charged point charge are radial and point towards the charge.

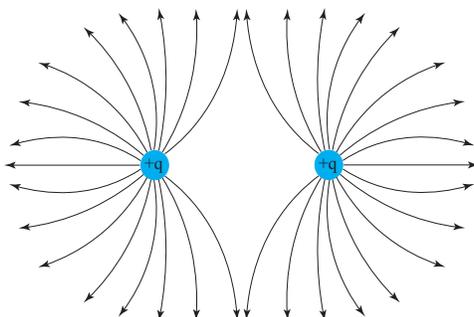


**Figure 2.2.** An electric dipole consists of opposite charges separated by a distance. The electric field flows from the positive to the negative charge.

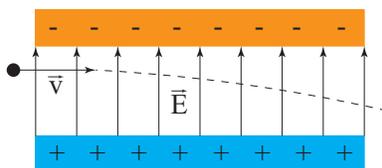
For two point charges, the electric field lines are created at the site of the positive charge and extend toward the negative charge, as shown in Fig. 2.2. The density of lines represents the strength of the electric field locally. For two charges of the same sign, the field lines form a repulsive pattern (Fig. 2.3).

For a parallel plate capacitor (two parallel electrodes, with opposite charges), the field lines are parallel, as shown in Fig. 2.4. The figure also shows that an electron traveling initially to the right will be attracted toward the positive electrode, according to the Lorentz law:  $\mathbf{F} = q\mathbf{E} = (-e)\mathbf{E}$ , i.e.,  $\mathbf{F}$  points downward if  $\mathbf{E}$  points upward.  $e$  is the elementary charge,  $1.602176 \times 10^{-19}$  C. The charge of the proton is  $e$  and the charge of the electron is  $-e$ .

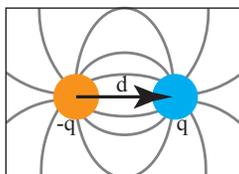
**2.1.1. Electric Dipole.** Let  $q > 0$  be an electric charge. A permanent electric dipole moment (EDM),  $\mathbf{p}$ , is a physical arrangement of a positive



**Figure 2.3.** Two electric charges of the same sign lead to repulsion. The electric field lines still flow from positive to negative charges, except that there are no negative charges here, so the lines go to infinity where the charge is eventually zero.



**Figure 2.4.** Parallel plate capacitor. Electric field lines flow from positive to negative charges (upward, in this example). A charge  $q$  enters the capacitor from the left with initial velocity  $\vec{v}$  along  $x$ . The dotted line shows the downward accelerating trajectory of the charge, implying that  $q < 0$ .



**Figure 2.5.** The EDM is a vector,  $\mathbf{p} = q\mathbf{d}$ , that points from the negative ( $-q$ ) to the positive ( $+q$ ) charge ( $q > 0$ ). Its length is  $q$  times  $|d|$ .

( $+q$ ) and a negative ( $-q$ ) charge separated by a distance  $d$ . The dipole moment is defined as  $\mathbf{p} = q\mathbf{d}$ . Its SI units are charge times distance [Coulomb  $\times$  meter]. It is a vector pointing along the intermolecular vector  $\mathbf{d}$ . By convention, we take it to point from the negative to the positive charge. This is illustrated in Fig. 2.5.

The CGS unit for dipole moment is Debye.  $1 \text{ D} \approx 3.336 \times 10^{-30} \text{ C}\cdot\text{m}$ . The Debye is defined to be equal to  $10^{-10} \text{ esu}\cdot\text{\AA}$ , where  $1 \text{ esu}$  (electrostatic units)  $\approx 3.336 \times 10^{-10} \text{ C}$ . Inter-atomic distances within molecules are typically measured in units of angstrom ( $\text{\AA}$ ), where  $1 \text{ \AA} = 10^{-10} \text{ m}$ .

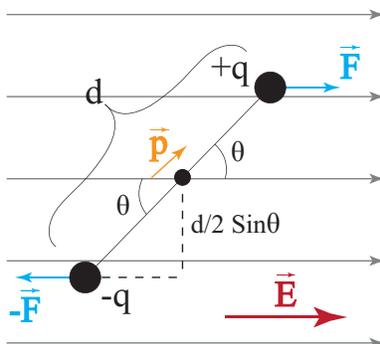


Figure 2.6. Torque on a dipole by an electric field.

Electronegativity (Pauling Scale)

0.7 4.0

1																	18
H																	He
2.1																	-
Li	Be											B	C	N	O	F	Ne
1.0	1.5											2.0	2.5	3.0	3.5	4.0	-
Na	Mg											Al	Si	P	S	Cl	Ar
0.9	1.2											1.5	1.8	2.1	2.5	3.0	-
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6	1.6	1.8	2.0	2.4	2.8	3.0
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5	2.6
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0.7	0.9	1.1	1.3	1.5	1.7	1.9	2.2	2.2	2.4	1.9	1.8	1.9	1.9	1.9	2.0	2.2	-
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub	113	Uuq	115	116	117	118
0.7	0.9	1.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

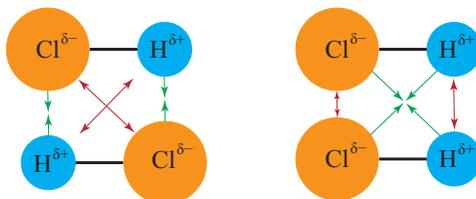
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1.1	1.1	1.1	1.2	1.2	1.1	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
1.3	1.5	1.7	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.5	-

Figure 2.7. Tables of Pauling electronegativities.

Dipole moments in a molecule can be permanent or induced.  $\text{H}_2\text{O}$ , for example, has a permanent EDM. Molecules without a permanent EDM can still be polarized by the application of an electric field (see Section 2.1.2). A consequence of  $\mathbf{p} \neq 0$  is that the electric dipole will want to orient itself along the electric field lines as a consequence of the Lorentz force  $\mathbf{F} = q\mathbf{E}$  which leads to a torque  $\boldsymbol{\tau} = \mathbf{p} \times \mathbf{E}$  ( $\times$ : cross product<sup>1</sup>) on the dipole, as shown in Fig. 2.6.

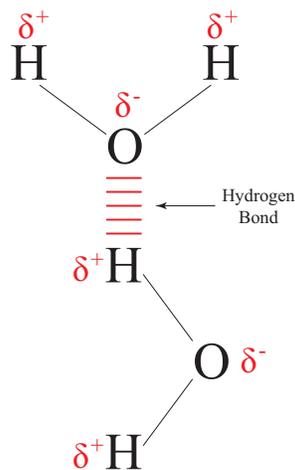
<sup>1</sup>The cross product  $\mathbf{x} \times \mathbf{y}$  of two vectors  $\mathbf{x} = (x_1, x_2, x_3)$  and  $\mathbf{y} = (y_1, y_2, y_3)$  is defined as the vector obtained from the determinant of the matrix

$$\mathbf{x} \times \mathbf{y} \equiv \begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ x_1 & x_2 & x_3 \\ y_1 & y_2 & y_3 \end{vmatrix} = \hat{\mathbf{x}}(x_2y_3 - x_3y_2) + \hat{\mathbf{y}}(x_3y_1 - x_1y_3) + \hat{\mathbf{z}}(x_1y_2 - x_2y_1).$$



**Figure 2.8.** Dipole-dipole interaction in HCl.

Dipole moments can occur between two ions in an ionic bond or between atoms in a covalent bond; dipole moments arise from differences in electronegativity. The larger the difference in electronegativity, the larger the dipole moment. The distance between the charge separation is also a deciding factor into the size of the dipole moment. The dipole moment is a measure of the polarity of the molecule. Electronegativities can be found online, e.g., <http://webelements.com>. Such a table is reproduced here (Fig. 2.7).



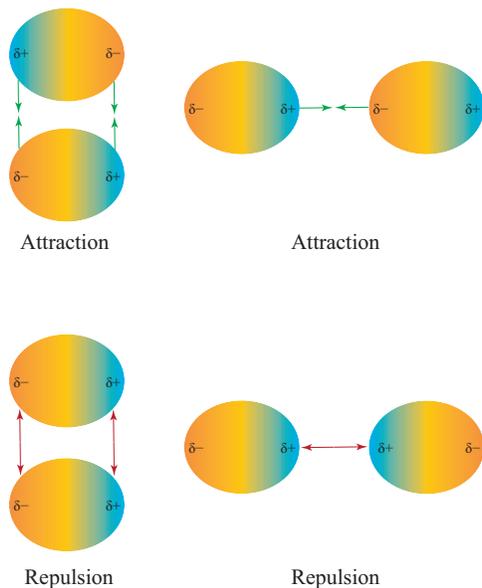
**Figure 2.9.** Hydrogen bonding interaction between  $\text{H}_2\text{O}$  molecules.

In Fig. 2.8 a molecule of HCl can be represented as having a small net negative charge on the Cl end, balanced by a small net positive charge on the H end. The overall charge is zero, however, the distribution of charges is spatially-dependent. The forces between two HCl molecules depend on their orientations. (a) The oppositely charged ends (green arrows) are closer

---

Its magnitude is  $|x||y|\sin\theta$ .  $\theta$  is the angle between  $\mathbf{x}$  and  $\mathbf{y}$ . Its geometric meaning is the area of the parallelogram traced with sides  $\mathbf{x}$  and  $\mathbf{y}$ . It is a vector pointing in a direction perpendicular to the plane spanned by  $\mathbf{x}$  and  $\mathbf{y}$ .  $\mathbf{x} \times \mathbf{y} = 0$  means the two vectors are parallel to each other.

than the ends with the same charge (red arrows). This gives a net attractive force. (b) Here, the opposite is true, and the net force is repulsive.



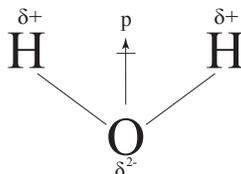
**Figure 2.10.** Permanent EDM in  $\text{H}_2\text{O}$  leads to attraction or repulsion between pairs of molecules, depending on the relative orientation of these molecules. Four different examples are shown here.

**Table 2.1.** Dipole moments for various molecules. Source: Israelachvili [2]

Compound	Dipole Moment (Debye)
NaCl	9.0 (meas. in gas phase)
$\text{CH}_3\text{Cl}$	1.87
$\text{H}_2\text{O}$	1.85
$\text{NH}_3$	1.47
$\text{CO}_2$	0
$\text{CCl}_4$	0

A popular example of permanent EDM is the water molecule  $\text{H}_2\text{O}$ , which has partial positive charge on the hydrogen and partial negative charges on its oxygen, leading to the formation of hydrogen bonds in water (see Fig. 2.9). The molecule  $\text{H}_2\text{O}$  is said to be polar because it possesses a permanent electric dipole moment indicated by the arrow in Fig. 2.11. This interaction can be interpreted in terms of Coulomb's law (like charges repel each other whereas unlike charges attract each other), as shown in Fig. 2.10.

Table 2.1 lists dipole moments of several popular compounds.



**Figure 2.11.** Net electric dipole moment of a water molecule forms as the vector sum of two dipole moments, each along the two H-O bonds, pointing from O to H, since O is more electronegative. According to our convention for the direction of the EDM, the vector  $\vec{p} = q\vec{d}$  points upward, from the negative partial charge to the positive side.

Tables 2.2, 2.3 and 2.4 are some values of permanent dipole moments of selected molecules. The unit is the Debye (D). Recall that  $1 \text{ D} = 3.336 \times 10^{-30} \text{ C}\cdot\text{m}$ . We note that hydrogen-bonding molecules can have different dipole moments in the gas, liquid, and solid phases, as well as in different solvents.

**Table 2.2.** Dipole moments of molecules. Source: Israelachvili [2]

Molecules			
Alkanes	0	H <sub>2</sub> O	1.85
C <sub>6</sub> H <sub>6</sub> (benzene)	0	C <sub>n</sub> H <sub>2n+1</sub> OH (alcohols)	1.7
CCl <sub>4</sub>	0	C <sub>6</sub> H <sub>11</sub> OH (cyclohexanol)	1.7
CO <sub>2</sub>	0	OMCTS	0.42
CO	0.11	CH <sub>3</sub> COOH (acetic acid)	1.7
CHCl <sub>3</sub> (chloroform)	1.06	C <sub>2</sub> H <sub>4</sub> O (ethylene oxide)	1.9
HCl	1.08	CH <sub>3</sub> COCH <sub>3</sub> (acetone)	2.9
HF	1.91	HCONH <sub>2</sub> (formamide)	3.7
NH <sub>3</sub>	1.47	C <sub>6</sub> H <sub>5</sub> OH (phenol)	1.5
CH <sub>3</sub> Cl	1.87	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> (aniline)	1.5
NaCl	8.5	C <sub>6</sub> H <sub>5</sub> Cl (chlorobenzene)	1.8
CsCl	10.4	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> (nitrobenzene)	4.2

**Table 2.3.** Bond Moments. Source: Israelachvili [2]

Bond Moments					
C-H <sup>+</sup>	0.4	C-C	0	C <sup>+</sup> -Cl	1.5-1.7
N-H <sup>+</sup>	1.31	C=C	0	N <sup>+</sup> -O	0.3
O-H <sup>+</sup>	1.51	C <sup>+</sup> -N	0.22	C <sup>+</sup> =O	2.3-2.7
F-H <sup>+</sup>	1.94	C <sup>+</sup> -O	0.74	N <sup>+</sup> =O	2.0

**Table 2.4.** Bond Moments. Source: Israelachvili [2]

Group Moments					
C <sup>+</sup> CH <sub>3</sub>	0.4	C <sup>+</sup> COOH	1.7	Adenine	~ 3
C <sup>+</sup> OH	1.65	C <sup>+</sup> OCH <sub>3</sub>	1.3	Thymine	~ 4
C <sup>+</sup> NH <sub>2</sub>	1.2-1.5	C <sup>+</sup> -NO <sub>2</sub>	3.1-3.8	Guanine	~ 7
				Cytosine	~ 8

**2.1.2. Electric Polarization.** Suppose that we have an electrically neutral molecule placed in an electric field  $\mathbf{E}$ . It can acquire a dipole moment  $\mathbf{p}$  through the action of the electric field by distorting its electron cloud. This is the case regardless of whether or not the molecule has a permanent EDM. The application of an electric field to a molecule gives rise to an induced EDM whose magnitude is proportional to  $\mathbf{E}$ :<sup>2</sup>

$$\mathbf{p} = \epsilon_0 \alpha \mathbf{E},$$

where  $\mathbf{E}$  is the “local” electric field at the site of the molecule,  $\epsilon_0 = 8.85 \times 10^{-12}$  Farad per meter [F/m] is the permittivity of free space and  $\alpha$  is the molecular polarizability (or simply, “polarizability”). The latter is a property that is specific to the molecule. Polarizabilities for several molecules can be found in Table 2.5.

*Question:* What must be the SI units of  $\alpha$ ?

*Solution:* From  $p = \epsilon_0 \alpha E$ ,  $\alpha = p/(\epsilon_0 E)$ , where  $E$  is V/m,  $p$  is C.m and  $\epsilon_0$  is F/m. Thus,  $\alpha$  has units C.m/(F.V/m/m) or  $\text{m}^3$ , since Farad is defined as Coulombs per Volt.

*Alternate Units:* Alternatively, we absorb  $\epsilon_0$  into  $\alpha$ , keeping SI units, and write  $\mathbf{p} = \alpha \mathbf{E}$  instead of  $\mathbf{p} = \epsilon_0 \alpha \mathbf{E}$ . In this case,  $\alpha$  has SI units of  $\text{C.m}^2/\text{V}$ .

*Closely Related Units:* A related set of units (which differs from the previous one by  $4\pi$ ), which we shall use in Section 2.6, is  $\mathbf{p} = \alpha \mathbf{E}$ , where  $\alpha$  is given in units of  $(4\pi\epsilon_0)\text{\AA}^3 = 1.11 \times 10^{-40} \text{ C.m}^2/\text{V}$ . (See Table 2.5.)

**Example 2.1.** Equation  $p = \alpha E$  is to be used with the data from Table 2.5. Let’s look at the case of  $\text{CCl}_4$ , which has a polarizability of 10.5 and units of  $(4\pi\epsilon_0)\text{\AA}^3$ . Suppose the electric field is 110 V between two electrodes separated 1 cm apart, i.e.  $E = (110 \text{ V})/(1 \text{ cm}) = 11,000 \text{ V/m}$ .

$$\begin{aligned} p &= \alpha E = (4\pi\epsilon_0)\text{\AA}^3 (10.5)(110 \text{ V}) \\ &= (1.11 \times 10^{-40} \text{ C.m}^2/\text{V})(10.5)(11,000 \text{ V/m}) \\ &= 1.282 \times 10^{-35} \text{ C.m} \end{aligned}$$

Because our formula uses SI units, the units of  $p$  are automatically C.m, as long as  $\alpha$  and  $E$  are in SI units. The SI units of  $E$  are V/m. The SI units of  $\alpha$  are  $\text{C.m}^2/\text{V}$  (and if polarizability values from Table 2.5 are used, we must multiply by the scaling factor  $1.11 \times 10^{-40}$ ). This magnitude can be compared to a permanent EDM. While  $\text{CCl}_4$  has no permanent EDM, other molecules such as NaCl or  $\text{H}_2$  do. According to Table 2.1,  $\text{H}_2\text{O}$  has

<sup>2</sup>Sometimes this is written in terms of the polarization density,  $\mathbf{P}$  (dipole moment per unit volume), where  $\mathbf{P} = \chi_e \epsilon_0 \mathbf{E}$ , where  $\chi_e$  is the electric susceptibility.  $\mathbf{p}$  is obtained from  $\mathbf{P}$  by multiplying the latter by volume.  $\chi_e$  and  $\alpha$  are related by  $\chi_e = \alpha N/V$ , where  $N/V$  is the number of molecules per unit volume.

**Table 2.5.** Electronic Polarizabilities of Molecules. Polarizabilities here are given in volume units of  $(4\pi\epsilon_0)\text{\AA}^3 = (4\pi\epsilon_0)10^{-30} \text{ m}^3 = 1.11 \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$ . 1 Joule = 1 Coulomb times Volt ( $\text{J}=\text{C.V}$ ). The numerical value of  $4\pi\epsilon_0$  is  $4\pi \times 8.854 \times 10^{-12} \sim 1.11 \times 10^{-10}$ . Note that when molecules are dissolved in a solvent medium, their polarizability can change by up to 10%. Source: Israelachvili [2]

Atoms and Molecules					
He	0.20	NH <sub>3</sub>	2.3	CH <sub>2</sub> =CH <sub>2</sub>	4.3
H <sub>2</sub>	0.81	CH <sub>4</sub>	2.6	C <sub>2</sub> H <sub>6</sub>	4.5
H <sub>2</sub> O	1.45-1.48	HCl	2.6	Cl <sub>2</sub>	4.6
O <sub>2</sub>	1.60	CO <sub>2</sub>	2.9	CHCl <sub>3</sub>	8.2
Ar	1.63	CH <sub>3</sub> OH	3.2	C <sub>6</sub> H <sub>6</sub>	10.3
CO	1.95	Xe	4.0	CCl <sub>4</sub>	10.5
Bond Polarizabilities					
C-C aliphatic	0.48	C-H	0.65	C-Cl	2.60
C $\simeq$ C aromatic	1.07	O-H	0.73	C-F	0.73
C=C	1.65	C-O	0.60	Si-Si	2.24
C $\equiv$ C	2.39	C=O	1.36	Si-H	1.27
Molecules Groups					
C-O-H	1.3	-CH <sub>2</sub> -	1.84	CF <sub>3</sub>	2.4
C-O-C	1.1	CH <sub>3</sub>	2.0	Si-O-Si	1.4
C-NH <sub>2</sub>	2.0	-CF <sub>2</sub> -	2.0	Si-OH	1.6

a permanent EDM of 1.85 Debye. Since  $1 \text{ D} \approx 3.3465 \times 10^{-30} \text{ C.m}$ , its permanent EDM in SI units is  $6.2 \times 10^{-30} \text{ C.m}$ .

**Example 2.2.** What is the magnitude of the electric field strength required to induce an EDM in H<sub>2</sub>O of the same magnitude as its permanent EDM? *Solution:* According to the data from Table 2.1, H<sub>2</sub>O has a permanent EDM of 1.85 Debye, which correspond to  $6.2 \times 10^{-30} \text{ C.m}$  in SI units. From Table 2.5, the polarizability of H<sub>2</sub>O is in the range 1.45-1.48, with units of  $1.11 \times 10^{-40} \text{ C.m}^2/\text{V}$ . Let's take 1.48. Equating the polarizations

$$6.2 \times 10^{-30} \text{ C.m} = (1.11 \times 10^{-40} \text{ C.m}^2/\text{V})(1.48)E$$

and solving for  $E$  gives:

$$E = \frac{6.2 \times 10^{-30} \text{ C.m}}{(1.11 \times 10^{-40} \text{ C.m}^2/\text{V})(1.48)} = 38 \times 10^9 \text{ V/m.}$$

**Example 2.3.** How does one generate an electric field of magnitude  $38 \times 10^9 \text{ V/m}$ ? *Solution:* One way is to apply a voltage across electrodes that are very close to each other. For example, if we apply 110 V across electrodes separated by 3 nm, we will get an electric field of this magnitude. In practice, this is difficult to achieve. On the other hand, let's look at the electric field of an ion. A point charge  $Q$  generates an electric field of magnitude

$E = Q/(4\pi\epsilon_0 r^2)$  some distance  $r$  away from the charge. Let's take  $Q = e$  (elementary charge). Solving for  $r$ :

$$r = \sqrt{\frac{1}{4\pi\epsilon_0} \frac{Q}{E}} = \sqrt{(9 \times 10^9 \text{ N.m}^2/\text{C}^2) \frac{(1.6 \times 10^{-19} \text{ C})}{38 \times 10^9 \text{ V/m}}} \approx 2 \times 10^{-10} \text{ m} = 2 \text{ \AA}.$$

Thus, in close proximity of an ion, such an electric field can be found.

Note: The units are m because we are using a formula in SI units and all our physical quantities have been provided in SI units. If you are unconvinced, you can work out the units yourself: inside the square root we have  $\text{C} \cdot (\text{N} \cdot \text{m}^2 / \text{C}^2) / (\text{V}/\text{m})$ , which equals  $\text{N} \cdot \text{m}^3 / (\text{C} \cdot \text{V})$ . However,  $1 \text{ J} = 1 \text{ C} \cdot \text{V}$ . Thus, our units are  $\text{N} \cdot \text{m}^3 / \text{J}$ , whereas  $1 \text{ J} = 1 \text{ N} \cdot \text{m}$ . This leaves us with  $\text{m}^2$ . Taking the square root gives m.

**2.1.3. Origin of the Coulomb's Law.** The Maxwell equations in free space are:

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0}, \quad \nabla \cdot \mathbf{B} = 0, \quad \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad \nabla \times \mathbf{B} = \mu_0 \left( \mathbf{J} + \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right)$$

The various quantities are:  $\mathbf{J}$ , current density (units: Ampères per square meter [ $\text{A}/\text{m}^2$ ]);  $\mu_0$ , permeability of free space (value:  $4\pi \times 10^{-7} \text{ V} \cdot \text{s}/(\text{A} \cdot \text{m})$  or  $\text{N}/\text{A}^2$ );  $\rho$ , charge density (units: Coulomb per cubic meter [ $\text{C}/\text{m}^3$ ]).

The Coulomb's law is a consequence of the first Maxwell equation, which we integrate over a volume  $vol$  enclosing an electrical charge  $Q$ :

$$\int_{vol} \nabla \cdot \mathbf{E} d^3\mathbf{r} = \int_{vol} \frac{\rho}{\epsilon_0} d^3\mathbf{r} = \frac{Q}{\epsilon_0}.$$

Here,

$$Q = \int_{vol} \rho(\mathbf{r}) d^3\mathbf{r}.$$

Consider the electric field of a *single charged particle* placed at the origin. Using the Gauss divergence theorem,<sup>3</sup> we may rewrite the left hand side as a surface integral:

$$\int_{\partial vol} \mathbf{E} \cdot d\mathbf{s} = \frac{Q}{\epsilon_0},$$

where  $d\mathbf{s}$  is a surface area element and  $\partial vol$  denotes the *boundary* of the volume  $vol$ . For example, if  $vol$  is a sphere, then  $\partial vol$  is a spherical shell.

<sup>3</sup>Let  $\mathbf{E}$  be a  $C^1$  (differentiable, with continuous derivative) vector field. Let  $\Omega \subset \mathbb{R}^3$  be a volume. The Gauss divergence theorem states that the volume integral can be reduced to a surface integral:

$$\int_{vol} (\nabla \cdot \mathbf{E}) d^3\mathbf{r} = \int_{\partial vol} \mathbf{E} \cdot d\mathbf{s}$$

The surface area element  $d\mathbf{s}$  is a vector pointing outward normal to the surface at each point. Another way to write the integrand of the second integral is  $\mathbf{E} \cdot \hat{\mathbf{n}} ds$ , where  $\hat{\mathbf{n}}$  is the unit vector that is outward normal to the surface.  $ds$  is an area element.

The electric field of a single charged particle is radial and does not depend on the spherical angles  $\theta, \phi$ .

Let  $vol$  be a sphere centered at the origin with radius  $R$ . Then, spherical coordinates

$$\int_{vol} f(\mathbf{r}) d^3\mathbf{r} \equiv \int_0^\pi d\theta \int_0^{2\pi} d\phi \int_0^R dr f(\theta, \phi, r) \sin \theta$$

render the integral trivial and the electric field is<sup>4</sup>

$$\mathbf{E} = \frac{Q}{4\pi\epsilon_0} \frac{1}{r^2} \hat{\mathbf{r}}.$$

Using the Lorentz law with  $\mathbf{B} = 0$ , the force is:

$$\mathbf{F} = q\mathbf{E} = k \frac{qQ}{r^2} \hat{\mathbf{r}},$$

where

$$k = \frac{1}{4\pi\epsilon_0} = 9 \cdot 10^9 \text{ Nm}^2/\text{C}^2.$$

This relationship is called the *Coulomb's law*. Since  $F \propto 1/R^2$ , we also say it's an *inverse square law*. Work is the line integral of force over distance. Let us integrate along a line/curve starting at the point  $P_i$  and ending at  $P_f$ .  $P_i$  is usually taken to be a "reference" point at infinity whereas  $P_f$  is the point of interest (where  $V$  is to be evaluated). We find:

$$(2.1) \quad V(\mathbf{R}) = - \int_{P_i}^{P_f} \mathbf{F} \cdot d\mathbf{r} = -k \int_\infty^R \frac{qQ}{r^2} dr = k \frac{qQ}{R}.$$

This is often written ( $q = q_1, Q = q_2$ ):

$$(2.2) \quad \boxed{V(\mathbf{R}) = k \frac{q_1 q_2}{R}}.$$

The negative sign (Eq. 2.1) describes the work we do *against* the electrical force to move the charge from point  $P_i$  (say, at infinity) to point  $P_f$ ; i.e., we have to apply a negative force  $-\mathbf{F}$ .

Here,  $\mathbf{R}$  is the distance vector between the two ions, as indicated in Fig. 2.12. In 3D,  $R \equiv |\mathbf{R}| \equiv \sqrt{X^2 + Y^2 + Z^2}$ , where  $X, Y, Z$  are the components of the vector  $\mathbf{R}$ .<sup>5</sup>

<sup>4</sup> $Q/\epsilon_0$  is needed so it matches what's on the right hand side. The  $1/(4\pi)$  is needed in order to cancel out the value of the integral over angles  $\theta, \phi$ , which gives  $4\pi$ :

$$\int_0^\pi d\theta \int_0^{2\pi} d\phi \sin \theta = \int_0^\pi d\theta \int_{-1}^1 d(\cos \theta) = 4\pi.$$

<sup>5</sup>For consistency, you can check that the force — the negative gradient of the potential energy  $V$  — gives the correct result:

$$\mathbf{F} = -\nabla V = k \frac{q_1 q_2}{R^2} \hat{\mathbf{r}}$$

where  $\hat{\mathbf{r}} \equiv \mathbf{R}/|\mathbf{R}|$ .

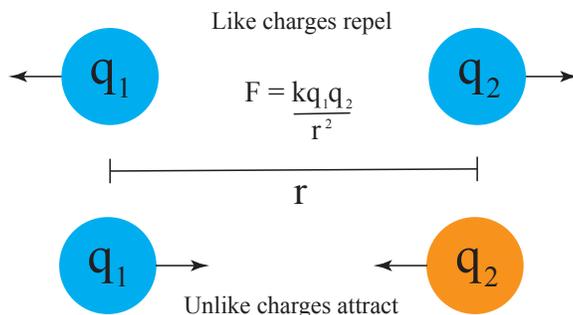


Figure 2.12. Coulomb interaction.

**2.1.4. Interacting Charge Distributions.** Suppose now that instead of two interacting point charges, we have two non-overlapping, continuous charge distributions ( $\rho_A$  and  $\rho_B$ ), as shown in Fig. 2.13 ( $\mathbf{R} = \mathbf{r}_B - \mathbf{r}_A$ ).

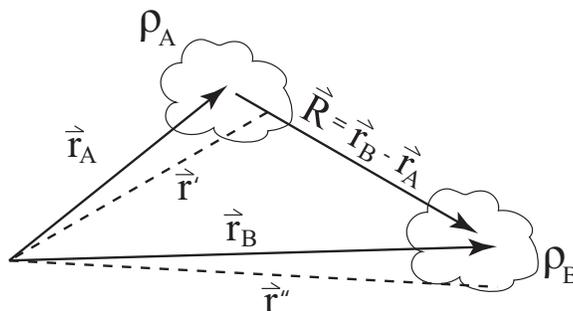


Figure 2.13. Two continuous electric charge distributions,  $\rho_A$  and  $\rho_B$ , shown here as clouds, interact via the Coulomb's law.

The vectors  $\mathbf{r}_B$  and  $\mathbf{r}_A$  are center-of-mass (*com*) coordinates for each charge distribution. Namely, if  $\mu_A(\mathbf{r})$  is the mass density for the charge distribution  $\rho_A$ , its center of mass is defined by

$$\mathbf{r}_A = \frac{1}{M_A} \int_{vol} \mu_A(\mathbf{r}) \mathbf{r} d^3\mathbf{r}$$

where  $M_A$  is the total mass of  $A$ , i.e.  $M_A = \int_{vol} \mu_A(\mathbf{r}) d^3\mathbf{r}$ . As an example, suppose that the mass distribution<sup>6</sup> describes a point mass  $m_1$  at  $\mathbf{r}_1$  and another point mass  $m_2$  located at  $\mathbf{r}_2$ . The center of mass is then:

$$\mathbf{r}_{com} = \frac{1}{m_1 + m_2} (m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2).$$

<sup>6</sup>In terms of Dirac delta functions (see A.23), the mass density is  $\mu(\mathbf{r}) = m_1 \delta(\mathbf{r} - \mathbf{r}_1) + m_2 \delta(\mathbf{r} - \mathbf{r}_2)$ . The total mass is  $\int_{\mathbb{R}^3} \mu(\mathbf{r}) d^3\mathbf{r} = m_1 + m_2$ . The center of mass is at  $\mathbf{r}_{com} = \frac{1}{m_1 + m_2} \int_{\mathbb{R}^3} \mu(\mathbf{r}) \mathbf{r} d^3\mathbf{r} = \frac{1}{m_1 + m_2} (m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2)$ .

The Coulomb energy describing the interaction of these two charge distributions is (c.f. Eq. 2.2):

$$V_{AB}(\mathbf{R}) = k \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_A(\mathbf{r}') \rho_B(\mathbf{r}'')}{|\mathbf{r}'' - \mathbf{r}'|} d^3 \mathbf{r}' d^3 \mathbf{r}''.$$

Now suppose that  $R$  is much larger than the radius of  $\rho_A$  and  $\rho_B$  (far field approximation). Let us rewrite the denominator  $|\mathbf{r}'' - \mathbf{r}'|$  as:

$$|\underbrace{\mathbf{R} - \mathbf{R}}_0 - \mathbf{r}' + \mathbf{r}''| = |\mathbf{R} - \underbrace{\vec{r}_B + \vec{r}_A}_{-\mathbf{R}} - \mathbf{r}' + \mathbf{r}''|,$$

and since  $R \gg |\vec{r}_B - \mathbf{r}''|$  and  $R \gg |\vec{r}_A - \mathbf{r}'|$  we may Taylor expand (see Section A.11) this factor about the point  $1/R$ , using the small parameter  $\boldsymbol{\epsilon} = \mathbf{r}_A - \mathbf{r}' - (\mathbf{r}_B - \mathbf{r}'')$ : (here, we use the shorthand notation  $\partial_\alpha \equiv \partial/\partial R_\alpha$  as well as summation over repeated indices; see Section A.10)

$$\frac{1}{|\mathbf{R} + \boldsymbol{\epsilon}|} = \frac{1}{R} + \epsilon_\alpha \partial_\alpha \left( \frac{1}{R} \right) + \frac{1}{2} \epsilon_\alpha \epsilon_\beta \partial_\alpha \partial_\beta \left( \frac{1}{R} \right) + O(\epsilon^3).$$

Let us keep zeroth and first moments for now since we want to discuss only the lowest order interactions (ion-ion, ion-dipole and dipole-dipole), i.e. we keep cross terms  $(r')(r'')$  and lower order  $(r')$  and  $(r'')$ . Terms such as  $(r')^2$  or  $(r'')^2$  and higher order describe quadrupole, octupole and higher order moments. Substitution of  $\boldsymbol{\epsilon}$  gives

$$(2.3) \quad \frac{1}{|\mathbf{R} + \boldsymbol{\epsilon}|} = \frac{1}{R} + \underbrace{(\mathbf{r}_A - \mathbf{r}' - (\mathbf{r}_B - \mathbf{r}''))_\alpha}_{\epsilon_\alpha} \partial_\alpha \left( \frac{1}{R} \right) \\ + \frac{1}{2} \{ -(\mathbf{r}_A - \mathbf{r}')_\alpha (\mathbf{r}_B - \mathbf{r}'')_\beta - (\mathbf{r}_B - \mathbf{r}'')_\alpha (\mathbf{r}_A - \mathbf{r}')_\beta \} \partial_\alpha \partial_\beta \left( \frac{1}{R} \right) + O(\epsilon^3)$$

where the derivatives are:

$$\partial_\alpha \left( \frac{1}{R} \right) = -\frac{R_\alpha}{R^3}, \quad \partial_\alpha \partial_\beta \left( \frac{1}{R} \right) = \partial_\alpha \left( -\frac{R_\beta}{R^3} \right) = \frac{3R_\alpha R_\beta}{R^5} - \frac{\delta_{\alpha\beta}}{R^3}.$$

The function  $\delta_{\alpha\beta}$  is called *Kronecker delta*. It is defined as 1 when  $\alpha = \beta$  and 0 when  $\alpha \neq \beta$ . The Kronecker delta arose because we encountered a situation that involved computing derivatives of the type:  $\partial x/\partial x = 1$  and  $\partial y/\partial x = 0$ , etc.

The integral

$$V_{AB}(\mathbf{R}) = k \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \rho_A(\mathbf{r}') \rho_B(\mathbf{r}'') |\mathbf{R} + \boldsymbol{\epsilon}|^{-1} d^3 \mathbf{r}' d^3 \mathbf{r}''$$

evaluates to:

$$k \left[ \underbrace{\frac{q_A q_B}{R}}_{\substack{\text{ion-ion} \\ \sim 1/R}} - \underbrace{\frac{q_A \mathbf{p}_B \cdot \mathbf{R}}{R^3} + \frac{q_B \mathbf{p}_A \cdot \mathbf{R}}{R^3}}_{\substack{\text{ion-dipole} \\ \sim 1/R^2}} + \underbrace{\left\{ \frac{\mathbf{p}_A \cdot \mathbf{p}_B}{R^3} - \frac{3(\mathbf{p}_A \cdot \mathbf{R})(\mathbf{p}_B \cdot \mathbf{R})}{R^5} \right\}}_{\substack{\text{dipole-dipole} \\ \sim 1/R^3}} + \dots \right].$$

We have made the following abbreviations:

$$\begin{aligned} q_A &= \int \rho_A(\mathbf{r}') d^3 \mathbf{r}', & q_B &= \int \rho_B(\mathbf{r}'') d^3 \mathbf{r}'' \quad (\text{monopole}) \\ \mathbf{p}_A &= \int \rho_A(\mathbf{r}')(\mathbf{r}' - \vec{r}_A) d^3 \mathbf{r}', & \mathbf{p}_B &= \int \rho_B(\mathbf{r}'')(\mathbf{r}'' - \vec{r}_B) d^3 \mathbf{r}'' \quad (\text{dipole}) \\ &\vdots & & (\text{higher order multipole moments}) \end{aligned}$$

This multipole expansion leads to a series of terms:

- (+) and (+): ion ion  $1/R$
- (+) and (+ -): ion dipole  $1/R^2$
- (+ -) and (+ -): dipole dipole  $1/R^3$
- (+) and (+<sub>-</sub> +): ion quadrupole  $1/R^3$
- (+ -) and (+<sub>-</sub> +): dipole quadrupole  $1/R^4$

For those who think we may have done this too quickly, here is a more detailed derivation. What we did is substitute Eq. (2.3) into the integral

$$k \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \rho_A(\mathbf{r}') \rho_B(\mathbf{r}'') |\mathbf{R} + \boldsymbol{\epsilon}|^{-1} d^3 \mathbf{r}' d^3 \mathbf{r}''$$

in place of  $|\mathbf{R} + \boldsymbol{\epsilon}|^{-1}$ . The first term in Eq. (2.3) is  $1/R$ . Its contribution to the integral is:

$$k \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{1}{R} \rho_A(\mathbf{r}') \rho_B(\mathbf{r}'') d^3 \mathbf{r}' d^3 \mathbf{r}'' = \frac{k}{R} \underbrace{\int_{\mathbb{R}^3} \rho_A(\mathbf{r}') d^3 \mathbf{r}'}_{q_A} \cdot \underbrace{\int_{\mathbb{R}^3} \rho_B(\mathbf{r}'') d^3 \mathbf{r}''}_{q_B} = \frac{k q_A q_B}{R}.$$

which is the term we sought. Next, according to Eq. (2.3) the second term in the expansion of  $|\mathbf{R} + \boldsymbol{\epsilon}|^{-1}$  is

$$(\vec{r}_A - \mathbf{r}' - (\vec{r}_B - \mathbf{r}''))_{\alpha} \partial_{\alpha} \left( \frac{1}{R} \right)$$

where  $\partial_{\alpha} \left( \frac{1}{R} \right) = -R_{\alpha} / R^3$ . Plugging this term into the integral gives

$$-k \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \rho_A(\mathbf{r}') \rho_B(\mathbf{r}'') (\vec{r}_A - \mathbf{r}' - (\vec{r}_B - \mathbf{r}''))_{\alpha} \left( \frac{R_{\alpha}}{R^3} \right) d^3 \mathbf{r}' d^3 \mathbf{r}''.$$

Next, we pull the term  $R_{\alpha} / R^3$  outside the integral, since it does not depend on the two variables of integration. We absorb the minus sign by reversing the order of  $\vec{r}_A - \mathbf{r}' \rightarrow \mathbf{r}' - \vec{r}_A$  and  $\vec{r}_B - \mathbf{r}'' \rightarrow \mathbf{r}'' - \vec{r}_B$ . Finally, we split the

integral into two terms (i.e.  $\int A + B = \int A + \int B$ ):

$$\begin{aligned} \frac{kR_\alpha}{R^3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \rho_A(\mathbf{r}') \rho_B(\mathbf{r}'') (\mathbf{r}' - \vec{r}_A)_\alpha d^3\mathbf{r}' d^3\mathbf{r}'' \\ - \frac{kR_\alpha}{R^3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \rho_A(\mathbf{r}') \rho_B(\mathbf{r}'') (\mathbf{r}'' - \vec{r}_B)_\alpha d^3\mathbf{r}' d^3\mathbf{r}'' . \end{aligned}$$

Writing the double integrals as products of integrals (one depending on  $r'$  only and the other, on  $r''$  only):

$$\begin{aligned} \frac{kR_\alpha}{R^3} \underbrace{\int_{\mathbb{R}^3} \rho_A(\mathbf{r}') (\mathbf{r}' - \vec{r}_A)_\alpha d^3\mathbf{r}'}_{(\mathbf{p}_A)_\alpha} \cdot \underbrace{\int_{\mathbb{R}^3} \rho_B(\mathbf{r}'') d^3\mathbf{r}''}_{q_B} \\ - \frac{kR_\alpha}{R^3} \underbrace{\int_{\mathbb{R}^3} \rho_A(\mathbf{r}') d^3\mathbf{r}'}_{q_A} \cdot \underbrace{\int_{\mathbb{R}^3} \rho_B(\mathbf{r}'') (\mathbf{r}'' - \vec{r}_B)_\alpha d^3\mathbf{r}''}_{(\mathbf{p}_B)_\alpha} \end{aligned}$$

which leads to:

$$\frac{kq_B \mathbf{p}_A \cdot \mathbf{R}}{R^3} - \frac{kq_A \mathbf{p}_B \cdot \mathbf{R}}{R^3}$$

since  $R_\alpha (\mathbf{p}_A)_\alpha$  (summation convention) denotes the dot product of the vectors  $\mathbf{R}$  and  $\mathbf{p}_A$ . Applying the same method you should be able to derive the dipole-dipole term. Do not panic when you encounter the term  $(\mathbf{p}_A)_\alpha \delta_{\alpha\beta} (\mathbf{p}_B)_\beta$ . The summation convention stands for:

$$(\mathbf{p}_A)_\alpha \delta_{\alpha\beta} (\mathbf{p}_B)_\beta \equiv \sum_{\alpha=1}^3 \sum_{\beta=1}^3 (\mathbf{p}_A)_\alpha \delta_{\alpha\beta} (\mathbf{p}_B)_\beta .$$

The Kronecker delta is zero unless  $\alpha = \beta$ , in which case it equals 1. Thus the double sum collapses into a single sum, yielding a dot product:

$$\sum_{\alpha=1}^3 (\mathbf{p}_A)_\alpha (\mathbf{p}_B)_\alpha \equiv \mathbf{p}_A \cdot \mathbf{p}_B .$$

## 2.2. Intermolecular Interactions and Their Ranges

Interactions between electrostatic charges are described by the Coulomb's law. So far we have considered electric charge distributions and interactions between charge distributions. The charge distributions can be molecules. Thus, the concepts introduced in the previous section can be applied to describe interactions between pairs of molecules. We often have that the molecular radius is small compared to  $R$ . For a dipole, this gives rise to the so-called "point dipole approximation; the separation between the two charges of the dipole is much smaller than  $R$ .

Molecules consist of many electrical charges. The spatial arrangement of charges on a molecule may include monopole (total charge), dipole moment, quadrupole moment, etc. Some molecules can dissociate into ions, in which case the ions have nonzero charge. Even if the total charge of a molecule is zero, there can be dipole, quadrupole or higher-order multipole moments, depending on how charges are spatially arranged. These spatial arrangements interact among each other, as described in the previous section by the multipole expansion.

The *range of interaction* is determined by how rapidly the interaction energy falls off as function of the intermolecular separation  $R$ . Slowly decreasing dependences of the form  $1/R$ ,  $1/R^2$  and  $1/R^3$  are considered “long-range interactions” because they extend far in space, much farther than the molecular dimensions.  $1/R^4$ ,  $1/R^5$  and  $1/R^6$  etc. are considered “short-range interactions” because they fall off rapidly with  $R$ .

**2.2.1. Ion-Ion (Charge-Charge) Interaction.** In Section 2.1.4 the lowest-order term describes the interaction of net charges  $q_1, q_2$  (of molecules “1” and “2”) according to Coulomb’s law,  $V(R) = kq_1q_2/R$ , where  $k \approx 9 \times 10^9 \text{ N.m}^2/\text{C}^2$ . The interaction is isotropic (spherically symmetric), as there is no angle dependence, only a radial ( $R$ ) dependence.

**Example 2.4.** NaCl is made of two ions: for  $\text{Na}^+$  and  $\text{Cl}^-$  we take  $q_1 = -e$  and  $q_2 = e$ , with  $e = 1.6 \times 10^{-19} \text{ C}$ . In the gas phase the interatomic separation is  $0.236 \text{ nm}$  ( $2.36 \text{ \AA}$ ). The interaction energy is then:

$$V(R) = k \frac{q_1 q_2}{R} = -(9 \times 10^9 \text{ N.m}^2/\text{C}^2) \frac{(1.6 \times 10^{-19} \text{ C})^2}{0.236 \times 10^{-9} \text{ m}} \approx -10^{-18} \text{ J}.$$

Since  $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ , the magnitude  $10^{-18} \text{ J} \sim 6.1 \text{ eV}$ . This “binding energy” can be viewed as the energy required to break this molecule apart.

The Coulomb interaction is said to be a long-range force because it falls off slowly with distance ( $\sim 1/R$ ). Ion-ion forces are relevant to electrolyte solutions. Its magnitude can be as strong as a covalent bond. We note that the Coulomb force vector,  $\mathbf{F}$ , is directed along the axis of the two ions; so the force does not depend on molecular orientation.

To have ionic interactions, we need a metal attached to a non-metal. Let’s look at the example of NaCl. Sodium is the metal. When NaCl is dissolved in solution, we get the ions  $\text{Na}^+$  and  $\text{Cl}^-$ . Here, the metal is sodium, and the non-metal is chlorine (Fig. 2.14). The structure of NaCl crystal is shown in Fig. 2.15.

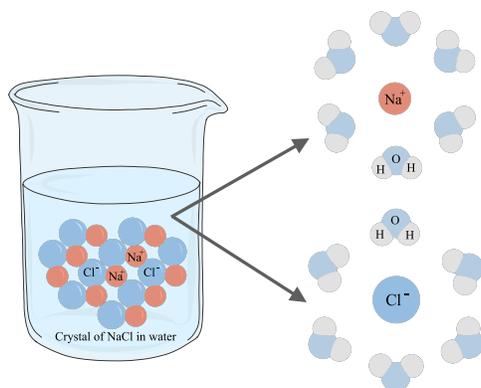


Figure 2.14. Dissolution of NaCl.

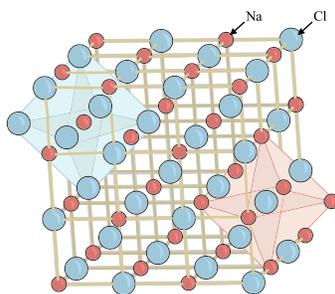


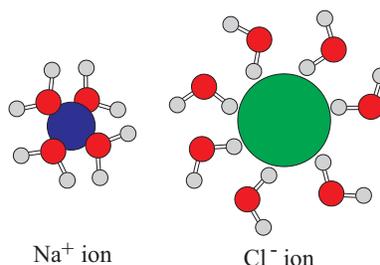
Figure 2.15. NaCl crystal.

### 2.3. Charge-Dipole Interaction

In Section 2.1.4, the next order term is the ion-dipole interaction, which depends on the angle between the dipole and the ion-dipole vector. When atoms in a molecule share electrons unequally, they create what is called a dipole moment. This occurs when one atom is more electronegative than another, resulting in that atom pulling more tightly on the shared pair of electrons, or when one atom has a lone pair of electrons and the difference of electronegativity vector points in the same way. One of the most common examples is the water molecule (Fig. 2.11), made up of one oxygen atom and two hydrogen atoms. The differences in electronegativity and lone electrons give oxygen a partial negative charge and each hydrogen a partial positive charge.

The interaction between a polar solvent molecule, such as water, and a dissolved ion is the most common case of ion-dipole interaction. This interaction energy scales as  $1/R^2$ , where  $R$  is the distance between the ion and

the dipole (with the dipole assumed to be a “point dipole”).<sup>7</sup> Figure 2.16 shows dissolved Na and Cl ions interacting with water dipoles. Positive ions ( $\text{Na}^+$ ) are attracted by the negative end of the dipole (the oxygen side of the  $\text{H}_2\text{O}$  molecule) and repelled by the positive end (H atoms); thus, the ( $\text{Na}^+$ ) ion is surrounded by a shell of water molecules whose oxygen (O) atoms are near the cation and whose hydrogen (H) atoms point outward into the solution (away from the cation). Likewise, the anion (here,  $\text{Cl}^-$ ) attracts the hydrogen atoms of the  $\text{H}_2\text{O}$  molecules, which are more positively charged than the oxygen atoms. The  $\text{H}_2\text{O}$  molecules are oriented around the anion in such a way that their negative ends (here, the O atoms of  $\text{H}_2\text{O}$ ) point away from the anion, and into the solution.



**Figure 2.16.** Ion-dipole interaction between  $\text{Na}^+$  and  $\text{Cl}^-$  ions and surrounding water molecules.

**Water Interacts With Dissolved Ions:** The water molecules have dipole moments; thus, the oxygen (O) atoms bear small, negative charges, whereas the hydrogen (H) atoms bear small, positive charges. (a) Positive ions are attracted to neighboring water molecules in aqueous solution by ion-dipole forces. (b) Negative ions form hydrogen bonds with water, with a nearly linear bond from O to H to the anion. (See Fig. 2.16.)

**2.3.1. Electrostatic Origin.** This interaction was derived in Section 2.1.4. Let us look at it from a different point of view. Consider a charge  $Q$  interacting with an electric dipole  $\mathbf{p} = q\mathbf{d}$  as shown in Fig. 2.17. The interaction energy is obtained from the Coulomb’s law: (self-interaction energy of the

<sup>7</sup>“Point dipole” in the present context means that the distance between the ion and any of the dipole’s charges is much larger than the length of the dipole itself (charge separation).

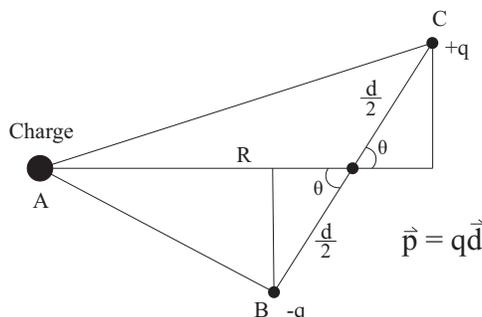


Figure 2.17. Ion-dipole interaction.

dipole is not included<sup>8</sup>)

$$V(\mathbf{R}) = -kqQ \left( \frac{1}{AB} - \frac{1}{AC} \right),$$

where (in the last step we make the *far-field* approximation  $R \gg d$ , such that only the first term inside the square root is kept)

$$AB = \sqrt{\left(R - \frac{1}{2}d \cos \theta\right)^2 + \left(\frac{1}{2}d \sin \theta\right)^2} \approx R - \frac{1}{2}d \cos \theta,$$

$$AC = \sqrt{\left(R + \frac{1}{2}d \cos \theta\right)^2 + \left(\frac{1}{2}d \sin \theta\right)^2} \approx R + \frac{1}{2}d \cos \theta.$$

Insert this into the expression for  $V$  and get:

$$\begin{aligned} V(\mathbf{R}) &= -kqQ \left( \frac{1}{R - \frac{1}{2}d \cos \theta} - \frac{1}{R + \frac{1}{2}d \cos \theta} \right) \\ &= -kqQ \left( \frac{d \cos \theta}{R^2 - \frac{1}{4}d^2 \cos^2 \theta} \right) \approx \frac{-kqQd \cos \theta}{R^2}. \end{aligned}$$

Thus, the charge-dipole energy is  $V(\mathbf{R}) = -\frac{kQp \cos \theta}{R^2}$ , which drops off as  $R^{-2}$  (inverse square law). Here,  $\cos \theta = \hat{\mathbf{R}} \cdot \hat{\mathbf{p}} \equiv \mathbf{R} \cdot \mathbf{p} / (|\mathbf{R}||\mathbf{p}|)$ .

**Example 2.5.** Suppose we have an aqueous solution with dissolved NaCl. What is the interaction energy between  $\text{Na}^+$  ions and water molecules? *Solutions:* This is an ion-dipole interaction. The  $\text{Na}^+$  and  $\text{Cl}^-$  ions are surrounded by water molecules. For sodium, complexes of the type  $[\text{Na}(\text{H}_2\text{O})_8]^+$

<sup>8</sup>Notice that we have not included a term for the Coulomb interaction of the dipole's charges  $+q$  and  $-q$ . This interaction is called the *self-energy* (of the dipole). Its inclusion causes conceptual difficulties, especially in the limit of a point dipole, where the self-energy causes singularities. We often sweep the self-energy under the rug and ignore it. For molecules, we are content with saying that they have finite size and the idealization of a point dipole is not needed. In this case, the self-energy contributes a constant term independent of  $R$ . (The zero of the energy is not important.)

form (with 8 water molecules bound to  $\text{Na}^+$  ions, on average), where the average Na-O distance is approximately 250 pm. According to Table 2.1 the permanent EDM of  $\text{H}_2\text{O}$  molecules is 1.85 D, where 1 D =  $3.336 \times 10^{-30}$  C.m. Using the formula,  $V(\mathbf{R}) = -\frac{kQp\cos\theta}{R^2}$ , we find that the interaction energy for each Na-O bond is:

$$\begin{aligned} V(\mathbf{R}) &= -\left(9 \times 10^9 \frac{\text{N.m}^2}{\text{C}^2}\right) \frac{(1.6 \times 10^{-19} \text{ C})(1.85 \times 3.336 \times 10^{-30} \text{ C.m})}{(250 \times 10^{-12} \text{ m})^2} \cos\theta \\ &= - (1.42 \times 10^{-19} \text{ J}) \cos\theta \end{aligned}$$

and since  $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ , this energy is  $\sim 0.9 \text{ eV}$ , about 7 times weaker than the interaction energy of NaCl. The factor  $\cos\theta$  has to do with orientation of the dipole relative to the ion-dipole vector. In solution, molecules tumble and this factor is averaged by rotations. For fixed orientation, and referring to Figure 2.17, we see that  $\theta = 0$  (dipole pointing away from the positive charge) has the lowest possible energy because the negative end of the dipole is closest to the  $\text{Na}^+$  ion. When  $\theta = \pi$ ,  $\cos\pi = -1$  and we have a state of high energy because  $\text{Na}^+$  repels the positive end of the dipole. When  $\theta = \pi/2$  or  $3\pi/2$ ,  $\cos\theta = 0$  and the interaction energy is zero (half-way point between the high energy and low energy states).

## 2.4. Dipole-Dipole Interaction

The dipole-dipole interaction can be thought of as describing the electrostatic coupling between the charges making up the dipoles. The dipole-dipole interaction falls off as  $\sim 1/R^3$ , which means that the force one dipole 1 due to dipole 2 falls off as  $1/R^4$ . This interaction energy is shorter range than the Coulomb interaction, but is still considered long-range.<sup>9</sup> The dipole-dipole interaction depends on the relative orientation of the two dipoles.

**2.4.1. Electrostatic Origin.** This interaction was derived in Section 2.1.4. Let us look at a slightly different method of derivation. Consider two dipoles

$$\mathbf{p}_A = q_A \vec{d}_A, \quad \mathbf{p}_B = q_B \vec{d}_B$$

interacting electrostatically, as shown in Fig. 2.18.

The interaction energy is obtained from Coulomb's law applied to all the charge pairs in the system ( $\mathbf{R} = \mathbf{r}_B - \mathbf{r}_A$ )

$$V(\mathbf{R}) = \frac{k(-q_A)(-q_B)}{|\mathbf{R}|} + \frac{k(-q_A)q_B}{|\mathbf{R} + \mathbf{d}_B|} + \frac{kq_A(-q_B)}{|\mathbf{R} - \mathbf{d}_A|} + \frac{kq_Aq_B}{|\mathbf{R} + \mathbf{d}_B - \mathbf{d}_A|}.$$

<sup>9</sup>Long range means that when integrated over all space, the integral of  $V(R)$  is finite and doesn't depend on the volume (which we denote here as  $vol$ ).  $1/r^3$  is long range because the integral  $\int_{vol} (1/r^3) d^3\vec{r}$  in spherical coordinates is  $(4\pi) \int_{vol} (1/r^3) r^2 dr \sim \int (1/r) dr \sim \log(vol)$ , which depends on volume ( $vol$ ). Integrals whose values depend on the volume of the region of integration are called *conditionally convergent*.

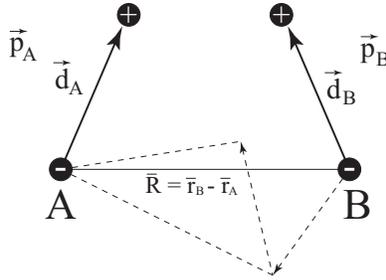


Figure 2.18. Two EDMs coupled electrostatically.

We then take the limit

$$|\mathbf{R}| \equiv |\mathbf{r}_A - \mathbf{r}_B| \gg |\mathbf{d}_A|, |\mathbf{d}_B|,$$

i.e., so we can neglect terms that are higher order in  $|\mathbf{d}_A|/|\mathbf{R}|$  and  $|\mathbf{d}_B|/|\mathbf{R}|$ , and expand the square roots as<sup>10</sup>

$$(1+x)^{-1/2} \approx 1 - \frac{x}{2} + \frac{3x^2}{8} + \dots$$

After some algebra, we get the famous result: (left as a homework exercise)

$$(2.4) \quad V(\mathbf{R}) = k \left\{ \frac{\mathbf{p}_A \cdot \mathbf{p}_B}{R^3} - \frac{3(\mathbf{p}_A \cdot \mathbf{R})(\mathbf{p}_B \cdot \mathbf{R})}{R^5} \right\}.$$

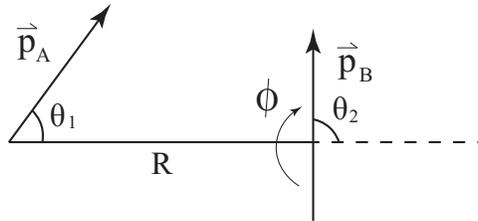


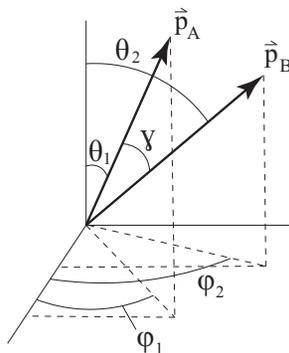
Figure 2.19. The relative orientation of two dipoles can be described using 3 angles:  $\theta_1, \theta_2$  and  $\phi$ . Both  $\theta_1$  and  $\theta_2$  are measured in-plane, whereas  $\phi$  is measured out-of-plane.

<sup>10</sup>The first term  $\frac{1}{|\mathbf{r}_A - \mathbf{r}_B|} = \frac{1}{|\mathbf{R}|} = \frac{1}{R}$  does not need to be expanded. The remaining three terms are the ones to be expanded. For example, the second term becomes:

$$\begin{aligned} \frac{1}{|\mathbf{R} + \mathbf{d}_B|} &= \frac{1}{|\mathbf{R} + \mathbf{d}_B|} = \frac{1}{\sqrt{R^2 + 2\mathbf{R} \cdot \mathbf{d}_B + d_B^2}} = \frac{1}{R} \frac{1}{\sqrt{1 + 2\mathbf{R} \cdot \mathbf{d}_B/R^2 + d_B^2/R^2}} \\ &\approx \frac{1}{R} \left[ 1 - (2\mathbf{R} \cdot \mathbf{d}_B/R^2 + d_B^2/R^2)/2 + 3(2\mathbf{R} \cdot \mathbf{d}_B/R^2 + d_B^2/R^2)^2/8 + \dots \right] \end{aligned}$$

where in the last line we have used the expansion  $(1+x)^{-1/2} \approx 1 - \frac{x}{2} + \frac{3x^2}{8} + \dots$

**2.4.2. Spherical Coordinates.** Equation (2.4) describes two dipoles  $\mathbf{p}_A$  and  $\mathbf{p}_B$  interacting according to the geometry shown in Fig. 2.19. Spherical coordinates will be useful later when we calculate angle-averaged interactions (see Fig. 2.20).



**Figure 2.20.** Alternative geometry to analyze the dipole-dipole interaction.

Using the identity:

$$\cos \gamma = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\varphi_1 - \varphi_2)$$

$V$  becomes: ( $\phi = \varphi_1 - \varphi_2$  since  $\hat{\phi} \cdot \hat{\theta} = 0$ )

$$V(\mathbf{R}) = k \left\{ \frac{p_A p_B}{R^3} [-2 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi] \right\}.$$

This follows from writing the first term as:

$$(2.5) \quad \frac{\mathbf{p}_A \cdot \mathbf{p}_B}{R^3} = \frac{p_A p_B \cos \gamma}{R^3} = \frac{p_A p_B}{R^3} \{ \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi \}$$

and the second term as

$$(2.6) \quad \frac{(\mathbf{p}_A \cdot \mathbf{R})(\mathbf{p}_B \cdot \mathbf{R})}{R^5} = \frac{(\mathbf{p}_A \cdot \hat{\mathbf{r}})(\mathbf{p}_B \cdot \hat{\mathbf{r}})}{R^3} = \frac{p_A p_B \cos \theta_1 \cos \theta_2}{R^3}$$

where  $\hat{\mathbf{r}} = \mathbf{R}/|\mathbf{R}|$ , and collecting the terms.

**Example 2.6.** Suppose we have two water molecules separated 3 Å apart and interacting (only) via the dipole-dipole interaction. What is the magnitude of this interaction? *Solution:* According to Table 2.1 the permanent EDM of H<sub>2</sub>O molecules is 1.85 D, where 1 D = 3.336 × 10<sup>-30</sup> C.m. The magnitude of the dipole-dipole interaction<sup>11</sup> is on the order of:

$$V(R) = k \frac{p_A p_B}{R^3} = (9 \times 10^9 \frac{\text{N.m}^2}{\text{C}^2}) \frac{(1.85 \times 3.336 \times 10^{-30} \text{ C.m})^2}{(5 \times 10^{-10} \text{ m})^3}$$

$$\approx 1.3 \times 10^{-20} \text{ J} \approx 0.08 \text{ eV}$$

<sup>11</sup>This formula is exact when  $\vec{p}_A$  and  $\vec{p}_B$  are parallel to each other (setting  $\gamma = 0$  in Eq. 2.5), and when  $\vec{p}_A$  and  $\vec{p}_B$  are both perpendicular to  $\vec{R}$  (setting  $\theta_1 = \theta_2 = 0$  in Eq. 2.6).

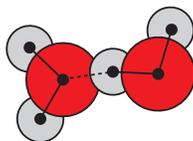
It is known from experiments that the hydrogen bond energy in water is 23.3 kJ/mol. The conversion to eV goes like this:

$$(23.3 \times 10^3 \frac{\text{J}}{\text{mol}}) \left( \frac{1 \text{ eV}}{1.6 \times 10^{-19} \text{ J}} \right) \left( \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \right) = 0.242 \text{ eV},$$

i.e. the conversion factor is 1 kJ/mol = 0.01037 eV. The dipole-dipole interaction only partially accounts for the interaction energy between pairs of water molecules. Covalent character is also present in the hydrogen bond.

## 2.5. Hydrogen Bonding

Hydrogen bonding is commonly found in water, between pairs of water molecules (Fig. 2.21), where the H atom bonds to the O atom of a neighboring molecule. The bond is partly ionic, due to the partial positive charge of the H atom and partial negative charge of the O atom, and partly covalent, due to the sharing of electrons from the oxygen's lone pair.



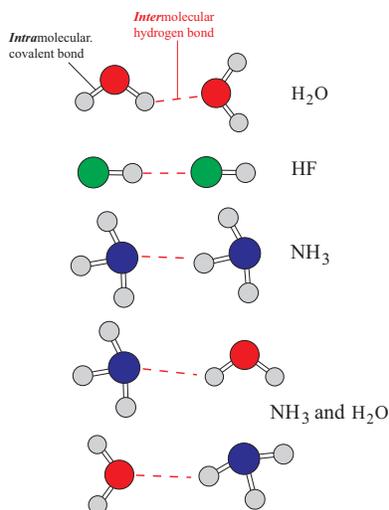
**Figure 2.21.** Hydrogen bonding between two water molecules.

Hydrogen (H) bonds can be thought of as especially strong dipole-dipole interactions involving the strongest electronegative elements of the periodic table. A hydrogen bond (H-bond) is the interaction between two polar groups that occurs when a hydrogen (H) atom covalently bound to a small, highly electronegative atom such as nitrogen (N), oxygen (O), or fluorine (F) experiences the electric field of another highly electronegative atom nearby. (Remember: FON.)

The molecule itself must possess either a N-H, N-O or N-F bond for this to work. As an example, H<sub>2</sub>O can undergo hydrogen bonding because it has H-O bonds. The H-bond itself will occur between pairs of neighboring H<sub>2</sub>O molecules. On the other hand, CH<sub>3</sub>F does not H-bond because there are no H-F bonds (CH<sub>3</sub>F only possesses C-F and H-C bonds).

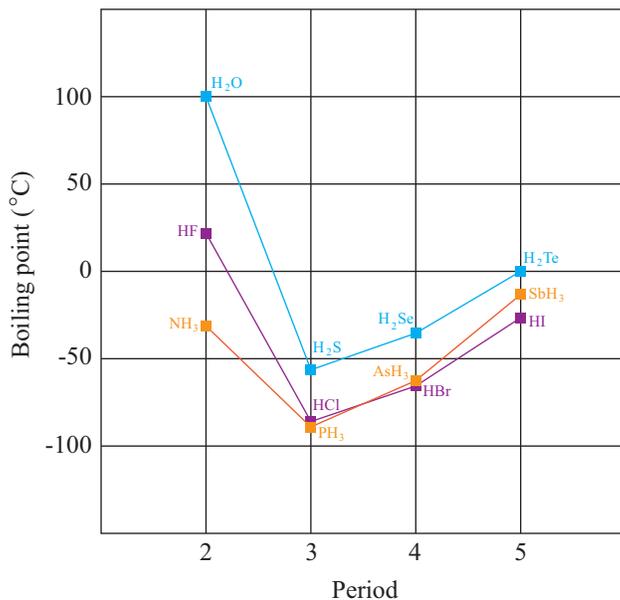
The H-bond is strong because the dipole is strong. The dipole is strong due to the large difference in electronegativity; the H-atom does not possess any core electrons to shield its positive charge.

Hydrogen bonding is typically stronger than VDW interactions, but weaker than covalent or ionic bonds. H-bonds can be intramolecular (within the same molecule) or intermolecular (between different molecules). Intermolecular hydrogen bonding is responsible for the high boiling point of water



**Figure 2.22.** Examples of hydrogen bonding.

(100°C) compared to the other group 16 hydrides that have much weaker hydrogen bonds. Intramolecular hydrogen bonding is partly responsible for the secondary and tertiary structures of proteins and nucleic acids. It also plays an important role in the structure of polymers, both synthetic and natural.

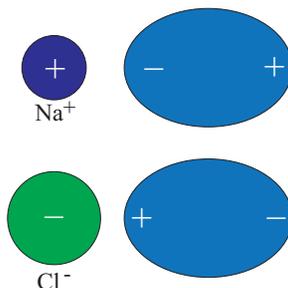


**Figure 2.23.** Effect of hydrogen bonding on boiling point. Group 15 (orange), 16 (blue) and 17 (purple) elements are compared.

The examples of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{HF}$  are shown in Fig. 2.22. Hydrogen bonding can also occur between different types of molecules, as shown in the last two lines in Fig. 2.22 (the case of intermolecular  $\text{NH}$  and  $\text{HO}$  bonding). Finally, we note that the boiling point is strongly affected by hydrogen bonding, as shown in Fig. 2.23. If  $\text{H}_2\text{O}$  did not possess the ability to form hydrogen bonds, its boiling point would likely be below  $-50^\circ\text{C}$ .

## 2.6. Ion-Induced Dipole

Ion-dipole interactions can also be found in non-polar solvents. We call these “ion-induced dipole” or “charge-induced dipole”. In that case, it is the ion’s electric field that induces a dipole moment in neighboring solvent molecules (electric polarization was explained in Section 2.1.2). This situation is illustrated in Fig. 2.24. We note that molecules can be polarized regardless of whether or not they already possess an EDM. In the case where the molecule has an EDM, the polarization would be an additional (albeit smaller) effect. So the ion-induced dipole interaction is present regardless of the existence of a permanent EDM.



**Figure 2.24.** Ion-induced dipole interaction.

When a molecule of polarizability  $\alpha$  is at distance  $R$  from an ion of charge  $ze$ , the electric field of the ion  $E = ze/4\pi\epsilon_0 R^2$  (electric charge is often written as a multiple of the elementary charge:  $q = ze$ ) will induce in the molecule a dipole moment of

$$p = \alpha E = \frac{\alpha ze}{4\pi\epsilon_0 R^2}$$

Here,  $\alpha$  is given in units of  $(4\pi\epsilon_0)\text{\AA}^3 = (4\pi\epsilon_0)10^{-30} \text{ m}^3 = 1.11 \times 10^{-40} \text{ C}^2\text{m}^2\text{J}^{-1} = 1.11 \times 10^{-40} \text{ C}\cdot\text{m}^2/\text{V}$  since 1 Joule = 1 Coulomb times Volt (1 J=1 C.V). (See Table 2.5.)

Let us look at the magnitude of this interaction. We shall estimate the distance by which the electron cloud of a methane ( $\text{CH}_4$ ) molecule is shifted relative to the center of the molecule due to the presence of a bare sodium ion whose center is 0.4 nm from the center of the molecule.

For a monovalent ion such as  $\text{Na}^+$ , the electric field at a distance of 0.4 nm from its center is

$$E = \frac{e}{4\pi\epsilon_0 R^2} = \frac{(1.602 \times 10^{-19})}{(4 \times 3.142 \times 8.854 \times 10^{-12})(0.4 \times 10^{-9})^2} = 9.0 \times 10^9 \text{ V/m}$$

The induced dipole moment on a methane molecule (see Table 2.5 for polarizability of  $\text{CH}_4$ ) is therefore,

$$\begin{aligned} p &= \alpha E = \underbrace{4\pi\epsilon_0(2.6 \times 10^{-30})}_{\text{Table 2.5}}(9.0 \times 10^9) = 2.60 \times 10^{-30} \text{ C.m} \\ &= 2.60 \times 10^{-30} / 3.336 \times 10^{-30} = 0.78 \text{ D.} \end{aligned}$$

Since a dipole moment is *charge*  $\times$  *distance*, this corresponds to a unit charge separation in the molecule of  $d = p/e = 0.016$  nm, which is about 8% of the molecular radius of methane (of 0.2 nm).

From this calculation, the induced dipole moment can be on the order of 1 Debye, which is quite large. We may therefore anticipate that the forces associated with induced dipole moments can also be large.

The scenario is the following. An ion is adjacent to a molecule, including a dipole moment  $p$ . The electric field of the induced dipole (which will act on the ion) is<sup>12</sup>

$$E(R) = -\frac{2p}{4\pi\epsilon_0 R^3} = -\frac{2\alpha E}{4\pi\epsilon_0 R^3} = -\frac{2\alpha(ze)}{(4\pi\epsilon_0)^2 R^5}$$

so that the attractive force and energy are:

$$\begin{aligned} F(R) &= (ze)E(R) = -\frac{2\alpha(ze)^2}{(4\pi\epsilon_0)^2 R^5}, \\ V(R) &= -\int_{\infty}^R F(r)dr = -\frac{\alpha(ze)^2}{2(4\pi\epsilon_0)^2 R^4} = -\frac{1}{2}\alpha E^2. \end{aligned}$$

where  $E(R) = ze/2\pi\epsilon_0 R^2$  is the field acting on the molecule. Thus,

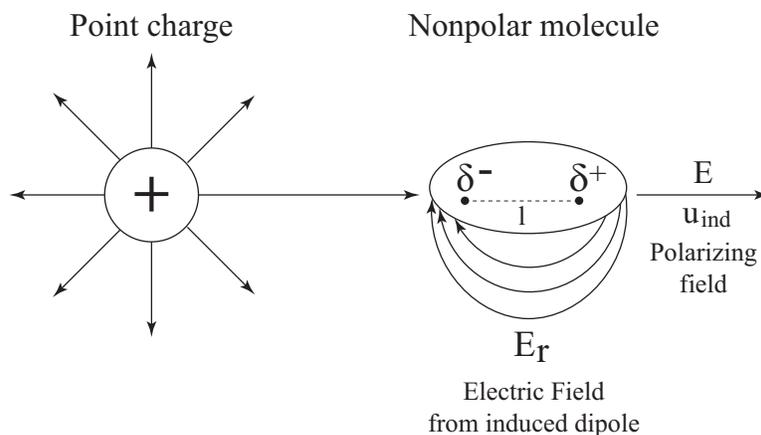
$$\boxed{V(\mathbf{R}) = -\frac{\alpha(ze)^2}{2(4\pi\epsilon_0)^2 R^4}}$$

The situation is illustrated in Fig. 2.25.

## 2.7. Ion-Quadrupole Interaction: Cation- $\pi$

An example of the ion-quadrupole interaction ( $V(R) \sim 1/R^3$ ) is the cation- $\pi$  interaction, which involves an electron-rich  $\pi$  system (e.g. benzene, ethylene, acetylene) and an adjacent cation (e.g.  $\text{Li}^+$ ,  $\text{Na}^+$ ). This interaction can be as strong as hydrogen bonding and salt bridges in proteins. Cation- $\pi$

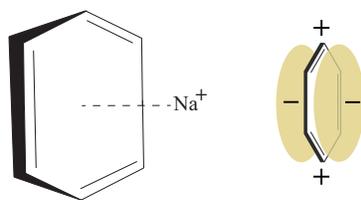
<sup>12</sup>The electric field of a dipole is  $\mathbf{E} = \frac{1}{4\pi\epsilon_0} \left( \frac{3(\mathbf{p} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{p}}{R^3} \right)$ .



**Figure 2.25.** Ion-induced dipole interaction.

interactions play important roles in protein structure, molecular recognition and enzyme catalysis.

Take the example of benzene. It has no permanent dipole moment because all dipoles (CH bonds) are weak and their interactions vanish due to symmetry. However, the  $\pi$  electrons above and below the benzene ring create a negative charge, which counterbalances the positive charge in the plane of the benzene ring. This leads to a quadrupole moment. The negative  $\pi$  electrons interact with the cation nearby, leading to the cation- $\pi$  interaction, which is a type of ion-quadrupole interaction. See Fig. 2.26.



**Figure 2.26.** Ion-quadrupole interaction: benzene interacting with  $\text{Na}^+$  ion (left). Benzene possesses an electric quadrupole moment (right).

## 2.8. Quadrupole-Quadrupole: $\pi$ -Stacking

$\pi$ -stacking is an example of quadrupole-quadrupole interaction. The benzene dimer is capable of quadrupole-quadrupole interaction because each benzene ring contains  $\pi$  electron clouds. These interactions are important in nucleobase stacking within DNA and RNA molecules, protein folding and molecular recognition. Three different conformations of the benzene dimer are shown in Fig. 2.27.

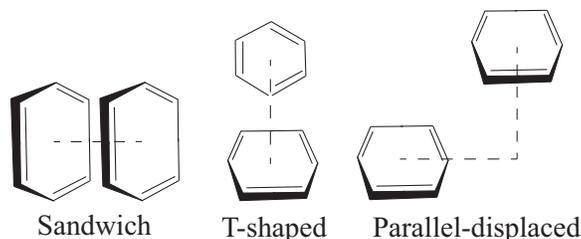


Figure 2.27. Three different conformations of the benzene dimer

## 2.9. Van Der Waals Force

Van Der Waals (VDW) interactions, which behave as  $V(\mathbf{R}) \sim 1/R^6$ , describe “dynamical effects” arising from quantum fluctuations, induced dipoles and molecular tumbling.  $1/R^6$  interactions include 3 contributions:

- London dispersion forces: Of quantum mechanical origin, they are a type of “induced dipole-induced dipole” interaction whereby dynamic motions of charge distributions around the molecule lead to a temporary dipole moment. Such a temporary dipole on one molecule will induce a temporary dipole in the other molecule. Example (He): For a non polar atom such as helium, the time average of its dipole moment is zero, but at any instant there exists a finite dipole moment given by the instantaneous positions of the electrons about the nucleus. This instantaneous dipole generates an electric field that polarizes any nearby neutral atom, inducing a dipole moment in it. The resulting interaction between the two dipoles gives rise to an instantaneous attractive force between the two atoms, and the time average of this force is finite. The overall dependence is  $1/R^6$ :

$$V(\mathbf{R}) = \frac{3}{2} \frac{\alpha_1 \alpha_2}{(4\pi\epsilon_0)^2 R^6} \frac{I_1 I_2}{(I_1 + I_2)}$$

where  $\alpha_1$  and  $\alpha_2$  are the polarizabilities of the two molecules,  $I_1$  and  $I_2$  are the first ionization potentials of the molecules,

- Keesom force: When molecules have permanent dipole moments and tumble, the Keesom force (derived in Section 2.10) is defined as the motionally-averaged dipole-dipole interaction. While static dipole-dipole interactions behave as  $V(R) \sim 1/R^3$ , the motionally-averaged interaction is weaker and  $V(R) \sim 1/R^6$ . It is the angular dependent part of the dipole-dipole interaction that causes a weakening of the dipole-dipole interaction.
- Debye force: A molecule with a permanent dipole moment (such as HCl or H<sub>2</sub>O) adjacent to a non-polar molecule can induce a dipole moment in the non-polar molecule. These two dipoles (permanent dipole-induced dipole) interact together, giving rise to the Debye force (see Section 2.12).

The strength of the induced dipole depends on the polarizability of the non-polar molecule.

By far, London dispersion forces comprise the largest and most important contribution to VDW forces. Because of this, VDW forces are often referred to as “London dispersion forces” interchangeably. In reality, Keesom and Debye forces can also contribute to the  $1/R^6$  dependence.<sup>13</sup>

Approximate contributions of the dispersion to the total intermolecular interaction energy are shown in Table 2.6.

**Table 2.6.** Contribution of the dispersion to the total intermolecular interaction energy.

Molecule pair	% of the total energy of interaction
Ne-Ne	100
CH <sub>4</sub> -CH <sub>4</sub>	100
HCl-HCl	86
HBr-HBr	96
HI-HI	99
CH <sub>3</sub> Cl-CH <sub>3</sub> Cl	68
NH <sub>3</sub> -NH <sub>3</sub>	57
H <sub>2</sub> O-H <sub>2</sub> O	24
HCl-HI	96
H <sub>2</sub> O-CH <sub>4</sub>	87

Source: [https://en.wikipedia.org/wiki/London\\_dispersion\\_force](https://en.wikipedia.org/wiki/London_dispersion_force)

### 2.9.1. Factors Affecting the Strength of London Dispersion Forces.

Dispersion forces are a mutual interaction between the polarizable charge distributions on two separate molecules, and they are always attractive. Very often, dynamic motions of charge around the molecule lead to a temporary dipole moment. Such a temporary dipole on one molecule will induce a temporary dipole in the other molecule. These transient, fluctuating dipoles attract one another in much the same way as do permanent dipoles.

Figure 2.28 provides a simple view of the source of this interaction. The polarizability increases with the number of electrons in the atom or molecule. Heavier atoms or molecules interact more strongly by dispersion forces than do lighter ones. These electrons are less strongly bound than those of the lighter elements, because they are shielded from the full attraction of the nucleus by intervening electrons. Consequently, they are more easily distorted by external fields of neighboring dipoles. Dispersion forces provide the attractive,  $1/R^6$ , term in the Lennard-Jones potential.

<sup>13</sup>Keesom and Debye interactions are not always present because they require permanent dipoles and sufficient polarizability (in the case of Debye). Not every molecule meet such criteria.

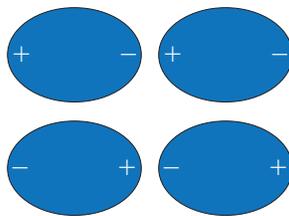


Figure 2.28. London interaction.

A fluctuation of the electron distribution on one atom induces a corresponding temporary dipole moment on a neighboring atom. The two dipole moments interact to give a net attractive force, called a “dispersion force.”

There are three main factors affecting the strength of London dispersion forces:

- **Contact area:** the closer we can bring two molecules together, get their electron clouds to touch, the stronger the dispersion force will be. For example, *n*-pentane has stronger dispersion forces than neopentane (Fig. 2.29), even though they have the same number and types of atoms. The *n*-pentane is shaped like a column (as opposed to spheres, as is the case for neopentane) and makes better contact with other like molecules. Thus, the boiling point of *n*-pentane will be higher than neopentane.

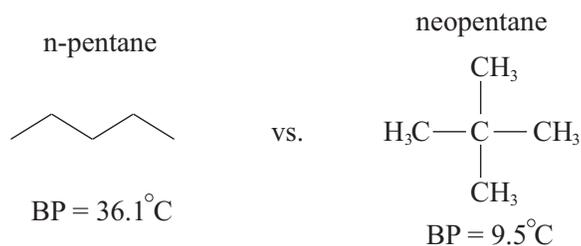


Figure 2.29. Boiling points of *n*-pentane vs neopentane.

- **Polarizability:** the more electrons we have, the stronger the polarizability of the molecule. Thus, molecular size matters. Think about proteins (very large molecules). Much of their 3D shapes originate from London dispersion forces. Another example is halogens going down the rows: F, Cl, Br, I. At ambient temperatures, F and Cl are gases, Br is a liquid and Iodine is a solid. As the atoms get bigger, they have more electrons, and the stronger the dispersion forces are.

Example: Silk Fibroin. Fibroin is the main protein in silk from moths and spiders. It consists of antiparallel  $\beta$ -sheet structure (Fig. 2.30). It

has small side chains (Ala and Gly) that allow the close packing of sheets. Its structure is stabilized by: 1) hydrogen bonding within sheets and 2) London dispersion interactions between the sheets:

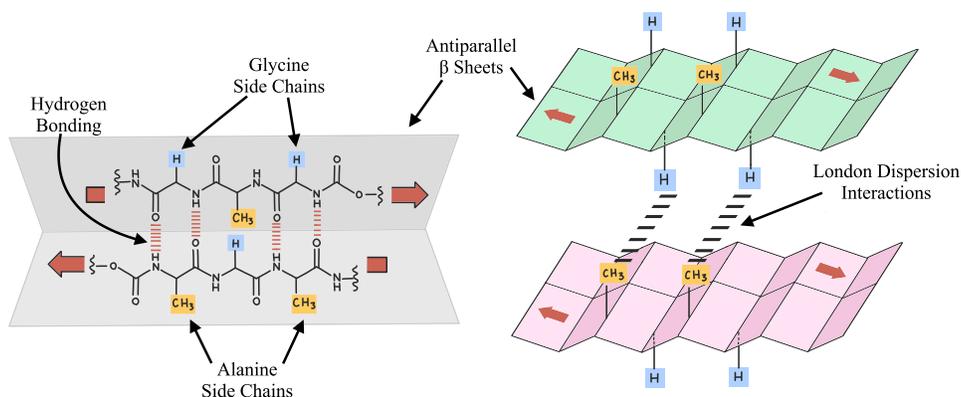


Figure 2.30. Structure of silk fibroin.

Note: for proteins, several interactions matter. These include: 1) the hydrophobic effect, 2) hydrogen bonding (peptide bond N-H and C=O interact to yield  $\alpha$ -helices and  $\beta$ -sheets), 3) London dispersion and 4) electrostatic interactions, such as interactions between permanently charged groups, e.g., salt bridges stabilize the protein.

- Pi-bonding: molecules with  $\pi$ -bonding will exhibit stronger London dispersion forces (Fig. 2.31).

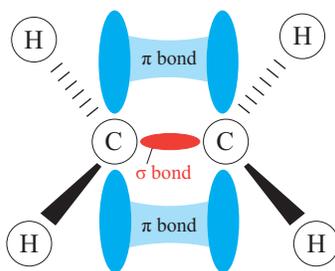


Figure 2.31.  $\pi$ -bonding.

## 2.10. Thermal Averaging of Intermolecular Interactions

When the interaction energy falls below  $k_B T$  the dipoles can rotate more or less freely. We are then interested in the Boltzmann average of these

interactions over the angles. At room temperature we have

$$k_B T \approx 0.03 \text{ eV} \sim 4 \cdot 10^{-21} \text{ J.}$$

We define the thermal average energy by angle-averaging the Boltzmann factor corresponding to some interaction energy  $V(R, \Omega)$  (Ref. [2]):

$$e^{-V(R)/k_B T} \equiv \left\langle e^{-V(R, \Omega)/k_B T} \right\rangle = \frac{\int e^{-V(R, \Omega)/k_B T} d\Omega}{\int d\Omega}$$

In spherical coordinates the solid angle element is  $d\Omega = \sin \theta d\theta d\phi$ , where  $\theta, \phi$  are polar and azimuthal angles, respectively. Thus,

$$e^{-V(R)/k_B T} \equiv \left\langle e^{-V(R, \Omega)/k_B T} \right\rangle = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi e^{-V(R, \theta, \phi)/k_B T} \sin \theta d\theta$$

When calculating such integrals the following results are useful<sup>14</sup>:

$$\langle \cos^2 \theta \rangle = \frac{1}{4\pi} \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi = \frac{1}{2} \int_{-1}^1 x^2 dx = \frac{1}{3}.$$

$$\langle \sin^2 \theta \rangle = \frac{1}{4\pi} \int_0^\pi \sin^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi = \frac{2}{3}$$

$$\langle \sin^2 \phi \rangle = \langle \cos^2 \phi \rangle = \frac{1}{2}$$

$$\langle \sin \theta \rangle = \langle \cos \theta \rangle = \langle \sin \theta \cos \theta \rangle = 0$$

$$\langle \sin \phi \rangle = \langle \cos \phi \rangle = \langle \sin \phi \cos \phi \rangle = 0$$

Averaging over the angles implies that the system (e.g. charge-dipole or dipole-dipole) samples all possible angles over some time period<sup>15</sup>.

When  $V$  is less than  $k_B T$  we may Taylor expand the exponential

$$e^{-V(R)/k_B T} = 1 - \frac{V(R)}{k_B T} + \dots = \left\langle 1 - \frac{V(R, \Omega)}{k_B T} + \frac{1}{2} \left( \frac{V(R, \Omega)}{k_B T} \right)^2 - \dots \right\rangle$$

<sup>14</sup>These are obtained using trigonometric identities or tables of integration. For example, the second relation follows from

$$\int \sin^3(ax) dx = \frac{\cos 3ax}{12a} - \frac{3 \cos ax}{4a} + C$$

<sup>15</sup>Instead of computing the time-average of some quantity, we invoke the idea of the ensemble average through the ergodic theorem

$$\frac{1}{T} \int_0^T (\cdot) dt \approx \frac{1}{vol} \int (\cdot) d^3 \vec{r},$$

where  $vol$ =volume (of some region of space comprising the ensemble of molecules). The left hand side is the time average of some quantity and the right hand side is the average of that quantity across an ensemble of molecules. The validity of the ergodic theorem is discussed in statistical mechanics and will not concern us here except to say that the ensemble average is used here by invoking the Boltzmann distribution.

## 2.11. Keesom Interaction (permanent dipole-permanent dipole, thermally averaged) 87

Thus,

$$V(R) = \left\langle V(R, \Omega) - \frac{V(R, \Omega)^2}{2k_B T} + \dots \right\rangle$$

Example: 1) Charge-dipole interaction: we recall the geometric picture for this interaction (Fig. 2.17) and the expression for its interaction energy

$$V(\mathbf{R}) = -\frac{qp \cos \theta}{4\pi\epsilon_0 R^2}.$$

Performing the thermal averaging we find:

$$V(R) = \left\langle \underbrace{-\frac{qp \cos \theta}{4\pi\epsilon_0 R^2}}_{\langle \cos \theta \rangle = 0} - \left( \frac{qp}{4\pi\epsilon_0 R^2} \right)^2 \frac{\cos^2 \theta}{2k_B T} + \dots \right\rangle = -\frac{q^2 p^2}{6(4\pi\epsilon_0)^2 k_B T R^4} \sim \frac{1}{R^4}$$

for  $k_B T > qp/(4\pi\epsilon_0 R^2)$ .

2) Dipole-dipole interaction: we recall the geometric picture for this interaction (Fig. 2.19) and its interaction energy in spherical coordinates (see Section 2.4.2 for derivation)

$$V(\mathbf{R}) = \frac{k p_A p_B}{R^3} \{-2 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi\}.$$

The first order term vanishes since  $\langle \cos \theta_1 \rangle = 0$ , etc. The second order term does not vanish and equals

$$\begin{aligned} V(R) &= \left\langle -\frac{k^2 p_A^2 p_B^2}{2R^6 k_B T} \left( \underbrace{4 \cos^2 \theta_1}_{1/3} \underbrace{\cos^2 \theta_2}_{1/3} + 0 + \underbrace{\sin^2 \theta_1}_{2/3} \underbrace{\sin^2 \theta_2}_{2/3} \underbrace{\cos^2 \phi}_{1/2} \right) + \dots \right\rangle \\ &= -\frac{k^2 p_A^2 p_B^2}{3k_B T R^6} \end{aligned}$$

for  $k_B T > k p_A p_B / R^3$ . Note: we did not include the cross term

$$-4 \cos \theta_1 \cos \theta_2 \sin \theta_1 \sin \theta_2 \cos \phi$$

since it is zero (because  $\langle \cos \theta_1 \rangle = 0$ , etc.). This is the *Keesom interaction* and it scales as  $\sim 1/R^6$ . The Keesom interaction is 1 of 3 different contributions to the VDW interaction.

### 2.11. Keesom Interaction (permanent dipole-permanent dipole, thermally averaged)

The Keesom interaction, which was derived in Section 2.10, is due to the interaction of permanent dipoles. It is temperature dependent. Such interactions consist of attractive interactions between an ensemble of dipoles that are averaged over different rotational orientations of the dipoles. It is assumed that the molecules are constantly rotating and are never get locked. The energy of a Keesom interaction depends on the inverse sixth power of the

distance, unlike the interaction energy of two spatially fixed dipoles, which depends on the inverse third power of the distance. The Keesom interaction can only occur among molecules that possess permanent dipole moments, i.e., two polar molecules. Also, Keesom interactions are very weak VDW interactions and do not occur in aqueous solutions that contain electrolytes. The angle-averaged interaction is given by:

$$V(\mathbf{R}) = \frac{-m_1^2 m_2^2}{24\pi^2 \epsilon_0^2 \epsilon^2 (k_B T) R^6},$$

where  $m$  is the charge per unit length and  $\epsilon$  is the dielectric constant of surrounding medium ( $\epsilon = 1$  for vacuum).

This force is inversely proportional to temperature. At low temperatures the dipoles want to be in the energetically favorable “ground state” whereas at high temperature they are found in random orientations (where the forces cancel out on average), causing a weakening of the force.

### 2.12. Debye Force (Dipole-Induced Dipole)

The interaction of a polar molecule with a non polar molecule is analogous to the ion-induced dipole interaction. Suppose that we have a fixed dipole  $p$  with orientation  $\theta$  with respect to the line joining it to a polarizable molecule, the electric field of the dipole acting on the molecule is (omitting the angular factor and other factors),  $E \propto R^{-3}$ , which means that the interaction energy is

$$(2.7) \quad V(R, \theta) = -\frac{1}{2} \alpha E^2 \propto \frac{\alpha}{R^6}$$

For two molecules possessing permanent dipole moment  $p_1$  and  $p_2$  and polarizabilities  $\alpha_1$  and  $\alpha_2$ , their net dipole-induced dipole energy is

$$V(\mathbf{R}) = -\frac{[p_1^2 \alpha_2 + p_2^2 \alpha_1]}{(4\pi\epsilon_0)^2 R^6}$$

This Debye interaction is one of three inverse sixth power contributions to the total VDW interaction energy between molecules.

The Debye force is an *angle averaged interaction* because it arises from interactions between *rotating permanent dipoles* and from the polarizability of atoms and molecules (induced dipoles). These induced dipoles occur when one molecule with a permanent dipole repels another molecule’s electrons. A molecule with permanent dipole can induce a dipole in a similar neighboring molecule and cause mutual attraction. Debye forces cannot occur between atoms, because atoms do not possess permanent electric dipole moments. The forces between induced and permanent dipoles are not as temperature dependent as Keesom interactions because the induced dipole is free to shift

and rotate around the non-polar molecule. The Debye induction effects and Keesom orientation effects are termed polar interactions.

One example of an induction-interaction between permanent dipole and induced dipole is the interaction between HCl and Ar. In this system, Ar experiences a dipole as its electrons are attracted (to the H side of HCl) or repelled (from the Cl side) by HCl.

This kind of interaction can be expected between any polar molecule and non-polar/symmetrical molecule. The induction-interaction force is far weaker than dipole-dipole interaction, but can be stronger than the London dispersion force, depending on the strength of the dipoles involved.

### 2.13. Boltzmann-Weighted Interactions

Here is an alternative approach to deriving thermally averaged interaction energies. It gives almost the same result as the previous method. We all agree that the interaction energy,  $V(R, \Omega)$ , should be averaged over the angles in some way (i.e. over the unit sphere). We also know that some angles are more likely than others, because certain configurations of the dipole-dipole interaction are lower in energy than others. It makes sense to weigh these angles more heavily in the average. This can be done using the Boltzmann factor:

$$V(R) = \frac{\langle V(R, \Omega) e^{-V(R, \Omega)/k_B T} \rangle}{\langle e^{-V(R, \Omega)/k_B T} \rangle} \equiv \frac{\int V(R, \Omega) e^{-V(R, \Omega)/k_B T} d\Omega}{\int e^{-V(R, \Omega)/k_B T} d\Omega},$$

where the denominator,  $\langle e^{-V(R, \Omega)/k_B T} \rangle$ , is a normalization factor.

Here,  $\Omega$  denotes any set of spherical angles, depending on the nature of the problem we want to solve. The ion-dipole interaction, for example, requires only one such set of angles whereas the dipole-dipole interaction requires two sets of spherical angles. Suppose that there are two sets of angles involved,  $\Omega = (\Omega_1, \Omega_2) = (\theta_1, \phi_1, \theta_2, \phi_2)$  then  $\Omega$  is shorthand notation for all spherical angles. The integral is over all unit spheres associated with each set of angles. For example, if  $\Omega \equiv (\Omega_1, \Omega_2) = (\theta_1, \phi_1, \theta_2, \phi_2)$ , then  $\int d\Omega$  stands for:

$$\int d\Omega = \int_0^\pi \sin \theta_1 d\theta_1 \int_0^\pi \sin \theta_2 d\theta_2 \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2.$$

In the high-temperature regime ( $V < k_B T$ ) we may employ a Taylor expansion for the exponential. The denominator approaches 1 if we keep only the zeroth order term  $e^{-V(R, \Omega)/k_B T} \approx 1$ . The numerator is expanded in powers of  $V/k_B T$ :

$$V(R) = \langle V(R, \Omega) \underbrace{e^{-V(R, \Omega)/k_B T}}_{\text{expand}} \rangle \approx \left\langle V(R, \Omega) \left( 1 - \frac{V(R, \Omega)}{k_B T} + \dots \right) \right\rangle$$

Substituting the dipole-dipole energy (see Section 2.4.2 for derivation)

$$V(\mathbf{R}) = (kp_{APB}/R^3)\{-2 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi\}$$

into this expression, the lowest order term  $\langle V(R, \Omega) \rangle$  vanishes for the same reasons as before<sup>16</sup>. The next order term gives

$$\begin{aligned} V(R) &= - \left\langle \frac{V(R, \Omega)^2}{k_B T} + \dots \right\rangle \\ &= - \frac{k^2 p_A^2 p_B^2}{(k_B T) R^6} \left\langle \underbrace{4 \underbrace{\cos^2 \theta_1}_{1/3} \underbrace{\cos^2 \theta_2}_{1/3} + 0 + \underbrace{\sin^2 \theta_1}_{2/3} \underbrace{\sin^2 \theta_2}_{2/3} \underbrace{\cos^2 \phi}_{1/2}}_{2/3} \right\rangle \end{aligned}$$

So,

$$V(R) = - \frac{2k^2 p_A^2 p_B^2}{3(k_B T) R^6}.$$

We are off by a factor of 2 but otherwise have obtained the correct formula with the  $1/R^6$  dependence.

## 2.14. $k_B T$ vs Interaction Strength

In the previous section, the Boltzmann factor is used to weigh the angles according to their energies. Angles that lead to lower energy configurations weigh more heavily: the Boltzmann factor,  $e^{-V/k_B T}$ , involves comparing the interaction energy strength  $V(R, \Omega)$  for a given angle configuration  $\Omega = (\theta, \phi)$  to  $k_B T$ . If  $V(R, \Omega)$  is small compared to the magnitude of  $k_B T$  (0.03 eV at room temperature), then the Boltzmann factor is large. Otherwise, its magnitude is small (compared to 1).

## 2.15. Relative Strengths of Intermolecular Forces

Table 2.7 gives typical dissociation energies ( $E_d$ ) for different types of bonds. It is best to think of these values as “typical” values, i.e. orders of magnitude. The actual strengths will vary depending on the molecules involved. Ionic bonding and covalent bonding will always be stronger than intermolecular forces in any given substance. To determine whether ionic bonding occurs, we must have a metal bound to a non-metal, e.g. NaCl.

The main intermolecular forces are summarized in Table 2.8.

<sup>16</sup>Recall:  $\langle \cos^2 \theta \rangle = 1/3$ ,  $\langle \sin^2 \theta \rangle = 2/3$ ,  $\langle \sin^2 \phi \rangle = \langle \cos^2 \phi \rangle = 1/2$  and  $\langle \sin \theta \rangle = \langle \cos \theta \rangle = 0$ ,  $\langle \sin \theta \cos \theta \rangle = 0$ ,  $\langle \sin \phi \rangle = \langle \cos \phi \rangle = 0$ ,  $\langle \sin \phi \cos \phi \rangle = 0$

**Table 2.7.** Typical dissociation energies for different types of chemical bonds. 1 cal = 4.184 J. 1 eV =  $1.6 \times 10^{-19}$  J.

Bond type	$E_d$ (kcal/mol)	$E_d$ (kJ/mol)	$E_d$ (eV)
Interatomic (intramolecular) bonds			
Ionic lattice (solid)	250-4,000	1,046-16,736	11-173
Ionic (molecular)	80-251	335-1,050	3.5-10.9
Covalent bond	15-260	63-1,088	0.653-11.2
Metallic	26.3-83.7	110-350	1.14-3.63
Intermolecular bonds			
Hydrogen bond	1-12	4.2-50.2	0.04-0.52
Dipole-dipole (excluding H-bond)	0.5-5.0	2.1-21	0.022-0.218
London dispersion	<1 to 15	<4.2-62.8	<0.04-0.65
Dipole-induced dipole	~0.48	~2.0	~0.021

## 2.16. Hard Sphere and Lennard-Jones Potentials

Insights into the physics of liquids, gases and solids have often come from computer simulations. Some of the very first scientific computer simulations back in the 1950s studied the hard-sphere (HS) liquid.

The hard-sphere potential is defined as:

$$V(\mathbf{R}) = \begin{cases} +\infty & R < a \\ 0 & R \geq a \end{cases}$$

where  $a$  is the distance of closest approach, twice the molecular radius and  $R = \mathbf{R}/|\mathbf{R}|$ . This potential only models the repulsive core, but no attractive tail. Because of the abrupt transition at  $r = a$  it describes perfectly non-overlapping spheres. The HS potential has proved valuable in the study of sphere packings. HS exhibit a fluid-solid phase transition at sufficiently high densities. An early surprise was that the HS system has a first-order freezing transition.

The simplest liquid models<sup>17</sup> are defined by pair potentials,  $V(\mathbf{R})$ . If  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$  is the distance between particles  $i$  and  $j$ , the potential energy  $V$  as a function of all particle coordinates is given by

$$V(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i < j} V(r_{ij}).$$

<sup>17</sup>We call them “liquid models” because in gases we mostly neglect collisions; thus the intermolecular potentials are not so important. In solids, these spherically symmetric models are not suitable because they fail to describe the many different possible spatially ordered arrangements in crystals. More sophisticated models are needed which describe reduced symmetry.

Table 2.8. Most common intermolecular forces. Source: Israelachvili [2]

Type of Interaction	Diagram	Interaction Energy
Covalent, Metallic		Complicated, short range
Charge-Charge		$+Q_1 Q_2 / 4\pi\epsilon_0 r$ (Coulomb Energy)
Charge-Dipole	(fixed)	$-Qp \cos \theta / 4\pi\epsilon_0 r^2$
	(freely rotating)	$-Q^2 p^2 / 6(4\pi\epsilon_0)^2 kT r^4$
Dipole-Dipole	(fixed)	$-p_1 p_2 (2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\phi) / 4\pi\epsilon_0 r^3$
	(freely rotating)	$-p_1^2 p_2^2 / 3(4\pi\epsilon_0)^2 kT r^6$ (Keesom energy)
Charge-Non-polar		$-Q^2 \alpha / 2(4\pi\epsilon_0)^2 r^4$
Dipole-Non-polar	(fixed)	$-p^2 \alpha (1 + 3\cos^2 \theta) / 2(4\pi\epsilon_0)^2 r^6$
	(rotating)	$-p^2 \alpha / (4\pi\epsilon_0)^2 r^6$ (Debye energy)
Non-polar - Non-polar		$-3/4 \frac{h\nu\alpha^2}{(4\pi\epsilon_0)^2 r^6}$ (London Dispersion energy)
Hydrogen Bond		Complicated, short range, proportional to $-1/r^2$

Such systems are traditionally referred to as ‘simple liquids’ because they describe point particles with isotropic interactions, i.e. with a mathematically simple Hamiltonian.

In many simulations one uses ad hoc pair potentials. The most famous one is the Lennard-Jones (LJ) pair potential (1924) defined by

$$V_{LJ}(\mathbf{R}) = 4\epsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^6 \right],$$

where  $\epsilon$  is the well depth<sup>18</sup>,  $\sigma$  is the distance at which  $V(R)$  passes through zero. The attractive part, which describes VDW forces, is proportional to

<sup>18</sup>The point where the slope is zero gives:

$$\frac{dV}{dR} = 4\epsilon \left[ 12(\sigma/R)^{11}(-\sigma/R^2) - 6(\sigma/R)^5(-\sigma/R^2) \right] = 0,$$

$R^{-6}$  whereas the repulsive part, which describes Pauli repulsion, is proportional to  $R^{-12}$  (Fig. 2.32).

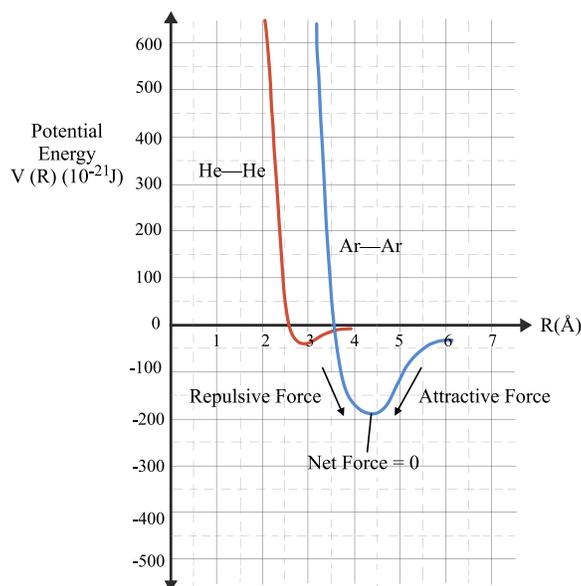


Figure 2.32. Lennard-Jones potential.

(Recall that the force  $F = -dV/dR$  in 1D or  $\mathbf{F} = -\nabla V$  in 3D.) The sixth-power term does not represent other kinds of bonding (non-VDW) well. The twelfth-power term appearing in the potential is chosen for its ease of calculation for simulations (by squaring the sixth-power term) and is not physically based. The LJ potential is a model for intermolecular forces designed to describe the interaction between neutral atoms or molecules.

The minimum value of  $V_{LJ}(\mathbf{R})$  is  $-\varepsilon$ , which is found at  $R = 2^{1/6}\sigma$  (check this by finding  $R$  such that  $dV_{LJ}/dR = 0$ ). Commonly simulated simple liquid models are: the LJ pair potential (sometimes cut off at the minimum, sometimes with other exponents than 12 and 6), the purely repulsive inverse-power law pair potentials  $V(\mathbf{R}) \propto (R/\sigma)^{-n}$ , the Yukawa “screened Coulomb” pair potential  $V(\mathbf{R}) \propto \exp(-R/\sigma)/R$ , the Morse pair potential that is a difference of two exponentials,  $V(\mathbf{R}) = D_e(e^{-2a(R-r_e)} - 2e^{-a(R-r_e)})$ , and the HS pair potential.

**2.16.1. PE Curves for Different Molecules (but same # of electrons).** The relative strengths and effective ranges of several intermolecular forces are illustrated in Fig. 2.33, which shows how the potential energy

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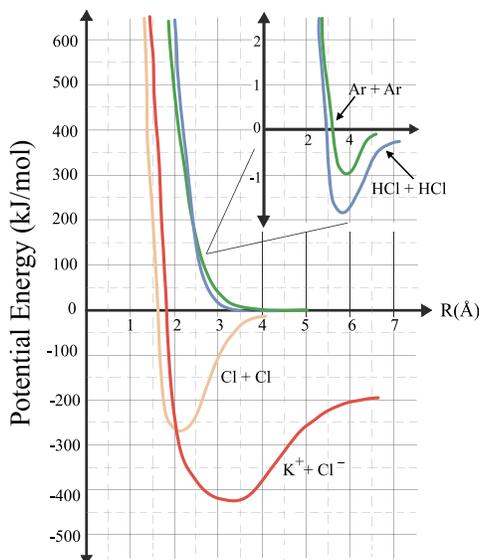
and solving for  $R$  leads to  $R = \sigma 2^{1/6}$ . Substitution of this  $R$  value into the Lennard-Jones equation gives  $V(\sigma 2^{1/6}) = -\varepsilon$ .

(PE) depends on the intermolecular separation (center-to-center distance) for several pairs of ions, atoms, and molecules.

The potentials illustrated in Fig. 2.33 include Coulomb ( $R^{-1}$ ), dipole-dipole ( $R^{-3}$ ), dispersion ( $R^{-6}$ ), and repulsive ( $R^{-12}$ ) potentials. The species shown were chosen so that the interacting atoms, ions, or molecules have the same number of electrons (Ar, Cl, K, HCl). For comparison, the covalent bond (intramolecular force) for  $\text{Cl}_2$  is also shown.

The ion-ion interaction of K with Cl is the strongest (stronger even than the covalent interaction in  $\text{Cl}_2$ ), followed by the interaction between two HCl molecules (dipole-dipole and dispersion) and the Ar-Ar interaction (dispersion only).

Notice in Fig. 2.33 the dramatically different depths of the wells (several orders of magnitude), as well as the distinctly different distances at which the minima occur.



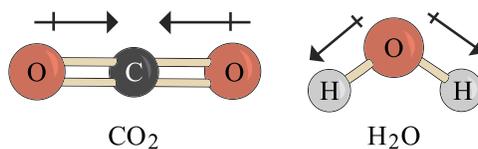
**Figure 2.33.** Potential energy curves showing attractive and repulsive forces for different types of interactions.

The potential energy of a pair of atoms, ions, or molecules depends on the distance between the members of the pair. Here, the potential energy at large separations (to the right side of the graph) is arbitrarily set to zero by convention. As pairs of particles approach each other, the potential energy becomes negative because attractive forces come into effect. The lowest point in each curve occurs at the distance where attractive and repulsive forces exactly balance. The relative potential energy values at these minima measure the relative strength of the attractive forces in the various cases

illustrated. Note the shallow potential energy minimum for HCl and Ar. The inset of Fig. 2.33 shows these same two curves with the vertical scale expanded by a factor of 100.

**2.16.2. Are CO<sub>2</sub> and H<sub>2</sub>O Polar or Nonpolar?** To determine whether dipole-dipole interactions are significant, we need to look at two things: 1) the dipole moment of each bond and 2) the geometry of the molecule. The net dipole moment, which determines if a molecule is polar or not, is the vector sum of all its constituent dipole moments (i.e. we vectorially add up the dipole moments of all bonds). When two atoms involved in a bond have a significant difference in electronegativity, the bond is polar, with a dipole moment that points toward the least electronegative atom (according to our convention). For example, the C=O bond is polar because the difference in electronegativity is  $\Delta E_N = 3.5 - 2.5 = 1.0$ , which is significant. In the C=O bond, the most electronegative atom is O; thus the dipole moment points from O to C.

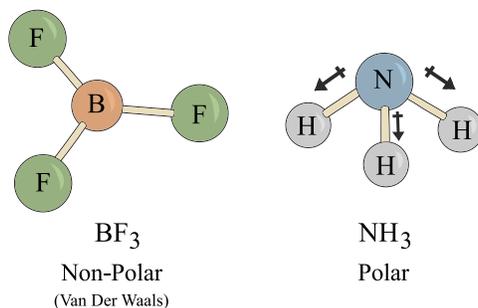
CO<sub>2</sub> has covalent bonds, each of which have a dipole moment, but its overall dipole moment is zero due to cancellation of the two dipole moment vectors, which point in opposite directions. The molecule is therefore nonpolar (Fig. 2.34). Only VDW forces exist. The molecule has no net dipole moment because even though CO bonds are polar, they cancel each other out due to the geometry of the molecule.



**Figure 2.34.** CO<sub>2</sub> has no permanent EDM (by symmetry) whereas H<sub>2</sub>O does.

CO<sub>2</sub> is linear because the C atom has a complete octet of valence electrons arising from covalent bonding to its two neighboring O atoms. H<sub>2</sub>O is bent because the octet around the O atom features 2 lone electron pairs.

**2.16.3. Are BF<sub>3</sub> and NH<sub>3</sub> Polar or Nonpolar?** Boron trifluoride (BF<sub>3</sub>) is perfectly nonpolar because the dipole vectors for each bond vectorially cancel out. Ammonia (NH<sub>3</sub>) has an overall dipole because the vectors point somewhat in one direction (Fig. 2.35).



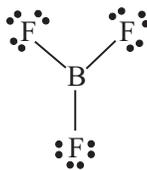
**Figure 2.35.**  $\text{BF}_3$  has no permanent EDM (by symmetry) whereas  $\text{NH}_3$  does.

2.16.3.1. *Ammonia ( $\text{NH}_3$ )*. Ammonia is nonplanar because of the presence of a lone pair of electrons on the nitrogen atom. This can be seen by drawing the Lewis structure (Fig. 2.36). Ammonia can also do hydrogen bonding since it has N-H bonds.



**Figure 2.36.** Lewis structure of  $\text{NH}_3$ .

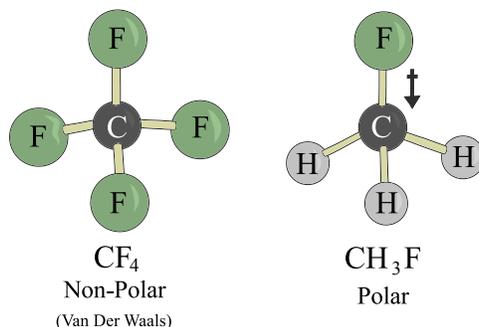
2.16.3.2. *Boron Trifluoride ( $\text{BF}_3$ )*. To see that  $\text{BF}_3$  is planar we draw its Lewis structure (Fig. 2.37). Boron has 3 valence electrons, whereas fluorine has 7. We have a total of  $3+3(7)=24$  valence electrons, which is a multiple of 8. There are no lone pairs on the central boron atom. Because fluorine is more electronegative than boron, boron will see its 3 electrons pulled away toward the F atoms.



**Figure 2.37.** Lewis structure of  $\text{BF}_3$ .

There are no ionic interactions here. There are no hydrogen atoms, so there cannot be any hydrogen bonds. This molecule is non-polar, because the 3 orientations of the dipole moments relative to the boron atom all cancel out vectorially.

ionic	H-bond	dipole	dispersion
no	no	no	yes



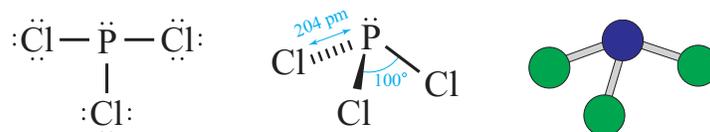
**Figure 2.38.** Structure of  $\text{CF}_4$  and  $\text{CH}_3\text{F}$ .  $\text{CF}_4$  is nonpolar because the vector sum of all bond dipoles is zero.  $\text{CH}_3\text{F}$  is polar due to its lower symmetry. The direction of the arrow indicates the orientation of the permanent EDM.

**2.16.4. Are  $\text{CF}_4$  and  $\text{CH}_3\text{F}$  Polar or Nonpolar?**  $\text{CF}_4$  is nonpolar because of geometry (Fig. 2.38).  $\text{CH}_3\text{F}$  has an overall dipole because of the CF bond. However, it does not participate in hydrogen bonding since it has no H-F bonds. For  $\text{CF}_4$  we have:

ionic	H-bond	dipole	dispersion
no	no	no	yes

For  $\text{CH}_3\text{F}$  we have:

ionic	H-bond	dipole	dispersion
no	no	yes	yes



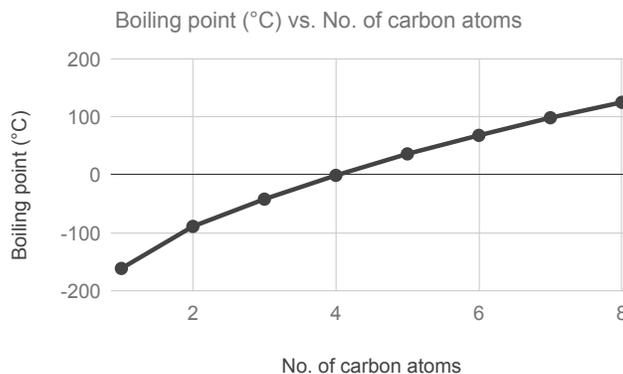
**Figure 2.39.** Structure of phosphorous trichloride.

**2.16.5. Phosphorous Trichloride ( $\text{PCl}_3$ ).** Phosphorous trichloride has the Lewis structure and 3D representation shown in Fig. 2.39. For  $\text{PCl}_3$ , phosphorous (P) has 5 valence electrons whereas chlorine (Cl) has 7, for a total of  $5 + 3(7) = 26$ . The highest multiple of 8 is 24. The difference is  $26 - 24 = 2$ , which tells us that there is 1 lone pair of 2 electrons on the central phosphorus atom. Because Cl has 7 valence electrons, it needs 1 more to get to 8, Cl wants to form 1 bond to acquire this extra electron. Therefore, we draw 3 lone pairs on each chlorine (Cl) atom so that each Cl atom has 8 electrons. If we count all valence electrons in the structure, we have a total of 26.

In  $\text{PCl}_3$  we don't have a metal attached to a non-metal. Thus, there are no ionic interactions. There are no hydrogen bonding interactions because there is no hydrogen atom. However, we do have dipolar interactions because the molecule is polar: P has a lone pair of electrons whereas Cl has 3 (P atom is more positively charged than Cl), leading to a dipole moment from each Cl atom (negatively charged) to the P atom (positively charged). Their vector sum (net dipole moment) points upward in Fig. 2.39. Finally, dispersion forces are always present.

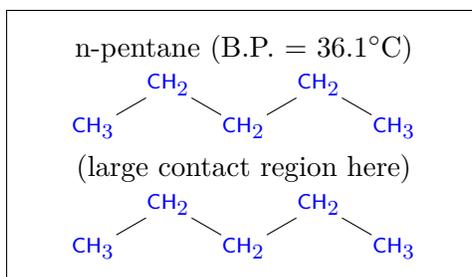
ionic	H-bond	dipole	dispersion
no	no	yes	yes

**2.16.6. Boiling Points (B.P.) of Alkanes: Effects of Molar Mass.** If we have only VDW interactions among molecules, it is important to look at other factors, such as number of electrons (polarizability), contact area and  $\pi$ -bonding. Consider molecules that are all linear but whose molar mass differs. In Fig. 2.40, the boiling points of  $n$ -alkanes increase with molar mass because the dispersion force is stronger due to increased contact area between dimers.

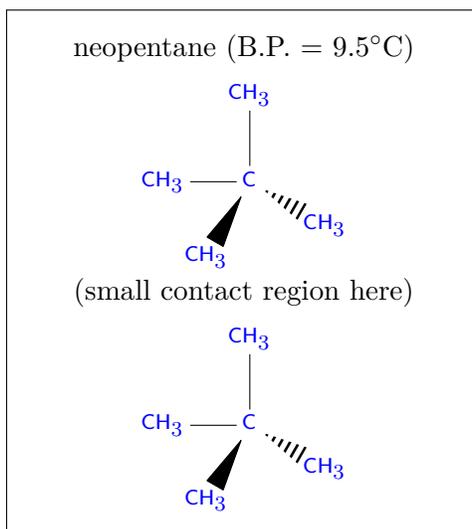


**Figure 2.40.** Boiling point of several alkanes.

**2.16.7. B.P. of  $n$ -pentane vs Neopentane: Effects of Molecular Shape.** Molar mass is not the only factor. Molecular shape also matters. For  $n$ -pentane, the boiling point (B.P.) is higher than neopentane because  $n$ -pentane makes contact with its neighbors using a larger contact area, increasing the number of interactions possible.



For neopentane the contact area is much smaller because the molecules are nearly spherical, therefore decreasing the boiling point by reducing the number of interactions possible:

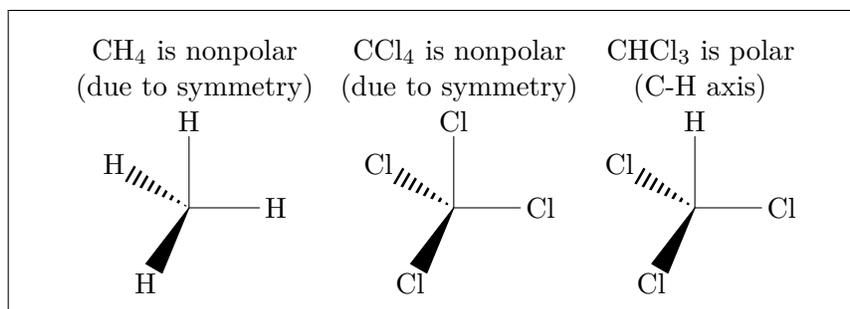


**2.16.8. Dipole-Dipole Examples.** For CH<sub>4</sub> the molecule is nonpolar because of its symmetry. We note that each C-H bond is very weakly polar, due to the very small difference in electronegativity  $\Delta E_N = 2.5 - 2.1 = 0.4$  between C and H.

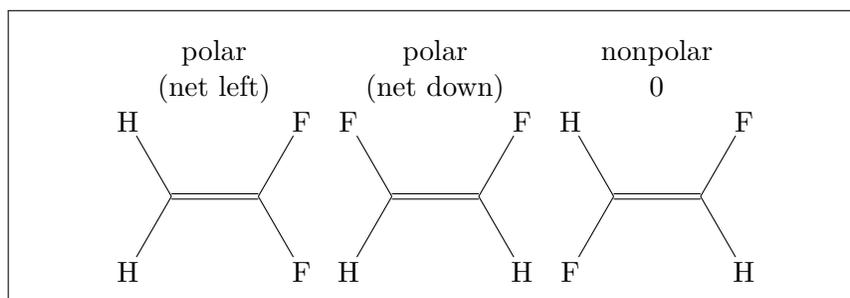
For CCl<sub>4</sub>, the molecule is also nonpolar for the same reason (geometry). Here, the difference in electronegativity in the C-Cl bonds is larger,  $\Delta E_N = 3.0 - 2.1 = 0.9$ .

Chloroform (CHCl<sub>3</sub>) is polar because of its lower symmetry. The net dipole moment points along the C-H bond direction.

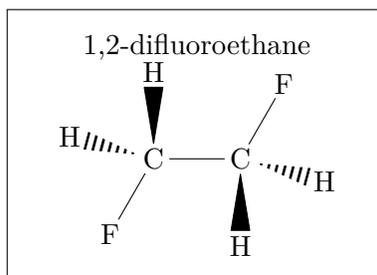
This is shown below:



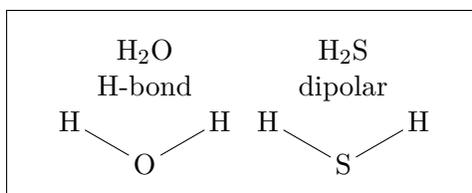
For C<sub>2</sub>H<sub>2</sub>F<sub>2</sub>, there are 3 possible isomers. Of the three shown, the first two are polar while the third one is nonpolar:



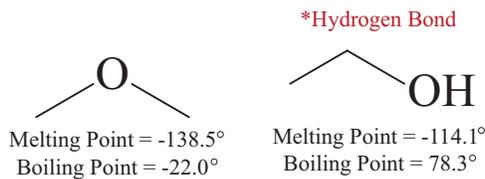
While CH<sub>2</sub>FCH<sub>2</sub>F looks nonpolar as drawn, a C-C single bond can rotate freely. Thus, there are times when the dipole moments do not cancel each other out. This residual (time-averaged) dipole moment is non-zero and the molecule is polar on the average.



**2.16.9. Examples that Involve Hydrogen Bonding.** H<sub>2</sub>O is more polar than H<sub>2</sub>S. In fact, it can undergo hydrogen bonding with other water molecules.



In Fig. 2.41, both molecules have the same atoms ( $C_2H_6O$ ), but different arrangements. Dimethyl ether is polar but its boiling point is lower than ethanol, which has a much higher boiling point because it undergoes hydrogen bonding (due to the terminal O-H).



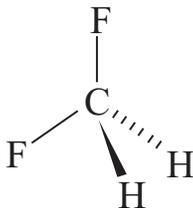
**Figure 2.41.** Effect of intermolecular bonding on boiling and melting points. (Temperatures shown are in Celsius degrees.)

**2.16.10. Combining it All: Ordering Compounds Based on Boiling Points.** Another typical question you may be asked to solve involves ordering compounds in order of their boiling points. In the example below, we have: NaCl, ethane, ethanol, difluoromethane.

You may be asked to arrange these molecules in order of increasing B.P. The first step is to identify the dominant intermolecular interaction:

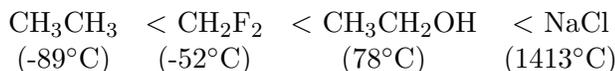
NaCl	$CH_3CH_3$	$CH_3CH_2OH$	$CH_2F_2$
ionic	nonpolar	H-bond	dipolar

Note:  $CH_2F_2$  does not form H-bonds. It's a tetrahedral structure where all H and F atoms are bound to the carbon (Fig. 2.42).

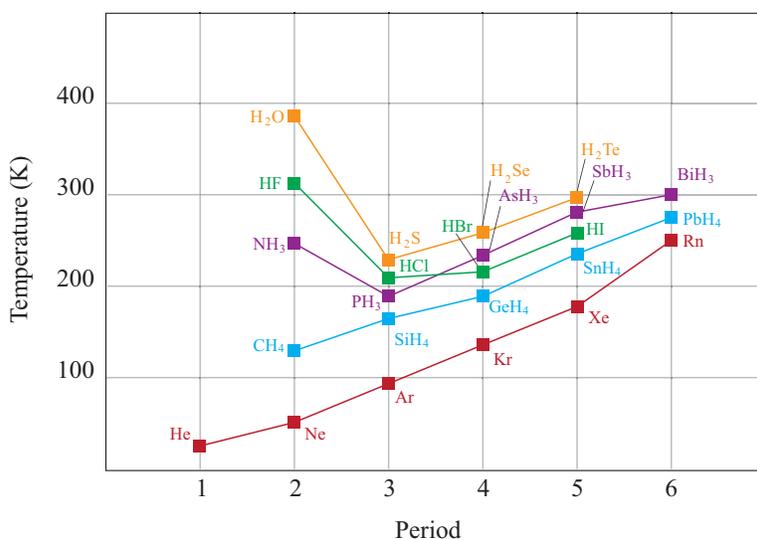


**Figure 2.42.** Structure of  $CH_2F_2$ .

Ordering according to B.P. gives:



2.16.10.1. *Boiling Point: Periodic Table Trends.* Substances with weaker intermolecular forces lead to lower boiling points,  $T_b$ . For example, ionic liquids have high boiling points because of the strong Coulomb interaction among ions. NaCl has  $T_b \sim 1,686$  K. Helium boils at  $\sim 4$  K. Xenon has a higher boiling point than helium because it has a higher polarizability. Polar liquids (e.g. HCl) have higher boiling points than non-polar liquids (e.g.  $\text{N}_2$ ). See Fig. 2.43.



**Figure 2.43.** Periodic table trends affecting the boiling points. Elements from five different groups are shown: group 18 (red), group 14 (blue), group 15 (purple), group 17 (green) and group 16 (orange).

2.16.10.2. *Example.* State which intermolecular forces dominate among pairs of molecules of the following substances: (a)  $\text{F}_2(\text{s})$ , (b)  $\text{HBr}(\text{l})$ , (c)  $\text{NH}_4\text{Cl}(\text{s})$ .

*Solution:* (a) Since  $\text{F}_2$  is nonpolar, VDW forces dominate. (b) Since HBr has an EDM, dipole-dipole dominates. HBr does not form H-bonds. (c) Within  $\text{NH}_4\text{Cl}(\text{s})$  there are ion-ion forces (between  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions). Between pairs of  $\text{NH}_4\text{Cl}$  molecules, there can be H-bonds (thanks to the N-H bonds).  $\text{NH}_4\text{Cl}$  also has a permanent EDM, so there are dipole-dipole forces. And of course, VDW forces. The strongest *intermolecular* forces would be the H-bonding.

## 2.17. Problems

**Problem 30.** Compare the magnitude of the gravitational force on a molecule to typical intermolecular forces. For the latter, assume an electrostatic

(Coulomb) interaction between two elementary charges separated 1 nm apart. There are 2 components to the gravitational force: the attraction of the Earth, the attraction from nearest-neighbor molecules. Take the distance between nearest-neighbor molecules to be 1 nm. Why do we discuss intermolecular forces in this chapter, but not gravity?

**Solution.** The gravitational force between two objects is  $F = G(m_1m_2)R^{-2}$ , where  $R$  is the distance between the centers of mass of the two objects,  $m_1, m_2$  are the masses of objects 1 and 2 (respectively) and  $G$  is the gravitational constant, whose magnitude is  $6.67 \times 10^{-11} \text{ N}\cdot\text{m}^2/\text{kg}^2$ . We first consider the gravitational force exerted on a molecule by planet Earth. Near the surface of the Earth,  $F = mg$ , where  $g \sim 9.81 \text{ m/s}^2$ . One proton weighs  $1.672 \times 10^{-27} \text{ kg}$ . Then,  $F \approx 1.64 \times 10^{-26} \text{ N}$ .

Second, we consider the gravitational attractive forces between two nearby molecules. For two hydrogen atoms separated  $R = 1 \text{ nm}$  apart, this force is  $F = (6.67 \times 10^{-11})(1.672 \times 10^{-27})^2 \cdot (1 \times 10^{-9})^{-2} \approx 1.86 \times 10^{-46} \text{ N}$ .

For electrostatic interactions, the forces are calculated from the Coulomb's law, which states that the force experienced by two charges  $q_1, q_2$  separated by a distance  $R$  has magnitude  $F = (4\pi\epsilon_0)^{-1}(q_1q_2)R^{-2}$ . Electrostatic charges of ions are on the order of  $1.6 \times 10^{-19} \text{ C}$ . Typical intermolecular distances are a few Angstroms. Take  $R = 1 \text{ nm}$  for example. Then,  $F = (1.11 \times 10^{-10})(1.6 \times 10^{-19})^2 \cdot (10^{-9})^{-2} \approx 2.8 \times 10^{-30} \text{ N}$ .

We conclude that intermolecular electrostatic forces are 16 orders of magnitude smaller than intermolecular gravitational forces. Thus, intermolecular gravitational forces can be neglected. On the other hand, the Earth's gravitational force is 4 orders of magnitude stronger than electrostatic forces. But unlike intermolecular forces, which have random directions, the Earth's gravitational field always points downward and has a net effect of causing substances to flow. ■

**Problem 31.** Calculate the force applied by one atom on another according to a Lennard-Jones potential. Evaluate the force at the distances of 3.0, 3.8, 4.5 Å for oxygen. (For oxygen  $\sigma = 3.58 \text{ Å}$  and  $\epsilon = 1.622 \times 10^{-21} \text{ J}$ .) Is the force attractive or repulsive at these points?

**Solution.** Starting from:

$$V_{LJ}(R) = 4\epsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^6 \right]$$

Take the (-ve) derivative of the LJ potential with respect to  $r$  to get the force

$$F_{LJ}(R) = -\frac{dV}{dR} = -4\epsilon \left( \frac{6\sigma^6}{R^7} - \frac{12\sigma^{12}}{R^{13}} \right)$$

For 3.0 Å:  $1.8 \times 10^{-9}$  J/m, which is repulsive. For 3.8 Å:  $2.9 \times 10^{-11}$  J/m, which is repulsive. For 4.5 Å:  $-1.1 \times 10^{-11}$  J/m, which is attractive. [Note: the unit J/m is equivalent to Newtons.] ■

**Problem 32.** How can NaCl crystal dissolve in water when ionic forces in the NaCl crystal (the “lattice energy” that holds the NaCl crystal together is approximately 8.2 eV; the ion-ion bond strength in NaCl is 1.52 eV) are stronger than ion-dipole forces? For the ion-dipole force between water molecules and the ions in the crystal, use the formula (SI units)

$$V(R) = -\frac{Qp}{4\pi\epsilon R^2},$$

where  $R$  is the distance between the ion and the dipole (we assume a “point dipole”),  $p$  is the electric dipole moment and  $Q$  is the ion charge (an electron has charge  $Q = -1.602 \times 10^{-19}$  C). The ion separation in NaCl crystal is 0.28 nm. For water molecules,  $p=1.85$  Debye or  $6.17 \times 10^{-30}$  C.m in SI units, since 1 D= $3.336 \times 10^{-30}$  C.m.  $\epsilon$  is the dielectric permittivity. For vacuum,  $\epsilon = 8.85 \times 10^{-12}$  F/m. Explain how it is possible for water to dissolve the NaCl crystal in spite of the fact that the ion-dipole interaction is weaker than the ion-ion interaction that holds the crystal together (since we know this to be true from experiments).

**Solution.** For vacuum,  $1/4\pi\epsilon_0 = 8.99 \times 10^9$  N.m<sup>2</sup>.C<sup>-2</sup>. For an ion-dipole distance of 2.5 Å, the interaction strength is

$$\frac{(1.85 * 3.336 \times 10^{-30})(1.6 \times 10^{-19})(8.99 \times 10^9)}{(2.5 \times 10^{-10})^2} = 1.42 \times 10^{-19} \text{ J} = 0.88 \text{ eV}$$

If we consider the lattice energy of NaCl (8.2 eV), approximately 9 water molecules are needed (on average) to break apart each ion in the NaCl structure. On the other hand, if we consider the ion-ion bond strength of NaCl (1.52 eV), about 2 water molecules are needed per ion. (So the actual number of water molecules per ion of NaCl is between 2 and 9.) ■

**Problem 33.** Imagine that NaCl crystal is completely dissolved in water. The more NaCl we dissolve, the more Na<sup>+</sup> and Cl<sup>-</sup> ions are present in water. The solution consists of metal aquo complexes with the formula [Na(H<sub>2</sub>O)<sub>8</sub>]<sup>+</sup>, with Na-O distance of 250 pm. The chloride ions are also strongly solvated, each being surrounded by an average of 6 molecules of water. When solvated the Na and Cl ions are stable. There will come a point where too many ions present in aqueous solution will lead to precipitation (Na<sup>+</sup> and Cl<sup>-</sup> ions will become so close to each other, in terms of average separation, that the formation of NaCl will be preferred over dissolution). What is this concentration, and how does it compare with the solubility limit of NaCl in water (357 mg/mL at 25°C)? (Hint: consider the point

where the ion-ion interaction energy becomes stronger than the ion-dipole interaction energy.)

**Solution.** *Notation:* We use  $V$  to denote volume and  $V(R)$  to denote intermolecular interaction strength. Let us assume  $n = 7$  water molecules on average per hydrated ion complex, so we can treat the case of Na and Cl simultaneously. (It's no problem to take  $n = 8$  and  $n = 6$ ; I am doing this simplification only to save space.) This calculation *can only be approximate* since we disregard the screening of charges and the dielectric constant of the medium. We also neglect any dynamical effects and neglect the hydrogen bonding between the inner and outer hydration layers.

It is instructive to look at two different limits. We start with the worst possible case scenario. Let us consider the size of water molecule,  $2.75 \text{ \AA}$ , and atomic radius of  $\text{Na}^+$  ( $1.02 \text{ \AA}$ ) and  $\text{Cl}^-$  ( $1.81 \text{ \AA}$ ). The worse case scenario is an ion-dipole separation of  $R = 2.75 + 1.81 = 4.56 \text{ \AA}$ . You can think of this as a rough attempt at modeling hydrogen bonding between the inner and outer hydration layers; the net effect being to "pull" inner water molecules away from the ion. Then,  $V(R) = -\frac{Qp}{4\pi\epsilon R^2}$  evaluates numerically to

$$= 8.99 \times 10^9 \cdot \frac{(1.85 * 3.336 \times 10^{-30})(1.6 \times 10^{-19})}{(456 \times 10^{-12})^2} = 4.23 \times 10^{-20} \text{ J},$$

Multiplying by 7 and solving for  $R$  in the Coulomb's law:

$$7 * (4.23 \times 10^{-20} \text{ J}) = \frac{q_1 q_2}{4\pi\epsilon R} = 8.99 \times 10^9 \cdot \frac{(1.6 \times 10^{-19})^2}{R}$$

which gives  $R=7.7 \text{ \AA}$ . Let's round this up to 1 nm. For inter-ion separation of 1 nm, the concentration of ions,  $\frac{N}{V} = 1 \bigg/ \frac{4}{3}\pi R^3$ , is

$$= 5.2 \times 10^{26} \text{ ions/m}^3 = 868 \text{ mol/m}^3 * (0.001 \text{ m}^3/\text{L}) = 0.868 \text{ mol/L}.$$

We want to compare this to the solubility of NaCl in water (359 g/L). The molar mass of Na or Cl ions is 25 or 35 g/mol, respectively (29 g/mol avg.). Then,

$$0.868 \text{ mol/L} * 29 \text{ g/mol} = 25 \text{ g/L}.$$

which is too low. This is ok because it is only an estimate for the worst case scenario.

Let us use instead the data provided in the problem ( $R=250 \text{ pm}$  for Na-O distance). The ion-dipole energy between ion and water,  $V(R) = -\frac{Qp}{4\pi\epsilon R^2}$ ,

is

$$= 8.99 \times 10^9 \cdot \frac{(1.85 * 3.336 \times 10^{-30})(1.6 \times 10^{-19})}{(250 \times 10^{-12})^2} = 1.42 \times 10^{-19} \text{ J} = 0.88 \text{ eV},$$

and since we have  $n = 7$  such water molecules bound to the ion, the total binding energy is 6.16 eV. Our task is to find  $R$  (distance between Na and Cl ions) such that the ion-ion interaction energy is larger than 6.16 eV. Setting  $E(\text{ion} - \text{ion}) = 6.16 \text{ eV}$  and invoking Coulomb's law:

$$7 * (1.42 \times 10^{-19} \text{ J}) = \frac{q_1 q_2}{4\pi\epsilon R} = 8.99 \times 10^9 \cdot \frac{(1.6 \times 10^{-19})^2}{R}$$

which gives  $R$  of approximately 2.3 Å. Then,  $\frac{N}{V} = 1 \bigg/ \frac{4}{3}\pi R^3$  is

$$= 1.96 \times 10^{28} \text{ ions/m}^3 = 32,583 \text{ mol/m}^3 * (0.001 \text{ m}^3/\text{L}) = 32.6 \text{ mol/L},$$

where

$$32.6 \text{ mol/L} * 29 \text{ g/mol} = 945 \text{ g/L}.$$

This overshoots the actual solubility limit of NaCl (359 g/L), but is off only by a factor of 3. We found that the solubility limit lies between 25 and 925 g/L. ■

**Problem 34.** Consider  $\beta$ -sheets that are stacked in a protein. While the strength of interaction between individual sheet elements is small, the overall interaction between sheets is strong because of cooperative effects (i.e. the sum of a very large number of small interactions leads to a strong interaction). Estimate the total energy of interaction (bonding energy) between pairs of  $\beta$ -sheets.

**Solution.** Let us consider the case of silk fibroin.  $\beta$ -sheets are stabilized by hydrogen bonding between peptide strands. In a  $\beta$ -sheet, regions of the polypeptide backbone lie parallel to each other and are connected by hydrogen bonds. The hydrogen bonds are formed between the carbonyl oxygen and the amine hydrogen of amino acid (AA) in adjacent strands in a polypeptide (i.e., the hydrogen bonds are inter-stand). The distance between adjacent amino acids is 3.5 Å.

The protein fibroin in silk has a repeating sequence of amino acids: mostly Gly-Ser-Gly-Ala-Gly-Ala, extending in length to over 5000 residues.<sup>19</sup> 5,000 residues correspond to a length of  $3.5 \text{ Å} * 5000 = 1,750 \text{ nm} = 1.75 \text{ }\mu\text{m}$ .

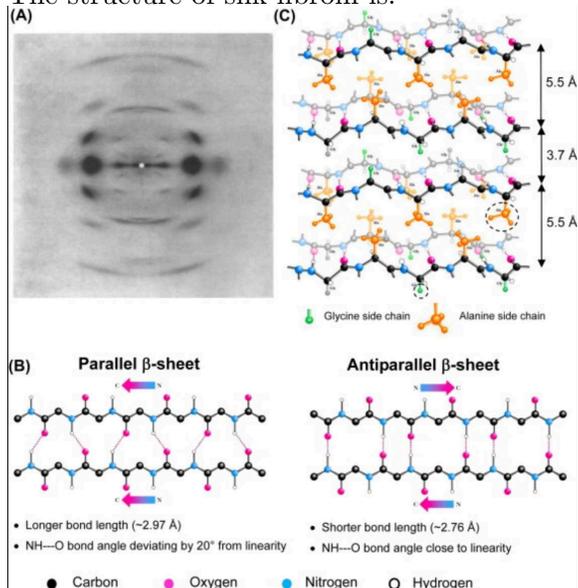
VDW interaction are weak (0.4-4.0 kJ/mol compared with 12-30 kJ/mol for a hydrogen bond).<sup>20</sup> Thus, along the first dimension (peptide chain), there

<sup>19</sup>From: <http://www.biopics.co.uk/jsmol/fibroin.html>

<sup>20</sup>From: [https://chem.libretexts.org/Core/Physical\\_and\\_Theoretical\\_Chemistry/Physical\\_Properties\\_of\\_Matter/Atomic\\_and\\_Molecular\\_Properties/Intermolecular\\_Forces/Specific\\_Interactions/Van\\_Der\\_Waals\\_Interactions](https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Physical_Properties_of_Matter/Atomic_and_Molecular_Properties/Intermolecular_Forces/Specific_Interactions/Van_Der_Waals_Interactions)

are 5000 residues; assume 1 hydrogen bond per residue (0.4-4.0 kJ/mol), and one VDW interaction (12-30 kJ/mol), the total interaction strength ranging from  $5000 \cdot (0.4 + 12) = 62,000$  kJ/mol to  $5000 \cdot (4 + 30) = 170,000$  kJ/mol. Along the second dimension, let's assume it is  $1.75 \mu\text{m}$  long, and that each neighboring AA chain are  $5.5 + 3.7 = 11.2 \text{ \AA}$  apart (see figure below).

The structure of silk fibroin is:<sup>21</sup>



Thus, there are approximately  $1,750 \text{ nm} / 11.2 \text{ \AA} = 1562$  AA chains.

For a pair of sheets, the total interaction energy is between

$$1562 \cdot 62,000 \text{ kJ/mol} = 96,844,000 \text{ kJ/mol to}$$

$$1562 \cdot 170,000 \text{ kJ/mol} = 265,540,000 \text{ kJ/mol.}$$

And since  $1 \text{ eV} = 96.485 \text{ kJ/mol}$ , this energy range is 1 to 2.7 MeV, a very large binding energy. If we assume only VDW bonding, the total energy is in the range

$$1562 \cdot 5000 \cdot (0.4) = 3,124,000 \text{ kJ/mol} = 32 \text{ keV to}$$

$$1562 \cdot 5000 \cdot (4) = 31,240,000 \text{ kJ/mol} = 323 \text{ keV.}$$

This should be compared against the strength of covalent bonds (200-1,000 kJ/mol) and ionic interactions (3,000 kJ/mol; for NaCl, 7.97 eV). We see that VDW interaction between  $\beta$ -sheets is several orders of magnitude stronger. This is a very strong bond, which is a consequence of the cooperative effect of many small interactions. Breaking such a bond would require enormous forces (or a suitable enzyme). ■

**Problem 35.** Hydrogen bonding is an intermolecular force often denoted by  $X - H \cdots X$  where  $X = \text{F, O, or N}$  and the dotted line is the intermolecular attraction between molecules of a dimer. This attraction involves a strongly

<sup>21</sup><https://www.sciencedirect.com/science/article/pii/S0079670015000155>

negative partial charge (in fact, a lone pair) on X pulling the positively charged H atom from the neighboring molecule.

(a) Does  $\text{H}_2\text{O}$  or  $\text{NH}_3$  form stronger hydrogen bonds with itself? State reasons to support your answer.

(b) Does  $\text{NH}_4^+$  hydrogen bond with itself, why or why not?

**Solution.** (a)  $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$  hydrogen bond is stronger than  $\text{NH}_3 \cdots \text{NH}_3$  bond because (1) the electronegativity difference between O and H is larger than that between N and H and (2) the hydrogen bonding in  $\text{H}_2\text{O}$  is linear whereas the hydrogen bonding in  $\text{NH}_3$  is bent.

(b) Draw the Lewis structure:  $\begin{array}{c} \text{H} \\ | \\ \text{H}:\text{N}:\text{H} \\ | \\ \text{H} \end{array}$ . There are no lone electron pairs!

Thus,  $\text{NH}_4^+$  does not hydrogen-bond with itself because it does not have lone pairs to participate in hydrogen bonding. ■

**Problem 36.** Consider the compounds  $\text{CHCl}_3$  and  $\text{CHBr}_3$  and compare the strengths of their dipole-dipole force and the strengths of their VDW forces. The respective boiling points are  $61^\circ\text{C}$  and  $149^\circ\text{C}$ . For these compounds, which type of intermolecular force (dipole-dipole or VDW) contributes more to the apparent difference in boiling points?

**Solution.**  $\text{CHCl}_3$  has a stronger dipole-dipole force among its dimers because Cl is more electronegative than Br. However, the difference in electronegativities  $\Delta E_N = 3.0 - 2.5 = 0.5$  for C-Cl versus  $\Delta E_N = 2.8 - 2.5 = 0.3$  for C-Br is small. Thus, differences in the dipole-dipole interaction strength are small (0.3 vs 0.5).  $\text{CHBr}_3$  has a stronger VDW force because Br is a heavier atom than Cl and has more electrons. But  $\text{CHBr}_3$  has the higher boiling point, so differences in VDW interactions must be stronger than differences in the d-d interaction. ■

**Problem 37.** Calculate the mean-square displacement (msd)  $\overline{x^2}$ , for a freely diffusing particle (no boundaries). The average of  $x^2$  is defined as  $\overline{x^2} = \int_{\mathbb{R}} x^2 p_t(x) dx$ , where  $p_t(x)$  is the PDF that solves the diffusion equation:

$$p_t(x) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(\frac{-x^2}{4Dt}\right)$$

The product  $p_t(x)dx$  is the probability that a particle will be found in the interval  $[x, x + dx]$  at time  $t$  when it was initially at  $x = 0$  at time  $t = 0$ . Using the formula for Gaussian integration I gave you in class you can easily check that this PDF is normalized, i.e.  $\int_{\mathbb{R}} p_t(x) dx = 1$ . Show by direct calculation that  $\overline{x^2} = 2Dt$ . Note: the reason we don't use  $\bar{x}$  to quantify the displacement of particles undergoing diffusion is that  $\bar{x}$  equals zero and is therefore trivial and non-informative. We instead use the second moment  $\overline{x^2}$ ,

which is nonzero because of the square. To get units of length we can take the square root,  $\sqrt{\overline{x^2}}$ , which is called the “root-mean-square” displacement.

**Solution.** By definition,

$$\overline{x^2} = \int_{\mathbb{R}} \frac{1}{\sqrt{4\pi Dt}} x^2 \exp\left(\frac{-x^2}{4Dt}\right) dx.$$

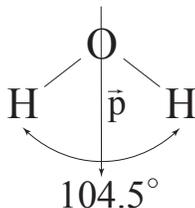
Let  $a = \frac{1}{4Dt}$ , and observe that (using formula for Gaussian integral provided in class)

$$\int_{\mathbb{R}} x^2 e^{-ax^2} dx = -\frac{d}{da} \int_{\mathbb{R}} e^{-ax^2} dx = -\frac{d}{da} \sqrt{\frac{\pi}{a}} = \frac{1}{2} \sqrt{\frac{\pi}{a^3}} = \frac{\sqrt{\pi(4Dt)^3}}{2}.$$

Thus,

$$\overline{x^2} = \frac{1}{\sqrt{4\pi Dt}} \frac{\sqrt{\pi(4Dt)^3}}{2} = 2Dt. \quad \blacksquare$$

**Problem 38.** The dipole moment  $\vec{p} = q\vec{d}$  is the product of the charge  $q$  and the displacement vector  $\vec{d}$  pointing from positive to negative charge. Use vector addition and the diagram below to calculate the dipole moment for a water molecule  $\vec{p}_{\text{H}_2\text{O}}$  given that the O-H<sup>+</sup> bond moment  $|\vec{p}_{\text{O-H}^+}| = 1.51$  D.



**Solution.**

$$|\vec{p}_{\text{H}_2\text{O}}| = 2 |\vec{p}_{\text{O-H}^+}| \cos\left(\frac{1}{2}\theta\right) = 2 \times (1.51 \text{ D}) \cos(52.25^\circ) = 1.85 \text{ D} \quad \blacksquare$$

**Problem 39.** The spherical coordinate expression for the dipole-dipole interaction energy in the point dipole approximation is (Section 2.4.2):

$$V(R, \theta_1, \theta_2, \phi) = -\frac{|\vec{p}_A||\vec{p}_B|}{4\pi\epsilon_0\epsilon R^3} [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]$$

where  $\vec{p}_A$  and  $\vec{p}_B$  are the dipole moments of dipoles  $A$  and  $B$ , respectively. They are vectors with length and orientation.  $|\vec{p}_A|$  and  $|\vec{p}_B|$  are the corresponding magnitudes (strengths) of the dipole moments.  $\epsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$  is the vacuum permittivity,  $\epsilon$  is the dimensionless dielectric constant of the solvent ( $\epsilon = 1$  in the case of vacuum) and  $R$  is the inter-dipole center-to-center separation length (assuming “point dipoles”,

i.e. infinitely small dipoles). The angles  $\theta_1$ ,  $\theta_2$  and  $\phi$ , which describe the relative orientations of the dipoles, are illustrated in Fig. 2.19.

(a) Determine the expression for the maximum attraction energy.

(b) Consider the situation when the dipoles are aligned anti-parallel to one another (still undergoing attractive interaction). Compare this energy to your answer in part (a).

(c) Are dipole-dipole forces alone strong enough to hold pure polar liquids of dipole moment 1 D together without the contribution of any other intermolecular forces? Compare your answer to part (a) or (b) at typical liquid-phase inter-dipole separations of 0.29 - 0.36 nm to room temperature thermal energy  $k_B T$  at 298 K.

**Solution.** (a) Maximum attraction occurs when  $\theta_1 = \theta_2 = 0$ . (Please note that attraction here is twice as strong as if we had  $\theta_1 = 90^\circ$ ,  $\theta_2 = 180^\circ$ .)

$$V(R, 0, 0, \phi) = -\frac{|\vec{p}_A||\vec{p}_B|}{(2\pi\epsilon_0\epsilon)R^3}$$

The negative sign denotes attractive force.

(b) If the dipoles are anti-parallel,  $\theta_1 = 90^\circ$  and  $\theta_2 = 180^\circ$ , the interaction energy is ( $\phi = 0$ ):

$$V(R, 0, 0, 0) = -\frac{|\vec{p}_A||\vec{p}_B|}{(4\pi\epsilon_0\epsilon)R^3}$$

which is still attractive because of the negative sign. Except that it differs by a factor of 2 from the expression in a.

(c) Yes, for strongly polar liquids of high dielectric constant. ■

**Problem 40.** In Section 2.10 we defined the thermally averaged energy by angle-averaging the Boltzmann factor corresponding to some interaction energy  $V(R, \Omega)$ :

$$e^{-V(R)/k_B T} \equiv \left\langle e^{-V(R, \Omega)/k_B T} \right\rangle = \frac{\int e^{-V(R, \Omega)/k_B T} d\Omega}{\int d\Omega}$$

In spherical coordinates the solid angle element is  $d\Omega = \sin\theta d\theta d\phi$ , where  $\theta, \phi$  are polar and azimuthal angles, respectively. Suppose we are interested in the low-temperature limit. Let us write  $V(R, \Omega_0)$  for the lowest energy configuration (ground state energy). We then write the remaining energies as differences from the lowest energy:  $\Delta V(R, \Omega) = V(R, \Omega) - V(R, \Omega_0)$ . The ground state energy corresponds to  $\Delta V = 0$ . Then,

$$e^{-V(R)/k_B T} = \frac{e^{-V_0(R, \Omega_0)/k_B T} \int e^{-\Delta V(R, \Omega)/k_B T} d\Omega}{\int d\Omega} \sim \text{const.} \times e^{-V(R, \Omega_0)/k_B T},$$

since when  $T \rightarrow 0$ , only the term  $e^{-\Delta V(R, \Omega_0)/k_B T} = 1$  contributes to the integral. The value of the integral depends on how fast  $\Delta V$  falls to zero as function of  $\Omega$ . Take log of both sides:

$$-V(R)/k_B T = \log(const) - V(R, \Omega_0)/k_B T.$$

In the low temperature limit, the term  $\log(const)$  is negligible compared to the  $1/T$  terms and we obtain the important result that the thermally averaged intermolecular energy is simply the ground state energy:

$$\boxed{V(R) = V(R, \Omega_0) \text{ as } T \rightarrow 0.}$$

(a) Let us take the case of the charge-dipole interaction. The interaction energy is

$$V(R, \Omega) = -\frac{Qp \cos \theta}{4\pi\epsilon_0 R^2},$$

where  $Q$  is the electric charge (in Coulombs),  $p$  is the strength of the dipole moment,  $R$  is the charge-dipole separation,  $\theta$  is the angle of the dipole tilt with respect to the charge-dipole axis, as shown in Fig. 2.17. Using the procedure outlined above, calculate the thermally averaged charge-dipole interaction strength in the low temperature limit.

(b) The high temperature regime occurs when  $V(R, \Omega) < k_B T$ . Calculate the charge-dipole interaction at high temperatures by expanding

$$e^{-V(R)/k_B T} \equiv \langle e^{-V(R, \Omega)/k_B T} \rangle = \frac{\int e^{-V(R, \Omega)/k_B T} d\Omega}{\int d\Omega}$$

Explain what happens to  $V(R)$  in the limit  $T \rightarrow \infty$ .

(c) The Boltzmann-averaged dipole-dipole interaction is known as the Keesom interaction and it is attractive and temperature dependent. Recall the dipole-dipole interaction potential for static dipoles can be written as (see Fig. 2.19):

$$V(R, \theta_1, \theta_2, \phi) = -\frac{|\vec{p}_A||\vec{p}_B|}{4\pi\epsilon_0\epsilon R^3} [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]$$

Explain the behavior of the interaction when  $k_B T$  is larger than the dipole-dipole interaction energy.

(d) Calculate the thermal energy  $k_B T$  at 298 K in eV and J.

(e) What is the inter-dipole separation at which orientational order breaks down for nitrobenzene in carbon tetrachloride?  $\epsilon_{\text{carbon tetrachloride}} = 2.24$ ,

$|\vec{p}_{\text{nitrobenzene}}| = 4.2 \text{ D}$  and at  $T = 298 \text{ K}$ .

(f) What is the value of the Keesom interaction energy at the high temperature limit (i.e., as  $T \rightarrow \infty$ )?

(g) Calculate the dipole-dipole interaction energy at the low temperature limit.

(h) Consider the  $1/R^2$  vs.  $1/R^4$  dependence of the charge-dipole interaction energy at the low- $T$  vs. high- $T$  limits, respectively. Also consider the dipole-dipole interaction at its low- $T$  limit ( $1/R^3$ ) and high- $T$  limit ( $1/R^6$ ). What is the significance of these differences in the  $R$ -dependence when  $T$  varies? Why is the interaction becoming more short-ranged in the high- $T$  limit?

**Solution.** (a) Since  $V(R) = V(R, \Omega_0)$ , we need to find  $V(R, \Omega_0)$ , the ground state energy. Suppose  $Q > 0$ . In that case, the minimum of  $V(R)$  with respect to  $\theta$  is found by inspection of the expression for  $V(R, \Omega)$ , which shows that the minimum value occurs when  $\cos \theta = 1$ , or when  $\theta = n2\pi$ ,  $n = 0, 1, 2, \dots$ . Then,  $V(R, \Omega_0) = -(Qp)/(4\pi\epsilon_0 R^2)$ . If  $Q < 0$ , we would need  $\cos \theta = -1$ , which would occur when  $\theta = \pi(2n + 1)$ ,  $n = 0, 1, 2, 3, \dots$ .

b) Since we are in the high- $T$  limit, we may Taylor-expand both sides

$$e^{-V(R)/k_B T} = 1 - \frac{V(R)}{k_B T} + \dots = \left\langle 1 - \frac{V(R, \Omega)}{k_B T} + \frac{1}{2} \left( \frac{V(R, \Omega)}{k_B T} \right)^2 - \dots \right\rangle$$

Cancelling out the 1's on both sides and multiplying out by  $k_B T$  leaves us with:

$$V(R) = \left\langle V(R, \Omega) - \frac{V(R, \Omega)^2}{2k_B T} + \dots \right\rangle$$

Substituting the charge-dipole interaction for  $V(R, \Omega)$

$$V(R) = \left\langle -\frac{Qp \cos \theta}{4\pi\epsilon_0 R^2} - \left( \frac{Qp \cos \theta}{4\pi\epsilon_0 R^2} \right)^2 \frac{\cos^2 \theta}{2k_B T} + \dots \right\rangle$$

The first term vanishes since the average  $\langle \cos \theta \rangle = 0$ . The second term survives:

$$V(R) \approx -\frac{Q^2 p^2}{6(4\pi\epsilon_0)^2 (k_B T) R^4}$$

where we used the fact that  $\langle \cos^4 \theta \rangle$  is a nonzero constant (you can easily check that  $\int_{-1}^1 x^4 dx$  is nonzero by symmetry of  $x^4$ , where  $x = \cos \theta$ ). When  $T \rightarrow \infty$ , the interaction energy  $V(R)$  vanishes. As the temperature of the system increases, more molecules have sufficient energy to occupy the less favorable configurations. The higher, less favorable, configurations are those

that give less favorable interactions between the dipoles (i.e., higher potential energy configurations).

(c) At thermal energies  $k_B T$  greater than the dipole-dipole interaction energy, the Keesom interaction averages over all angles and dipoles no longer have orientational preference to one another. The angle-averaged Keesom interaction potential and its condition is given below.

$$V(R)_{\text{Keesom}} = -\frac{|\vec{p}_A|^2 |\vec{p}_B|^2}{3(4\pi\epsilon_0\epsilon)^2 (k_B T) R^6} \quad \text{for} \quad k_B T > \frac{|\vec{p}_A| |\vec{p}_B|}{(4\pi\epsilon_0\epsilon) R^3}$$

(d)

$$k_B T = (1.38 \times 10^{-23} \text{ J/K})(298 \text{ K}) = 4.11 \times 10^{-21} \text{ J}$$

$$4.11 \times 10^{-21} \text{ J} \left( \frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} \right) = 0.0257 \text{ eV}$$

(e)

$$R = \left( \frac{|\vec{p}|^2}{(4\pi\epsilon_0\epsilon) k_B T} \right)^{1/3}$$

$$= \left( \frac{((3.34 \times 10^{-30} \text{ C.m.D}^{-1})(4.2 \text{ D}))^2}{4\pi(8.85 \times 10^{-12} \text{ F m}^{-1})(2.24)(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})} \right)^{1/3}$$

$$= 0.577 \text{ nm}$$

(f) As  $T \rightarrow \infty$ ,  $V(R)_{\text{Keesom}} \rightarrow 0$ .

g) In the low temperature limit, the energy is just the ground state energy. This is the result obtained in (a).

(h) As discussed in lecture, in the high- $T$  limit, there is an equal mix of ground and excited state configurations. When these average-out the interaction, it leads to partial cancellation and weakening of the interaction. This partial cancellation takes the long-range interaction ( $1/R^3$ ) and turns it into a short-range ( $1/R^6$ ) interaction. ■

**Problem 41.** Model the dissolution of NaCl in water by comparing the lattice energy of an NaCl crystal to the number of ion-dipole interactions of  $\text{Na}^+$  and  $\text{Cl}^-$  with the dipole of water that it would take to equal this energy according to the steps below.

(a) Calculate the ion-ion interaction energy between sodium cation and chloride anion by taking  $R = 0.282 \text{ nm}$  as the distance between the ion centers (an experimental value determined by crystallography) in the NaCl crystal lattice and using the Coulomb interaction (ion-ion) below. Assume vacuum so  $\epsilon = 1$ . The variable  $z$  refers to the charge valency of the ion (e.g.,  $z = 1$  for  $\text{Cl}^-$ ,  $z = 2$  for  $\text{Ca}^{2+}$ ,  $z = 3$  for  $\text{Fe}^{3+}$ , etc.).  $z$  times the elementary

charge of the electron,  $e$ , gives the charge of the ion. The experimentally determined value for the NaCl lattice energy is 787 kJ/mol. How close does your estimate compare to the experimental lattice energy? Propose reasons why your answer may deviate from the experimental value.

$$V(R)_{\text{ion-ion}} = \frac{z_1 z_2 e^2}{4\pi\epsilon_0\epsilon R}$$

(b) Calculate how many molecules of water it would take to equal the experimentally determined lattice energy of 787 kJ/mol for an NaCl crystal based entirely on ion-dipole interactions between water,  $\text{Na}^+$  and  $\text{Cl}^-$ . Use the value  $R = 0.354$  nm, the average distance between the center of sodium or chloride ions and the water dipole, in your calculation. Take the angle  $\theta$  to be equal to  $0^\circ$ , the ion-dipole orientation that yields a maximum value for the potential energy. Assume vacuum so  $\epsilon = 1$  for a more direct comparison to the lattice energy conditions. Note that in the diagram,  $Q$  represents the magnitude of the charge participating in the charge-dipole interaction. For the case of monovalent ions such as  $\text{Na}^+$  and  $\text{Cl}^-$ ,  $ze = Q$  where  $z$  represents ion valency and  $e$  represents the elementary charge  $e = 1.602 \times 10^{-19}$  C. See Fig. 2.17 for geometry.

$$V(R)_{\text{ion-dipole}} = -\frac{ze|\vec{p}| \cos \theta}{4\pi\epsilon_0\epsilon R^2}$$

(c) Convert the solubility limit of NaCl in water (36.0 g/100. mL) to a mole fraction and compare your answer to the mole fraction of 1 mol NaCl per mol  $\text{H}_2\text{O}$  from your answer to part (b). How close was your estimate to the experimental value?

**Solution.** (a)

$$\begin{aligned} V(R)_{\text{ion-ion}} &= \frac{(1)(1)(1.602 \times 10^{-19} \text{ C})^2(6.022 \times 10^{23} \text{ mol}^{-1})}{4\pi(8.854 \times 10^{-12} \text{ F m}^{-1})(1)(0.282 \times 10^{-9} \text{ m})} \\ &= 493 \text{ kJ/mol} \end{aligned}$$

This answer is not bad for a first order estimate but deviates significantly due to the long-range nature of Coulombic interactions. Ions other than nearest neighbors can interact with one another and must be considered. In more rigorous models of lattice energies, the term that accounts for this long-range interaction is called the Madelung constant. Furthermore, repulsions between ions of the same charge in the lattice are also significant.

(b)

$$\frac{n_{\text{H}_2\text{O}}}{n_{\text{NaCl}}} \times V(R)_{\text{ion-dip.}} = V(R)_{\text{ion-ion}}$$

where  $V(R)_{\text{ion-dip.}}$  evaluates to:

$$\begin{aligned} &= -\frac{ze|\vec{p}| \cos \theta}{4\pi\epsilon_0\epsilon R^2} \\ &= -\frac{(1)(1.602 \times 10^{-19} \text{ C})(6.17 \times 10^{-30} \text{ C.m})(1)(6.022 \times 10^{23} \text{ mol}^{-1})}{4\pi(8.854 \times 10^{-12} \text{ F.m}^{-1})(1)(0.354 \times 10^{-9} \text{ m})^2} \\ &= -42.7 \text{ kJ/mol} \end{aligned}$$

Considering only the absolute magnitudes of the energies and solving for moles of water

$$\frac{n_{\text{H}_2\text{O}}}{n_{\text{NaCl}}} = \frac{787 \text{ kJ/mol}}{42.7 \text{ kJ/mol}} = 18.4$$

We find that it would take 18 molecules of water to dissolve 1 molecule of NaCl. In other words, 9 molecules of water per ion. Please note that in this problem and in the previous one, we have assumed that  $\epsilon = 1$  (vacuum). We would get different results if we used the dielectric constant of each respective medium.

(c)

$$\begin{aligned} \frac{36.0 \text{ g NaCl}}{100. \text{ mL H}_2\text{O}} &\approx \frac{36.0 \text{ g NaCl}}{100. \text{ g H}_2\text{O}} \\ \frac{36.0 \text{ g NaCl}}{100. \text{ g H}_2\text{O}} \left( \frac{18.02 \text{ g/mol H}_2\text{O}}{58.44 \text{ g/mol NaCl}} \right) &= 0.111 \end{aligned}$$

Taking the reciprocal of this mole fraction gives a number of 9 moles of water for every mole of NaCl at the solubility limit which is surprisingly close to the coarse estimate of 18.4 from part (b). Please note that this assumes ions are homogeneously and randomly distributed in solutions. This is not the case (ions of opposing charge associate loosely, and there is also an ionic atmosphere forming). ■

**Problem 42.** At  $90^\circ\text{C}$ , the vapor pressure of methylbenzene is 400. Torr and that of 1,2-dimethylbenzene is 150. Torr. What is the composition of the liquid mixture that boils at  $90^\circ\text{C}$  when the pressure is 0.50 atm? Calculate the composition of the vapor produced.

**Solution.** Combine Dalton's law and Raoult's law.

$$P_{\text{total}} = P_A + P_B = X_A P_A^\circ + (1 - X_A) P_B^\circ$$

$$P_{\text{MB}}^\circ = 400. \text{ Torr}$$

$$P_{1,2\text{-DMB}}^\circ = 150. \text{ Torr}$$

Solve for  $X_{\text{MB}} = X_A$

$$X_A = \frac{P_{\text{total}} - P_B^\circ}{P_A^\circ - P_B^\circ}$$

Boiling occurs when

$$P_{\text{total}} = 0.50 \text{ atm} \left( \frac{760. \text{ Torr}}{1 \text{ atm}} \right) = 380 \text{ Torr}$$

Substituting

$$X_A = \frac{380 \text{ Torr} - 150. \text{ Torr}}{400. \text{ Torr} - 150. \text{ Torr}} = 0.920$$

$$X_{1,2\text{-DMB}} = X_B = 1 - 0.920 = 0.080$$

Vapor phase composition is given by

$$Y_{\text{MB}} = Y_A = \frac{X_A P_A^\circ}{P_B^\circ + (P_A^\circ - P_B^\circ) X_A}$$

$$= \frac{(0.920)(400. \text{ atm})}{150. \text{ atm} + (400. \text{ atm} - 150. \text{ atm})(0.920)} = 0.968$$

$$Y_{1,2\text{-DMB}} = Y_B = 1 - 0.968 = 0.032$$

■

**Problem 43.** Isothermal compressibility is a material property defined by:

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

- (a) Calculate  $\kappa$  for an ideal gas.  
 (b) Calculate  $\kappa$  for a VDW gas.

**Solution.** (a)

$$V = \frac{nRT}{P}, \quad \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{P}{nRT} \left( -\frac{nRT}{P^2} \right) = \frac{1}{P}$$

(b)

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left( \frac{\partial P}{\partial V} \right)_T^{-1}, \quad P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

$$\left( \frac{\partial P}{\partial V} \right)_T = -\frac{nRT}{(V - nb)^2} + \frac{2an^2}{V^3}$$

$$\kappa = -\frac{1}{V} \frac{1}{\left( -\frac{nRT}{(V - nb)^2} + \frac{2an^2}{V^3} \right)} = \frac{(V - nb)^2 \cdot V^{-1}}{nRT - 2an^2(V - nb) \cdot V^{-3}}$$

■

**Problem 44.** Calculate the thermal expansion coefficient,  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$ , for ideal and VDW gas.

**Solution.** Idea gas was done in class,  $\alpha = 1/T$ . Regarding  $V$  as a function of temperature,  $V = V(T)$ , we can solve for  $\left( \frac{\partial V}{\partial T} \right)_P$  by differentiation:

$$\frac{\partial}{\partial T} \left[ \left( P + a \frac{n^2}{V^2} \right) (V - nb) = nRT \right]_P$$

$$\begin{aligned} \frac{\partial}{\partial T} \left[ PV - Pnb + a \frac{n^2}{V} - ab \frac{n^3}{V^2} = nRT \right]_P \\ \left( \frac{\partial V}{\partial T} \right)_P \left( P - a \frac{n^2}{V^2} + 2ab \frac{n^3}{V^3} \right) = nR \\ \left( \frac{\partial V}{\partial T} \right)_P = \frac{nR}{P - a \frac{n^2}{V^2} + 2ab \frac{n^3}{V^3}} \end{aligned}$$

and then divide by  $V$  to arrive at the result.

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{nR}{PV - a \frac{n^2}{V} + 2ab \frac{n^3}{V^2}}$$

■

**Problem 45.** The Lennard-Jones potential is as follows:  $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ , where  $\epsilon$  and  $\sigma$  are constants. The  $\epsilon$  corresponds to the potential well depth at the equilibrium intermolecular (interatomic) distance. (i.e. where the potential energy is a minimum). Calculate the intermolecular (interatomic) distance in Å that corresponds to  $\epsilon$  for a He..He interaction. Derive an expression in terms of  $\sigma$  for this distance for any atomic/molecular interaction.

**Solution.** You might start out by sketching a potential energy curve. From such a graph we see that the distance we need to calculate occurs at the minimum of the function, so one technique to calculate this  $r$  is to take the derivative of the function and set it equal to zero and solve for an  $r$  value that makes the derivative equal to zero.

You may also want to find the constants for He.

$$\epsilon = 1.41 \times 10^{-22} \text{ J}, \quad \sigma = 2.56 \times 10^{-10} \text{ m} = 2.56 \text{ \AA}.$$

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

$$V(r) = 4\epsilon\sigma^{12}r^{-12} - 4\epsilon\sigma^6r^{-6}.$$

$$\frac{dV(r)}{dr} = (-12)(4\epsilon)\sigma^{12}r^{-11} - (-6)(4\epsilon)(\sigma^6)(r^{-5})$$

$$= (-6)(4\epsilon)(\sigma) \left[ 2 \left( \frac{\sigma}{r} \right)^{11} - \left( \frac{\sigma}{r} \right)^5 \right] = 0$$

When the square bracket equals zero,  $dV/dr = 0$ . Thus,  $2(\sigma^{11}/r^{11}) - (\sigma^5/r^5) = 0$  and  $2(\sigma^{11}/r^{11}) = (\sigma^5/r^5)$  which gives  $2(\sigma)^6 = (r)^6$  and  $r = (2\sigma^6)^{1/6} = \sigma(2)^{1/6} = \sigma(1.122)$ . This is the general expression in terms of  $\sigma$  for the distance  $r$ . Now, plug in  $\sigma$  for He to obtain the specific answer

$$(2.56 \text{ \AA})(1.122) = 2.87 \text{ \AA}$$

for the He...He interaction. ■



# Properties of Matter

The bulk properties of gases, liquids and solids — molar volume, density, compressibility, and thermal expansion, among others — differ widely, often by orders of magnitude. All of these properties depend on temperature and pressure. Gases, liquids and solids differ by their local structure. We have outlined the most important forces responsible for interactions between molecules. These forces help determine the structure of solids and liquids, solubility limits for different solutes, surface tension, boiling points, melting points, etc.

## 3.1. Structure of Liquids, Solids and Gases

Figure 3.1 illustrates the packing structure of solids (left), liquids (middle) and gases (right). As the Figure illustrates, gases are isolated molecules. Liquids are packed molecules, but the packing shows little ordering. Solids can be ordered.

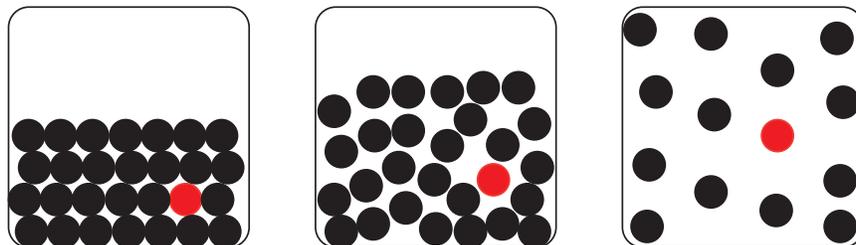


Figure 3.1. Structure of solids, liquids and gases.

**3.1.1. Density.** Liquids and solids are dense: their density is about 1,000 times larger than gases. However, they differ in their ordering: solids are often crystalline whereas liquids are usually disordered. Solids can also be disordered (amorphous). Gases are dilute and disordered.

**3.1.2. Compressibility.** Gases are compressible whereas liquids and solids are said to be incompressible. (Liquids and solids can be compressed slightly, but much less than gases can be compressed.) The isothermal compressibility  $\kappa$  of a substance is the change in its volume in response to a change in the applied pressure under conditions of constant temperature. The formal definition is:

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \approx -\frac{1}{V} \left( \frac{\Delta V}{\Delta P} \right)_T$$

where the approximation is good in the limit of small  $\Delta P$  and  $\Delta V$ . This says that  $\kappa$  is the (negative) fractional change in volume in response to a small pressure change. Its unit are inverse pressure. The value of  $\kappa$  for a real gas will depend on molecular properties such as molecular size and intermolecular interactions: for example, we expect that  $\kappa$  decreases with molecular size but increases as intermolecular interaction strength increases. On the other hand, let us take the ideal gas. Since  $PV = nRT$ ,  $V = nRT/P$ . Thus, the derivative with respect to  $P$  is  $\partial V/\partial P = -nRT/P^2$ . Then,  $\kappa = -(1/V)(-nRT/P^2)$ , and inserting  $V = nRT/P$  gives:

$$\kappa = \frac{1}{P}.$$

Thus, the lower the pressure, the higher the compressibility. The higher the pressure (in the container) the less compressible the gas is. Also, note that  $\kappa$  is independent of the gas type, as expected for an ideal gas.

Homework problem: calculate the isothermal compressibility of a VDW gas and compare with the case of an ideal gas.

**3.1.3. Mean Free Path.** The mean free path is defined as the average distance traveled by a molecule (or atom/particle) between successive collisions. In Section 1.5.2 we derived an expression for the mean free path in gases using arguments from kinetic theory. The collision causes the particles/molecules to change direction or energy. If the collisions are elastic, total momentum and total energy are conserved quantities. At ambient pressure, there are approximately  $10^{19}$  molecules/cc and the mean free path is on the order of 70 nm. The mean free path is inversely proportional to the gas density.

In a gas, the mean free path ( $\lambda$ ) is much larger than the molecular diameter  $d$ :  $\lambda \gg d$ . In a liquid, the mean free path is less than  $d$ :  $\lambda < d$ . In a solid there exists no concept of mean free path.

**3.1.4. Volume.** In a gas, the volume is inversely proportional to the pressure:  $V \propto P^{-1}$ . In a liquid or solid, the volume remains mostly constant.

**3.1.5. Thermal Expansion.** When a material such as a solid is heated it will expand because of the increase in interatomic distances within the lattice as a result of increased thermal vibrations (phonons). This is quantified by the coefficient of thermal expansion:

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \approx \frac{1}{V} \left( \frac{\Delta V}{\Delta T} \right)_P,$$

where the approximation holds in the limit of small  $\Delta T$  and  $\Delta V$ . The subscript  $P$  indicates constant pressure. For solids and liquids, this coefficient is on the order of 0.02% per degrees Celsius, which is much smaller than in the case of a gas.

**3.1.6. Diffusion Coefficient.** In Section 1.5.2 we derived an expression for the diffusion coefficient of gases using arguments from kinetic theory. In a gas, molecular diffusion is fast:  $D \sim 0.2 \text{ cm}^2/\text{s}$ . In a liquid, the diffusion is moderate:  $D \sim 2 \times 10^{-5} \text{ cm}^2/\text{s}$ . In a solid, diffusion is slow:  $D \sim 2 \times 10^{-9} \text{ cm}^2/\text{s}$  for hydrogen in iron or  $D \sim 10^{-30} \text{ cm}^2/\text{s}$  for aluminum in copper.

Note: “aluminum in copper” refers to the diffusion of aluminum atoms in a copper lattice. When specifying diffusion coefficients one must indicate the diffusing substance and the surrounding matrix. If only one substance is specified, this refers to the “self-diffusion” coefficient, i.e. how fast atoms/molecules move within the same substance.

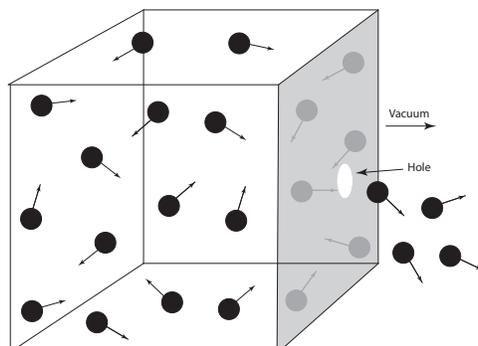
## 3.2. Effusion

Effusion is the flow of gas out of a container through a tiny hole (pinhole) as illustrated in Fig. 3.2. The effusion rate can be computed from the rate of collisions at the wall. The latter is proportional to:

$$\frac{N}{V} \bar{v} A \propto \frac{N}{V} \sqrt{\frac{8k_B T}{\pi m}} A.$$

Suppose that a container of volume  $V$  is held at temperature  $T$  and contains a mixture of two gases  $A$  and  $B$  ( $N_A$  molecules of  $A$  and  $N_B$  molecules of  $B$ ). This leads to:

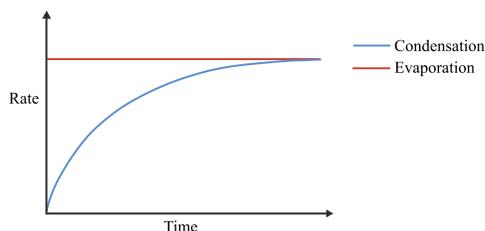
$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{N_A}{N_B} \sqrt{\frac{m_B}{m_A}}.$$



**Figure 3.2.** Effusion of a gas from a box through a small nozzle (hole).

This is Graham's law of effusion. A rigorous derivation requires arguments from the kinetic theory of gases. It was used in the past as a technique to separate isotopes by consecutive stages of enrichment. This technique was later replaced by the gas centrifuge method where the centrifugal force creates a gradient of molecules/atoms of different weights. Nowadays, the technique of laser isotope separation is the method of choice because of its much higher efficiency.

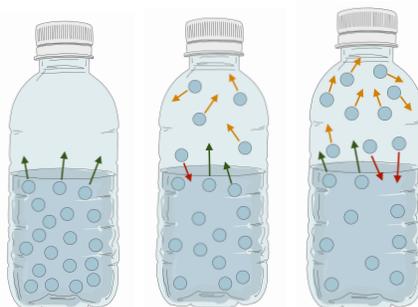
### 3.3. Phase Equilibrium



**Figure 3.3.** Approach to equilibrium in evaporation and condensation. Initially, the pressure above the liquid is very low, and many more molecules leave the liquid surface than return to it. As time passes, more molecules fill the gas phase until the equilibrium vapor pressure is approached; the rates of evaporation and condensation then become equal. Three points in time are illustrated in Fig. 3.4.

More than one phases (solid, liquid, gas) can co-exist. Suppose we evacuate a flask and put liquid water in it, with the temperature held at  $25^{\circ}\text{C}$ . We then monitor the pressure of water vapor inside the flask. At time  $t = 0$ , the pressure of water vapor begins to rise from zero. It increases with time and gradually levels off at a value of  $0.03126 \text{ atm}$ , which is the vapor pressure of water at  $25^{\circ}\text{C}$ . The contents of the flask have reached equilibrium, a condition in which no further changes in macroscopic properties occur as

long as the system remains isolated. If some of the water vapor that has formed is removed, additional water evaporates from the liquid to reestablish the same vapor pressure,  $P_{vap}(\text{H}_2\text{O})=0.03126$  atm.



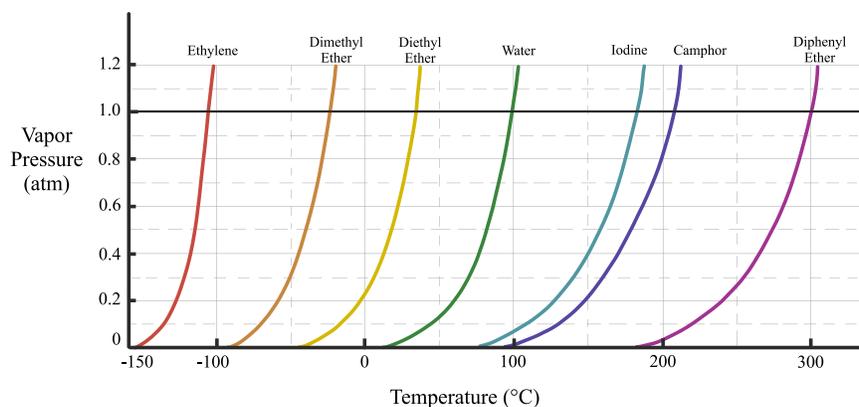
**Figure 3.4.** Schematic representation of the dynamics illustrated in Fig. 3.3, at three different points in time: (left)  $t = 0$ , (middle)  $t$ =intermediate and (right)  $t = \infty$ .

What is happening on a microscopic scale to cause this spontaneous movement of the system toward equilibrium? According to kinetic theory, the molecules of water in the liquid are in a constant state of thermal motion. Some of those near the surface are moving fast enough to escape the attractive forces holding them in the liquid; this process of evaporation causes the pressure of the water vapor to increase. As the number of molecules in the vapor phase increases, the reverse process begins to occur: molecules in the vapor strike the surface of the liquid, and some are captured, leading to condensation. As the pressure of the gas increases, the rate of condensation increases until it balances the rate of evaporation from the surface (see Figs. 3.3 and 3.4). Once this occurs, there is no further net flow of matter from one phase to the other; the system has reached phase equilibrium, characterized by a particular value of the water vapor pressure. Water molecules continue to evaporate from the surface of the liquid, but other water molecules return to the liquid from the vapor at an equal rate. A similar phase equilibrium is established between an ice cube and liquid water at the freezing point.

Vapor pressure depends on temperature and type of substance, as shown in Fig. 3.5. For fixed volume and number of moles, the temperature at which the vapor pressure equals 1 atm defines the **normal boiling point of a liquid** and the **normal sublimation point of a solid**.

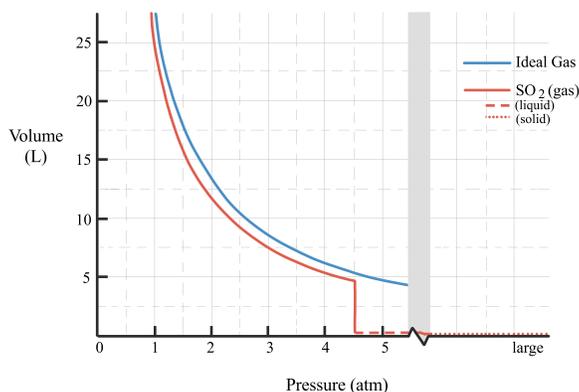
### 3.4. Phase Transitions

Suppose 1 mol of gaseous sulfur dioxide is compressed at fixed temperature of  $30^\circ\text{C}$ . The volume of the substance is measured at each pressure, and a



**Figure 3.5.** Temperature dependence of vapor pressure for different substances.

graph of volume against pressure is constructed (Fig. 3.6). At low pressures, the graph shows the inverse dependence ( $V \propto 1/P$ ) predicted by the ideal gas law. As the pressure increases, deviations appear because the gas is not ideal.

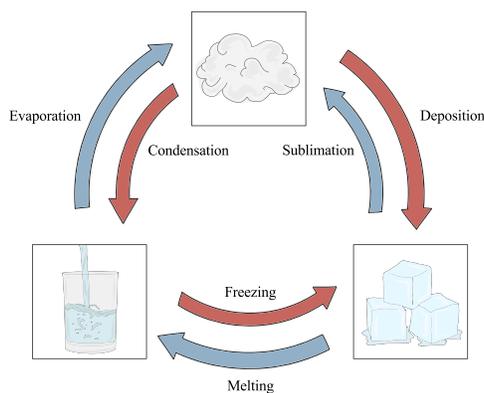


**Figure 3.6.** P-V diagram of  $\text{SO}_2$ .

For pressures up to 4.52 atm, this behavior is quite regular and can be described by the VDW equation. At 4.52 atm, something dramatic occurs: The volume decreases abruptly by a factor of 100 and remains small as the pressure is increased further. The gas underwent a phase transition from gas to liquid as a result of the applied pressure. If the compression of  $\text{SO}_2$  is continued, another abrupt (but small) change in volume will occur as the liquid freezes to form a solid.

Condensed phases also arise when the temperature of a gas is reduced at constant pressure. If steam (water vapor) is cooled at 1 atm pressure, it condenses to liquid water at  $100^{\circ}\text{C}$  and freezes to solid ice at  $0^{\circ}\text{C}$ . Liquids and solids form at low temperatures once the attractive forces between molecules become strong enough to overcome the kinetic energy of random thermal motion.

Six phase transitions occur among the three states of matter (see Fig. 3.7).



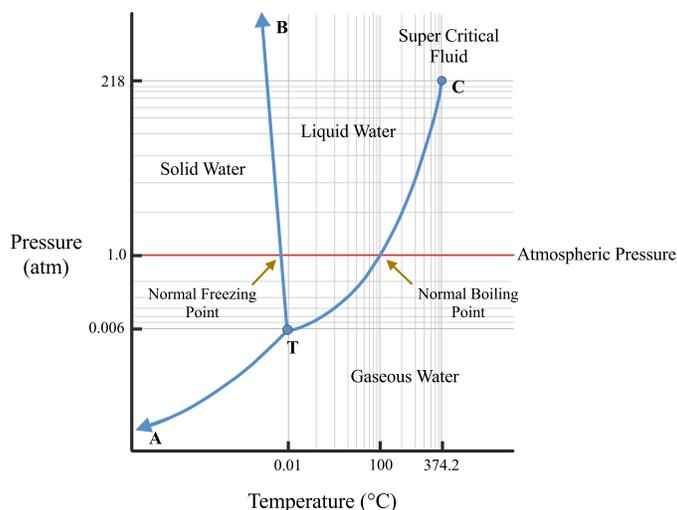
**Figure 3.7.** The most commonly encountered phase transitions in chemistry describe structural transitions between the liquid, solid and gas states.

### 3.5. Phase Diagrams

If the temperature of a substance is held constant and the applied pressure is changed, phase transitions between two phases will be observed at particular pressures. Making the same measurements at a number of different temperatures provides the data necessary to draw the phase diagram for that substance – a plot of pressure against temperature that shows the stable state for every pressure – temperature combination. Figure 3.8 shows a sketch of the phase diagram for water. For each substance there is a unique combination of pressure and temperature, called the triple point (marked “T”), at which the gas, liquid, and solid phases coexist in equilibrium. Extending from the triple point are three lines, each denoting the conditions for the coexistence of two phases at equilibrium. Along the line TA, solid and gas are in equilibrium; along TB, solid and liquid; and along TC, liquid and gas. The regions bounded by these lines represent conditions where only one phase exists.

The P-T diagram for  $\text{H}_2\text{O}$  at fixed volume is shown in Fig. 3.8.

Notice how the solid-liquid coexistence line tilts leftward. This is a result of the anomalous properties of water (owing to its abilities for hydrogen



**Figure 3.8.** P-T diagram of  $\text{H}_2\text{O}$ .

bonding and directionality of the bonding); for  $\text{H}_2\text{O}$ , the ice phase is less dense than the liquid phase. Other substances tilt towards the right, because the solid phase is denser than the liquid phase.

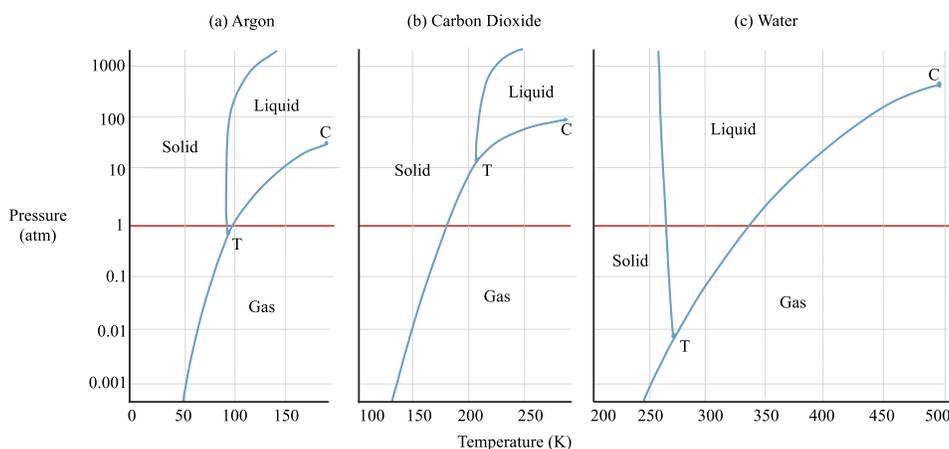
A P-V-T diagram may look like the one shown in Fig. 1.5. Note: This surface plot is definitely *not* for water, because the solid-liquid coexistence line does not tilt leftward. To learn more about the anomalous properties of water, see:

[http://www1.lsbu.ac.uk/water/water\\_anomalies.html](http://www1.lsbu.ac.uk/water/water_anomalies.html)

The gas-liquid coexistence curve extends upward in temperature and pressure from the triple point. This line (similar to a parabola) is the vapor pressure curve of the liquid substance. The gas-liquid coexistence curve does not continue indefinitely, but instead terminates at the critical point (labelled). Along this coexistence curve there is an abrupt, discontinuous change in the density and other properties from one side to the other. The differences between the properties of the liquid and the gas become smaller as the critical point is approached and disappear altogether at that point.

For pressures above the critical pressure (218 atm for water), it is no longer possible to identify a particular state as gas or liquid. A substance beyond its critical point is called a supercritical fluid because the term fluid includes both gases and liquids. The liquid-solid coexistence curve does not terminate as the gas-liquid curve does at the critical point, but continues to indefinitely high pressures. In practice, such a curve is almost vertical because large changes in pressure are necessary to change the freezing temperature of a liquid. For most substances, this curve inclines slightly to the

right (Fig. 3.9a,b): An increase in pressure increases the freezing point of the liquid. In other words, at constant temperature, an increase in pressure leads to the formation of a phase with higher density (smaller volume), and for most substances, the solid is denser than the liquid. Water and a few other substances are anomalous (see Fig. 3.9c); for them, the liquid-solid coexistence curve slopes up initially to the left, showing that an increase in pressure causes the solid to melt. This anomaly is related to the densities of the liquid and solid phases: ice is less dense than water (which is why ice cubes float on water), so when ice is compressed at  $0^{\circ}\text{C}$ , it melts.



**Figure 3.9.** P-T diagrams for argon (a), carbon dioxide (b) and water (c).

## 3.6. Solutions

Solutions are homogeneous systems that contain two or more substances. Usually, it consists of a solvent (liquid) in which we have dissolved a second substance (solid, gas or liquid). “Solid solutions” are also possible in which more than two different substances are mixed, such as bismuth and selenium.<sup>1</sup> The host substance is called the solvent and the added substance is the solute.<sup>2</sup>

**3.6.1. Composition: Mole Fraction, Molarity and Molality.** The **mole fraction**,  $X_1$ , of a substance, 1, in a mixture is the number of moles of that substance,  $n_1$ , divided by the total number of moles of all substances

<sup>1</sup>In solid solutions, it is more difficult to maintain homogeneity of the system, depending on the degree of miscibility of the constituent substances. We often observe a certain amount of phase separation.

<sup>2</sup>The usual convention is to label as “solvent” the most abundant substance.

present  $n_1 + \dots + n_N$ :

$$X_1 = \frac{n_1}{n_1 + n_2 + \dots + n_N}$$

where  $N$  is the number of substances present (including the solvent) and  $n_i$  is the number of moles of the  $i$ -th substance.

The **concentration** of a substance is the number of moles per unit volume. The basic unit is **molarity**, defined as number of moles of solute per liter of solution:

$$\text{molarity} = \frac{\text{moles solute}}{\text{liters solution}} = \text{mol L}^{-1} \equiv \text{M}.$$

Because volume depends on temperature, some prefer to use **molality**, which is defined as the number of moles of solute per kilogram of solvent:

$$\text{molality} = \frac{\text{moles solute}}{\text{kilograms solvent}} = \text{mol kg}^{-1}.$$

We note that at 20° C the two concepts are identical for water, since its density is 1.00 g/cm<sup>3</sup> (so that 1.00 L of water weighs 1.00 kg).

**3.6.2. Preparing Solutions.** Suppose that a solution of 1 M (molar) concentration is prepared. One possible method is to weigh 1 mol of solute, then add slightly less than 1 L of solvent (to avoid overshooting our target volume of 1 L). We then add solvent continuously until we reach a final volume of exactly 1 L.

In chemistry, we often prepare “stock solutions” which are highly concentrated, then dilute the stock solution to obtain the desired concentration. Suppose that the stock solution contains  $n_1 = c_1 V_1$  moles of solute, where  $c_1$  is the concentration of solute and  $V_1$  is the volume of stock solution. To get a solution of concentration  $c_2$  from this, all we need to do is realize that if we dilute the solution, it will still contain  $n_1$  moles of solute. Thus,  $n_1 = n_2$ , where  $n_2 = c_2 V_2$ . So, we may write:

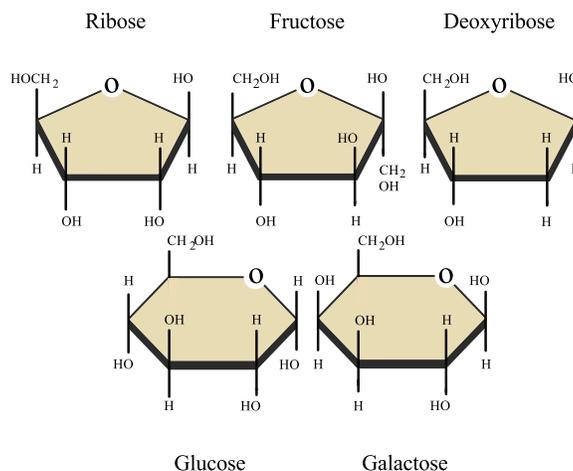
$$c_2 = \frac{\text{moles of solute}}{\text{final solution volume}} = \frac{c_1 V_1}{V_2}.$$

### 3.7. Non-Electrolyte Solutions

In organic and inorganic chemistries, different solvents than water are normally used. Here, we shall mainly discuss solutions of the aqueous type. When dissolving a solute, such as  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , in water, we write it as  $\text{C}_{12}\text{H}_{22}\text{O}_{11}(aq)$  to mean that the environment is aqueous. Solutions can be classified as electrolytes and non-electrolytes, due to the very different nature of the intermolecular interactions.

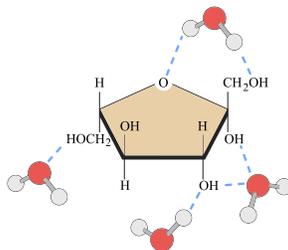
Non-polar molecules such as hydrocarbons do not dissolve significantly in water. Hydrocarbons are *hydrophobic* and tend to phase-separate. Molecules

that are polar are readily dissolved in water. A typical example is sugar,  $C_m(H_2O)_n$ . Some examples of common sugars are shown in Fig. 3.10.



**Figure 3.10.** Pentoses.

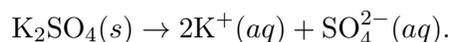
As can be seen in Fig. 3.10 these molecules include OH (hydroxyl) groups bonded to carbon atoms, which provide sites for hydrogen bonding interactions with water molecules. Figure 3.11 shows the example of the fructose molecule whose hydroxyl groups readily form a hydrogen bonding network with surrounding water molecules. Also shown is a hydrogen bond between a water molecule and an oxygen atom in the fructose ring.



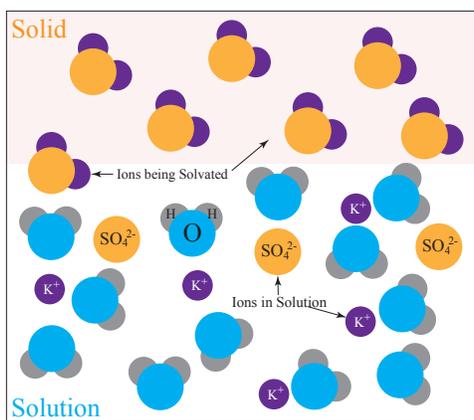
**Figure 3.11.** Hydrogen bonding between fructose and surrounding water molecules.

### 3.8. Electrolyte Solutions

3.8.0.1. *Dissolution of Electrolytes.* In electrolyte solutions the ion-dipole solute-solvent bonding can be much stronger than the case of dipole-dipole interactions (or hydrogen bonding) for non-electrolyte solutions. Consider the dissolution of potassium sulfate:

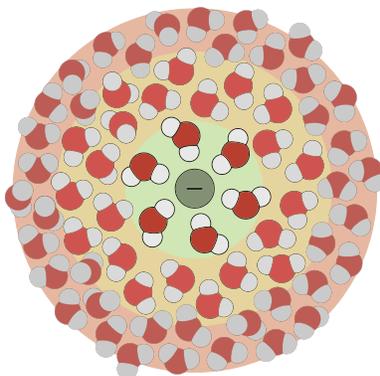


The dissolution occurs through the ion-dipole forces. Each positive ion is surrounded by water molecules with the negative end of their dipole moments toward the positive ion. For most ionic solids, several water molecules are needed to pull an ion from the lattice. In Problem 32 (p. 104) you are asked to calculate how many water molecules are needed to dissolve  $\text{Na}^+$  and  $\text{Cl}^-$  ions from the  $\text{NaCl}$  lattice.



**Figure 3.12.** Electrolyte solution.

In Fig. 3.12, each  $\text{SO}_4^{2-}$  anion in solution is surrounded by water molecules oriented with the positive end of their dipole moments toward the anion. Likewise, each  $\text{K}^+$  ion is surrounded by water molecules oriented with the negative end of their dipole moments toward the cation.



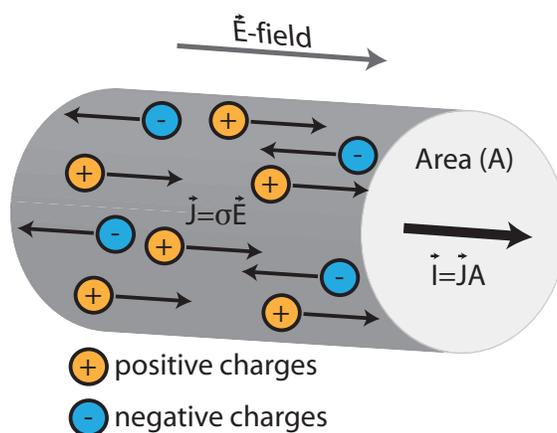
**Figure 3.13.** Hydrated ion.

3.8.0.2. *Hydration Shell of Ion.* The ability of salts to dissolve in water depends strongly on their stabilization by the solvent molecules. This process is known generally as solvation, and in the case of water, as hydration. All ions dissolved in water are hydrated (see Fig. 3.13).

In the standard model for hydrated ions (Fig. 3.13), the water molecules (red) closest to the negative ion (green) are the most tightly bound, and constitute the primary hydration shell.  $\text{H}_2\text{O}$  molecules in the outer hydration shell experience local ordering by hydrogen bonding, but this is opposed by the electrostatic field of the central cation. As one moves farther out and the electrostatic field due to the central ion weakens, local hydrogen bonded-clusters enlarge and begin to dominate, finally becoming the sole source of local ordering within the bulk water region of the solution.

The attractive forces that are operational here [hydrogen bonding (dipole-dipole) and even the stronger ion-dipole forces that bind the waters in the primary shell to the central ion] are continually subject to disruption by thermal motions. This affects even the waters within the primary shell; residence times of these  $\text{H}_2\text{O}$  molecules are usually less than  $10^{-4}$  s.

### 3.9. Ionic Conduction



**Figure 3.14.** Electrical conductivity in a material. The current density  $\vec{J} = \sigma \vec{E}$  is proportional to the conductivity  $\sigma$  and applied electric field  $\vec{E}$ . Multiplication of  $\vec{J}$  by the cross-sectional area of the conductor,  $A$ , gives the total current  $\vec{I}$ . The direction of  $\vec{J}$  points along  $\vec{E}$ . The units of  $\vec{J}$  are  $\text{A}/\text{m}^2$ . Since the units of  $\vec{E}$  are  $\text{V}/\text{m}$ , the SI unit for conductivity are Siemens per meter ( $\text{S}/\text{m} = \text{A}/\text{V}\cdot\text{m}$ ), where  $1 \text{ S} = 1 \Omega^{-1} = 1 \text{ A}/\text{V}$ .

The phenomenon of electrical conductivity is illustrated in Fig. 3.14. Electrical charges experiencing an electric field  $\vec{E}$  accelerate due to the Lorentz force,  $\vec{F} = Q\vec{E}$ , but are slowed down because of scattering<sup>3</sup>. The net effect

<sup>3</sup>While electrons in the conduction band of a conductor do not interact with each other (the “free electron gas” model), they do scatter at the positively charged lattice sites via the Coulomb interaction.

is to eliminate acceleration, leaving charges that are moving at constant velocity. This is the statement of Ohm's law,  $\vec{J} = \sigma \vec{E}$ , where  $\sigma$  is the electrical conductivity of the medium in which charges flow. Multiplication of  $\vec{J}$  by the cross-sectional area of the conductor,  $A$ , gives the total current,  $\vec{I}$ .

Suppose that our conductor has a square cross-sectional area,  $A = L^2$ , where  $L$  is the side length. Multiplication of  $\vec{J} = \sigma \vec{E}$  by  $A$  gives  $\vec{I} = (\sigma L)(\vec{E}L)$ . Denoting  $\vec{E}L$  as the voltage  $V$  and  $(\sigma L)$  as  $R^{-1}$  (the inverse resistance). This gives  $I = R^{-1}V$  or  $V = RI$ , which is the familiar form of Ohm's law. The units of  $R$  are Ohm ( $\Omega$ ). The inverse of conductivity,  $\sigma^{-1}$ , is called the resistivity. The units of  $\sigma^{-1}$  are  $\Omega \cdot \text{m}$ .

The units of  $\vec{I}$  are C/s; thus charges are flowing at constant rate as long as  $\vec{E}$  remains constant. The sign convention is that positive charges move along  $\vec{E}$  (and therefore,  $\vec{I}$ ) whereas negative charges move in the opposite direction. In a metallic conductor, negative charges are electrons and positive charges are holes. In ionic solutions, positive charges are the positively charged ions whereas negative charges are the negatively charged ions.

The conduction of electricity through an ionic solution differs from metallic conduction in two fundamental ways:

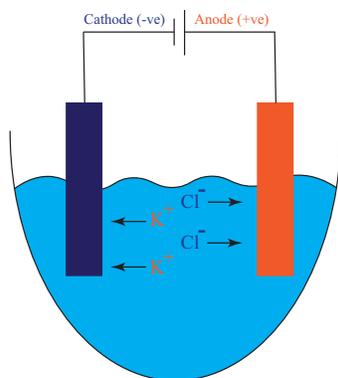
- The current is associated with the transport of relatively large and massive hydrated ions, rather than by nearly weightless electrons. Compared to ions, electrons move largely unimpeded through the metal. But ions, with their closely-held waters of hydration and more diffuse secondary hydration shell and oppositely-charged counterions, must disrupt the local hydrogen-bonded water structure as they move through the solution.
- Transfer of electric charge into and out of the solution occurs at electrodes, and is accompanied by chemical reactions at these interfaces.

Electrolytic conduction involves the transport of electric charge in the form of hydrated ions. Movement of these ions in response to an electric potential gradient is known as migration. Transport of electric charge is measured in Ampère (A).  $1 \text{ A} \equiv 1 \text{ C/s}$ . Current ( $I$ ) is the flow of charge per unit time:  $I = dQ/dt$ , where  $Q(t)$  describes is the electric charge in a given region as function of time.

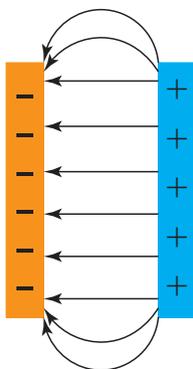
An ion of charge  $Q$  undergoes a drift from cathode to anode in solution, under the action of an electric field  $\mathbf{E}$ . In chemistry, the convention is to call the cathode the electrode which attracts positive ions and the anode the electrode which attracts negative ions.<sup>4</sup> See Fig. 3.15.

When a voltage (potential difference),  $V = V(\text{cathode}) - V(\text{anode})$ , is applied an electric field is created between the two electrodes. The  $E$ -field

<sup>4</sup>In physics, the convention is reversed: the anode is the negatively charged electrode and the cathode is the positively charged electrode.



**Figure 3.15.** Experimental setup for the electrolysis of KCl.



**Figure 3.16.** Electric field between two parallel plates (anode and cathode).

arrows point from the positive electrode to the negative electrode. The  $E$ -field lines are shown in Fig. 3.16.

This electric field gives rise to a force  $\mathbf{F} = Q\mathbf{E}$ . While  $\mathbf{F} = m\mathbf{a}$ , the ions accelerate under the  $E$ -field, but also slow down because of random thermal motion and viscous drag (collision with fluid molecules). The overall motion is that of a constant velocity rather than acceleration.

Using this sign convention, in Fig. 3.16, the anode (positive electrode) is on the right, the cathode (negative electrode) is on the left, and the  $E$ -field arrows between the two electrodes point from right to left (with  $E$ -field lines always originating from the + charges at the electrodes). According to  $\mathbf{F} = Q\mathbf{E}$ , the negative ions ( $Q < 0$ ) drift from left to right (direction opposite to the  $E$ -field), i.e. from the cathode to the anode.

Force over distance leads to work:<sup>5</sup>

$$W(\text{work}) = \int_a^b \mathbf{F} \cdot d\mathbf{l} = Q \int_a^b \mathbf{E} \cdot d\mathbf{l}$$

where the integral is carried out along a path (line or curve) connecting  $a$  to  $b$ . If  $\mathbf{E}$  is parallel to the path  $d\mathbf{l}$ ,  $\mathbf{E} \cdot d\mathbf{l} = E dl$  and we get

$$W = Q \int_a^b E dl = Q[V(b) - V(a)].$$

where  $V(b) - V(a)$  is the potential difference (voltage) between the two electrodes (one at  $a$  and one at  $b$ ). Electric field has units of V/m; if we have two electrodes separated by a distance  $d$ , then the  $E$ -field has magnitude  $V/d$ , where  $V$  is the potential difference between the two electrodes,  $V = V(b) - V(a)$ .

Electric charge is measured in units of Coulombs. One Coulomb (1 C) is one ampère-second (1 A.s); if a current of one ampère (1 A) flows for one minute (60 s), the quantity of charge transported will be 60 C.

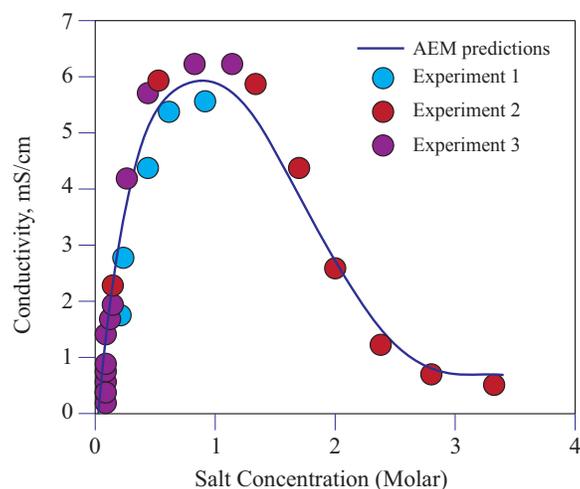
When charges migrate in an electric field, thermodynamic work is done. One Coulomb (1 C) of charge moving through a potential difference of one volt results in the performance of one joule (1 J) of work.

*Ideal solutions* are solutions whose properties depend linearly on the concentration of a dissolved species. Water is not electrically conductive unless we add electrolytes. The dissolved ions conduct electricity. We would expect that the electric conductivity  $\sigma$  of the solution increases linearly with the concentration of ions  $[A^+]$ , i.e.  $\sigma \propto [A^+]$ . This is true at low ion concentrations. However, the more ions are dissolved in solution, the more they interact among each other, leading to deviations from ideal behavior. In fact, for “strong” electrolytes, at high concentrations, the conductivity begins to *decrease*, as shown in Fig. 3.17.

In general, ionic solutions are *not ideal*, meaning that we can expect interaction among the ions leading to deviations from ideal behavior. The non-ideality character of a solution occurs at ion concentrations above 10–100  $\mu\text{M}$ ; the exact point of onset depends on the strength of intermolecular interactions.

Significant early developments in the theory of electrolyte solutions are due to Debye and Hückel (1923) as well as Lars Onsager. The decrease in the molar conductivity of a strong electrolyte was attributed to the mutual interference of the ions, which becomes more pronounced as the concentration increases. Because of the strong attractive forces between ions of opposite

<sup>5</sup>I removed the minus signs to keep things simple. In physics books, the sign convention is slightly different:  $\mathbf{E} = -\nabla V$  ( $\nabla =$  gradient, or derivative with respect to space),  $V(b) - V(a) = \int_a^b (\nabla V) \cdot d\mathbf{l} = -\int_a^b \mathbf{E} \cdot d\mathbf{l}$ . Then,  $W = \int_a^b \mathbf{F} \cdot d\mathbf{l} = -Q \int_a^b \mathbf{E} \cdot d\mathbf{l} = Q[V(b) - V(a)]$ .

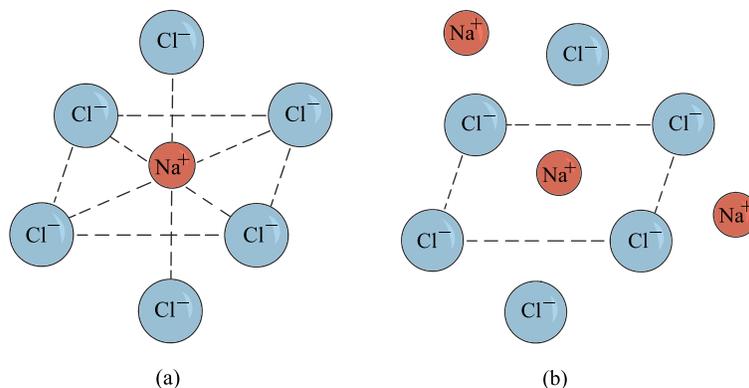


**Figure 3.17.** Conductivity of saline solution and comparison to theory (AEM, Advanced Electrolyte Model by Kevin Gering, R&D 100, FLC Far West, and Idaho Innovation awards, 2014). In the low concentration limit, conductivity increases with ion concentration. However, at higher ion concentrations, the conductivity decreases due to significant ion-ion interactions. The SI unit for conductivity is Siemens per meter (S/m).  $1 \text{ S} = 1 \text{ } \Omega^{-1} = 1 \text{ A/V}$ , or  $1 \text{ S} = 1 \text{ A}^2/(\text{kg}\cdot\text{m}^2\cdot\text{s}^3)$ .

signs, the arrangement of ions in solution is not completely random. In the immediate neighborhood of any positive ion, there tend to be more negative than positive ions, whereas for a negative ion there are more positive than negative ions. Onsager accounted for thermal effects leading to random motion of the ions.

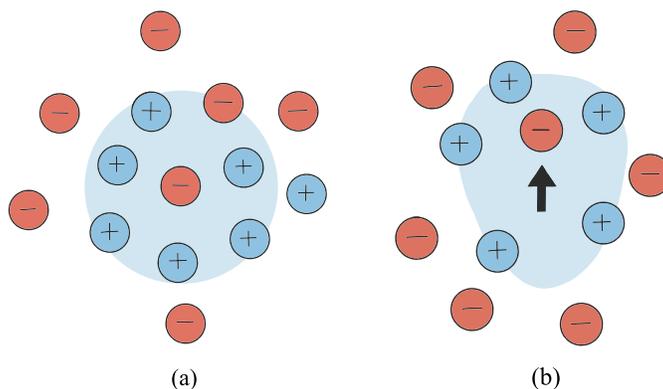
The specific example of NaCl is shown in Fig. 3.18. As seen in Fig. 3.18(a), each sodium ion has six chloride ions as its nearest neighbor. When the sodium chloride is dissolved in water, this ordering is still preserved to a very slight extent [Fig. 3.18(b)]. The ions are much farther apart than in the solid; the electrical attractions are therefore much smaller and the thermal motions cause irregularity. The small amount of ordering that does exist, however, is sufficient to exert an important effect on the conductivity of the solution.

The effect of the ionic atmosphere is to exert a drag on the movement of a given ion. If the ion is stationary, the atmosphere is arranged symmetrically about it and does not tend to move it in either direction. See Fig 3.19(a). However, if a potential that tends to move the ion (indicated by the upward arrow) is applied, the atmosphere will decay to some extent under the ion and build up more above it. See Fig. 3.19(b). Since it takes time for these *relaxation* processes to occur, there will be an excess of ionic atmosphere



**Figure 3.18.** Structure of NaCl in solid (crystalline) form (a) and in solution (b). The solution structure is time-averaged.

below the ion (i.e., behind it) and a deficit above (in front of it). This asymmetry of the atmosphere will have the effect of dragging the central ion back. This is the relaxation or asymmetry effect.



**Figure 3.19.** (a) The ionic atmosphere surrounds an ion. (b) When the ion moves, the ionic atmosphere follows the ion as it moves in solution.

There is a second reason why the existence of the ionic atmosphere impedes the motion of an ion. Ions are attracted to solvent molecules mainly by ion-dipole forces; therefore, when they move, they drag solvent along with them. The ionic atmosphere, however, having a charge opposite to that of the central ion, moves in the opposite direction to it and therefore drags solvent in the opposite direction. This means that the central ion has to travel upstream, and it therefore travels more slowly than if there were no effect of this kind. This is the electrophoretic effect (Fig. 3.20).

The theory of Debye and Hückel supposes the ions travel through the solution in straight lines, neglecting zigzag Brownian motion brought about by

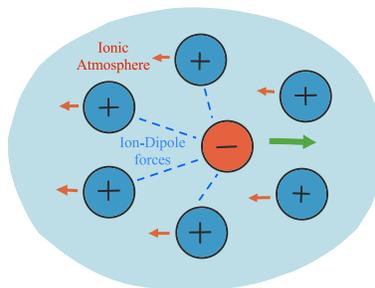


Figure 3.20. Electrophoretic effect.

collisions of surrounding solvent molecules. Lars Onsager in 1926 improved the theory to account for these “thermal effects.”

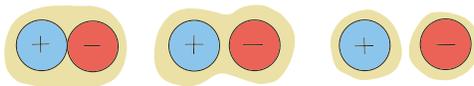
**3.9.1. Ionic Solutions Generally Exhibit Non-Ideal Behavior.** The conceptual definition of an ideal solution requires that the interactions of solvent-solvent, solvent-solute, and solute-solute molecules are identical, something that is clearly not possible in ionic solutions. As a consequence, the operational criteria of solution ideality (linear dependence of colligative and other properties on nominal concentrations), does not apply. In general, we cannot realistically expect calculations based on equilibrium constants to reliably predict the compositions of solutions having significant concentrations of ions.

The actual quantity we use to express the summed concentrations of ions of all kinds in a solution is the ionic strength. See this Wikipedia article for a definition and examples: [http://en.wikipedia.org/wiki/Ionic\\_strength](http://en.wikipedia.org/wiki/Ionic_strength) What “significant” means in this context depends on the charges of the ions, and this includes “spectator” ions that are not directly involved in a reaction. A very crude rule-of-thumb is that ion concentrations in excess of 0.0001 M are likely to exhibit non-ideal behavior.

**3.9.2. Interactions Among Dissolved Ions.** It is not possible using conventional synthetic chemistry techniques to introduce a single kind of ion into water. Bulk matter cannot possess a significant net electric charge. Thus, all ionic solutions contain both anions and cations in the proportions required to ensure electroneutrality. Coulombic interactions between charged particles fall off with separation distance far more slowly than do the weaker ion-dipole forces responsible for water ordering, and *are thus operative even in solutions that we would normally regard as quite dilute*, down to about  $10^{-4}$  M.

3.9.2.1. *Oppositely-Charged Ions Tend to Pair Up.* Depending on the sizes and charges of the two kind of ions, they may form relatively stable ion

pairs in which the “bonding” is purely electrostatic and independent of the chemical properties of the ions (Fig. 3.21).



**Figure 3.21.** Oppositely-charged ions in solution tend to pair up.

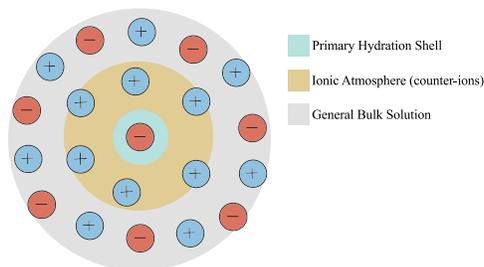
Neglect of ion-pairing can lead to erroneous assumptions about the concentrations of “free” ions in solutions, and misinterpretation of calculations involving solubility. Here are a few examples:

- In addition to forming the sparingly-soluble solid  $\text{CdI}_2$ , part of the cadmium in a solution in equilibrium with the two ions will exist as the soluble species  $\text{CdI}^+(aq)$  and  $\text{CdI}_2^0(aq)$ .
- Similarly, solutions in equilibrium with  $\text{Ca(OH)}_2(s)$  will also contain species  $\text{CaOH}^+(aq)$  and  $\text{Ca(OH)}_2^0(aq)$ .
- The ion-pair  $\text{CaCO}_3^0(aq)$  is believed to tie up a significant fraction of the total carbonate when water is in equilibrium with solid calcium carbonate.

The ions in the more strongly-bound pairs will be in contact and within a common hydration shell, whereas others may have only their shells in contact.

### 3.9.2.2. *Electrostatic Forces Lead to Local Charge Imbalances Near an Ion.*

Simple electrostatics predicts that oppositely-charged ions are more likely to be found close to a given ion, while like-charged ions tend to be farther away. Thus in addition to hydration shells, ions in solution are surrounded by a region containing an excess of counter-ions, known as the *ionic atmosphere*. The latter tends to move along with the ion as it diffuses or migrates through the solution.



**Figure 3.22.** Ionic atmosphere.

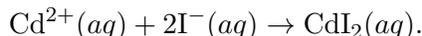
- In Fig. 3.22, the ionic atmosphere corresponds to the yellow region just outside the primary hydration shell [blue].

- Although only the positive counter-ions are explicitly represented in the ionic atmosphere in the diagram, it is important to understand that the atmosphere contains ions of both charges; the positive ions are just present in greater quantity. Near the outer boundary of the ionic atmosphere, the displaced negative ions are in excess. Only in the bulk solution are their concentrations identical.
- The atmosphere surrounding an cation will of course have the opposite charge. Because cations tend to be smaller than anions, the volume and charge density of the atmosphere is expected to be bigger.

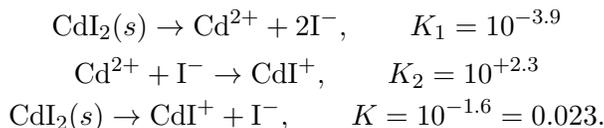
**3.9.3. Most Salts are Not Completely Dissociated in Water.** The dissolution of cadmium iodide in water is commonly represented as



This is actually wrong.<sup>6</sup> To most people, this would imply that a 0.1 M solution of this salt would contain 0.1 M of  $\text{Cd}^{2+}(aq)$ ? This would be wrong because it fails to take into account that the two ions react with each other. Firstly, they combine to form neutral, largely-covalent molecular species:



This non-ionic form accounts for 76% of the Cd present in the solution. In addition, they form a molecular ion  $\text{CdI}^+(aq)$  according to the following scheme (the  $K$ 's are equilibrium constants, see Section 4.1.0.1):



As a consequence, the concentration of “free”  $\text{Cd}^{2+}(aq)$  in an aqueous cadmium iodide solution is only about 2% of the value you would calculate by taking  $K_1$  as the solubility product. The principal component of such a solution is actually (covalently-bound)  $\text{CdI}_2(aq)$ . It turns out that many salts, especially those of metals beyond Group 2, are similarly only partially ionized in aqueous solution. See Table 3.1.

**Table 3.1.** Species present in various ionic solutions. This is Table 2 from [13].

Solute	Molarity	Ionic Strength		Fraction of Metal Present as Each Species		
KCl	0.52	0.5	$\text{K}^+$	0.95	KCl	0.05
CsCl	0.55	0.5	$\text{Cs}^+$	0.9	CsCl	0.1
KI	0.58	0.5	$\text{K}^+$	0.87	KI	0.13
CsI	0.61	0.5	$\text{Cs}^+$	0.82	CsI	0.18
$\text{Na}_2\text{SO}_4$	0.25	0.5	$\text{Na}^+$	0.76	$\text{NaSO}_4^-$	0.24

<sup>6</sup>The data shown here and in the table are from Ref. [13]. This fact was stated by Arrhenius in 1887, but has been largely ignored and is almost never mentioned in standard textbooks.

K <sub>2</sub> SO <sub>4</sub>	0.36	0.7	K <sup>+</sup>	0.7	KSO <sub>4</sub> <sup>-</sup>	0.3		
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.23	0.5	NH <sub>4</sub> <sup>-</sup>	0.8	NH <sub>4</sub> SO <sub>4</sub> <sup>-</sup>	0.2		
MgSO <sub>4</sub>	0.043	0.1	Mg <sup>2+</sup>	0.58	MgSO <sub>4</sub>	0.42		
MgCl <sub>2</sub>	0.44	1.0	Mg <sup>2+</sup>	0.7	MgCl <sup>+</sup>	0.3		
BeCl <sub>2</sub>	0.27	0.7	Be <sup>2+</sup>	0.8	BeCl <sup>+</sup>	0.2		
CaCl <sub>2</sub>	0.44	1.0	Ca <sup>2+</sup>	0.7	CaCl <sup>+</sup>	0.3		
SrCl <sub>2</sub>	0.42	1.0	Sr <sup>2+</sup>	0.7	SrCl <sup>+</sup>	0.3		
BaCl <sub>2</sub>	0.39	1.0	Ba <sup>2+</sup>	0.8	BaCl <sup>+</sup>	0.2		
Pb(NO <sub>3</sub> ) <sub>2</sub>	0.021	0.05	Pb <sup>2+</sup>	0.65	PbNO <sub>3</sub> <sup>+</sup>	0.33	Pb(NO <sub>3</sub> ) <sub>2</sub>	0.02
CuSO <sub>4</sub>	0.045	0.1	Cu <sup>2+</sup>	0.56	CuSO <sub>4</sub>	0.44		
FeSO <sub>4</sub>	0.047	0.1	Fe <sup>2+</sup>	0.53	FeSO <sub>4</sub>	0.47		
CuCl <sub>2</sub>	0.42	1.0	Cu <sup>2+</sup>	0.7	CuCl <sup>+</sup>	0.3		
CdCl <sub>2</sub>	2.86	1.0	Cd <sup>2+</sup>	0.014	CdCl <sup>+</sup>	0.31	CdCl <sub>2</sub>	0.67
CdI <sub>2</sub>	0.50	0.14	Cd <sup>2+</sup>	0.02	CdI <sup>+</sup>	0.22	CdI <sub>2</sub>	0.76

**3.9.4. Activities and Activity Coefficients.** The quantitative treatment of ionic solutions is based on the Debye-Hückel theory, which was developed in the 1920s. This theory models the electrostatic interactions between ions and their ionic atmospheres, and can predict mean ionic activity coefficient for solutions whose ionic strengths are not very high. Many extensions to this model have been suggested; all are mathematically complicated and all fail for “highly concentrated” solutions.

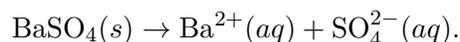
The practical approach to the problem of non-ideality is to introduce a quantity known as the activity, which can be thought of as the thermodynamically-effective concentration. The relation between activity  $a$  and the “analytical” concentration  $c$  is given by the activity coefficient  $\gamma$  (gamma), where  $a = \gamma c$ .

An ideal solution has  $\gamma = 1$ . As ionic concentrations increase, activity constants diminish. Activity coefficients approach unity in the limit of zero concentration. Because solutions containing ions of a single charge species cannot be prepared, all experimental measurements can only yield mean ionic activity coefficients (i.e. the coefficient describes both positive *and* negative ions simultaneously).

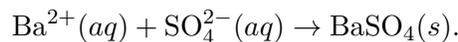
**3.9.5. Reactions: Halide Compounds.** An unknown solution that is suspected to contain halide compounds such as KCl, KBr and KI can be identified with silver nitrate solution, AgNO<sub>3</sub>. The halogen will react with Ag<sup>+</sup> and form a precipitate, with varying color depending on the halogen:

- AgF: No Precipitate
- AgCl: White
- AgBr: Pale Yellow
- AgI: Bright Yellow

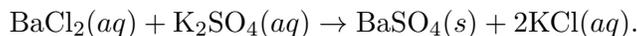
**3.9.6. Reactions: Precipitation.** Barium sulfate is not very soluble in water at room temperature. The following reaction is very unfavorable:



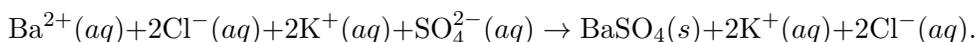
Instead, the reverse reaction is much more likely to happen. It is called a **precipitation reaction**



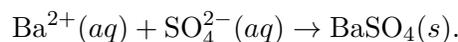
One possible way to obtain this reaction is to mix barium chloride and potassium sulfate:



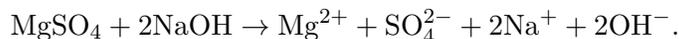
What happens during this reaction is that the ions dissociate, followed by precipitation:



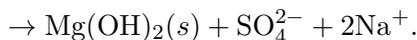
The potassium and chloride ions appear on both sides of the equation. They are called **spectator ions**, as they do not take part in the reaction. We can omit the spectator ions and write the **net ionic equation**:



**3.9.7. Reactions: Ionic Exchange.** Suppose that we dissolve magnesium sulfate and sodium hydroxide in aqueous solution. The ions dissolve to some extent:



Of those ions that do dissolve there is a strong tendency for precipitation. In this particular case, the following precipitation reaction takes place:



**Example calculation (electrolyte solution):**

*Problem:* For the  $\text{MgSO}_4$  with  $\text{NaOH}$  reaction, suppose we start with 20 mL (0.020 L) of 2.0 M solution of  $\text{MgSO}_4$ . How much 1.0 M  $\text{NaOH}$  is needed to precipitate all  $\text{Mg}(\text{OH})_2(s)$ ? What is the final  $[\text{Na}^{+}]$ ?

*Solution:* We calculate the number of moles at the start:

$$n_{\text{MgSO}_4} = [\text{MgSO}_4] \cdot V = 2 \text{ mol/L} \cdot 0.020 \text{ L} = 0.040 \text{ mol} \quad (2 \text{ sig. figs.})$$

Based on this amount of  $\text{MgSO}_4$ , we require a minimum of

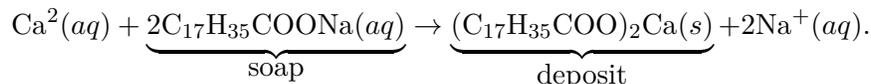
$$n_{\text{NaOH}} = 2 \cdot n_{\text{MgSO}_4} = 2 \cdot 0.040 \text{ mol} = 0.080 \text{ mol}.$$

We solve  $n_{\text{NaOH}} = [\text{NaOH}] \cdot V$  for  $V$ :

$$V = \frac{n_{\text{NaOH}}}{[\text{NaOH}]} = \frac{0.080 \text{ mol}}{1.0 \text{ mol/L}} = 0.080 \text{ L} = 80 \text{ mL},$$

$$[\text{Na}^{+}] = \frac{n_{\text{Na}}}{V} = \frac{0.080 \text{ mol}}{(0.080 + 0.020) \text{ L}} = 0.80 \text{ M}.$$

Another example is water softening by ion exchange. Water that contains divalent cations, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  causes problems. First, they combine with fatty-acid anions in soaps to produce hard deposits on clothes, washing machines and kitchen sinks:



Secondly, when bicarbonate ( $\text{HCO}_3^+$ ) is present in water, the hard-water cations cause a buildup of deposits in boilers, pots and pipes, which not only looks dirty but can damage the plumbing:



The removal of hard-water ions (water softening) is accomplished by exchanging soft-water  $\text{Na}^+$  ions for the hard-water ions. Ion-exchange resins are insoluble polymers with covalently bound anion groups, such as  $-\text{SO}_3^-$  or  $-\text{COO}^-$ , with  $\text{Na}^+$  ions attached to balance the charge. The divalent cations in hard water are attracted to the resin's anionic groups and displace the  $\text{Na}^+$  ions into the water. One type of ion is exchanged for another. The resin is replaced when all the resin sites are occupied, or it can be *regenerated* by treating it with a very concentrated  $\text{Na}^+$  solution, which exchanges  $\text{Na}^+$  ions for the bound  $\text{Ca}^{2+}$ .

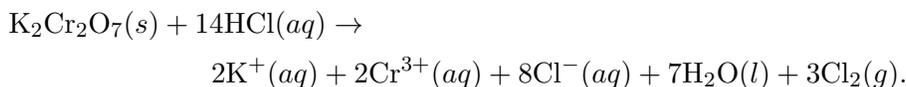
### 3.9.8. Importance of Matching the Number of Moles in Reactions.

When solving problems, pay attention to the data given to you, such as masses of substances, volumes of solutions and concentrations. For example, a problem may ask you which volume or concentration of a solution is required to neutralize or precipitate a given substance. The problem frequently boils down to matching the number of moles and inspecting the stoichiometry of the chemical reaction to ensure the correct number of moles are used. For a given stoichiometry, the number of moles is calculated using the formula  $n = c \cdot V$ , where  $n$  is the number of moles,  $c$  is concentration and  $V$  is volume. The example of the previous section is typical.

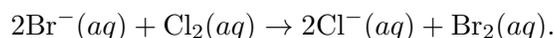
One more thing you will need to check is whether or not a substance has fully dissociated in the solvent or not. Knowing the extent of a reaction (how far it goes) is essential to knowing the correct number of moles.

Oxtoby [1] (p. 481-2) discusses the following two reactions:

Potassium dichromate with hydrochloric acid:



Preparation of elemental bromine from its salts in solution:



### 3.10. Ideal Solutions: Raoult's and Henry's Laws

Vapor pressure (Fig. 3.23) is the pressure of a substance as measured in the space above the liquid or solid substance. It is easiest to measure this pressure in closed container in the gas space above the substance that is initially (at time  $t = 0$ ) vacuum-pumped. Vapor pressure of a substance arises because of thermal energy ( $k_B T$ ), which imparts some fraction<sup>7</sup> of molecules with kinetic energy large enough to leave the liquid or solid<sup>8</sup> phase and escape into the gas phase.

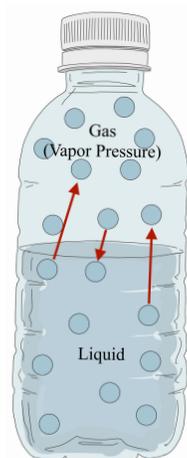


Figure 3.23. Vapor pressure.

A *solution* is a homogeneous phase that contains more than one component. Although if both components are in the same phase, e.g. liquids<sup>9</sup>, and the solution is homogeneous, there is no fundamental difference between components in a solution as far as labeling them solvent vs solute. It is then common practice to label the component that constitutes the larger proportion of the solution as the solvent; the component in lesser proportion is commonly called the solute.

<sup>7</sup>For a given temperature and molecular mass, you should be able to calculate this fraction from the Maxwell-Boltzmann speed distribution. The energy should be larger than intermolecular forces that keep the liquid (or solid) together.

<sup>8</sup>At sufficiently low temperature and pressure, a solid substance may sublime to the gas phase without passing through the liquid phase (*c.f.* Fig. 1.4).

<sup>9</sup>Solid solutions are also possible when there are one or more solutes in a solvent, and the chemical components remain in a single homogeneous phase.

Partial vapor pressures of the individual components of the solution yield information about the individual components in solution. This is because the partial vapor pressure measures the escaping tendency of a molecule from solution, which is in turn a measure of the cohesive forces present in solution. Thus, measurements of the vapor pressure of each component as a function of pressure, temperature, and mole fraction lead to some understanding of the system, namely, the intermolecular forces and the physical properties affected by them (e.g. boiling point, freezing point, etc).

*Ideal solutions* are homogeneous mixtures of substances that have physical properties linearly related to the amount of solute present. The classic statement of this condition is Raoult's law, which is valid for many highly dilute solutions and for a limited class of concentrated solutions, namely, those in which the interactions between the molecules of solute and solvent are the same as those between the molecules of each substance by itself. Solutions of benzene and toluene, which have very similar molecular structures, are ideal solutions: any mixture of the two has a volume equal to the sum of the volumes of the separate components, and the mixing process occurs without absorption or evolution of heat. The vapor pressures of the solutions are mathematically represented by a linear function of the molecular composition. Ideal solutions are analogous to ideal gases ( $P_i = n_iRT/V$ , which expresses the linear dependence of the partial pressure,  $P_i$ , of the  $i$ -th component of a gas mixture on gas density  $n_i/V$  of that component at fixed  $T$ ).

When the components of nonideal solutions are mixed, the volume of the mixture ordinarily differs from the sum of the volumes of the pure components, and heat is evolved or absorbed. The properties of such solutions often are described in terms of their deviations from those of ideal solutions. Mixtures of acetone and chloroform, for example, are said to show negative deviations from ideality: their vapor pressures are lower than those calculated on the assumption of a linear relationship to the molecular composition. Solutions of acetone and carbon disulfide, on the other hand, have higher vapor pressures than those that would characterize an ideal solution. The cases of chloroform in acetone and chloroform in ethanol will be discussed later in the context of Fig. 3.28.

**3.10.1. Raoult's Law (François Marie Raoult, 1830-1916).** Raoult's law says that the vapor pressure of a component (1),  $P_1$ , in solution is the product of the pure substance's vapor pressure,  $P_1^\circ$  (may depend on temperature), and its mole fraction,  $X_1$ :

$$P_1 = X_1P_1^\circ.$$

A solution which obeys this law is called an **ideal solution**. Solutions that deviate from this law are called non-ideal solutions. For non-ideal solution, this linear relationship only holds in the dilute limit ( $X_2 \rightarrow 0$ ,  $X_1 \rightarrow 1$ , for a 2-component solution). Mathematically, this law is expressed as a limit:

$$(3.1) \quad P_1^\circ = \lim_{X_1 \rightarrow 1} \frac{P_1}{X_1}.$$

Real solutions may show positive deviations (with vapor pressures higher than those predicted by Raoult's law) or negative deviations (with lower vapor pressures).

The total vapor pressure, of a solution consisting of  $N$  components will be the sum of the vapor pressures:

$$P_{tot} = P_1 + P_2 + \cdots + P_N,$$

where  $1, 2, \dots, N$  include all components of the solution (all solutes plus solvent). Using Raoult's law this can be written as:

$$P_{tot} = X_1 P_1^\circ + X_2 P_2^\circ + \cdots + X_N P_N^\circ,$$

where  $X_1 + X_2 + \cdots + X_N = 1$ . This relationship look similar to the Dalton's law, but applies to ideal solutions.

For a 2-component system, where "1" is the solvent and "2" is the solute,

$$X_1 = \frac{n_1}{n_1 + n_2}.$$

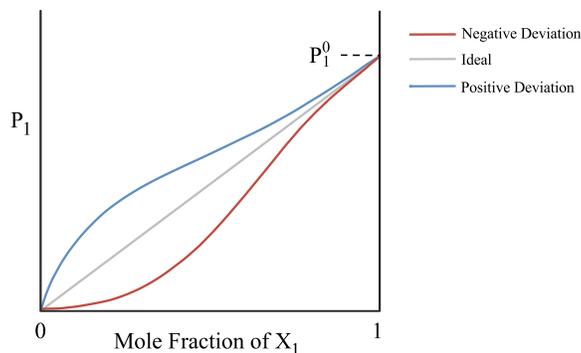
Here,  $n_1$  is the number of moles of solvent and  $n_2$  is the number of moles of solute.  $n_1 + n_2$  is the total number of moles in solution.  $X_1 + X_2 = 1$ .

Raoult's law is a statement regarding the behavior of solvents when a solute is added. Raoult was known for his research on solutions. He published papers on solute-induced freezing point depression of solutions, depression of a solvent's vapor pressure, and various experiments involving solvents, such as benzene and acetic acid, in addition to water. The laws he published concern the properties of the solvent, enable the determination of the molecular weights of dissolved substances, and are valid in the limit of dilute solutions.

Raoult's law is typically only valid at low solute concentrations. The relationship  $P_1 = X_1 P_1^\circ$  is analogous to the ideal gas law,  $P_1 = n_1 RT/V$ . Both laws express the linear dependence of  $P_1$  on the amount of substance 1, namely  $X_1$  (or  $n_1$  for gases).

### 3.11. Deviations From Raoult's Law

Real solutions deviate from ideal behavior, as shown in Fig. 3.24.



**Figure 3.24.** In an ideal solution, a graph of solvent vapor pressure  $P_1$  versus mole fraction of solvent  $X_1$  is a straight line. Nonideal solutions behave differently; examples of positive and negative deviations from the ideal solution are shown. The vapor pressure of pure solvent is  $P_1^0$ .

**3.11.1. Negative Deviations.** On a molecular level, *negative deviations* arise when the solute attracts solvent molecules especially strongly, reducing their tendency to escape into the vapor phase. The substance wants to stay a liquid. (Recall our discussion of the VDW equation, where attractive forces lower the pressure.)

**3.11.2. Positive Deviations.** Positive deviations arise in the opposite case, when solvent and solute molecules are not strongly attracted to each other. The substance wants to be a gas, so its pressure is higher than it should be. Even non-ideal solutions with non-dissociating solutes approach Raoult's law as  $X_1$  approaches 1, just as all real gases obey the ideal gas law at sufficiently low densities.

No deviations: A number of pairs of liquids obey Raoult's law over a wide range of compositions:

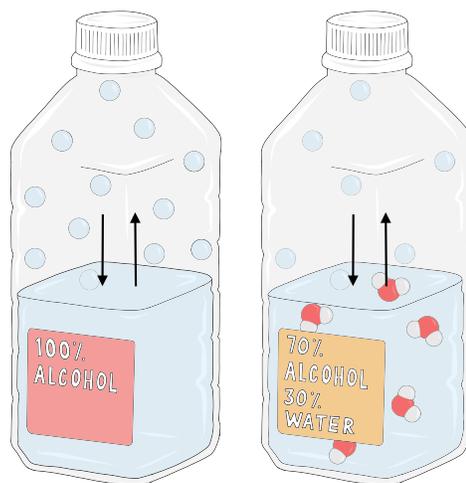
- benzene — toluene
- ethylene bromide — ethylene chloride
- carbon tetrachloride — trichloroethylene
- acetic acid — isobornyl acetate

It should be noted that air is generally present above the solution at a pressure that makes up the difference between the total vapor pressure and atmospheric pressure. The fact that air is present can generally be ignored in the vapor phase.

**3.11.3. How Raoult's Law Works.** While studying colligative properties of solvents, Raoult discovered that adding a solute lowers the vapor pressure. This is because the additional solute particles occupy space (volume

fraction) in solution. Vapor pressure is due to surface molecules escaping into the gas phase. If some of these solvent molecules are replaced by solute molecules, there will be fewer solvent molecules able to escape into the gas phase (due to obstruction), lowering the vapor pressure of the solvent.

When a liquid is in a sealed container, evaporation proceeds until there are as many molecules returning to the liquid as there are escaping (per unit time). At this point the vapor is said to be saturated, and the pressure of that vapor is called the **saturated vapor pressure**. Figure 3.25 shows the case where we start from 100% alcohol and dilute it by adding water (the case of 70% alcohol, 30% water is shown). Figure 3.25 shows that there are fewer alcohol molecules in the gas phase after dilution with water.

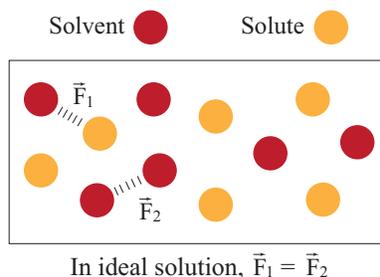


**Figure 3.25.** (left) Dynamic equilibrium between volatile molecules in the liquid and gas phase. (right) Dynamic equilibrium of a solution consisting of volatile solvent molecules (blue circles) and non-volatile solute molecules (water molecules in this case). Note that fewer molecules exist in the gas phase compared to the pure solvent. (The 70-30 alcohol-water solution may deviate slightly from Raoult's law because of the high concentration of water.)

As mentioned earlier, some fraction of the solvent molecules have sufficient energy to escape from the surface and enter the gas phase. If the number of solvent molecules on the liquid's surface is reduced by the addition of solute, there will be a smaller number of solvent molecules that will be able to escape during any given time interval. On the other hand, molecules in the gas phase can always return to the solution regardless of how much solute is present (assuming an ideal solution). The net effect of this is that when equilibrium is established, there will be fewer solvent molecules in the vapor phase, and the vapor pressure is lowered.

**3.11.4. Limitations of Raoult's Law.** In practice, there's no such thing as an ideal solution! However, features of one include:

- Ideal solutions satisfy Raoult's law over a wide range of concentrations, meaning that some key macroscopic properties (such as vapor pressure, boiling point, freezing point, etc.) depend linearly on the amount of solute added and not on the nature of the solute itself.
- In an ideal solution (Fig. 3.26), it takes exactly the same amount of energy for a solvent molecule to break away from the surface of the solution as it did in the pure solvent. The forces of attraction between solvent and solute are exactly the same as between the original solvent molecules.
- There are very few cases of truly ideal solutions where Raoult's law holds precisely over the entire range of concentrations. When solutions deviate from ideal solutions, the Raoult's law will still hold, but in the dilute limit (see Eq. 3.1).



**Figure 3.26.** Ideal solution. The intermolecular forces shown are average forces (averaged over all such interactions, and over time).

**3.11.5. Henry's Law (William Henry, 1774-1836).** While Raoult's law applies to solvents, Henry's law applies to the solute. Henry's law is the statement that the vapor pressure of a volatile dissolved substance is proportional to the mole fraction (or concentration) of that substance in solution. Suppose we have a solute "2" with low mole fraction  $X_2$ . Its vapor pressure (even in non-ideal solution) is proportional to  $X_2$ :<sup>10</sup>

$$P_2 = k_2 X_2,$$

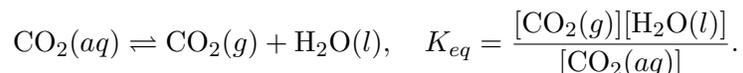
where  $k_2$  is a constant (the Henry's law constant), which is usually denoted  $k_H$ . The SI units of the Henry's law constant are Pa. Its value depends on both solute and solvent. A volatile substance is one for which the Henry's law constant is non-zero. In mathematical terms, Henry's law is the statement

<sup>10</sup>Since  $X_2 = 1 - X_1$ , we can also express this as  $P_2 = k_2 X_2 = k_2(1 - X_1)$ .

that the following limit exists:

$$(3.2) \quad k_2 = \lim_{X_2 \rightarrow 0} \frac{P_2}{X_2}.$$

We also find Henry's law expressed in concentration units,  $P_2 = k_2 \cdot c_2$ , where  $k_2$  has units of pressure per unit concentration (e.g. L.atm/mol) and  $c_2$  has concentration units (mol/L). Concentration units arise as follows: suppose we have a gas, such as  $\text{CO}_2$  dissolved in water. The chemical equilibrium is:



The concentration of water is a constant, so we can combine it with  $K_{eq}$  by dividing both sides by  $[\text{H}_2\text{O}(l)]$ :

$$k_H = \frac{K_{eq}}{[\text{H}_2\text{O}(l)]} = \frac{P_{\text{CO}_2}}{[\text{CO}_2(aq)]}.$$

Thus,  $k_H$  has units of atm/M if  $P_{\text{CO}_2}$  is in atm. Chemical equilibrium will be covered in Chapter 4.

**Henry's law: (Applicability)**

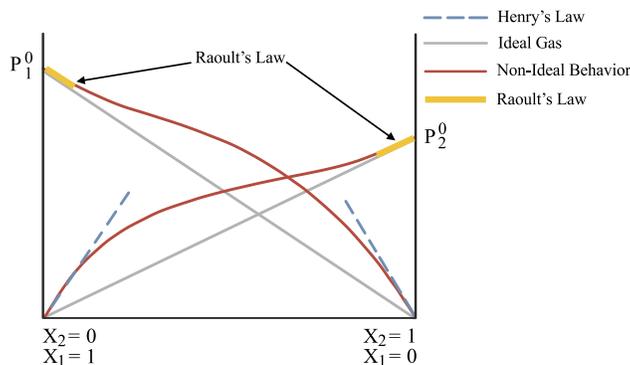
- Henry's law applies in the limit of low concentrations of the solute.
- Henry's law can be used to infer the concentration of dissolved gas in a solvent from the knowledge of the vapor pressure of this solute, provided of course, that Henry's law constant is known.

Whenever Raoult's law is valid for a solvent, Henry's law is valid for a solute (see Fig. 3.27). Henry's law may be applied to dilute solutions of a binary liquid system. It is found that in the limit of infinite dilution, most liquid solvents obey Raoult's law but that under the same conditions the solute obeys Henry's law.

One application of Henry's law is the carbonation of beverages: by knowing the partial pressure of a given gas in the space above a solution, we can estimate how much of the substance is dissolved in solution. This is best understood by working an example.

3.11.5.1. *Example.* Suppose that we have a carbonated drink (soda).  $\text{CO}_2$  gas is dissolved and the can is pressurized. The partial pressure of  $\text{CO}_2$  above the soda (in the soda can) is 0.01 atm (this can be taken as the total gas pressure, since water is far less volatile than  $\text{CO}_2$ ). Henry's law constant for  $\text{CO}_2$  dissolved in water at  $20^\circ\text{C}$  is 29.4 L.atm/mol. Find the amount of  $\text{CO}_2$  dissolved in solution.

*Solution:* If the Henry's law constant is specified in units of L.atm/mol, this means the Henry's law is in the form  $P = k_H \cdot c$ , where  $P$  is the partial pressure of the solute above the solution and  $c$  is the concentration of the solute in solution. From  $c = P/k_H$ , we find  $c = 0.01 \text{ atm}/29.4 \text{ L.atm/mol} = 0.34 \text{ mM}$ .



**Figure 3.27.** Vapor pressures above a mixture of two volatile liquids. Both ideal (blue lines) and non-ideal behaviors (red curves) are shown. Positive deviations from ideal solution behavior are illustrated, although negative deviations are observed for other non-ideal solutions. Raoult's and Henry's laws are shown as dilute solution limits for the non-ideal mixture; the markers explicitly identify regions where Raoult's law and Henry's law represent actual behavior.

*Note:* This problem is slightly more complicated when  $k_H$  is specified in pressure units, e.g.  $k_H = 0.163 \times 10^4$  atm. We instead use the form,  $X_{\text{CO}_2} k_H = P_{\text{CO}_2}$ . The mole fraction is:

$$X_{\text{CO}_2} = \frac{P_{\text{CO}_2}}{k_H} = \frac{0.01 \text{ atm}}{0.163 \times 10^4 \text{ atm}} = 0.061 \times 10^{-4}.$$

The mole fraction is defined as:

$$X_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_{\text{H}_2\text{O}} + n_{\text{CO}_2}} = \frac{c_{\text{CO}_2}}{c_{\text{H}_2\text{O}} + c_{\text{CO}_2}} \approx \frac{c_{\text{CO}_2}}{c_{\text{H}_2\text{O}}} = \frac{c_{\text{CO}_2}}{55 \text{ M}}$$

Inserting the numerical value for  $X_{\text{CO}_2}$  and solving for  $c_{\text{CO}_2}$ :

$$0.061 \times 10^{-4} = \frac{c_{\text{CO}_2}}{55 \text{ M}} \rightarrow c_{\text{CO}_2} = (0.061 \times 10^{-4})(55 \text{ M}) = 0.34 \text{ mM}.$$

This suggests another expression for the Henry's law:

$$P_2(\text{atm}) = k_H(\text{atm}) X_2 \frac{[\text{H}_2\text{O}]}{[\text{H}_2\text{O}]} = \frac{k_H(\text{atm})}{[\text{H}_2\text{O}]} \cdot c_2(\text{M}).$$

where  $[\text{H}_2\text{O}] = 55 \text{ M}$  and  $c_2(\text{M}) = X_2 \cdot [\text{H}_2\text{O}]$ .

**3.11.6. Henry's Law Constant.** Henry's law constant  $k_H$  depends on the **solvent, solute and temperature**. You can find such constants tabulated under various conditions. See, for example, <http://www.henrys-law.org/henry.pdf>

If a gas is dissolved in a solvent, the pressure of the gas in equilibrium with the solution is proportional to the amount of gas dissolved. (And

vice-versa.) Likewise, if several gases from a mixture of gases dissolve in a solution, Henry's law applies to each gas independently, *regardless of the pressure of the other gases present in the mixture* (meaning, for example, that air could be present as well, and we can neglect air).

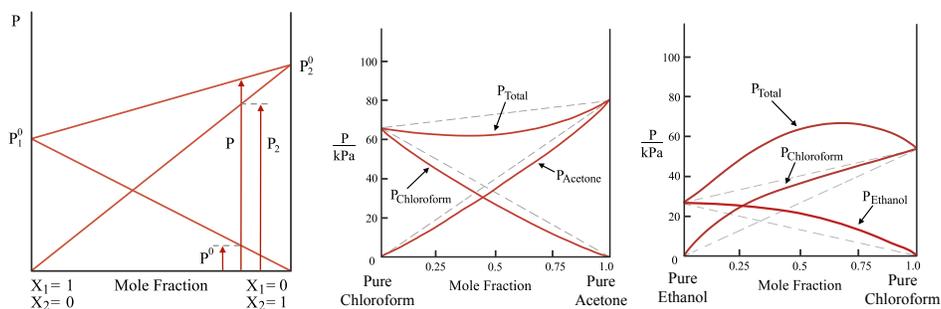
**Henry's law constant is the vapor pressure of the liquified gas at the temperature of the solution.** The dissolved gas may be viewed in terms of its solubility under the pressure  $P_2$ , or  $P_2$  may be taken as the vapor pressure of the volatile solute.

**Temperature dependence of Henry's law constant:** An expression for the temperature dependence of the Henry's law constant is (see Problem 52 or Atkins [14] for derivation):

$$k_H(T) = k_H^\ominus \exp\left(-\frac{\Delta_{\text{soln}}H}{R} \left[\frac{1}{T} - \frac{1}{T^\ominus}\right]\right)$$

where  $\Delta_{\text{soln}}H$  is the enthalpy of solution (in molar units here, since the denominator uses  $R$ ). We will introduce enthalpy later (see Section 6.10.2).  $T^\ominus$  is a reference temperature and  $k_H^\ominus$  is the value of  $k_H$  measured at this reference temperature. **Note:** The value of  $k_H^\ominus$  depends on both the solvent *and* the solute. For example  $k_H^\ominus$  differs for oxygen in water compared to nitrogen in water. Likewise,  $k_H^\ominus$  is different for oxygen in benzene versus oxygen in water.

**3.11.7. Summary: Raoult's and Henry's Laws.** The three plots in Fig. 3.28 summarize the behavior of Raoult's and Henry's laws.



**Figure 3.28.** Summary of Raoult's and Henry's laws. (left) Vapor pressure of two liquids obeying Raoult's law. The total pressure at constant temperature is obtained from  $P = X_1P_1^0 + (1 - X_1)P_2^0$ . (middle) Vapor pressure of the system acetone-chloroform at 328 K showing negative deviations from Raoult's law. Dashed lines show Raoult's law behavior. (right) Vapor pressure of the system ethanol-chloroform at 318 K showing positive deviations from Raoult's law. Dashed lines show Raoult's law behavior.

**3.11.8. Henry's Law Example.** Dry air contains 78.084 mol % N<sub>2</sub> and 20.946 mol % O<sub>2</sub>. Calculate the relative proportion of N<sub>2</sub> and O<sub>2</sub> dissolved in water under a total pressure of 1.000 bar. Henry's law constants for N<sub>2</sub> and O<sub>2</sub> are  $6.51 \times 10^7$  Torr and  $3.30 \times 10^7$  Torr, respectively, at 25°C.

*Solution:* Application of Dalton's law gives

$$P_{\text{N}_2} = 0.78084 \times 750.06 \text{ Torr} = 585.7 \text{ Torr}$$

$$P_{\text{O}_2} = 0.20946 \times 750.06 \text{ Torr} = 157.1 \text{ Torr}$$

We then apply Henry's law to get the mole fractions

$$X_{\text{N}_2} = \frac{P_{\text{N}_2}}{k_H(\text{N}_2)} = \frac{585.7 \text{ Torr}}{6.51 \times 10^7 \text{ Torr}} = 9.00 \times 10^{-6}$$

$$X_{\text{O}_2} = \frac{P_{\text{O}_2}}{k_H(\text{O}_2)} = \frac{157.1 \text{ Torr}}{3.30 \times 10^7 \text{ Torr}} = 4.76 \times 10^{-6}$$

Since  $X_{\text{N}_2} = n_{\text{N}_2}/n_{\text{tot}}$  and  $X_{\text{O}_2} = n_{\text{O}_2}/n_{\text{tot}}$ , the relative proportions are:

$$\text{for N}_2 \quad \frac{n_{\text{N}_2}}{n_{\text{N}_2} + n_{\text{O}_2}} = \frac{9.00 \times 10^{-6}}{9.00 \times 10^{-6} + 4.76 \times 10^{-6}} = \frac{9.00 \times 10^{-6}}{1.376 \times 10^{-6}} = 0.654$$

$$\text{for O}_2 \quad \frac{n_{\text{O}_2}}{n_{\text{N}_2} + n_{\text{O}_2}} = \frac{4.76 \times 10^{-6}}{9.00 \times 10^{-6} + 4.76 \times 10^{-6}} = 0.346$$

This is approximately a ratio of 2 N<sub>2</sub> to 1 O<sub>2</sub>.

### 3.12. Colligative Properties: Non-Volatile Solutions

Raoult's law forms the basis for the four **colligative** properties of dilute solutions. Colligative means that the properties depend on the *number* of dissolved particles, independently of the *nature* of the particles themselves. These properties are:

- Lowering of vapor pressure
- Boiling point elevation
- Freezing point depression
- Osmotic pressure

**3.12.1. Lowering of Vapor Pressure (Raoult's Law).** Suppose we have a two-component solution where "1" is the solvent and "2" is the solute. Raoult's law for the solvent component says that:

$$\Delta P_1 = P_1 - P_1^\circ = X_1 P_1^\circ - P_1^\circ = (X_1 - 1)P_1^\circ \equiv -X_2 P_1^\circ,$$

where  $X_1 = 1 - X_2 = n_1/(n_1 + n_2)$  is the solvent mole fraction,  $P_1^\circ$  is the pure solvent vapor pressure and  $X_2 = n_2/(n_1 + n_2)$  is the solute's mole fraction. Because the sign is negative, we have a lowering of the vapor pressure. Thus,

the vapor pressure is always lower when we add a solute, as compared to the pure solvent.

Note that  $\Delta P_1 = -X_2 P_1^\circ$  depends only on  $X_2$ , the mole fraction of the solute. It does not depend at all on the nature of the solute. This is an example of a colligative property.

**3.12.2. Boiling Point Elevation (Raoult's Law).** A consequence of the lowering of vapor pressure is the elevation of the boiling point. This fact has been used as a way to determine molar masses. In Fig. 3.29,  $\Delta P_1$  is the decrease in vapor pressure at  $T_b$  and  $\Delta T_b$  is the change in temperature needed to keep the vapor pressure at 1 atm. The quantity

$$\Delta T_b = T'_b - T_b$$

is the increase in boiling point caused by the addition of solute to the pure solvent. Let us look at the slope of this graph near 1 atm, assuming that the two curves are parallel near that point:

$$-\frac{\Delta P_1}{\Delta T_b} = \text{slope of curve} = S \quad \rightarrow \quad \Delta T_b = -\frac{\Delta P_1}{S} = \frac{X_2 P_1^\circ}{S} = \frac{1}{S} \left( \frac{n_2}{n_1 + n_2} \right)$$

from Raoult's law with  $P_1^\circ = 1$  atm.  $S$  is a property of the solvent (independent of the solute) because we assumed the two curves were parallel. For dilute solutions ( $n_1 \gg n_2$ ) we have

$$\Delta T_b = \frac{1}{S} \frac{n_2}{n_1} = \frac{1}{S} \left( \frac{m_2/\mathcal{M}_2}{m_1/\mathcal{M}_1} \right),$$

where  $m_1$  and  $m_2$  are the masses of the solvent and solute (in grams) and  $\mathcal{M}_1$  and  $\mathcal{M}_2$  are their molar masses in grams per mole. Because  $\mathcal{M}_1$  is a property of the solvent, it can be lumped into  $S$ . We define a new constant:

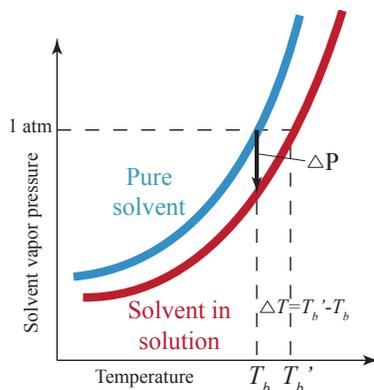
$$K_b = \frac{\mathcal{M}_1}{(1000 \text{ g.kg}^{-1})S}$$

**Boiling point elevation:**

$$\Delta T_b = K_b \left( \frac{m_2/\mathcal{M}_2}{m_1/(1000 \text{ g.kg}^{-1})} \right) = K_b m.$$

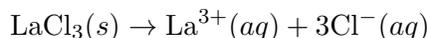
If  $m_1$  is in grams,  $m_1/(1000 \text{ g.kg}^{-1})$  is the number of kilograms of solvent.  $m_2/\mathcal{M}_2$  is the number of moles of solute. Hence, this expression is equal to  $K_b m$  where  $m$  is the molality of the solution.

Note: if the substance *dissociates* in solution, we must count the total molality. For example, if we dissolve NaCl, we get two species:  $\text{Na}^+$  and  $\text{Cl}^-$ . Thus, the molality should be doubled, as we now have 2 moles of ions for each mole of NaCl dissolved.



**Figure 3.29.** The vapor pressure of the solvent above a dilute solution is lower than that of the pure solvent at all temperatures. As a result, for the solution to boil (that is, for the vapor pressure to reach 1 atm), a higher temperature is required for the solution than for the pure solvent. This amounts to an elevation of the boiling point,  $\Delta T_b = T_b' - T_b > 0$ .

**3.12.3. Example w/ Multiple Ions.** Lanthanum(III) chloride ( $\text{LaCl}_3$ ) is a salt that completely dissociates into ions in dilute aqueous solution,



yielding 4 mol of ions per mole of  $\text{LaCl}_3$ . Suppose 0.2453 g of  $\text{LaCl}_3$  is dissolved in 10.00 g of  $\text{H}_2\text{O}$ . What is the boiling point of the solution at atmospheric pressure, assuming ideal solution behavior?

*Solution:* The molar mass of  $\text{LaCl}_3$  is 245.3 g/mol. The moles of  $\text{LaCl}_3$  are  $\frac{0.2453 \text{ g}}{245.3 \text{ g/mol}} = 1.000 \times 10^{-3}$  mol. The molality,  $m$ , is  $\frac{(4)(1.000 \times 10^{-3}) \text{ mol ions}}{0.0100 \text{ kg solvent}} = 0.400$  mol/kg. We look up the value of  $K_b$  from tables and insert this molality into the equation for the boiling-point elevation:

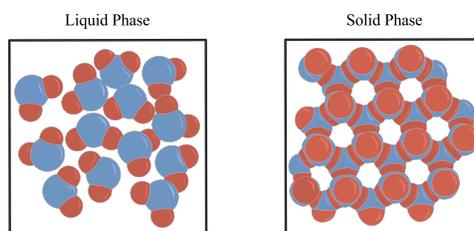
$$\Delta T_b = K_b m = (0.512 \text{ K}\cdot\text{kg/mol})(0.400 \text{ mol/kg}) = 0.205 \text{ K}.$$

This is the boiling point elevation. The new boiling point of the solvent (water) is increased to  $100.000^\circ\text{C} + 0.205^\circ\text{C} = 100.205^\circ\text{C}$ . The actual boiling point is slightly lower than this because the solution is nonideal.

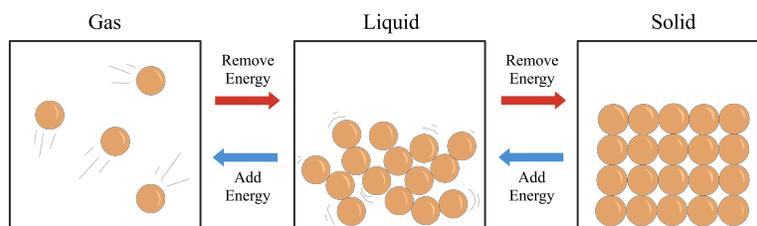
**3.12.4. Freezing Point Depression (Raoult's Law).** In a pure solvent, such as water, the formation of the solid phase usually<sup>11</sup> involves the creation of a crystalline structure. The example of water is shown in Fig. 3.30.

The process of going from gas to liquid, or from liquid to solid, requires us to remove energy from the system (i.e. via cooling), as shown in Fig. 3.31.

<sup>11</sup>Not all solids are crystalline. Some are amorphous.

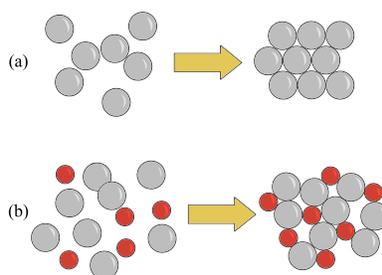


**Figure 3.30.** Structure of water in the liquid and crystalline (solid) phases.



**Figure 3.31.** Phase transitions between different states of matter require the addition or removal of energy.

When a solute is added, however, the mere presence of the solute interferes with the formation of the solid crystalline structure (see Fig. 3.32). Indeed, the solute added (red) in the solvent (grey) prevents the rigid, ordered arrangement of a solid from being achieved. The particles of solute block the crystallization of the solvent, at least up until a certain point, causing a depression in the freezing point of the water. This is an entropic effect (see Problem 56).

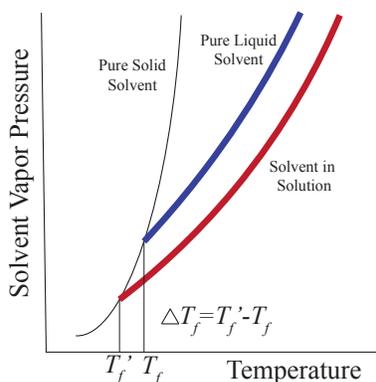


**Figure 3.32.** Freezing point depression. (a) Pure solvent (b) Solvent plus solute.

Application 1: Why do we add ethylene glycol,  $\text{CH}_2\text{OHCH}_2\text{OH}$ , to water in a car radiator in winter? Without any additive the water would freeze at  $0^\circ\text{C}$  and the resulting increase in volume would crack the radiator. Since ethylene glycol is very soluble in water, it can form a solution with a freezing point low enough to prevent freezing even on the coldest winter day.

Application 2: In many countries, salt is added to melt the ice on the sidewalk. The ice melts because the NaCl added lowers the freezing point of water. Of course, this only works at mild temperatures. At temperatures well below the freezing point, salt only has the effect of increasing friction.

Vapor pressure diagram. At the **freezing point** the vapor pressure of the *solid solvent* is equal to the vapor pressure of the *solvent in solution*. The freezing temperature of the solution is the temperature at which the vapor-pressure curve of the pure solid solvent intersects that of the solution (see Fig. 3.33). As solute is added to the solution, the vapor pressure of the solvent falls and the freezing point drops.  $\Delta T_f = T'_f - T_f$  is negative.



**Figure 3.33.** Change in the temperature associated with the freezing point depression.  $\Delta T_f = T'_f - T_f < 0$ .

By analogy with the case of the boiling point elevation we write:

$$\Delta T_f = T'_f - T_f = -K_f m.$$

If the substance dissociates in solution, we must use the *total molality*, as the example below shows:

**3.12.5. Example Problem.** The number of moles of the major dissolved species in a 1.000-L sample of seawater are as follows:

$\text{Na}^+$  0.458 mol.  $\text{Mg}^{2+}$  0.052 mol.  $\text{Ca}^{2+}$  0.010 mol.  $\text{K}^+$  0.010 mol.  $\text{Cl}^-$  0.533 mol.  $\text{SO}_4^{2-}$  0.028 mol.  $\text{HCO}_3^-$  0.002 mol.  $\text{Br}^-$  0.001 mol. Neutral species: 0.001 mol.

Estimate the freezing point of the seawater, assuming  $K_f = 1.86 \text{ K}\cdot\text{kg}/\text{mol}$  for water.

*Solution:* Because water has a density of  $1.00 \text{ g}/\text{cm}^3$ , 1.00 L of water weighs 1.00 kg. For dilute *aqueous* solutions, the number of moles per kilogram of solvent (the molality,  $m$ ) is therefore approximately equal to the number of moles per liter. The total molality, obtained by adding the individual

species molalities just given, is  $m = 1.095$  mol/kg. Then

$$\Delta T_f = -K_f m = -(1.86 \text{ K}\cdot\text{kg/mol})(1.095 \text{ mol/kg}) = -2.04 \text{ K}.$$

The seawater should freeze at approximately  $-2^\circ\text{C}$ . Nonideal solution effects make the actual freezing point slightly higher than this.

The graph of Fig. 3.34 shows freezing point of water vs molality of solute added. This graph appears to suggest that the freezing point of water depends not only on molality but also on the dissolved substance. This difference in slopes is actually due to the fact that different substances decompose into different numbers of ions (one:  $M$ , two:  $MX_1$ , three:  $MX_2$  and four:  $MX_3$ ). When using the formula  $\Delta T_f = -K_f m$ , the molality  $m$  must account for the total number of moles of all solute species added to the solvent. For example, if 1 mol of  $\text{NaCl}$  added to water completely dissociates into  $\text{Na}^+$  and  $\text{Cl}^-$ , then  $m$  should count 2 mol of ions. If the substance added does not dissociate, then  $m$  only counts the number of moles of undissociated substance. If the substance partially dissociates, then we must add all the moles of reactants and products according to the chemical equilibrium describing the partial dissociation of the solute added.

Table 3.2 lists freezing point depressions and boiling point elevations for different solvents.

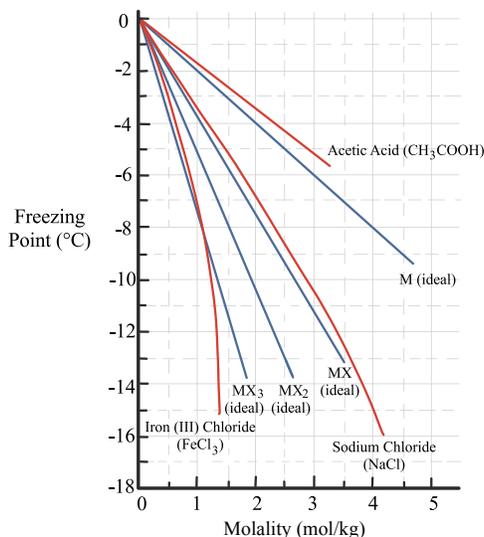
**Table 3.2.** Boiling-point elevation and freezing-point depression constants.

Solvent	Formula	$T_b(^{\circ}\text{C})$	$K_b(\text{K}\cdot\text{kg/mol})$	$T_f(^{\circ}\text{C})$	$K_f(\text{K}\cdot\text{kg/mol})$
Acetic acid	$\text{CH}_3\text{COOH}$	118.1	3.07	17	3.9
Benzene	$\text{C}_6\text{H}_6$	80.1	2.53	5.5	4.9
Carbon tetrachloride	$\text{CCl}_4$	76.7	5.03	-22.9	32
Diethyl ether	$\text{C}_4\text{H}_{10}\text{O}$	34.7	2.02	-116.2	1.8
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	78.4	1.22	-114.7	1.9
Naphthalene	$\text{C}_{10}\text{H}_8$	—	—	80.5	6.8
Water	$\text{H}_2\text{O}$	100	0.512	0.0	1.86

### 3.13. Binary Mixtures of Liquids

Suppose that we have an “ideal binary mixture”, i.e. two liquids ( $A$  and  $B$ ) that behave together as ideal solution. Both liquids are volatile and thus generate a non-zero vapor pressure. Figure 3.35 shows vapor pressure vs mole fraction of  $A$ . Traces shown are for the two partial vapor pressures of the mixture components ( $A, B$ ) as well as the total vapor pressure, which is the sum of both partial pressures. For an ideal solution the Raoult’s and Henry’s laws have the same form, featuring the same slope. The only difference is that Raoult’s law refers to the solvent whereas Henry’s law refers to the solute. Otherwise, their form is identical (i.e., they both describe straight line behavior vs mole fraction).

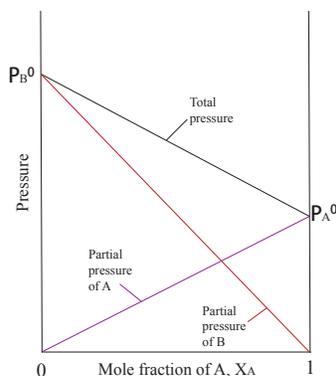
Figure 3.36 shows the behavior of a real solution compared to an ideal solution. The real solution is the curved trace. The ideal solution is the



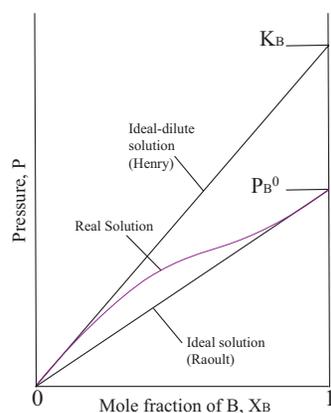
**Figure 3.34.** Freezing point vs molality. Molality as the number of moles of solute added (per kg solvent). The red colored lines give the observed depression of the freezing point of water by acetic acid, NaCl, and FeCl<sub>3</sub> as the molality of the solutions increases. Straight blue lines sketch the predicted ideal behavior for one through four moles of particles per mole of solute added to the solution. The experimental curve for NaCl (which gives two moles of dissolved particles per mole of NaCl added) stays close to the ideal straight line for MX; the experimental curve for FeCl<sub>3</sub> (which gives four moles of dissolved particles) stays fairly close to the ideal straight line for MX<sub>3</sub>. The pattern suggests that acetic acid dissolves to give one mole of particles per mole of solute. As molality increases, the observed freezing-point depressions deviate in varying ways from the straight lines.

straight line. There are two straight lines: one for Raoult's law and one for Henry's law. The Raoult's law is the straight line that is tangent to the real solution curve near mole fraction  $X_B = 1$  (the limit of nearly pure solvent). It extrapolates to zero mole fraction. The Henry's law is the case of a dilute solution, and refers to the solute. It is a straight line that is tangent to the curve at  $X_B = 0$  and extrapolates at  $X_B = 1$  to the pressure required to liquify the solute substance at the same temperature. Thus, the two slopes are different and carry different meanings. (The Henry's law constant is a measure of the volatility of the solute in a particular solvent, whereas the Raoult's law constant is just the vapor pressure of the pure solvent.)

Figure 3.37 illustrates the behavior of three different "real solutions": carbon disulfide in acetone, benzene in methylbenzene and chloroform in acetone. For carbon disulfide in acetone, there is a positive deviation from the ideal



**Figure 3.35.** The total vapor pressure and the two vapor pressures of an ideal binary mixture are proportional to the mole fractions of the components.

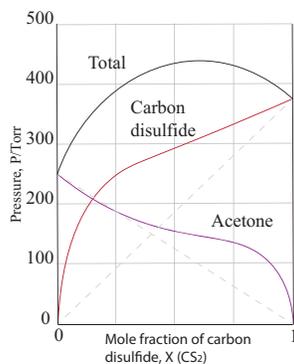


**Figure 3.36.** When a component (the solvent) is nearly pure, it has a vapor pressure that is proportional to its mole fraction with a slope  $P_B^0$  (Raoult's law). When it is the minor component (the solute) its vapor pressure is still proportional to the mole fraction, but the constant of proportionality is now  $K_B$  (Henry's law).

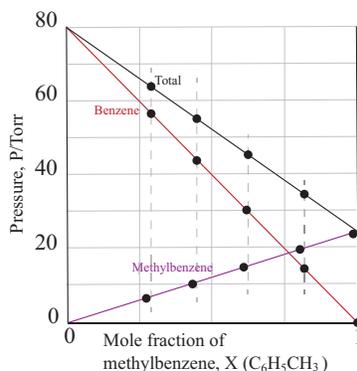
solution. Neither substance likes each other, and intermolecular forces are weak, hence the high volatility.

For benzene in methylbenzene, we see behavior that is close to ideal solution. Both substances are very similar in terms of intermolecular bonding, yet the attraction forces are moderate. See Fig. 3.38.

For chloroform in acetone, the intermolecular forces between them are strong, as both substances are polar. Hence, the deviations are negative. See Fig. 3.39.



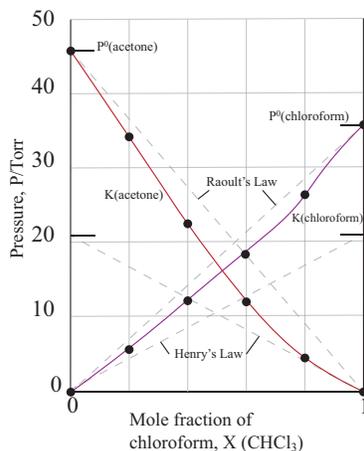
**Figure 3.37.** Strong deviations from ideality are shown by dissimilar liquids (in this case carbon disulfide and acetone, propanone).



**Figure 3.38.** Two similar liquids, in this case benzene and methylbenzene (toluene), behave almost ideally, and the variation of their vapor pressures with composition resembles that for an ideal solution.

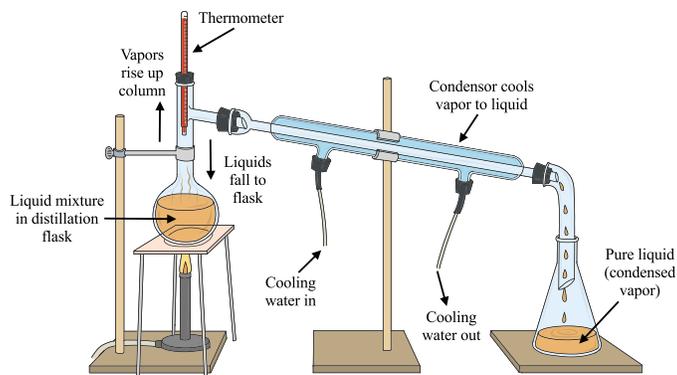
**3.13.1. Volatile Solutes: Distillation.** Henry's law applies to volatile solutes, because without volatility, the partial pressure of the solute in the gas space would be zero. Henry's law enables us to calculate the amount of solute dissolved in a solution (mole fraction) based on the knowledge of its vapor pressure and the Henry's law constant for that substance and solvent at a given temperature.

Using Henry's law we can explain the phenomena of distillation, which is a method for separating component substances from liquid mixtures through vaporization and condensation. It is a separation process that is based on differences in volatility (vaporization point) of components in the mixture. The main applications of distillation include separation of crude oil into its components, desalination of sea water, purification of liquid chemicals (e.g.



**Figure 3.39.** The experimental partial vapor pressures of a mixture of chloroform (trichloromethane) and acetone (propanone).

solvents) and the production of distilled beverages with a higher alcohol content.



**Figure 3.40.** In a distillation column (still), temperature decreases with height in the column. The less volatile components condense and fall back to the flask, but the more volatile ones continue up the column into the water-cooled condenser, where they condense and are recovered in the receiver.

The equipment used for distillation is called a *still* (Fig. 3.40). The process is based on differences in volatility, as quantified by the vapor pressure of the substances at some given temperature.

**3.13.2. Example.** Consider a mixture of hexane and heptane. At ambient temperatures, the vapor pressure of pure hexane is 0.198 atm whereas that

of pure heptane is 0.060 atm. Suppose that a mixture consists of mole fractions  $X_{hexane} = 0.4$  and  $X_{heptane} = 0.6$ , the partial pressures are:

$$P_{hexane} = X_{hexane}P_{hexane}^{\circ} = (0.4)(0.198 \text{ atm}) = 0.0792 \text{ atm}$$

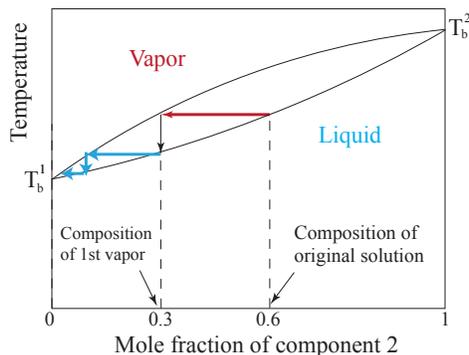
$$P_{heptane} = X_{heptane}P_{heptane}^{\circ} = (0.6)(0.060 \text{ atm}) = 0.0360 \text{ atm}$$

From Dalton's law the total pressure is  $P = P_{hexane} + P_{heptane} = 0.1152$  atm. The mole fractions in the vapor are:

$$X'_{hexane} = \frac{0.0792 \text{ atm}}{0.1152 \text{ atm}} = 0.688$$

$$X'_{heptane} = 1 - X'_{hexane} = 0.312$$

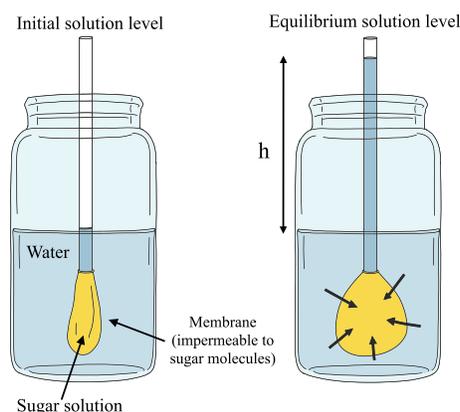
Thus, *the vapor is enriched in the more volatile component*. In a temperature-mole fraction plot (see Fig. 3.41), the distillation process at constant total pressure is illustrated. The component with the lower vapor pressure (component 2) has the higher boiling point ( $T_b^2$ ). If a solution starts at mole fraction 0.6 (see plot) and we raise its temperature until it touches the liquid line in the plot, the vapor in equilibrium with the solution is richer in the more volatile component 1. Its composition lies at the intersection of the horizontal constant-temperature line and the equilibrium vapor curve. Component 1 is enriched, as indicated by the component 2 mole fraction which is down to 0.312. The process is repeated until the desired enrichment is attained.



**Figure 3.41.** The boiling point of an ideal solution varies with the composition of the solution. The upper curve is the boiling temperature referred to the vapor composition, and the lower curve is the boiling temperature referred to the liquid composition. The vapors boiling off a solution that has a 0.600-mol fraction of component 2 are enriched in the more volatile component 1 to the extent that their mole fraction of component 2 is only 0.312 (red arrow). The subsequent blue arrows show the further steps used in obtaining nearly pure component 1 by fractional distillation.

### 3.14. Osmotic Pressure

Osmosis describes the transport of small molecules through membranes. It is important in biology and reverse osmosis (a commercial process to desalinate water). Suppose a solution is contained in an inverted tube, the lower end of which is covered by a semipermeable membrane. This solution has a solute concentration of  $c$  moles per liter. When the end of the tube is inserted in a beaker of pure solvent (see Fig. 3.42), solvent flows from the beaker into the tube. The volume of the solution increases, and the solvent rises in the tube until, at equilibrium, it reaches a height,  $h$ , above the solvent in the beaker.



**Figure 3.42.** Osmotic pressure builds up when concentrations across a membrane are unequal.

The pressure on the solution side of the membrane is greater than the atmospheric pressure on the surface of the pure solvent by an amount given by the **osmotic pressure**,  $\pi$ :

$$\pi = \rho gh$$

where  $\rho$  is the density of the solution (water:  $1.00 \text{ g/cm}^3$ ) and  $g$  is the gravitational acceleration constant ( $9.8 \text{ m/s}^2$ ). For example,  $h=0.17 \text{ m}$  in a dilute aqueous solution gives:

$$\begin{aligned} (3.3) \quad \pi &= (1.00 \text{ g/cm}^3)(10^{-3} \text{ kg/g})(10^6 \text{ cm}^3\text{m}^{-3})(9.8 \text{ m/s}^2)(0.17 \text{ m}) \\ &\approx 1.7 \times 10^3 \text{ kg/m/s}^2 = 1.7 \times 10^3 \text{ Pa} = \frac{1.7 \times 10^3 \text{ Pa}}{1.013 \times 10^5 \text{ Pa/atm}} = 0.016 \text{ atm.} \end{aligned}$$

van't Hoff (1887) discovered a relationship between osmotic pressure  $\pi$ , concentration  $c$  and absolute temperature  $T$ :

$$\pi = cRT$$

since  $c = n/V$  we can write this in a form similar to the ideal gas law:

$$\pi V = nRT.$$

The following example illustrates the use of the van't Hoff formula to find the molar mass of a chemical species, if an osmometer provides the osmotic pressure in units of atm.

**3.14.1. Example.** We dissolve 2.00 g of a protein in 0.100 L water. The osmotic pressure is 0.021 atm at 25°C. What is the approximate molar mass of the protein?

*Solution:* The concentration in moles per liter is

$$c = \frac{\pi}{RT} = \frac{0.021 \text{ atm}}{(0.08206 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298 \text{ K})} = 8.6 \times 10^{-4} \text{ mol/L}$$

The number of moles ( $n = c \cdot V$ ,  $V=0.100 \text{ L}$ ) is:

$$n = c \cdot V = 8.6 \times 10^{-4} \text{ mol/L} \cdot 0.100 \text{ L} = 8.6 \times 10^{-5} \text{ mol}.$$

The molar mass, by definition, is:

$$\mathcal{M} = \frac{m}{n} = \frac{2.00 \text{ g}}{8.6 \times 10^{-5} \text{ mol}} = 23,000 \text{ g/mol}.$$

*Remark:* If you are confused about the constant  $R = 0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$ , when we earlier using  $R = 8.31 \text{ J}/\text{mol}\cdot\text{K}$ , the relationship between the two is easily obtained by realizing that J (Joules) are a unit of energy, and energy is  $PV$  (pressure  $\times$  volume). In SI units, the units of pressure are Pa, whereas those of volume are  $\text{m}^3$ . Converting  $1 \text{ J}=(1 \text{ Pa})\cdot(1 \text{ m}^3)$  to L.atm:

$$(1 \text{ Pa}) \cdot (1 \text{ m}^3) \cdot \frac{1 \text{ atm}}{101325 \text{ Pa}} \cdot \frac{1000 \text{ L}}{1 \text{ m}^3} = \frac{1}{101.325} \text{ L}\cdot\text{atm}$$

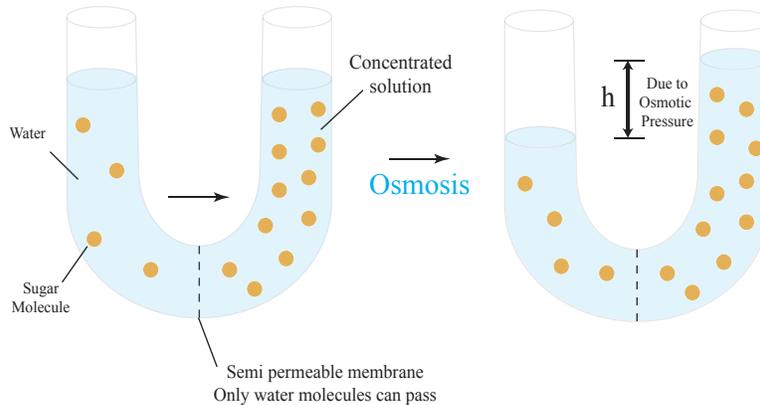
So that the gas constant becomes (in the new units):

$$8.31 \text{ J}/\text{K}\cdot\text{mol} \cdot \frac{1}{101.325} \frac{\text{L}\cdot\text{atm}}{\text{J}} = 0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}.$$

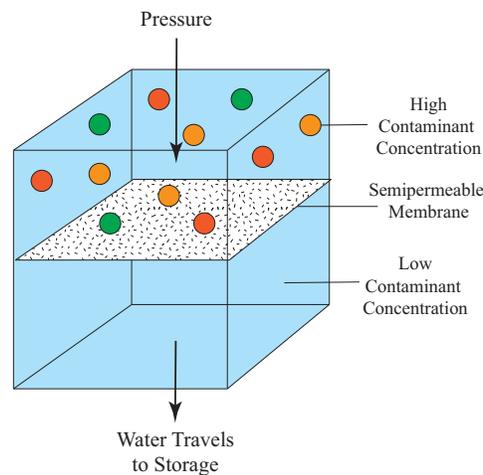
### 3.15. Osmosis and Reverse Osmosis

Before we conclude our discussion on colligative properties we will provide a few remarks concerning the driving forces behind the osmotic process. Osmosis is illustrated in Fig. 3.43. Reverse osmosis is shown in Fig. 3.44.

Let's look at the driving forces involved. Suppose that we have two compartments, one which contains the pure solvent (see Fig. 3.45, left) and another which contains a solvent with solute (right):

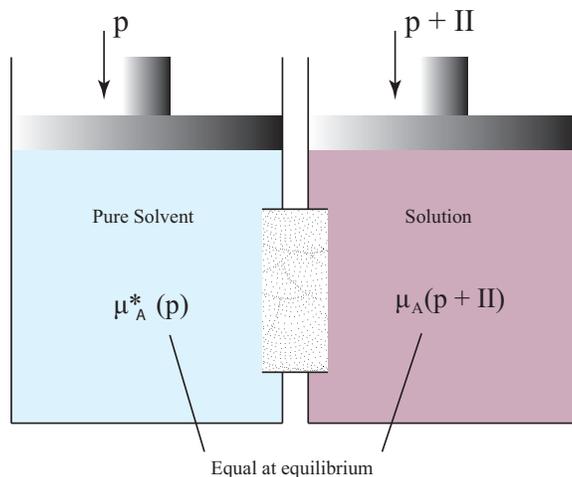


**Figure 3.43.** Osmotic pressure builds up when concentrations across a membrane are unequal. This schematic shows the situation before (left) and after (right) equilibrium is reached.



**Figure 3.44.** Osmotic pressure builds up when concentrations across a membrane are unequal.

Reverse osmosis (Fig. 3.44) can be described in terms of chemical potentials. A *potential* gives rise to a flux or force of some kind. In a way analogous to the gravitational potential which leads to objects falling from high places and the electric potential which leads to the flow of charges between electrodes, the chemical potential leads to chemical or physical transformations involving molecules. It is *differences* in the potential that lead to these forces. For example, we need a positively charged electrode and a negatively charged electrode for electric currents to flow through a conductive medium. Likewise, differences in the chemical potential of a substance between two compartments (or points in space) will lead to the flow of molecules.



**Figure 3.45.** Experimental apparatus for reverse osmosis.

In general, the chemical potential of a substance indicates its potential for physical or chemical transformation. In the absence of a chemical reaction, chemical potential differences drive physical transport such as diffusion. You can think of the chemical potential as indicative of the concentration of a given molecular species. Diffusion describes the random movement of chemical species. The consequence of this random motion is that it leads to uniform distributions of concentrations: gases diffuse away from regions of high concentrations toward regions of low concentrations<sup>12</sup>. Equilibrium is reached when the concentration of each chemical species is uniform everywhere in space. Thus, we can think of each substance as having a chemical potential which indicates the local concentration of this particular substance. In Fig. 3.44 the solute is found in high concentration in the right-most compartment and has zero concentration in the left-most compartment. Thus, the solute wants to move from the right compartment to the left compartment. However, the semi-permeable membrane in the middle does not allow this diffusion to take place. Therefore, the flux of solute particles toward the left is zero because of this membrane. On the other hand, there is a higher concentration of solvent in the left compartment compared to the right compartment. This is because of the presence of solute molecules in the right compartment, which leads to a lower concentration of solvent molecules. Thus, the solvent wants to move from the left compartment toward the

<sup>12</sup>The flux of the  $i$ th component,  $J_i$  is driven by gradients in the chemical potentials according to relationships of the type  $J_i = -\sum_k M_{ik} \nabla \mu_k$ , where  $\mu_k$  is the chemical potential of the  $k$ th component and  $M_{ik}$  is a coupling coefficient between fluxes in  $i$  and gradients in  $k$ . In the case where there is no coupling between the components ( $M_{ik} = 0$  for  $i \neq k$ ) we have  $J_i = -M_{ii} \nabla \mu_i$ .

right compartment, in an attempt to equate the solvent concentrations everywhere. This flux of solvent from the left to the right leads to a higher pressure on the right compartment: the osmotic pressure. At equilibrium, the chemical potentials of the solvent are equal in both compartments. This causes the gradient (difference) in chemical potentials to be zero and the driving force vanishes.

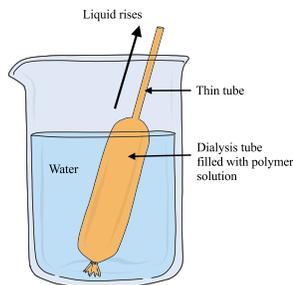
**Reverse osmosis:** What happens if we apply an external pressure to overcome the osmotic pressure? In this case, the solvent will want to move from the top compartment to the bottom compartment. The solute will also want to move from the top to the bottom. However, it will not be able to do so because of the semi-permeable membrane. Thus, only the solvent will be transferred. This process leads to an accumulation of pure solvent in the bottom compartment. This process, called *reverse osmosis*, can be used to purify water and other solvents.

Reverse osmosis is a technique that can be used to purify water. When a sufficiently high pressure is applied to overcome the osmotic pressure across a membrane, water is forced back through the membrane, leaving ions and other dissolved substances behind. In a sense, this method filters out the ions and other unwanted substances at the molecular level.

Even after municipal water treatment, drinking water still contains heavy metal ions such as  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  that are toxic. Commercial reverse osmosis systems can be purchased for domestic use to remove these toxic ions. Reverse osmosis can also be used to desalinate (remove ions) from seawater. Seawater is pumped under high pressure into tubes containing hollow fiber membranes. Water molecules (but not ions) pass through the membranes into the fiber to be collected. This method can purify seawater to less than 400 ppm of total dissolved solids in one pass, making it suitable for drinking.

### 3.16. Problems

**Problem 46.** The average molar masses of unknown polymers can be determined through osmotic pressure experiments. Several aqueous solutions of non-volatile poly(ethylene) oxide of an unknown molar mass were prepared and the osmotic pressure expressed in terms of height of the solvent in a thin tube according to the experimental setup below. You may take the density of water to be  $1.004 \text{ g cm}^{-3}$ ,  $P = 1.00 \text{ atm}$ , and  $T = 298.15 \text{ K}$ .



concentration ( $\text{g L}^{-1}$ )	2.042	6.613	9.521	12.602
height (cm)	0.592	1.910	2.750	3.600

Calculate the molar mass of the dissolved poly(ethylene) oxide sample. Hint: plotting the data will be helpful.

**Solution.** From the graph of height vs concentration, a straight line is fit through the data points. We should force the intercept to be zero, since  $\pi = cRT$  has no offset. Rearranging,

$$\pi = cRT = \frac{mRT}{V\mathcal{M}} \text{ and } \pi = \rho gh$$

Therefore,

$$h = \left( \frac{RT}{\rho g \mathcal{M}} \right) c$$

The slope of the fitting curve is equal to the above quantity in parentheses. Rearranging, converting to mks units, and plugging in the slope,

$$\mathcal{M} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{(1.004 \times 10^3 \text{ kg m}^{-3})(9.81 \text{ m s}^{-2})(0.29 \times 10^{-2} \text{ m}^4 \text{ kg}^{-1})} = 87 \text{ kg mol}^{-1}$$

■

**Problem 47.** You determine the osmotic pressure of an aqueous solution at 300 K to be 120 kPa. Calculate the freezing point of the solution based on this data.

**Solution.** The freezing point depression equation

$$\Delta T_f = K_f m$$

and osmotic pressure equation

$$\pi = cRT$$

can be combined based on the following relationships

$$m = \frac{n_{\text{solute}}}{\text{kg}_{\text{H}_2\text{O}}} \approx \frac{n_{\text{solute}}}{V \rho_{\text{H}_2\text{O}}}, \quad c = \frac{n}{V}, \quad n = \frac{\pi V}{RT}$$

to form the following expression for temperature change

$$\Delta T_f = \frac{K_f \pi}{RT\rho}$$

The freezing point depression constant and density for H<sub>2</sub>O are  $K_f=1.86$  K.kg.mol<sup>-1</sup> and 10<sup>3</sup> kg.m<sup>-3</sup>, respectively.

$$\Delta T_f = \frac{(1.86 \text{ K.kg.mol}^{-1})(120 \times 10^3 \text{ Pa})}{(8.314 \text{ J.K}^{-1} \text{ mol}^{-1})(300. \text{ K})(10^3 \text{ kg.m}^{-3})} = 0.0895 \text{ K}$$

so solution will freeze at -0.0895°C. ■

**Problem 48.** Each increase in pressure of 100 atm decreases the melting point of ice by about 1.0°C.

(a) Estimate the temperature at which liquid water freezes under a pressure of 400 atm.

(b) One possible explanation of why a skate moves smoothly over ice is that the pressure exerted by the skater on the ice lowers its freezing point and causes it to melt. The pressure exerted by an object is the force (its mass × the acceleration of gravity, 9.8 m.s<sup>-2</sup>) divided by the area of contact. Calculate the change in freezing point of ice when a skater with a mass of 75 kg stands on a blade of area 8.0 × 10<sup>-5</sup> m<sup>2</sup> in contact with the ice. Is this sufficient to explain the ease of skating at a temperature of, for example, -5°C (23°F)?

**Solution.** (a)

$$T_f = 0^\circ\text{C} + \Delta T_f = 0^\circ\text{C} - \left(\frac{400}{100}\right) \times 1^\circ\text{C} = -4^\circ\text{C}$$

(b)

$$P = \frac{(75 \text{ kg})(9.8 \text{ m.s}^{-2})}{8.0 \times 10^{-5} \text{ m}^2} \times \frac{1 \text{ atm}}{101325 \text{ Pa}} = 90.67 \text{ atm}$$

No, this pressure is not high enough for this effect to explain the relative ease of skating at -5°C. ■

**Problem 49.** Glycerol was once used in antifreeze because it can lower the freezing point of water below 0°C. What mass percentage of glycerol in water must be used to reduce the freezing point of the mixture to -5.0°C, assuming ideal solution behavior? ( $K_f = 1.87$  K.kg/mol.)

**Solution.** Using  $\Delta T_f = -K_f m$  with  $\Delta T_f = -5.0$  K and the value of  $K_f$  provided, yields  $m = 2.7$  mol/kg (moles of glycerol per kg of solvent). Multiplication of  $m$  by the molecular weight of glycerol (92.09 g/mol) gives 248.6 g glycerol per kg (1,000 g) solvent. (Let's round this to 250 g to get round numbers; in practice, don't round.) We have 250 g glycerol in 1,000 g water.

The total mass of the solution is  $250 \text{ g} + 1,000 \text{ g} = 1,250 \text{ g}$ . The mass fraction is  $250 / 1,250 = 0.20$ , or 20% of total solution by mass. ■

**Problem 50.** Show that for one nonvolatile ionic molecule, that completely ionizes into  $x$  ions per molecule, the formula for the vapor pressure lowering is  $\Delta P = -xX_{salt}P_B^\circ$  as the limit of the solute concentration approaches zero.  $X_{salt}$  is the ratio of the number of moles of the ionic salt in solution to the total number of moles if the compound were to not ionize.

**Solution.**  $n_0 :=$  moles of  $\text{H}_2\text{O}$

$n_1 :=$  moles of ionic compound

$X_B :=$  mole fraction when the compound completely dissociates

$X_{salt} :=$  mole fraction the compound does not dissociate

$$\begin{aligned} X_{salt} &= \frac{n_1}{n_1 + n_0} \approx \frac{n_1}{n_0} \\ X_B &= \frac{xn_1}{xn_1 + n_0} \approx \frac{xn_1}{n_0} \\ \Delta P_B &= -X_B P_B^\circ = -x \frac{n_1}{n_0} P_B^\circ = -x X_{salt} P_B^\circ \end{aligned}$$

■

**Problem 51.** You have a non-volatile solvent Q, with a molar mass of  $97.80 \text{ g mol}^{-1}$ , dissolved in 0.551 pounds of water (water is a solvent as well, but it is volatile compared to Q). The solution has a vapor pressure of 23.8 torr. Take the vapor pressure of water to be 0.056 atm at the temperature of the solution. Determine how many grams of Q are present in the solution.

**Solution.** The only volatile component is water. Thus, the vapor pressure of the solution,  $P_{vap}$  is due to the water solvent. The Raoult's law is applied to the water solvent:

$$\begin{aligned} P_{vap} &= X_{solvent} P_{solvent}^\circ, \\ X_{solvent} &= P_{vap} / P_{solvent}^\circ = 0.031 \text{ atm} / 0.056 \text{ atm} = 0.56. \end{aligned}$$

Since we have 0.551 lb (249.92 g) of water and its molar mass is 18 g/mol, this implies we have  $n_{\text{H}_2\text{O}} = 249.92/18 = 13.9$  mol of water. Then,

$$\begin{aligned} 0.56 &= \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_Q} = \frac{13.9}{n_Q + 13.9}, \\ n_Q &= 10.9 \text{ mol}, \\ n_Q \times 97.8 \text{ g.mol}^{-1} &= 1066 \text{ g}. \end{aligned}$$

■

**Problem 52.**<sup>13</sup> A total of 10 g of nonvolatile solute are added to five moles of a solvent whose total volume is 200 cm<sup>3</sup>. The freezing point of the solvent is 280 K, while its molar enthalpy of fusion is 2,000 cal mol<sup>-1</sup>. It's found that the solvent in the solution freezes at 279.894 K. By assuming the solution is ideal, compute the osmotic pressure at 300 K.

**Solution.** This is a freezing point depression problem, a colligative property (Raoult's law). Consider the heterogeneous equilibrium where we have a solid  $A(s)$  melting into a liquid  $A(l)$ , but the liquid phase has some amount of solute  $B$  dissolved.  $A(s)$  is in equilibrium with  $A(l)$ ; this means that the chemical potentials of  $A$  in the two phases are equal:

$$\mu_A^*(s) = \mu_A^*(l) + RT \log X_A$$

where  $X_A$  is the mole fraction of  $A$  and  $*$  denotes the pure substance. This leads to the formula for freezing point depression  $\Delta T_f = K' X_B$  presented in class,  $K' = RT_f^2/(\Delta_{fus}H)$ , because differentiation of:

$$\log X_A = \frac{\mu_A^*(s) - \mu_A^*(l)}{RT} = \frac{\Delta_{fus}G}{RT}$$

with respect to  $T$ :

$$\frac{d \log X_A}{dT} = \frac{d}{dT} \frac{\Delta_{fus}G}{RT}$$

Then we use the Gibbs-Helmholtz equation,  $\partial(\Delta G/T)/\partial T|_P = -\Delta H/T^2$ , to get  $\frac{d \log X_A}{dT} = -\Delta_{fus}H/(RT^2)$ . Multiply both sides by  $dT$  and integrate from  $X_A = 1$  to  $X_A$ , and from  $T = T_f$  to  $T$ :

$$\int_0^{\log X_A} d \log X_A = -\frac{1}{R} \int_{T_f}^T \frac{\Delta_{fus}H}{T^2} dT$$

The left hand side integrates to  $\log X_A$ , which equals  $\log(1 - X_B)$ , but for small values of  $X_B$ , this is approximately equal to  $-X_B$ . Then, assuming that  $\Delta_{fus}H$  is constant across this temperature range,

$$X_B = \frac{\Delta_{fus}H}{R} \left( \frac{1}{T_f} - \frac{1}{T} \right),$$

where  $X_B = X_{solute}$ . Writing  $\frac{1}{T_f} - \frac{1}{T} = \frac{T - T_f}{TT_f} \approx \frac{\Delta T_f}{T_f^2}$  (since  $T \approx T_f$ ),  $\Delta T_f = T - T_f$ , yields the result  $\Delta T_f = K' X_B$ , where  $K' = RT_f^2/(\Delta_{fus}H)$ . (Note: this convention results in  $\Delta T_f > 0$ .)

<sup>13</sup>This problem requires Chapter 6 as a pre-requisite; it is placed here because it deals with the topic of freezing point depression. Upon first reading, you can skip the derivations and merely use the boxed equation.

Finally,

$$X_{solute} = \frac{2000 \text{ cal mol}^{-1}}{1.987 \text{ cal K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{279.894 \text{ K}} - \frac{1}{280 \text{ K}} \right) = 0.0013614$$

and

$$\pi = \frac{RTX_{solute}}{V_n} = \frac{(0.0821 \text{ atm.L.K/mol})(300 \text{ K})(0.0013614)}{\frac{0.2 \text{ L}}{5 \text{ mol}}} = 0.8379 \text{ atm}$$

NOTE: We have employed two results. The first is the Gibbs-Helmholtz equation,  $\partial(\Delta G/T)/\partial T|_P = -\Delta H/T^2$ . This equation is derived as follows:

$$\left( \frac{\partial(G/T)}{\partial T} \right)_P = \frac{1}{T} \left( \frac{\partial G}{\partial T} \right)_P + G \frac{d(1/T)}{dT} = \frac{1}{T} \left( \frac{\partial G}{\partial T} \right)_P - \frac{G}{T^2} = \frac{1}{T} \left[ \left( \frac{\partial G}{\partial T} \right)_P - \frac{G}{T} \right]$$

Then, from  $dG(P, T) = VdP - SdT$ ,  $(\partial G/\partial T)_P = -S$ , by definition  $G = H - TS$ , or  $S = (H - G)/T$ ,  $(\partial G/\partial T)_P = (G - H)/T$ , we get for the square bracket:

$$\left( \frac{\partial G}{\partial T} \right)_P - \frac{G}{T} = \frac{G - H}{T} - \frac{G}{T} = -\frac{H}{T}.$$

Thus,

$$\left( \frac{\partial(G/T)}{\partial T} \right)_P = -\frac{H}{T^2},$$

which holds for each term in  $\Delta G = G_f - G_i$ ; hence we can replace  $G$  by  $\Delta G$  and  $H$  by  $\Delta H$ . The second result is the Gibbs energy at constant temperature ( $dT = 0$ ),  $dG = VdP$ , integrated from initial to final state:

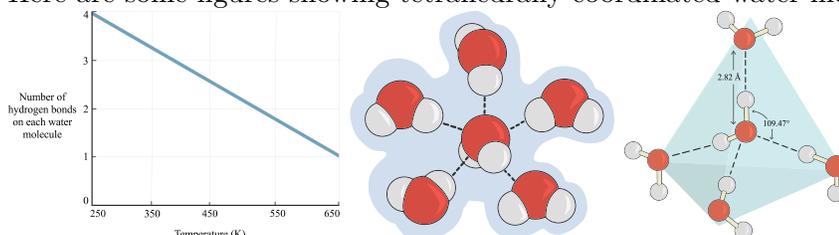
$$G(P_f) = G(P_i) + \int_{P_i}^{P_f} VdP$$

which, for an ideal gas, gives  $G(P_f) = G(P_i) + RT \int_{P_i}^{P_f} (1/P)dP = G(P_i) + RT \log(P_f/P_i)$ . The corresponding molar quantity is called the molar Gibbs energy (Gibbs energy per mole of substance), or chemical potential; hence  $\mu = \mu^\ominus + RT \log(P/P^\ominus)$ , where  $\ominus$  denotes a reference state. For simplicity, we write  $P \equiv P/P^\ominus$ . Denoting the quantities relating to pure substances by a \*, so the chemical potential of pure  $A$  is written  $\mu_A^*$  or  $\mu_A^*(l)$  to denote a liquid. Because the vapor pressure of the pure liquid is  $P_A^*$ , it follows that the chemical potential of  $A$  in the vapor (treated as perfect gas) is  $\mu_A^\ominus + RT \log P_A^*$  (with  $P_A$ , a relative pressure  $P_A/P^\ominus$ ). If another substance, a solute, is also present in the liquid, the chemical potential of  $A$  in the liquid is changed to  $\mu_A$  and its vapor pressure is  $P_A$ . The vapor and solvent are in equilibrium, so we can equate the chemical potentials,  $\mu_A = \mu_A^\ominus + RT \log P_A$ . Combining these two equations to eliminate  $\mu_A^\ominus$ , we get  $\mu_A = \mu_A^* - RT \log(P_A^*) + RT \log P_A = \mu_A^* + RT \log(P_A/P_A^*)$ . Invoking Raoult's law,  $P_A = X_A P_A^*$ , we get  $\mu_A = \mu_A^* + RT \log X_A$ . This derivation is from Atkins [14]. ■

**Problem 53.** Let's estimate the rate of evaporation for water at RT. 1) Calculate the energy,  $\Delta H$ , that binds water molecules in a liquid. You can find more information about the structure of water at the link below:

[http://www1.lsbu.ac.uk/water/water\\_hydrogen\\_bonding.html](http://www1.lsbu.ac.uk/water/water_hydrogen_bonding.html)

Here are some figures showing tetrahedrally coordinated water molecules:



As always, such structures are understood in the sense of time-averages. The actual picture is very dynamic. You may also consult any other useful articles you may find. 2) Then calculate the fraction,  $f$ , of water molecules with kinetic energies sufficiently large to break the hydrogen bonding structure apart and escape to the gas phase. Let's assume that water molecules in the liquid phase also obey Maxwell-Boltzmann statistics. Feel free to use Wolfram Alpha to compute the relevant integrals numerically. 3) Use the fraction calculated in #2 to estimate the rate of evaporation in kg per square meter per second. The approach we shall use is loosely inspired by the Langmuir theory of adsorption on surfaces. How many molecules are there per unit area on the water's surface? Call this quantity,  $\sigma$ , for area density (units: # molecules/m<sup>2</sup>). Consider the following formula:

$$E = \frac{1}{6} \cdot \sigma \cdot \tau_0^{-1} e^{-\Delta H/RT} \cdot f$$

The factor of 1/6 is a geometric factor I've added to account for the fraction of water molecules moving upwards (imagine a cube with 6 faces, and only those moving towards the top face go towards the gas region; the rest stay in solution). The factor  $f$  gives the "area coverage", that is, the fraction of water molecules that are eligible to escape from the solution because their kinetic energies are large enough to enable a jump.  $\tau_0$  is a "residence time", which we take to be the average lifetime of a water molecule in a hydrogen-bonded cluster. The paper below cites hydrogen bond lifetimes in the range 1-20 ps:

<https://arxiv.org/pdf/0706.1355>

Let's take  $\tau_0=20$  ps, the worst case scenario (very long lived clusters). The Arrhenius factor  $e^{-\Delta H/RT}$  gives the fraction of eligible water molecules that will actually jump (at a given temperature  $T$ ); this fraction grows larger with  $T$ .  $\Delta H$  is the energy barrier required to break the hydrogen bonded cluster (see part #1). You can check that the units of  $E$  are molecules/m<sup>2</sup>/s.

**Solution.** 1) Per articles

<https://arxiv.org/pdf/0706.1355>

[http://www1.lsbu.ac.uk/water/water\\_hydrogen\\_bonding.html](http://www1.lsbu.ac.uk/water/water_hydrogen_bonding.html)

the energy required to break the bonds is on the order of a few kJ/mol. One value cited was 9.80 kJ/mol. Let's take 9.80 kJ/mol.

2) For water,  $M = 18 \text{ g/mol} = 0.018 \text{ kg/mol}$ .

$$\sqrt{8RT/\pi M} = \sqrt{8(8.31)(293)/(\pi \cdot 0.018)} \approx 587 \text{ m/s.}$$

This is the average speed of a water molecule. From part 1), the kinetic energy must exceed 9.80 kJ/mol. From  $K = \frac{1}{2}Mv^2$ , this corresponds to a speed of  $\sqrt{2K/M} = \sqrt{2(9800 \text{ J/mol})/(0.018 \text{ kg/mol})} = 1043 \text{ m/s}$ .

We must integrate

$$f(v) = \sqrt{\left(\frac{M}{2\pi RT}\right)^3} 4\pi v^2 e^{-Mv^2/(2RT)}$$

from 1043 m/s to  $\infty$ , using  $T = 293 \text{ K}$ :

$$f = \sqrt{\left(\frac{M}{2\pi RT}\right)^3} 4\pi \int_{1043}^{\infty} v^2 e^{-Mv^2/(2RT)} dv$$

Numerically, the prefactor  $\sqrt{\left(\frac{M}{2\pi RT}\right)^3}$  evaluates to  $1.276 \times 10^{-9}$ .

Also,  $M/(2RT) = 3.696 \times 10^{-6}$ . In Wolfram Alpha, the integral can be evaluated by typing:

`integrate (v^2)*exp(-(v^2)*(3.696e-4)) from 1043 to infinity`

This gives the result:  $2.81 \times 10^6$ . Multiplication by  $4\pi \times 1.276 \times 10^{-9}$  gives:

$$f = 0.045$$

so about 4.5% of molecules have enough kinetic energy to escape the solution and go into the gas phase.

3) Water has mass density  $\rho_m = 1 \text{ g/cc} = 10^6 \text{ g/m}^3 = 10^3 \text{ kg/m}^3$ . Number density is  $(10^3 \text{ kg/m}^3) \cdot (6.022 \times 10^{23} \text{ molecules/mol}) / (0.018 \text{ kg/mol})$ . Elevating this to the power 2/3 gives an area density of  $\sigma = 1.038 \times 10^{19} \text{ molecules/m}^2$ .

$$E = \frac{1}{6} \sigma \cdot \tau_0^{-1} \cdot e^{-\Delta H_{vap}/RT} \cdot f = 1.39 \times 10^{27} \text{ molecules/m}^2/\text{s.}$$

where  $\Delta H_{vap} = 9.8 \text{ kJ/mol}$ .  $RT = (8.31 \text{ J/mol/K})(293 \text{ K}) = 2.434 \text{ kJ/mol}$ . Then,  $e^{-\Delta H_{vap}/RT} \approx 0.01784$ . To get units of  $\text{kg/m}^2/\text{s}$  we must convert molecules to kg, using molar mass (0.018 kg/mol) and Avogadro's constant:

$$E_{mass} = \frac{E}{N_A} \cdot (0.018 \text{ kg/mol}) = 2.07 \text{ kg/m}^2/\text{s}$$

This value is close to the experimental value of  $1.97 \text{ kg/m}^2/\text{s}$  cited here:

<http://likesundanese.blogspot.com/2013/09/water-evaporation-rate-per-surface-area.html> ■

**Problem 54.** Use the evaporation rate,  $E$ , you found in Problem 53 to estimate the amount of water evaporated around the planet by all bodies of water during 1 day. (You will need to look up this information about the total surface area of the Earth that is water.) Assume that all water is at RT and that the temperature is uniform (held at RT) everywhere. (This assumption is probably OK, since the average temperature on Earth is  $16^\circ\text{C}$ , per <https://www.space.com/17816-earth-temperature.html>, so not too far off from RT.) Compare the amount of water evaporated in 1 day to the total rainfall in 1 day. (Look up the average annual rainfall, and divide by 365 days to get the daily rate.) These two numbers should balance each other, right? (If not, explain why not.)

**Solution.** About 70% of the Earth's surface is water-covered (with the oceans accounting for 95.6% of all Earth's water). The surface area of the Earth is 196.9 millions of square miles, or  $5.1 \times 10^8 \text{ km}^2$ . So 70% of this works out to 361 million  $\text{km}^2$  (or 139.4 million  $\text{mi}^2$ ). This data is from: <https://www.universetoday.com/25756/surface-area-of-the-earth/> Multiplication of  $E$  by  $361 \times 10^{12} \text{ m}^2$  and by 1 day (86,400 seconds) gives:

$$(2.07 \text{ kg/m}^2/\text{s})(361 \times 10^{12} \text{ m}^2)(86,400 \text{ s}) = 6.45 \times 10^{19} \text{ kg}$$

The Earth's average annual precipitation is approximately  $5.36 \times 10^{14} \text{ m}^3$ . Source: <https://hypertextbook.com/facts/2008/VernonWu.shtml> Divided by 365 days, this gives  $1.47 \times 10^{12} \text{ m}^3$  per day. Because water has density of  $1000 \text{ kg/m}^3$ , this corresponds to  $1.47 \times 10^{15} \text{ kg}$  of water.

The estimate is off by 4 orders of magnitude ( $1.47 \times 10^{15} \text{ kg}$  vs.  $6.45 \times 10^{19} \text{ kg}$ ). We neglected the rate of condensation. We can estimate the rate of condensation if we know the amount of water in the air (humidity level),  $[\text{H}_2\text{O}]$  (in  $\text{moles/m}^3$ ), the average (say, rms) speed  $v_{rms}$  of the air molecules, and  $\gamma$  the uptake coefficient.  $\gamma$  is the probability that a molecule hitting the water surface will be reabsorbed into the solution. Then,

$$J = \frac{\gamma}{6} \cdot v_{rms} \cdot [\text{H}_2\text{O}]$$

where the factor  $1/6$  is introduced for the same reason as before. Let's assume the air temperature is the same as the solution temperature and take  $\gamma = 1$ . Taking  $v_{rms} = 1043 \text{ m/s}$ . According to <https://www.cactus2000.de/uk/unit/masshum.shtml> if the relative humidity were 51.73%, which appears to be some ideal value "comfortable to humans"

[https://en.wikipedia.org/wiki/Relative\\_humidity](https://en.wikipedia.org/wiki/Relative_humidity)

the water concentration at normal pressure and temperature (25°C and 101.325 kPa) is  $3.9798 \times 10^{17}$  molecules/cc, or  $3.9798 \times 10^{23}$  molecules/m<sup>3</sup>. Then,  $J$  in units of kg/m<sup>2</sup>/s is:

$$\frac{J}{N_A} \cdot (0.18 \text{ kg/mol}) = \frac{1}{6} \cdot (1043) \cdot (3.9798 \times 10^{23}) \cdot \frac{0.018}{6.022 \times 10^{23}} \approx 2.067 \text{ kg/m}^2/\text{s}$$

Then, condensation accounts for the difference. Note: the choice of 51.73% is semi-arbitrary here and the exact value chosen matters. The moral of the story here is that precipitations alone do not account for the difference, by a long shot. We must include the rate of condensation at the very least. ■

**Problem 55.** Suppose you want to build a swimming pool in your backyard (assume a surface area of 500 square foot) and you want to estimate how much water it will consume. How many gallons of water per day do you lose by evaporation? (Assume RT.) Note: this calculation (and the one in Problem 54) neglects the effects of direct sunlight.

**Solution.** 500 square feet = 46.5 square meters. Multiplication of  $E$  by 46.5 m<sup>2</sup> and by 1 day (86,400 seconds) gives:

$$(2.07 \text{ kg/m}^2/\text{s})(46.5 \text{ m}^2)(86,400 \text{ s}) = 8.32 \times 10^6 \text{ kg}$$

Again, this number is much too high. If instead, we account for condensation and air humidity (51% r.h.), we get a much smaller loss

$$(2.07 - 2.067 \text{ kg/m}^2/\text{s})(46.5 \text{ m}^2)(86,400 \text{ s}) = 12,053 \text{ kg}$$

A pool of this size (say 5 m wide x 10 m long, 1.5-3.5 m deep) may have a volume of 125,000 liters (kg). This represents about 10% loss of water volume per day. Losses may be less if the pool temperature is lower. ■

**Problem 56.** Freezing point depression. The addition of a (non-volatile) solute to the solvent lowers the freezing point because the solute impedes the formation of the crystalline solid. This is mainly an entropic effect that describes the space (configurations) occupied by the solute, thereby forcing the solvent molecules to rearrange themselves around the solute particles to accommodate them. Recall that the freezing point depression is given by the formula  $\Delta T_f = K_f \cdot m$ , where  $m$  is the molality of the solute and  $K_f$  is a constant. (With this convention,  $\Delta T_f > 0$ .) This formula is a statement of the fact that  $\Delta T_f$  a *colligative property*. (a) Explain why?  $K_f$  has a name; it is called the *cryoscopic constant*. It can be shown

[http://www1.lsbu.ac.uk/water/colligative\\_properties.html](http://www1.lsbu.ac.uk/water/colligative_properties.html)

that the cryoscopic constant can be written in the form:

$$K_f = \frac{MRT_f^2}{\Delta H_{fus}}$$

where  $\Delta H_{fus}$  is the enthalpy of fusion,  $M$  is the molar mass of the solvent,  $R$  is the gas constant,  $T_f$  is the fusion temperature of the pure solvent. It can also be shown

[www4.ncsu.edu/~franzen/public\\_html/CH433/lecture/](http://www4.ncsu.edu/~franzen/public_html/CH433/lecture/)

Colligative\_Prop\_h.pdf

[https://en.wikipedia.org/wiki/Entropy\\_of\\_fusion](https://en.wikipedia.org/wiki/Entropy_of_fusion)

that the enthalpy of fusion is related to the entropy of fusion,  $\Delta S_{fus}$ :

$$\Delta S_{fus} = \Delta H_{fus}/T_f,$$

because  $\Delta G_{fus} = \Delta H_{fus} - T_f \Delta S_{fus} = 0$  at equilibrium. The entropy of fusion,  $\Delta S_{fus} = S(\text{liquid}) - S(\text{solid})$ , is the increase in entropy when melting a substance. For a pure substance, this is almost always positive [meaning that  $S(\text{liquid}) > S(\text{solid})$ ] since the degree of disorder increases in the transition from an organized crystalline solid to the disorganized structure of a liquid; the only known exception is helium. Suppose for simplicity that  $S(\text{liquid})$  does not change significantly with addition of the solute [i.e. it may change a bit, but not as much as  $S(\text{solid})$ , so that  $S(\text{liquid})$  is always larger than  $S(\text{solid})$ ; this is, of course, an approximation, but good enough to illustrate the main point].

Thus,  $K_f$  (and thereby,  $\Delta T_f$ ) depend on  $\Delta S_{fus}$ . Let us look at the origins of these entropic effects from a very simple picture. Our task here shall be to examine the effect of solute addition on  $S(\text{solid})$ . Imagine a 2D fluid, for example, a  $3 \times 3$  matrix (square array). When the solvent is pure, this

array looks like:

```

  ○ ○ ○

```

where  $\circ$  denotes a solvent particle. When a solute

```

  ○ ○ ○

```

```

  ● ○ ○

```

particle is added, this matrix may look like

```

  ○ ○ ○
  ○ ○ ○

```

particle. In fact, there can be 9 different configurations, corresponding to all possible ways to insert a  $\bullet$  in any of the 9 positions. The entropy of the solid, according to Boltzmann, is proportional to the logarithm of the number of configurations of fixed energy,  $\Omega$ :  $S(\text{solid}) = k_B \log(\Omega)$ , where  $\log$ =natural log. For pure solvent,  $\Omega = 1$ , since there is only 1 possible configuration,

```

  ○ ○ ○

```

namely,  $\circ \circ \circ$ . Since  $\log(1) = 0$ ,  $S_0 = 0$ . For 1 solute particle,  $\Omega = 9$

```

  ○ ○ ○

```

and  $S_1 = k_B \log(9)$ . Thus,  $S_1 > S_0$ , i.e. the entropy for 1 solute particle is greater than the entropy of the pure solvent.

(b) What do you conclude about the effect of solute on  $S(\text{solid})$ , and its impact on  $\Delta T_f$ , the freezing point depression? Now let's go to 3D. Imagine a  $3 \times 3 \times 3$  array/cube (27 total lattice positions).

(c) What is the entropy,  $S_0$  of the pure solvent. What is the entropy,  $S_1$ , of the solution containing 1 solute particle? What is the entropy,  $S_2$  of the solution containing 2 particles? etc. (Continue this process up to  $S_{27}$ , the case of the pure solute.) What can you conclude about  $S_n$ ,  $n = 1, \dots, 27$ , and its effect on  $\Delta T_f$ , the freezing point depression?

(d) Here, we have considered a solid of size  $3 \times 3 \times 3$  for simplicity; what happens in the limit of large volume  $V$ ?

**Solution.** (a) Colligative property only depends on the mole fraction of the solute, not on its nature. (b) As solute is added,  $S(\text{solid})$  increases, up to the point where the amount of solute equals the amount of solvent (50-50 mixture). At the same time,  $S(\text{liquid}) - S(\text{solid})$  decreases. This causes  $\Delta T_f$  to increase.

(c) There are  $\Omega(27, 1) = \binom{27}{1} = 27$  ways of placing 1 particle in a  $3 \times 3 \times 3$  lattice,  $\Omega(27, 2) = \binom{27}{2} = 27 \cdot 26/2 = 351$  ways of placing 2 particles in a  $3 \times 3 \times 3$  lattice,  $\Omega(27, 3) = \binom{27}{3} = 27 \cdot 26/2 = 2925$  ways of placing 3 particles in a  $3 \times 3 \times 3$  lattice,  $\dots$ ,  $\Omega(27, 26) = 27$ ,  $\Omega(27, 27) = 1$ . So the entropy increases as we add more solute, up to the point where the amount of solute equals the amount of solvent (at which point the solute becomes the solvent), followed by a decrease. As far as the freezing point depression,  $\Delta T_f$ , is concerned, the effect becomes more pronounced as more solute is added.

(d) In the limit of large volume, the same idea applies to the freezing point depression. The discrete variables become continuous parameters. ■

**Problem 57.** Find out what conditions ( $T, P$ ) are used to carry out ammonia synthesis in industrial processes. Explain why the reaction is carried out under those conditions. How do these conditions affect the chemical equilibrium?

**Solution.** The conditions are approximately 200 atm and  $450^\circ\text{C}$ . Carrying out the reaction at high pressure shifts the equilibrium towards the product, per Le Châtelier's principle. However, the reaction is exothermic, so lower temperatures are better. However, the reaction rate can be pretty slow at low temperatures. Why  $450^\circ\text{C}$  then? At high temperatures, the reaction rate increases.  $450^\circ$  represents a compromise (between equilibrium and reaction rate). This compromise results in a significant amount of ammonia produced, in a very short time. More details can be found here:

<https://chemguide.co.uk/physical/equilibria/haber.html> ■

**Problem 58.** Dialysis relies on a membrane to separate molecules in a solution. Consider a system in equilibrium consisting of a flexible dialysis vessel filled with a solution of a purified protein sitting in water. Describe

what happens to the system if:

- You increase the concentration of the protein in the vessel.
- You decrease the concentration of the protein in the vessel.
- Add a small, impure protein sample (containing salts and dyes) to the vessel.

**Solution.** Let us invoke Le Châtelier's principle:

- The vessel expands as more water enters to balance the increased concentration.
- The vessel contracts as water leaves in response to the reduced concentration.
- The salt and dyes diffuse through the dialysis vessel, leaving a more pure sample of the protein. The vessel also likely expands some due to the increased concentration. ■

**Problem 59.** The vapor pressures of each component in a mixture of propanone (acetone, A) and trichloromethane (chloroform, C), were measured at 35° C with the following results:

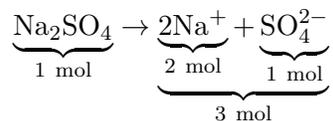
$\chi_c$	0	0.2	0.4	0.6	0.8	1.0
$P_C/\text{torr}$	0	35	82	142	219	293
$P_A/\text{torr}$	347	270	185	102	37	0

Confirm that the mixture “conforms” to Raoult's law for the component in large excess and to Henry's law for the component that is minor. Estimate the Henry's law constants,  $K_A$  and  $K_C$ .

**Solution.** You should graph this data and realize that it shows a general conformity to Raoult's law by both components. Both components exhibit a negative deviation to Raoult's law. So, at large mole fractions the component obeys Raoult's law (experimental data will approach the line) and at small mole fractions the component obeys Henry's law. ■

**Problem 60.** Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) has a normal boiling point,  $T_b$  of 78.4°C. When 46.58 g of  $\text{Na}_2\text{SO}_4$  (sodium sulfate) is dissolved in the ethanol (mass = 1000 g) the boiling point becomes 79.6°C. Calculate the  $K_B$  for ethanol (including appropriate units). Assume the salt completely dissolves in the ethanol and behaves as a strong electrolyte.

**Solution.** We will use:  $\Delta T_b = K_b \cdot m$ . The solute,  $\text{Na}_2\text{SO}_4$  has a molar mass of 142.04 g/mol. There is 1000 g of solvent (1.000 kg solvent). Therefore, the molality can be calculated. Strong electrolyte:



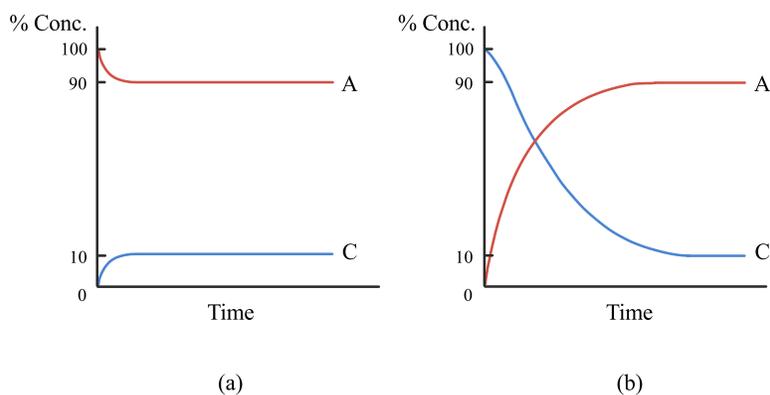
$$(46.58 \text{ g Na}_2\text{SO}_4) \left( \frac{1 \text{ mol Na}_2\text{SO}_4}{142.04 \text{ g Na}_2\text{SO}_4} \right) = 0.3279 \text{ mol Na}_2\text{SO}_4 \times 3 \\ = 0.9837 \text{ mol particles}$$

$$m = \frac{\text{moles of solute particles}}{\text{kg of solvent}} = \frac{0.9837}{1.000 \text{ kg}} = 0.9837 \text{ m}$$

So,  $\Delta T = T_{\text{new}} - T_b = K_b \cdot m = 79.6^\circ\text{C} - 78.4^\circ\text{C} = 1.2^\circ\text{C}$ . So,  $1.2^\circ\text{C} = (K_b)(0.9837 \text{ mol/kg})$  and  $K_b = \frac{1.2^\circ\text{C}}{0.9837 \text{ mol/kg}} = 1.22^\circ\text{C kg/mol}$  which gives  $1.2^\circ\text{C kg/mol}$ . ■

# Chemical Reactions

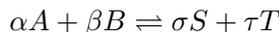
Suppose we have a chemical reaction which describes a cobalt-HCl system (see Fig. 4.1), where at time  $t = 0$  we only have reactants and zero products. As time evolves, the reactants are depleted and the products are formed. A possible time course of this reaction is illustrated in the left hand plot (a) of Fig. 4.1, where the time courses of concentration of a reactant (A) and product (C) are shown. In the right hand plot (b) the roles are reversed: species A is produced whereas species C is depleted. This plot could correspond to the case where at time  $t = 0$  we only have products present and zero reactants, in which case only the reverse reaction initially takes place. In both cases (a,b) some equilibrium concentrations are reached after sufficiently long time. At that point, species A and C do not “remember” the initial conditions anymore.



**Figure 4.1.** Chemical reactions reach equilibrium over time. The dynamics of the reaction are determined by its kinetics.

### 4.1. Chemical Reactions and Equilibrium

Suppose that we have a reversible chemical reaction:



- The forward reaction rate is  $k_f[A]^\alpha[B]^\beta$ ,
- The backward reaction rate is  $k_r[S]^\sigma[T]^\tau$ .

Here,  $k_r$  and  $k_f$  are called affinity constants.

At *equilibrium* the reaction rates for forward and backward reaction are equal:

$$k_f[A]_{\text{eq}}^\alpha[B]_{\text{eq}}^\beta = k_r[S]_{\text{eq}}^\sigma[T]_{\text{eq}}^\tau,$$

where the subscript  $_{\text{eq}}$  denotes equilibrium concentrations.

4.1.0.1. *Law of Mass-Action.* If we call  $K$  the *equilibrium constant* and set it equal to  $k_f/k_r$ , we have:

$$K \equiv \frac{k_f}{k_r} = \frac{[S]_{\text{eq}}^\sigma [T]_{\text{eq}}^\tau}{[A]_{\text{eq}}^\alpha [B]_{\text{eq}}^\beta}.$$

This equation for  $K$  is called the **law of mass-action**. Sometimes the law of mass-action refers to the “chemical force” (affinity) between two reactants reacting together, in the above case, this force is proportional to  $k_f[A]^\alpha[B]^\beta$ .

**Chemical equilibrium:** At equilibrium, the concentrations do not change in time:

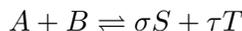
$$\frac{d[\text{reactants}]}{dt} = \frac{d[\text{products}]}{dt} = 0.$$

There are still chemical transformations taking place at equilibrium, but the net change is zero: this is where the rates of the forward and backward reaction are equal.

**4.1.1. Comment on Reaction Rates.** That the forward reaction rate is of the form

$$k_f[A]^\alpha[B]^\beta$$

can easily be understood as follows. Suppose  $\alpha = \beta = 1$  for simplicity. The reaction is of the form:

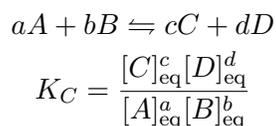


1 molecule of  $A$  reacts with 1 molecule of  $B$  to produce some quantities of  $S$  and  $T$ . Thus, this event depends on the binary collision of  $A$  and  $B$ . For a binary collision to happen in a given volume element, the rate of this reaction should be proportional to the product of probabilities of finding a molecule of type  $A$  in that volume times the probability of finding a molecule of type  $B$  in that same volume. (Assuming “statistical independence” of these individual

events, i.e. the presence of a molecule of type  $A$  within a volume element does not influence, and is not influenced by the presence of a molecule of type  $B$  within that same volume, which is the case for dilute concentrations), but these probabilities are proportional to the concentrations of each species. Namely, the probability of finding  $A$  in a volume element is proportional to  $[A]$ , the concentration of  $A$ . Same for the probability of finding a molecule of type  $B$  within that same volume, which is also proportional to  $[B]$ . Hence, the rate is proportional to the product  $[A][B]$ . When the stoichiometric coefficients  $\alpha$  and  $\beta$  are different from 1, this means we have three-body, four-body, etc. collisions. But in those instances, the same reasoning can be applied. In a three-body collision requiring the encounter of  $A$ ,  $A$  and  $B$ , the rate of this event is proportional to  $[A][A][B] = [A]^2[B]$ . This idea is easily generalized to arbitrary  $\alpha$  and  $\beta$  to give  $[A]^\alpha[B]^\beta$ .

#### 4.1.2. For Solution Phase Reactions.

**4.1.3. Notation.**  $K_C$  is the equilibrium constant in terms of concentrations. This applies to solutions. For example,



where the subscript eq denotes the concentrations at equilibrium (in steady state, where concentrations do not change with time anymore).

**4.1.4. For Gas-Phase Reactions.** For a gas-phase reaction, the law of mass-action is written in terms of gas pressures (all pressures are taken at equilibrium)

$$K_P = \frac{(P_C)_{\text{eq}}^c (P_D)_{\text{eq}}^d}{(P_A)_{\text{eq}}^a (P_B)_{\text{eq}}^b}$$

and likewise we can omit the subscript eq from this.

**4.1.5. Gas-Phase Reactions.** For reasons of convenience and compatibility with concepts from thermodynamics (which we will cover later in the course), all pressures are expressed in units of atm, relative to a reference pressure  $P_{\text{ref}}$  of 1 atm and we define a dimensionless quantity  $K$ :

$$K = \frac{(P_C/P_{\text{ref}})_{\text{eq}}^c (P_D/P_{\text{ref}})_{\text{eq}}^d}{(P_A/P_{\text{ref}})_{\text{eq}}^a (P_B/P_{\text{ref}})_{\text{eq}}^b}$$

$$K(P_{\text{ref}})^{(c+d-a-b)} = \frac{(P_C)_{\text{eq}}^c (P_D)_{\text{eq}}^d}{(P_A)_{\text{eq}}^a (P_B)_{\text{eq}}^b}$$

where, with  $P_{ref} = 1$  atm, the  $K$  is identical to  $K_P$  (i.e. they both have the same *numerical value*):

$$K = K_P = \frac{(P_C)_{eq}^c (P_D)_{eq}^d}{(P_A)_{eq}^a (P_B)_{eq}^b}.$$

(The equality  $K = K_P$  holds as long as  $P_{ref}=1$  atm and partial pressures are in units of atm.)

**4.1.6. Liquid Phase Reactions.** Likewise if we define a  $K$  value in terms of concentrations referenced to a reference concentration  $c_{ref}$

$$K = \frac{([C]_{eq}/c_{ref})^c ([D]_{eq}/c_{ref})^d}{([A]_{eq}/c_{ref})^a ([B]_{eq}/c_{ref})^b}$$

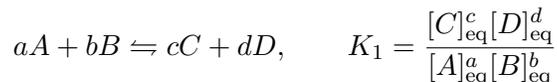
and express our concentrations in units of molar (M) and take  $c_{ref}=1$  M,  $K$  has the same *numerical value* as  $K_C$ :

$$K = K_C = \frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b}.$$

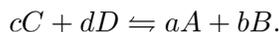
(The equality  $K = K_C$  holds as long as  $c_{ref}=1$  M and concentrations are in units of M.)

## 4.2. Operations on Reaction

**4.2.1. Inverse Reaction.** Suppose we have a reaction



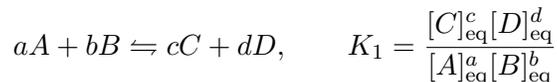
and another reaction, which is the inverse of the first one:



Then the rate constants are inverses of each other:

$$K_2 = \frac{[A]_{eq}^a [B]_{eq}^b}{[C]_{eq}^c [D]_{eq}^d} = \frac{1}{K_1}.$$

**4.2.2. Multiplication of the Stoichiometric Coefficients.** Suppose that we multiply the reaction:



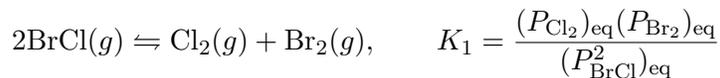
by a factor of 2,



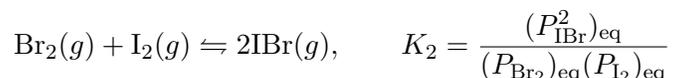
The effect is to raise the equilibrium constant to the power 2:

$$K_2 = \frac{[C]_{eq}^{2c} [D]_{eq}^{2d}}{[A]_{eq}^{2a} [B]_{eq}^{2b}} = (K_1)^2$$

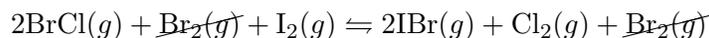
**4.2.3. Adding Two Reactions.** If we add:



to the equation



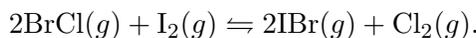
we get an overall reaction:



and its corresponding rate constant:

$$K_3 = \frac{(P_{\text{IBr}}^2)_{\text{eq}}(P_{\text{Cl}_2})_{\text{eq}}\cancel{(P_{\text{Br}_2})_{\text{eq}}}}{(P_{\text{I}_2})_{\text{eq}}\cancel{(P_{\text{Br}_2})_{\text{eq}}}(P_{\text{BrCl}}^2)_{\text{eq}}} = \frac{(P_{\text{IBr}}^2)_{\text{eq}}(P_{\text{Cl}_2})_{\text{eq}}}{(P_{\text{I}_2})_{\text{eq}}(P_{\text{BrCl}}^2)_{\text{eq}}}$$

Deleting  $\text{Br}_2(g)$  from both sides:



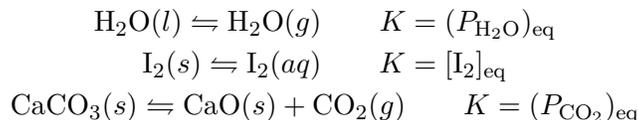
Thus, we see that the equilibrium constants multiply each other:

$$K_3 = K_1 \cdot K_2$$

**4.2.4. Subtracting Two Reactions.** By the same token subtracting two reactions leads to the division of the equilibrium constants. This follows from the fact that subtracting a reaction is equivalent to adding the reverse of the second one, which we saw leads to taking the inverse of its equilibrium constant.

### 4.3. Multi-Phase (Heterogeneous) Reactions

For reactions that involve some mixture of solid, liquid, and gas phases (also known as heterogeneous reactions), we have the following equilibrium constants

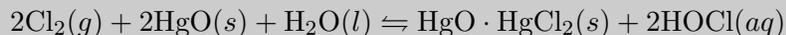


To write down the equilibrium constant for such a heterogeneous reaction we must follow certain conventions:

- Gases enter the equilibrium expression as partial pressures, measured in units of atm
- Dissolved species enter as concentrations, in units of mol/L (M)
- Pure solids and pure liquids do not appear in equilibrium expressions. Neither does a solvent that participates in a chemical reaction provided the solution is dilute.

- Partial pressures and concentrations of products appear in the numerator, and those of reactants in the denominator. Each is raised to a power equal to its coefficient in the balanced chemical equation for the reaction.

**Example:** For



we write:

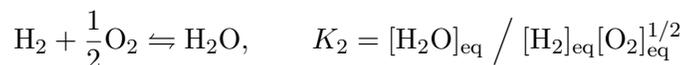
$$K = \frac{[\text{HOCl}]_{\text{eq}}^2}{(P_{\text{Cl}_2})_{\text{eq}}^2}$$

The HgO and HgO·HgCl<sub>2</sub> do not appear because they are solids, and water does not appear because it is a pure liquid. Chlorine gas enters as its partial pressure in atm. The HOCl appears as its concentration in M. Both the concentration of HOCl and the partial pressure of Cl<sub>2</sub> are raised to the second power because their coefficients in the balanced chemical reaction are 2.

**4.3.1. Dependence on Stoichiometry.** It matters how you write the equation. For example,



and



implies that  $K_1 \neq K_2$ . In fact, we have  $K_2 = \sqrt{K_1}$ . However, both equations describe the same chemical reaction, so it would make sense that their equilibrium constants be the same constant. This ambiguity can be avoided by following the convention of using “stoichiometric coefficients that are the smallest possible whole numbers”.

The convention we learned so far is: 1) express partial pressures in the equilibrium constant in units of 1 atm, concentrations in units of 1 M, 2) omit pure solids and pure liquids from the equilibrium constant, 3) use smallest possible whole numbers as stoichiometric coefficients. This convention removes ambiguities in the many possible values and units of the equilibrium constant. In this course, we shall not necessarily follow this convention. The reason for this is because many textbooks do not; hence, you should be prepared to deal with different conventions. For example, in the first reaction,  $K_1$  could have units of atm<sup>-1</sup> or M<sup>-1</sup>, depending on whether the quantities are expressed in units of partial pressures or concentrations. Likewise,  $K_2$  could have units of 1/√atm or 1/√M.

**4.3.2. Detailed Balance.** If two reactions are in equilibrium:



Then the whole thing is in equilibrium:



Thus, if each step is in equilibrium (balanced) then the whole thing is in equilibrium.

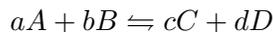
This is a consequence of the addition of chemical reactions. The equilibrium constant of the first two equations are:

$$K_1 = \frac{[E]^e}{[A]^a[B]^b} \quad \text{and} \quad K_2 = \frac{[C]^c[D]^d}{[E]^e}$$

The sum of the two reactions is:



Cancelling  $eE$  on both sides leads to the desired result:



whose equilibrium constant is

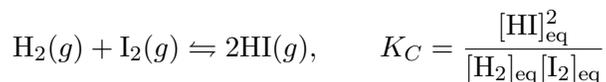
$$K_3 = \frac{[C]^c[D]^d}{[A]^a[B]^b}.$$

We note that this is also equal to the equilibrium constant of (\*):

$$K_{1+2} = \frac{[C]^c[D]^d[E]^e}{[A]^a[B]^b[E]^e} = K_1 \cdot K_2 = \frac{[C]^c[D]^d}{[A]^a[B]^b} = K_3.$$

#### 4.4. Direction of a Reaction

Suppose we have a reaction



for which  $K_C = 46$  at 783 K. Let's say we mix  $\text{H}_2$ ,  $\text{I}_2$  and  $\text{HI}$  at each 0.0020 mol/L at 783 K. (We'll use concentrations instead of pressures.) There is a way to predict whether or not  $\text{HI}$  will have a tendency to form.

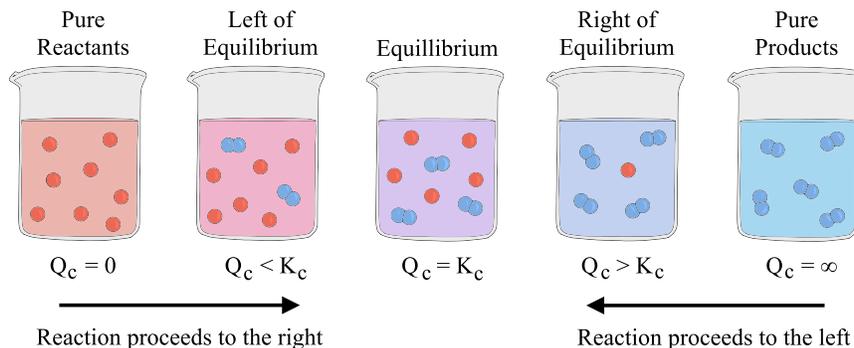
*Strategy:* As you will recall  $K_C$  is products over reactants. If the quantity  $[\text{HI}]^2/([\text{H}_2][\text{I}_2])$  at non-equilibrium is greater than  $K_C$  this means there is too much product, so reactants will form. Thus, our strategy is to calculate the reaction quotient

$$Q_C = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.0020)^2}{0.0020 \times 0.0020} = 1.0$$

and compare to  $K_C$ . Here, we find  $Q_C < K_C$  and conclude that the reaction will tend to form more product and consume reactants.

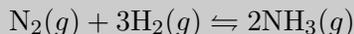
$Q_C$  is called the quotient of the reaction. It is calculated under the conditions given by the problem (not necessarily at equilibrium). Comparison of  $Q_C$

to  $K_C$  tells us which direction the reaction will proceed. This concept is illustrated in Fig. 4.2.



**Figure 4.2.** The value of  $Q$  relative to  $K_C$  (equilibrium constant) tells us if the reaction needs to favor the reactants or products. Red: reactants; blue: products.

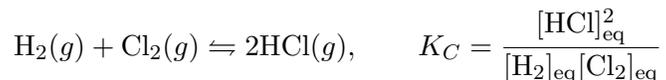
**Exercise:** A mixture of  $\text{H}_2$ ,  $\text{N}_2$  and  $\text{NH}_3$  with molar concentrations  $3.0 \times 10^{-3}$  mol/L,  $1.0 \times 10^{-3}$  mol/L and  $2.0 \times 10^{-3}$  mol/L, respectively, was prepared and heated to 500 K, at which temperature  $K_C = 61$  for the reaction



Decide whether ammonia tends to form or decompose. [Answer:  $Q_C = (2.0 \times 10^{-3})^2 / (3 \times 10^{-3})^3 (1.0 \times 10^{-3}) = 1.48 \times 10^5$ , so it tends to decompose.]

Note: certain textbooks would express  $K_C$  and  $Q_C$  in units of  $1/\text{M}^2$ .

**4.4.1. Solving for Equilibrium Concentrations.** Suppose that in equilibrium between  $\text{HCl}$ ,  $\text{Cl}_2$  and  $\text{H}_2$ ,



the concentrations are:

$$[\text{H}_2]_{\text{eq}} = 1.0 \times 10^{-17} \text{ mol} \cdot \text{L}^{-1} \quad \text{and} \quad [\text{Cl}_2]_{\text{eq}} = 2.0 \times 10^{-16} \text{ mol} \cdot \text{L}^{-1}.$$

What is the equilibrium molar concentration of  $\text{HCl}$  given  $K_C = 4.0 \times 10^{31}$  for the reaction?

*Strategy:* At equilibrium, the molar concentrations of the reactants and products satisfy the expression for  $K_C$ . Rearrange the expression to give the unknown concentration, and substitute the data.

From the expression  $K_C = \frac{[\text{HCl}]_{\text{eq}}^2}{[\text{H}_2]_{\text{eq}}[\text{Cl}_2]_{\text{eq}}}$  we solve for  $[\text{HCl}]_{\text{eq}}$ :

$$[\text{HCl}]_{\text{eq}} = \sqrt{K_C[\text{H}_2]_{\text{eq}}[\text{Cl}_2]_{\text{eq}}},$$

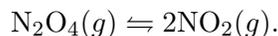
and substitute the data given

$$[\text{HCl}]_{\text{eq}} = \sqrt{(4.0 \times 10^{31})(1.0 \times 10^{-17})(2.0 \times 10^{-16})} = 0.28.$$

That is, the molar concentration of HCl at equilibrium is 0.28 mol/L. This result means that, at equilibrium, the amount of product in the system is overwhelming compared to the amounts of reactants.

#### 4.4.2. Effecting a Change From Initial to Equilibrium Pressures.

The reversible reaction between dinitrogen tetroxide and nitrogen dioxide is written as:



1 L  $\text{N}_2\text{O}_4$  (at 25°C, 1 atm) is allowed to come to equilibrium.  $K=0.14$  atm at 25°C. What are  $P_{\text{N}_2\text{O}_4}$ ,  $P_{\text{NO}_2}$  and  $P_{\text{tot}}$  at equilibrium?

*Strategy:* Chemical reaction gives relationship between the partial pressures. We setup  $x$  as the progress variable.

$$P_{\text{N}_2\text{O}_4} = 1 \text{ atm} - x \quad \text{and} \quad P_{\text{NO}_2} = 2x.$$

From our knowledge of the equilibrium constant (its value is given to us)

$$K = 0.14 \text{ atm} = \frac{(P_{\text{NO}_2})_{\text{eq}}^2}{(P_{\text{N}_2\text{O}_4})_{\text{eq}}}$$

$$0.14 \text{ atm} = \frac{(2x)^2}{1 \text{ atm} - x}$$

$$0.14 \text{ atm}^2 - 0.14x \text{ atm} = 4x^2$$

$$4x^2 + 0.14x \text{ atm} - 0.14 \text{ atm}^2 = 0.$$

Thus we need to solve a quadratic equation of the form  $Ax^2 + Bx + C = 0$  whose roots are:

$$x^{\pm} = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A}.$$

We get two roots, only one of which makes physical sense (the other root,  $-0.21$  is rejected because  $x$  cannot be negative if product must be formed):

$$x = 0.17 \text{ atm}.$$

From this, we get:

$$(P_{\text{NO}_2})_{\text{eq}} = 2x = 0.34 \text{ atm}, \quad (P_{\text{N}_2\text{O}_4})_{\text{eq}} = 1 - 0.17 = 0.83 \text{ atm},$$

$$(P_{\text{tot}})_{\text{eq}} = (0.34 + 0.83) \text{ atm} = 1.17 \text{ atm}.$$

### 4.5. Le Châtelier's Principle: Response to (small) Changes (from Equilibrium)

Henri Louis Le Châtelier (1850-1936) stated a general principle that lets us predict how the composition of a reaction mixture at equilibrium tends to change when the conditions are perturbed:

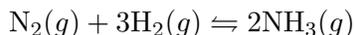
**Le Châtelier's principle:** When a stress is applied to a system in dynamic equilibrium, the equilibrium tends to adjust to minimize the effect of the stress.

Other statements you may encounter include: 1) When any system at equilibrium is subjected to change in concentration, temperature, volume, or pressure, then the system readjusts itself to counteract (partially) the effect of the applied change and a new equilibrium is established. 2) Any change in status quo prompts an opposing reaction in the responding system.

The main points to remember are:

- System initially at equilibrium (“dynamic equilibrium” = steady state)
- It is perturbed *slightly* from equilibrium (big changes not allowed)
- DIRECTION: Response is such that the change is opposed

**4.5.1. Adding and Removing Reagents.** Suppose that the following reaction has reached equilibrium:



So at time  $t = 0$  we are at equilibrium. Suppose that we pump in more hydrogen gas. According to Le Châtelier's principle, the reaction will tend to minimize the increase in the number of hydrogen molecules. Hydrogen will tend to react with nitrogen. As a result, ammonia will be formed. If instead of hydrogen, we were to add ammonia, then the reaction would tend to form reactants.

The explanation is found in the previous discussion of  $Q$  and  $K$ . When reactants are added,  $Q$

$$Q = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]}$$

falls below  $K$  momentarily, because the reactant concentrations appear in the denominator of  $Q$ . As we have seen, when  $Q < K$ , the reaction mixture responds by forming products. Likewise when products are added  $Q$  rises above  $K$ . Because  $Q > K$  the reaction mixture responds by forming reactants at the expense of the products until  $Q = K$  again.

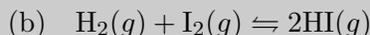
**4.5.2. Compressing a Reaction Mixture.** A gas-phase equilibrium responds to compression (a reduction in volume) of the reaction vessel. According to Le Châtelier's principle, the composition will tend to change in a

way that minimizes the increase in pressure resulting from the compression. For instance, the formation of  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2$  decreases the number of gas-phase molecules in the container because 4 mol of reactant molecules produce 2 mol of product molecules. The forward reaction therefore decreases the pressure the mixture exerts. When the mixture is compressed, the equilibrium composition will tend to shift in favor of the products, for that minimizes the increase in pressure. The opposite response, a tendency for products to decompose, occurs in an expansion. In order to increase the yield of ammonia, the synthesis must be carried out with highly compressed gases. The industrial process uses pressures of 250 atm and more.

**Predicting the Effect of Compression:** Predict the effect of compression on the equilibrium composition of the reaction mixture in which the equilibria



and

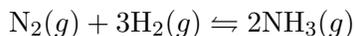


have been established.

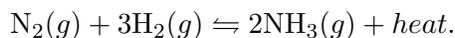
**Solution:** (a) In the reverse reaction, two  $\text{NO}_2$  molecules combine to form one  $\text{N}_2\text{O}_4$  molecule. Hence, compression favors the formation of  $\text{N}_2\text{O}_4$ . (b) Because neither direction corresponds to the reduction of gas-phase molecules, compressing the mixture should have little effect on the composition of the equilibrium mixture.

**Comment:** We can deduce the Le Châtelier principle by comparing the  $Q$  value to  $K$ . For the first reaction we have  $Q = [\text{NO}_2]^2/[\text{N}_2\text{O}_4]$ . Upon compression all concentrations increase by the same factor. However, the numerator will grow faster than the denominator because it is squared. Thus,  $Q$  will increase. We end up with  $Q > K$ , which implies the reaction will want to go in the  $\leftarrow$  direction to form more reactants in order to lower the number of moles to counter the increase in pressure.

**4.5.3. Temperature.** The effect of temperature is most easily understood by writing the heat of the reaction as a reactant or product according to whether the reaction is endothermic or exothermic. The reaction of ammonia synthesis:



is exothermic with  $\Delta H = -92 \text{ kJ/mol}$  at some temperature. This heat is produced, meaning that we can write it on the product side:

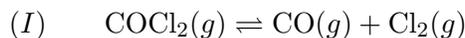


Thus, with the equation written as such we easily see that upon increasing the temperature the reaction will want to shift toward the reactants and

consume heat in the process to counter-act the increase in heat supplied to the reaction (due to the elevated temperature).

#### 4.6. Problems

**Problem 61.** Consider the following reactions:



Write an expression for the equilibrium constant for each reaction.

**Solution.** For reaction I

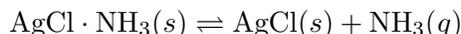
$$K_p = \frac{P_{\text{CO}}P_{\text{Cl}_2}}{P_{\text{COCl}_2}} \quad K = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]}$$

for reaction II

$$K_p = P_{\text{CO}}P_{\text{CO}_2} \quad K = [\text{CO}][\text{CO}_2]$$

■

**Problem 62.** Write an expression for the equilibrium constant for the endothermic reaction



What is the effect on  $P_{\text{NH}_3}$  at equilibrium if additional  $\text{AgCl}(s)$  is added or if additional  $\text{NH}_3$  is pumped into or out of the system, provided that neither of two solids phases shown in the chemical equation are completely used up? What is the effect on the  $P_{\text{NH}_3}$  of lowering the temperature? Why?

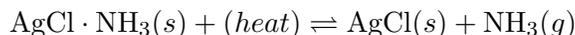
**Solution.**

$$K = [\text{NH}_3(g)] \quad K_p = P_{\text{NH}_3}$$

Addition of  $\text{AgCl}(s)$  has no effect on  $P_{\text{NH}_3}$ .

If  $P_{\text{NH}_3}$  increases, it will react with solid  $\text{AgCl}(s)$  to relieve the stress on the system. The reaction shifts to the left (from equilibrium) to achieve a new equilibrium condition. The opposite will occur if  $P_{\text{NH}_3}$  is decreased.

The reaction is endothermic and can be written as



In this context, lowering the temperature means removing heat. The reaction shifts to the left and  $P_{\text{NH}_3}$  is reduced. ■

**Problem 63.** At  $627^\circ\text{C}$  and 1 atm,  $\text{SO}_3$  is partly dissociated into  $\text{SO}_2$  and  $\text{O}_2$ :  $\text{SO}_3(g) \rightleftharpoons \text{SO}_2(g) + (1/2) \text{O}_2(g)$ . The density of the equilibrium mixture is 0.925 g/liter. What is the degree of dissociation of  $\text{SO}_3$  under these circumstances?

**Solution.** Let  $y$ =equilibrium  $P_{\text{dimer}}$ . Let  $x$ =equilibrium  $P_{\text{monomer}}$ .  $P_{\text{total}} = 0.725$  atm (at equilibrium).

$$P_{\text{total}} = P_{\text{dimer}} + P_{\text{monomer}} \quad (\text{Dalton's law})$$

$$\therefore P_{\text{dimer}} + P_{\text{monomer}} = 0.725 \text{ atm}$$

$$y + x = 0.725 \text{ atm}$$

We also know that:

$$K_p = 3.72 = \frac{P_{\text{dimer}}}{(P_{\text{monomer}})^2}$$

So:

$$3.72 = \frac{(0.725 - x)}{x^2}$$

Use the quadratic equation to solve for  $x$ .  $x = 0.327$ .  $y = 0.398$ .  $P_{\text{monomer}} = 0.327$  atm.  $P_{\text{dimer}} = 0.398$  atm.

If none of the monomer is dimerized the  $P_{\text{monomer}}$  at equilibrium would be

$$0.327 \text{ atm} + (2 \times 0.398 \text{ atm}) = 1.123 \text{ atm}$$

There is actually 0.327 atm of monomer present at equilibrium

$$\frac{0.327 \text{ atm}}{1.123 \text{ atm}} \times 100 = 29.1\%$$

$$\therefore 100\% - 29.1\% = 90.9\% \text{ dimerized}$$

■



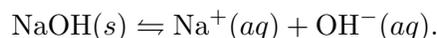
# Acids and Bases

## 5.1. Definitions of Acids: Arrhenius, Lewis, Brønsted-Lowry

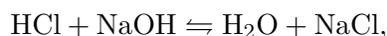
**5.1.1. Arrhenius Acid.** The definition of acid and base, according to Swedish chemist Svante Arrhenius (1859-1927), classifies acids as substances that increase the concentration of  $[\text{H}_3\text{O}^+]$  ions, e.g.



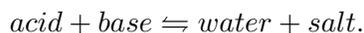
and bases as substances that increase the concentration of  $[\text{OH}^-]$  ions, e.g.



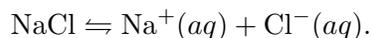
If we combine these two reactions, we get an *acid-base neutralization reaction*



which is seen to be of the form:



This creates an electrolyte solution, since



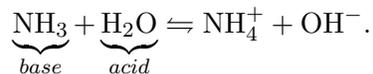
The neutralization reaction involves the combination of hydrogen ions and hydroxide ions to form water:  $\text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l)$ .

This strong acid/base reaction produces a strong electrolyte solution in the sense that its dissociation constant is very large:  $K \gg 1$ , i.e. the equilibrium constant heavily favors the formation of products.

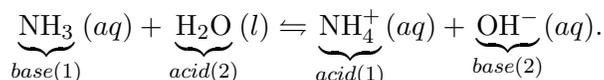
One problem with this Arrhenius definition is it makes only reference to water as the solvent. What if the solvent is different from water? Another problem arises with the weak base ammonia,  $\text{NH}_3$ , because Arrhenius theory suggests that all bases contain  $\text{OH}^-$ . Where is  $\text{OH}^-$  in  $\text{NH}_3$ ? Moreover,

the Arrhenius theory does not account for the behavior of amphiprotic substances.<sup>1</sup>

**5.1.2. Brønsted-Lowry Definition.** A slightly more general definition of an **acid** is a *proton donor* and a **base** is a *proton acceptor*. To describe the behavior of ammonia:



In this reaction,  $\text{H}_2\text{O}$  acts as an *acid*, giving up a proton  $\text{H}^+$ , which is taken up by  $\text{NH}_3$ , the *base*. As a result of this, the ions  $\text{OH}^-$  and  $\text{NH}_4^+$  are formed. The pair  $\text{NH}_3/\text{NH}_4^+$  is called a *conjugate pair*.  $\text{NH}_4^+$  is the conjugate acid of  $\text{NH}_3$ , the conjugate base. Similarly,  $\text{H}_2\text{O}/\text{OH}^-$  is a conjugate pair where  $\text{H}_2\text{O}$  is the acid and  $\text{OH}^-$  is the conjugate base. Pairs (1) and (2) are explicitly identified below:

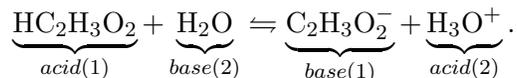


The equilibrium constant for this reaction is:

$$K_b = \frac{[\text{NH}_4^+]_{\text{eq}}[\text{OH}^-]_{\text{eq}}}{[\text{NH}_3]_{\text{eq}}} = 1.8 \times 10^{-5}.$$

Some authors prefer to call  $K_b$  the *ionization constant* rather than the equilibrium constant, where the latter is the ratio  $\frac{[\text{NH}_4^+]_{\text{eq}}[\text{OH}^-]_{\text{eq}}}{[\text{NH}_3]_{\text{eq}}[\text{H}_2\text{O}]_{\text{eq}}}$ . But according to our rules for writing down equilibrium constants  $[\text{H}_2\text{O}]_{\text{eq}}$  does not appear in the expression since it is a pure liquid.  $K_b$  is normally called the *base ionization constant*. See Fig. 5.1.

5.1.2.1. *Example: ionization of acetic acid.*

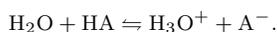


The acetate ion  $\text{C}_2\text{H}_3\text{O}_2^-$  is the conjugate base of the acid  $\text{HC}_2\text{H}_3\text{O}_2$ . Here,  $\text{H}_2\text{O}$  acts as a base. Its conjugate acid is the hydronium ion  $\text{H}_3\text{O}^+$ .

The ionization of acetic acid can be described in the following way:

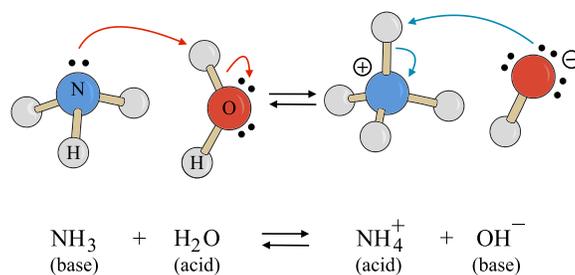
$$K_a = \frac{[\text{C}_2\text{H}_3\text{O}_2^-]_{\text{eq}}[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HC}_2\text{H}_3\text{O}_2]_{\text{eq}}} = 1.8 \times 10^{-5}.$$

<sup>1</sup>An amphiprotic substance is one that can act as an acid or a base. The most common example is water, which acts as a base in the presence of an acid:



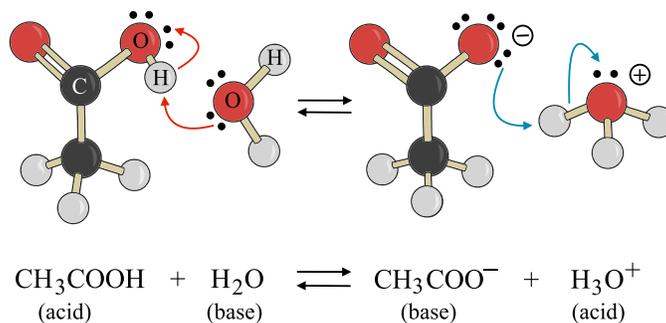
It also acts as an acid in the presence of a base:





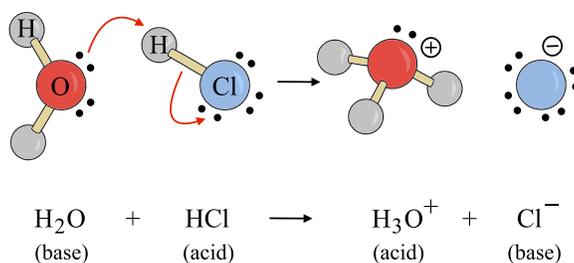
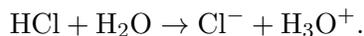
**Figure 5.1.** Both forward and backward “proton transfer” reactions proceed because  $\text{NH}_4^+$  is a stronger acid than  $\text{H}_2\text{O}$  and  $\text{OH}^-$  is a stronger base than  $\text{NH}_3$ .  $\text{NH}_3$  is only slightly ionized.

$K_a$  is called the *acid ionization constant*. See Fig. 5.2.



**Figure 5.2.** Weak acid.

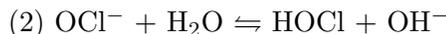
5.1.2.2. *Example: ionization of HCl.* The reaction is shown in Fig. 5.3. Here  $K_a$  is so large (about  $10^6$ ) so the ionization equation is written with a single arrow



**Figure 5.3.** Strong acid.

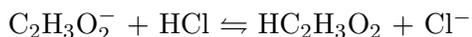
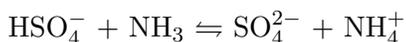
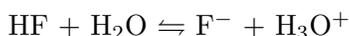
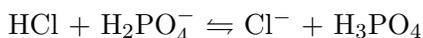
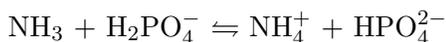
5.1.2.3. *Identifying Brønsted-Lowry acids and bases and their conjugates.* Chlorous acid reacts with water to give chlorine dioxide and hydronium ion: (1)  $\text{HClO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{ClO}_2^- + \text{H}_3\text{O}^+$ .

$\text{HClO}_2$  gives up a proton,  $\text{H}^+$ , to become  $\text{ClO}_2^-$ , therefore,  $\text{HClO}_2$  is an acid and  $\text{ClO}_2^-$  is its conjugate base.  $\text{H}_2\text{O}$  takes the proton from  $\text{HClO}_2$  and becomes  $\text{H}_3\text{O}^+$ . Thus  $\text{H}_2\text{O}$  is a base and  $\text{H}_3\text{O}^+$  is its conjugate acid.



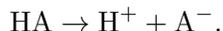
$\text{OCl}^-$  is a base and gains a proton from water.  $\text{OH}^-$  produced in this reaction is the conjugate base of  $\text{H}_2\text{O}$ .

Consider the reactions below; can you identify the conjugate acids and bases?



## 5.2. Acid-Base Titrations

According to the Arrhenius definition of acid and base, an acid is a substance that donates a proton:



whereas a base is a proton acceptor:



$\text{OH}^-$  is a base because it accepts a proton:



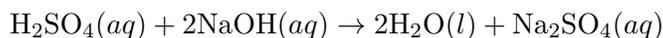
An *acid-base titration* reaction is one where acid is added to base (or vice-versa) to neutralize the original species and form  $\text{H}_2\text{O}$ . An example of an *acid-base titration* is the reaction of *nitric acid* with *ammonium hydroxide*:



In acid-base reactions we are often asked to neutralize an acid using a base or vice-versa. This is done by matching the number of moles.

5.2.0.1. *Example Calculation (Acid-Base Titration)*. Suppose that we are asked to titrate a solution which contains 10 mL of 3.0 M sulfuric acid,  $\text{H}_2\text{SO}_4(\text{aq})$ , using a sodium hydroxide solution of unknown concentration. We find that 20 mL NaOH was required. What is the molarity  $c_{\text{NaOH}}$  of the NaOH solution?

*Solution:* The reaction is:



The units of molarity  $c_{\text{NaOH}}$  are mol/L. The concentration of NaOH was (we need to obtain  $n_{\text{NaOH}}$ ):

$$c_{\text{NaOH}} = \frac{n_{\text{NaOH}}}{20 \text{ mL}}$$

The number of moles of sulfuric acid is:

$$\begin{aligned} n_{\text{H}_2\text{SO}_4} &= c_{\text{H}_2\text{SO}_4} \cdot 10 \text{ mL} \\ &= (3.0 \text{ M})(10 \text{ mL}) = (3.0 \text{ M})(0.010 \text{ L}) = 0.03 \text{ mol.} \end{aligned}$$

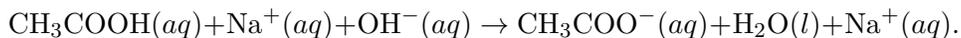
The minimum number of moles needed,  $n_{\text{NaOH}}$ , is (according to the stoichiometry of the equation, we must have 2 moles of NaOH for each mole of sulfuric acid)

$$n_{\text{NaOH}} = 2n_{\text{H}_2\text{SO}_4} = 0.06 \text{ mol.}$$

So the concentration of NaOH is

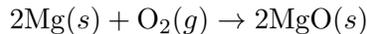
$$c_{\text{NaOH}} = \frac{n_{\text{NaOH}}}{20 \text{ mL}} = \frac{0.06 \text{ mol}}{0.020 \text{ L}} = 3.0 \text{ M.}$$

Another example (Oxtoby [1], Example 11.6, p. 484) is the titration of acetic acid using NaOH:



### 5.3. Redox Reactions

An **oxidized** substance is one that gives up its electrons. Its oxidation number increases, whereas a reduced substance is one which accepts electrons. Example:



where magnesium is oxidized: it gives up two electrons. Its oxidation number increases from 0 (as in elemental Mg) to +2 (in MgO). Oxygen accepts these electrons and its oxidation number decreases from 0 to -2. The transfer of electrons can be emphasized using arrows (Fig. 5.4).

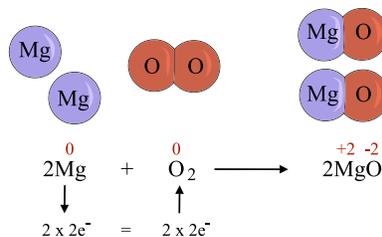
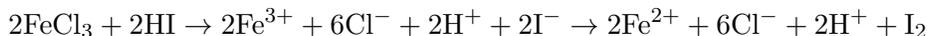


Figure 5.4. Redox reaction.

Another example is the reaction of iron(III) chloride with hydrogen iodide (hydroiodic acid),



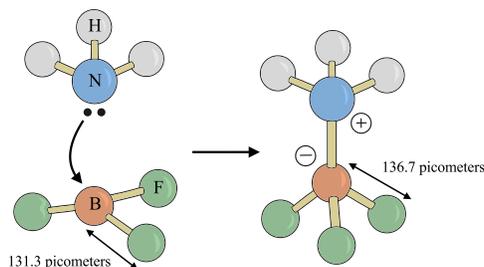
Which involves the following intermediate steps:



where the electron was transferred from I to Fe.

#### 5.4. Lewis Acids & Bases

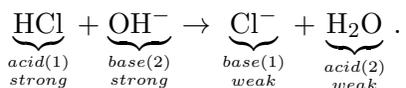
A Lewis acid (Gilbert N. Lewis, 1985-1946) is a chemical species that contains an empty orbital which is capable of accepting an electron pair from a Lewis base to form a Lewis adduct. A Lewis base, then, is any species that has a filled orbital containing an electron pair which is not involved in bonding but may form a dative bond<sup>2</sup> with a Lewis acid to form a Lewis adduct. For example,  $\text{NH}_3$  is a Lewis base, because it can donate its lone pair of electrons. Trimethylborane ( $\text{Me}_3\text{B}$ ) is a Lewis acid as it is capable of accepting a lone pair. In a Lewis adduct, the Lewis acid and base share an electron pair furnished by the Lewis base, forming a dative bond. In the context of a specific chemical reaction between  $\text{NH}_3$  and  $\text{Me}_3\text{B}$ , the lone pair from  $\text{NH}_3$  will form a dative bond with the empty orbital of  $\text{Me}_3\text{B}$  to form an adduct  $\text{NH}_3 \cdot \text{BMe}_3$  (the dot here simply denotes a bond, not an electron). Another example is shown in Fig. 5.5. See also Problem 66.



**Figure 5.5.** Major structural changes accompany binding of the Lewis base to the coordinatively unsaturated, planar Lewis acid  $\text{BF}_3$ .

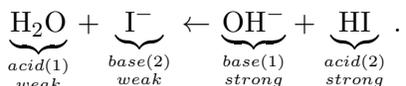
##### 5.4.1. For Acids & Bases, What is the Direction of the Reaction?

*In an acid-base reaction, the favored direction of the reaction is from the stronger to the weaker member of a conjugate acid-base pair.* For example:



<sup>2</sup>A dative bond is also known as a coordinate covalent bond.

Likewise, the following reaction proceeds almost exclusively in reverse:

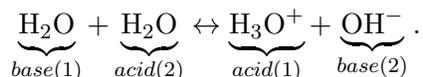


In general, we need to use a table of acid and base strengths, such as the one in Fig. 5.6, which also incidentally shows that *the stronger an acid, the weaker its conjugate base*.

	Acid		Conjugate Base
↑	HClO <sub>4</sub> Perchloric Acid HI Hydroiodic Acid HBr Hydrobromic Acid HCl Hydrochloric Acid H <sub>2</sub> SO <sub>4</sub> Sulfuric Acid HNO <sub>3</sub> Nitric Acid H <sub>3</sub> O <sup>+</sup> Hydronium Ion HSO <sub>4</sub> <sup>-</sup> Hydrogen Sulfate Ion HNO <sub>2</sub> Nitrous Acid CH <sub>3</sub> COOH Acetic Acid H <sub>2</sub> CO <sub>3</sub> Carbonic Acid NH <sub>4</sub> <sup>+</sup> Ammonium Ion HCO <sub>3</sub> <sup>-</sup> Hydrogen Carbonate Ion H <sub>2</sub> O Water CH <sub>3</sub> OH Methanol NH <sub>3</sub> Ammonia	↓	ClO <sub>4</sub> <sup>-</sup> Perchlorate Ion I <sup>-</sup> Iodide Ion Br <sup>-</sup> Bromide Ion Cl <sup>-</sup> Chloride Ion HSO <sub>4</sub> <sup>-</sup> Hydrogen Sulfate Ion NO <sub>3</sub> <sup>-</sup> Nitrate Ion H <sub>2</sub> O Water SO <sub>4</sub> <sup>2-</sup> Sulfate Ion NO <sub>2</sub> <sup>-</sup> Nitrite Ion CH <sub>3</sub> COO <sup>-</sup> Acetate Ion HCO <sub>3</sub> <sup>-</sup> Hydrogen Carbonate Ion NH <sub>3</sub> Ammonia CO <sub>3</sub> <sup>2-</sup> Carbonate Ion OH <sup>-</sup> Hydroxide Ion CH <sub>3</sub> O <sup>-</sup> Methoxide Ion NH <sub>2</sub> <sup>-</sup> Amide Ion

Figure 5.6. Strengths of acids and bases.

**5.4.2. Water and the pH Scale.** Pure water is nonconducting. This is because the concentration of ions is far too low. The reaction of *self-ionization* (auto-ionization, auto-protolytic)



The equilibrium constant for *pure water* is therefore,

$$K_C = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}[\text{OH}^-]_{\text{eq}}}{[\text{H}_2\text{O}]_{\text{eq}}^2} .$$

However, it is customary to absorb the factor  $[\text{H}_2\text{O}]_{\text{eq}}^2$  into the definition of  $K$  and call this the *ionic product* or water-dissociation equilibrium constant,

$$K_w = [\text{H}_3\text{O}^+]_{\text{eq}}[\text{OH}^-]_{\text{eq}} .$$

This is a consequence of our rules for writing down  $K$  (pure liquids are not included in the expression). The numerical value of the ionic product is

$$K_w = 1.0 \times 10^{-14} . \quad (\text{pure water, } 25^\circ\text{C})$$

Thus, the equilibrium is heavily shifted to the left, i.e., there are very few ionized species. The stoichiometry of the equation indicates that  $[\text{H}_3\text{O}^+]_{\text{eq}}$

and  $[\text{OH}^-]_{\text{eq}}$  are equal in pure water. Therefore,

$$[\text{H}_3\text{O}^+]_{\text{eq}} = [\text{OH}^-]_{\text{eq}} = 10^{-7} \text{ M}, \quad (\text{pure water, } 25^\circ\text{C})$$

which is exceedingly low: this means that only about 1 molecule in 200 million is ionized. This concentration is far too low for significant electrical conductivity. The pH of a solution is:

**pH stands for “potential of hydrogen ion” (Sørensen, 1909):**

The pH is defined as the negative logarithm of  $[\text{H}^+]_{\text{eq}}$ :

$$\text{pH} = -\log_{10} [\text{H}^+]_{\text{eq}} = -\log_{10} [\text{H}_3\text{O}^+]_{\text{eq}}.$$

The concentration of hydronium ions is a result of the ionization of water plus any other species present that may contribute or remove  $\text{H}^+$  ions (e.g. acids or bases).

In a solution of 0.0025 M HCl,

$$[\text{H}_3\text{O}^+]_{\text{eq}} = 2.5 \times 10^{-3} \text{ M} \quad \text{and} \quad \text{pH} = -\log_{10}(2.5 \times 10^{-3}) = 2.60.$$

Conversely in a solution with pH=4.50 we have:

$$[\text{H}_3\text{O}^+]_{\text{eq}} = 10^{-4.50} = 3.2 \times 10^{-5} \text{ M}.$$

**pOH:** The pOH is defined as the negative of the logarithm of  $[\text{OH}^-]_{\text{eq}}$ :

$$\text{pOH} = -\log_{10} [\text{OH}^-]_{\text{eq}}.$$

Let us take the negative log of  $K_w = [\text{H}_3\text{O}^+]_{\text{eq}}[\text{OH}^-]_{\text{eq}} = 1.0 \times 10^{-14}$ :

$$\begin{aligned} \text{p}K_w &= -\log_{10} [\text{H}_3\text{O}^+]_{\text{eq}}[\text{OH}^-]_{\text{eq}} = -\log_{10} [\text{H}_3\text{O}^+]_{\text{eq}} - \log_{10} [\text{OH}^-]_{\text{eq}} \\ &= \text{pH} + \text{pOH}. \end{aligned}$$

Thus,

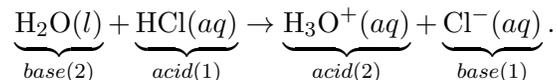
$$\text{p}K_w = \text{pH} + \text{pOH} = 14.00. \quad (25^\circ\text{C})$$

An aqueous solution with  $[\text{H}_3\text{O}^+]_{\text{eq}} = [\text{OH}^-]_{\text{eq}}$  is said to be *neutral*. In pure water at  $25^\circ\text{C}$ ,  $[\text{H}_3\text{O}^+]_{\text{eq}} = [\text{OH}^-]_{\text{eq}} = 1.0 \times 10^{-7} \text{ M}$  and pH=7.00. If the pH is less than 7.00 the solution is *acidic* and if the pH is greater than 7.00 it is *basic* or alkaline.

The following remark reinforces the notion that an equilibrium *constant* is indeed a constant. However, note that it is temperature-dependent.

Because  $K_w$  is an equilibrium constant, the product of the molarities of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions is always equal to  $K_w$ . We cannot increase the molarities of both hydronium and hydroxide ions. We can increase the concentration of  $\text{H}_3\text{O}^+$  ions by adding acid, in which case the concentration of  $\text{OH}^-$  ions must decrease to preserve the value of  $K_w$ . Alternatively, we can increase the concentration of  $\text{OH}^-$  ions by adding base, but then the concentration of  $\text{H}_3\text{O}^+$  ions must decrease. The auto-protolysis equilibrium links the molarities of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions so that when one goes up, the other goes down.

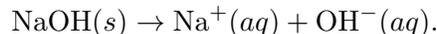
**5.4.3. Strong Acid (Strong Base).** A strong acid is one for which the dissociation constant is very large (i.e.  $K \gg 1$ ). At equilibrium it is completely dissociated (deprotonated). Similarly for a base, a strong base is one which is entirely protonated at equilibrium. Let's look at an example:



In this case, the pH of this solution will be determined solely by the amount of acid dissolved. This applies to any strong acid. In other words, a 0.10 M solution of any strong acid that donates one proton per molecule is simply 0.10 M =  $10^{-1}$  M, whose pH equals 1. The pOH is found from the equation for  $K_w$ :

$$[\text{OH}^-]_{\text{eq}} = \frac{K_w}{[\text{H}_3\text{O}^+]_{\text{eq}}} = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13} \text{ M},$$

which gives pOH=13. Likewise a strong base means we get complete dissociation to yield  $\text{OH}^-$  ions:



If we have a 0.10 M NaOH solution, we have

$$[\text{OH}^-]_{\text{eq}} = 0.10 \text{ M} \quad [\text{H}_3\text{O}^+]_{\text{eq}} = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13} \text{ M}.$$

**Remark:** We have neglected the autoionization of water in both cases on the basis that the contribution of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  from this process is very small ( $\sim 10^{-7}$  M). When very small amounts of a strong acid or base is added to pure water (for example,  $\sim 10^{-7}$  M), we have to include the autoionization of water to describe the concentration of hydronium and hydroxide ions accurately.

## 5.5. The pH Scale

In experiments the concentrations of hydronium ions can range from 10 M to  $10^{-15}$  M and even smaller. Thus, the range of concentrations extends over an enormous range. This is why we define the pH scale: the scale is compressed to a much smaller range as a result of taking the logarithm. The logarithm is indicative of the exponent of the concentration.

**Can we have negative pH values?:** It is certainly possible to have a negative pH value. For example, if the concentration of hydronium ions is  $10\text{ M} = 10^1\text{ M}$ , this corresponds to the negative value  $\text{pH} = -1$ .

**5.5.1. Example: Calculating pH.** What is the pH of (a) human blood, in which the molarity of  $\text{H}_3\text{O}^+$  ions is  $4.0 \times 10^{-8}$  mol/L; (b) 0.020 M  $\text{HCl}(aq)$ ; (c) 0.040 M  $\text{KOH}(aq)$ ?

*Strategy:* Apply the definition of pH. For strong acids, the molarity of  $\text{H}_3\text{O}^+$  is equal to the molarity of the acid. For strong bases we must first find the molarity of  $\text{OH}^-$  then convert to molarity of  $\text{H}_3\text{O}^+$  using the equation for  $K_w$ .

*Solution:* (a) For a solution in which the molarity of  $\text{H}_3\text{O}^+$  ions is  $4.0 \times 10^{-8}$  mol/L, we write  $[\text{H}_3\text{O}^+]_{\text{eq}} = 4.0 \times 10^{-8}$  and obtain

$$\text{pH} = -\log_{10}(4.0 \times 10^{-8}) = 7.40$$

(b) Because  $\text{HCl}$  is a strong acid, the molarity of  $\text{H}_3\text{O}^+$  is 0.020 mol/L. Hence,

$$\text{pH} = -\log_{10} 0.020 = 1.70$$

(c) Each formula unit of  $\text{KOH}$  (a strong base) provides one  $\text{OH}^-$  ion; therefore the molarity of  $\text{OH}^-$  is 0.040 mol/L and

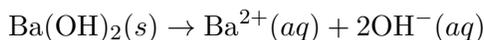
$$[\text{H}_3\text{O}^+]_{\text{eq}} = \frac{K_w}{[\text{OH}^-]_{\text{eq}}} = \frac{1.0 \times 10^{-14}}{0.040} = 2.5 \times 10^{-13}$$

Hence  $\text{pH} = -\log_{10}(2.5 \times 10^{-13}) = 12.60$ .

**5.5.2. Example Problem: Strong Base.** What are the molarities of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  in a 0.0030 M  $\text{Ba}(\text{OH})_2$  solution at  $25^\circ\text{C}$ ? [ $\text{Ba}(\text{OH})_2$  is a hydroxide of an alkaline earth metal and is therefore a strong base.]

*Strategy:* Strong bases are almost entirely present as  $\text{OH}^-$  in water. How many  $\text{OH}^-$  ions per formula unit? Calculate the molarity of these ions in solution. Find molarity of  $\text{H}_3\text{O}^+$  ions using the equation for  $K_w$ .

*Solution:* The equation

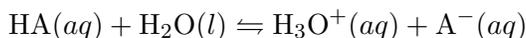


tells us that each  $\text{Ba}(\text{OH})_2$  gives  $2\text{OH}^-$ . Because the molarity of  $\text{Ba}(\text{OH})_2(aq)$  is 0.0030 mol/L, it follows that the molarity of  $\text{OH}^-$  is twice that value, or 0.0060 mol/L. Then, for the molarity of  $\text{H}_3\text{O}^+$  ions, we write

$$[\text{H}_3\text{O}^+]_{\text{eq}} = \frac{K_w}{[\text{OH}^-]_{\text{eq}}} = \frac{1.0 \times 10^{-14}}{0.0060} = 1.7 \times 10^{-12}$$

That is, the molarity of  $\text{H}_3\text{O}^+$  ions in the solution is only  $1.7 \times 10^{-12}$  mol/L.

**5.5.3.  $\text{p}K_a$  and  $\text{p}K_b$ .** According to the Brønsted-Lowry theory of an acid (HA), its ionization in aqueous solution is written as



where  $\text{A}^-$  is the conjugate base of HA. The equilibrium expression for this chemical reaction is

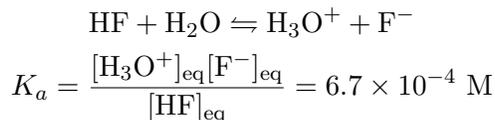
$$K_a = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}[\text{A}^-]_{\text{eq}}}{[\text{HA}]_{\text{eq}}}$$

where  $K_a$  is the **acid ionization constant**. The negative of its log is the  $\text{p}K_a$  value of this acid:

$$\text{p}K_a = -\log_{10} K_a.$$

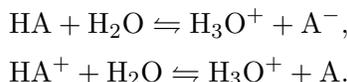
This is a quantitative measure of the strength of the acid in a particular solvent (here, water). Weak acids do not react completely and the concentrations of product are low at equilibrium and so  $K_a$  is small. By contrast, a strong acid reacts nearly completely and  $K_a$  is large ( $K_a \gg 1$ ).

A specific example is:

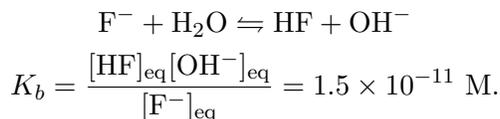


where HF is a *weak acid* and  $\text{F}^-$  is a *weak base*.

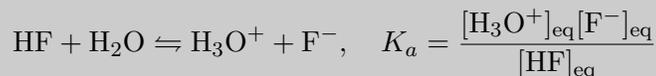
In general, the concept of  $\text{p}K_a$  applies to two types of reactions:



There is a similar concept for bases. For example, consider the reaction involving the weak base  $\text{F}^-$ :



**Relationship between  $K_a$  and  $K_b$ :** For the two reactions describing the equilibria in water of each conjugate acid-base pair considered above:



and



We have the product:

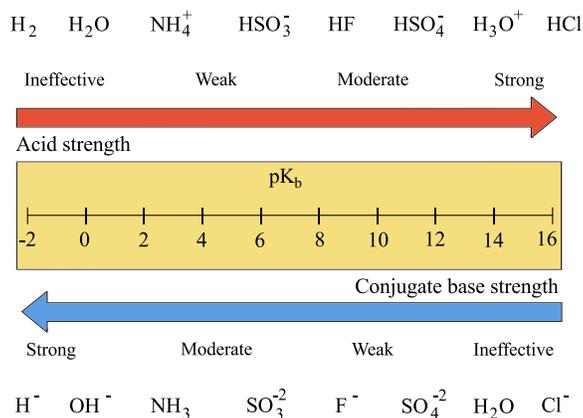
$$K_a \cdot K_b = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}[\text{F}^-]_{\text{eq}}}{[\text{HF}]_{\text{eq}}} \cdot \frac{[\text{HF}]_{\text{eq}}[\text{OH}^-]_{\text{eq}}}{[\text{F}^-]_{\text{eq}}} = [\text{H}_3\text{O}^+]_{\text{eq}}[\text{OH}^-]_{\text{eq}} = K_w.$$

This relationship  $K_w = K_a \cdot K_b$  is general and indicates an inverse relationship between the strength of a base and its conjugate acid. Taking the logs of both sides of the equation we get:

$$\text{p}K_w = \text{p}K_a + \text{p}K_b.$$

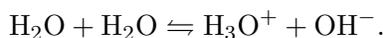
Note: this relationship only applies to conjugate pairs, such as HF and  $\text{F}^-$ . It does not relate  $\text{p}K_a$  and  $\text{p}K_b$  of, for example, HI and  $\text{F}^-$ , respectively, since they are not a conjugate pair.

This trend is illustrated in Fig. 5.7.



**Figure 5.7.** Acid strength vs conjugate base strength.  $\text{p}K_a$  is obtained from  $\text{p}K_b$  from the relationship  $\text{p}K_w = \text{p}K_a + \text{p}K_b$ .

We see from Fig. 5.7 that when  $\text{H}_2\text{O}$  is viewed as the acid,  $\text{p}K_a$  is 14. What is the significance of this?  $\text{p}K_a$  of 14 implies that  $K_a = 10^{-14}$ . This value of  $K_a$  is the equilibrium constant for the auto-ionization reaction of water:



Here,

$$K_a = [\text{H}_3\text{O}^+]_{\text{eq}}[\text{OH}^-]_{\text{eq}} = 10^{-14}.$$

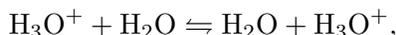
This value indicates that  $\text{H}_2\text{O}$  has a poor tendency to ionize. Why? Because  $\text{H}_2\text{O}$  is a very stable molecule and in order to ionize it, we would need to break an O-H bond. The O-H bond dissociation energy in water is approximately 5.15 eV per bond, which is considered very strong. In order to break this bond, the ion-dipole interaction between  $\text{H}^+$  and another  $\text{H}_2\text{O}$  molecule would need to be comparable or stronger. In Example 2.5 (see p. 73), we calculated this interaction energy for sodium and water; we can do a similar calculation here. The distance between nearest-neighbor water molecules in liquid water (1.85 D) is approximately 2.8 Å. At time  $t = 0$ , this gives the interaction energy between the ion-dipole that could potentially compete against the O-H bond energy. This ion-dipole interaction energy is:

$$(9 \times 10^9 \frac{\text{N}\cdot\text{m}^2}{\text{C}^2}) \frac{(1.6 \times 10^{-19} \text{ C})(1.85 \times 3.336 \times 10^{-30} \text{ C}\cdot\text{m})}{(2.8 \times 10^{-10} \text{ m})^2} = 8.9 \times 10^{-19} \text{ J},$$

and since  $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ , this energy is  $\sim 0.7 \text{ eV}$ , which is much weaker than the O-H bond dissociation energy (5.15 eV). Thus, this energy is highly unlikely to break the O-H bond of water and lead to ionization. This is why the equilibrium favors reactants, i.e. water is an ineffective acid.

From the relationship  $\text{p}K_w = \text{p}K_a + \text{p}K_b$ , we find that  $\text{p}K_b = 0$ . The  $\text{p}K_a$  should not be confused with the pH. The pH is  $-\log_{10}[\text{H}_3\text{O}^+]$ . For pure water at 25°C the pH is 7; however, hydronium ion concentration can be altered if other proton donors or acceptors are also present in solution. It is best to think of  $\text{p}K_a$  as a property of a given acid (proton donor in a given solvent), whereas pH is a property of the solution (accounting for all species present). For example, the  $\text{p}K_a$  of HF in water at 25°C will always equal 3.18. However, the pH of the solution depends on the amount of HF in solution (and any other combination of acids and/or bases that may be present).

Let us now look at the acid  $\text{H}_3\text{O}^+$ . The  $\text{p}K_a$  of  $\text{H}_3\text{O}^+$  is 0. What is the significance of  $\text{p}K_a=0$ ? In the reaction:

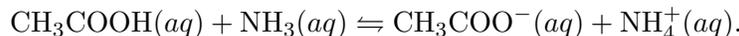


we have (by definition),

$$K_a = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}[\text{H}_2\text{O}]_{\text{eq}}}{[\text{H}_3\text{O}^+]_{\text{eq}}[\text{H}_2\text{O}]_{\text{eq}}} \equiv 1,$$

which implies that  $\text{p}K_a=0$  (strong acid). In other words, a proton is donated from one hydronium ion to a neighboring water molecule. But this is the same as proton transfer in the reverse direction. We therefore suspect that the energy cost of swapping the proton from one  $\text{H}_2\text{O}$  to the next is minimal, hence the reason why  $\text{H}_3\text{O}^+$  is a strong acid. Can you quantitatively explain this behavior in terms of interaction energies?

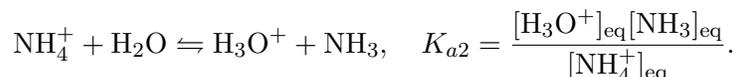
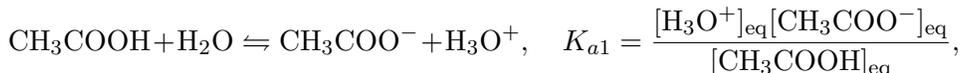
**5.5.4. Example.** Suppose we have a reaction:



Its equilibrium constant is

$$K = \frac{[\text{CH}_3\text{COO}^-]_{\text{eq}}[\text{NH}_4^+]_{\text{eq}}}{[\text{CH}_3\text{COOH}]_{\text{eq}}[\text{NH}_3]_{\text{eq}}}.$$

This reaction is the difference between two acid ionization reactions:



The equilibrium constant for the net reaction is the ratio of the equilibrium constants for the separate reactions:

$$K = \frac{K_{a1}}{K_{a2}}.$$

This method can be used to predict the outcome of the net reaction, provided it can be decomposed as the difference between two elementary reactions. Equilibrium constants for elementary acid ionization reactions can be found in Table 5.1. Looking up values from the Table for  $\text{CH}_3\text{COOH}$  and  $\text{NH}_4^+$ , we find:

$$K = \frac{1.76 \times 10^{-5}}{5.6 \times 10^{-10}} \approx 31,428.$$

**Table 5.1.** Ionization constants of acids at 25°C. For a given conjugate pair,  $\text{p}K_b$  is obtained from  $\text{p}K_a$  from the relationship  $\text{p}K_w = \text{p}K_a + \text{p}K_b$ .

Acid	HA (acid)	A <sup>-</sup> (conjugate base)	K <sub>a</sub>	pK <sub>a</sub>
Hydroiodic	HI	I <sup>-</sup>	~ 10 <sup>11</sup>	~ -11
Hydrobromic	HBr	Br <sup>-</sup>	~ 10 <sup>9</sup>	~ -9
Perchloric	HClO <sub>4</sub>	ClO <sub>4</sub> <sup>-</sup>	~ 10 <sup>7</sup>	~ -7
Hydrochloric	HCl	Cl <sup>-</sup>	~ 10 <sup>7</sup>	~ -7
Chloric	HClO <sub>3</sub>	ClO <sub>3</sub> <sup>-</sup>	~ 10 <sup>3</sup>	~ -3
Sulfuric (first ionization)	H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	~ 10 <sup>2</sup>	~ -2
Nitric	HNO <sub>3</sub>	NO <sub>3</sub> <sup>-</sup>	~ 20	~ -1.3
Hydronium ion	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O	1	0.0
Iodic	HIO <sub>3</sub>	IO <sub>3</sub> <sup>-</sup>	1.6 × 10 <sup>-1</sup>	0.80
Oxalic (first ionization)	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	HC <sub>2</sub> O <sub>4</sub> <sup>-</sup>	5.9 × 10 <sup>-2</sup>	1.23
Sulfurous (first ionization)	H <sub>2</sub> SO <sub>3</sub>	HSO <sub>3</sub> <sup>-</sup>	1.54 × 10 <sup>-2</sup>	1.81
Sulfuric (second ionization)	HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	1.2 × 10 <sup>-2</sup>	1.92
Chlorous	HClO <sub>2</sub>	ClO <sub>2</sub> <sup>-</sup>	1.1 × 10 <sup>-2</sup>	1.96
Phosphoric (first ionization)	H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	7.52 × 10 <sup>-3</sup>	2.12
Arsenic (first ionization)	H <sub>3</sub> AsO <sub>4</sub>	H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup>	5.0 × 10 <sup>-3</sup>	2.30
Chloroacetic	CH <sub>2</sub> ClCOOH	CH <sub>2</sub> ClCOO <sup>-</sup>	1.4 × 10 <sup>-3</sup>	2.85
Hydrofluoric	HF	F <sup>-</sup>	6.6 × 10 <sup>-4</sup>	3.18
Nitrous	HNO <sub>2</sub>	NO <sub>2</sub> <sup>-</sup>	4.6 × 10 <sup>-4</sup>	3.34
Formic	HCOOH	HCOO <sup>-</sup>	1.77 × 10 <sup>-4</sup>	3.75
Benzoic	C <sub>6</sub> H <sub>5</sub> COOH	C <sub>6</sub> H <sub>5</sub> COO <sup>-</sup>	6.46 × 10 <sup>-5</sup>	4.19
Oxalic (second ionization)	HC <sub>2</sub> O <sub>4</sub> <sup>-</sup>	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	6.4 × 10 <sup>-5</sup>	4.19
Hydrazoic	HN <sub>3</sub>	N <sub>3</sub> <sup>-</sup>	1.9 × 10 <sup>-5</sup>	4.72
Acetic	CH <sub>3</sub> COOH	CH <sub>3</sub> COO <sup>-</sup>	1.76 × 10 <sup>-5</sup>	4.75

Propionic	CH <sub>3</sub> CH <sub>2</sub> COOH	CH <sub>3</sub> CH <sub>2</sub> COO <sup>-</sup>	1.34 × 10 <sup>-5</sup>	4.87
Pyridinium ion	HC <sub>5</sub> H <sub>5</sub> N <sup>+</sup>	C <sub>5</sub> H <sub>5</sub> N	5.6 × 10 <sup>-6</sup>	5.25
Carbonic (first ionization)	H <sub>2</sub> CO <sub>3</sub>	HCO <sub>3</sub> <sup>-</sup>	4.3 × 10 <sup>-7</sup>	6.37
Sulfurous (second ionization)	HSO <sub>3</sub> <sup>-</sup>	SO <sub>3</sub> <sup>2-</sup>	1.02 × 10 <sup>-7</sup>	6.91
Arsenic (second ionization)	H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup>	HAsO <sub>4</sub> <sup>2-</sup>	9.3 × 10 <sup>-8</sup>	7.03
Hydrosulfuric	H <sub>2</sub> S	HS <sup>-</sup>	9.1 × 10 <sup>-8</sup>	7.04
Phosphoric (second ionization)	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	HPO <sub>4</sub> <sup>2-</sup>	6.23 × 10 <sup>-8</sup>	7.21
Hypochlorous	HClO	ClO <sup>-</sup>	3.0 × 10 <sup>-8</sup>	7.53
Hydrocyanic	HCN	CN <sup>-</sup>	6.17 × 10 <sup>-10</sup>	9.21
Ammonium ion	NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>	5.6 × 10 <sup>-10</sup>	9.25
Carbonic (second ionization)	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	4.8 × 10 <sup>-11</sup>	10.32
Arsenic (third ionization)	HAsO <sub>4</sub> <sup>2-</sup>	AsO <sub>4</sub> <sup>3-</sup>	3.0 × 10 <sup>-12</sup>	11.53
Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	HO <sub>2</sub> <sup>-</sup>	2.4 × 10 <sup>-12</sup>	11.62
Phosphoric (third ionization)	HPO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	2.2 × 10 <sup>-13</sup>	12.67
Water	H <sub>2</sub> O	OH <sup>-</sup>	1.0 × 10 <sup>-14</sup>	14.00

**5.5.5. The Meaning of  $K_a$  and Strength of the Acid.** Let us clarify the meaning of  $K_a$ .  $K_a$  is a property of an acid. Its numerical value depends on the type of acid and solvent. It quantifies the tendency (affinity) of an acid to give up a proton. Strong acids have large  $K_a$  values whereas weak acids have small  $K_a$  values. The precise value of  $K_a$  reflects the strength of intermolecular interactions binding the proton to its acid relative to the ability (strength of interaction) of the solvent molecules to pull this proton away from the acid. For ionization to occur, the solvent must be able to overcome the bond dissociation energy that's keeping this proton bound to its acid. In the dilute limit, the  $K_a$  *does not* depend on acid concentration, and *does not* significantly depend on other species dissolved in that solution. For a given solvent, and keeping the concentration of an acid fixed (say, 1 M), the pH of the solution depends on  $K_a$ . For example, the pH of a 1 M HCl aqueous solution at 25°C will be 0. According to Table 5.1, the  $pK_a$  of HCl is -7. The  $pK_a$  and pH are different: the pH will change if [HCl] changes (the more acid we add, the lower the pH), but the  $pK_a$  itself will not change.

In contrast, a 1 M solution of CH<sub>3</sub>COOH ( $pK_a=4.75$ ) has a pH which is determined from the equilibrium:

$$K_a = 1.76 \times 10^{-5} = [\text{CH}_3\text{COO}^-]_{\text{eq}}[\text{H}^+]_{\text{eq}}/[\text{CH}_3\text{COOH}]_{\text{eq}},$$

where the concentrations are equilibrium concentrations. If we start at time  $t = 0$  with 1 M of CH<sub>3</sub>COOH. At equilibrium,  $x$  amount of CH<sub>3</sub>COOH will dissociate. At the same time  $x$  amount of CH<sub>3</sub>COO<sup>-</sup> and H<sup>+</sup> will be produced. Thus,  $1.76 \times 10^{-5} = x^2/(1 - x) \approx x^2$  since  $x \ll 1$ . This leads to  $x = \sqrt{1.76 \times 10^{-5}} \approx 0.0042$  M. The pH is therefore,

$$-\log_{10}(\sqrt{1.76 \times 10^{-5}}) \approx 2.5.$$

Here, we had the acid concentration fixed (1 M). But the two acids (HCl vs CH<sub>3</sub>COOH) had a different  $pK_a$ . The acid with the lowest  $pK_a$  (HCl at -7)

had the lowest pH (0). The acid with the highest  $pK_a$  ( $\text{CH}_3\text{COOH}$  at 4.75) had the highest pH (2.4).

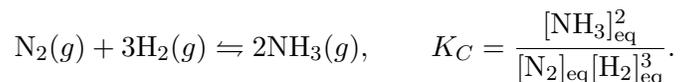
## 5.6. “ICE” Tables

In subsequent sections, we will use the concept of an “ICE table”. The ICE table is a convenient way to organize your equilibrium calculations. They are used in cases where initial and final conditions are to be related to one another. ICE stands for (I)initial, (C)hange and (E)quilibrium. First, we have the initial (I) conditions of a reaction. Then, these reactants react to form products. This “change” (C) leads to a new equilibrium (E). So I, C and E form the rows of an ICE table. The columns are the reactants and products of a reaction. The entries of the table are the amounts (moles) or concentrations (molar or molal), of reactants and products at a given time (initial or final conditions). We sometimes don’t know the “extent” of the reaction; however, it can be inferred algebraically by analyzing the ICE table and relating initial and final conditions using known equilibrium constants. ICE tables are frequently used in problems of acid-base titration.

**5.6.1. Example 1.** Suppose that we start with a mixture of 0.500 mol/L of  $\text{N}_2$  and 0.800 mol/L  $\text{H}_2$  and allow it to reach equilibrium with the product, ammonia. It is found that, at equilibrium at a certain temperature, the molar concentration of  $\text{NH}_3$  is 0.150 mol/L. Calculate the equilibrium constant for the reaction at that temperature.

*Strategy:* Write down an equation for the equilibrium constant. Identify the change in concentration of one substance, use reaction stoichiometry to calculate the implied changes in the other substances. Solve for new concentrations and plug into equation for  $K_C$ .

The reaction is



where  $K_C$  has units of  $1/(\text{concentration})^2$ , due to the particular stoichiometry of this reaction (2 mol on products side, 4 mol on reactants side).

The reaction implies that 1 mol  $\text{N}_2 = 2$  mol  $\text{NH}_3$  and 3 mol  $\text{H}_2 = 2$  mol  $\text{NH}_3$ . Therefore, because the molar concentration of  $\text{NH}_3$  increases by 0.150 mol/L to reach equilibrium, the concentration of  $\text{N}_2$  decreases by half that much, 0.075 mol/L, and the concentration of  $\text{H}_2$  by 1.5 times, 0.225 mol/L. We have:

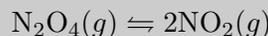
	N <sub>2</sub>	H <sub>2</sub>	NH <sub>3</sub>
1. Initial molar concentration	0.500	0.800	0
2. Change in molar concentration	-0.075	-0.225	+0.150
3. Equilibrium molar concentration	0.425	0.575	0.150

It follows that:

$$K_C = \frac{[\text{NH}_3]_{\text{eq}}^2}{[\text{N}_2]_{\text{eq}}[\text{H}_2]_{\text{eq}}^3} = \frac{(0.150)^2}{0.425 \times (0.575)^3} = 0.278$$

where the units are L<sup>2</sup>/mol<sup>2</sup>. If you are given the value of an equilibrium constant with no units, it will either have no units (due to normalization to 1 atm or 1 mol/L) or its units will be in terms of the concentration (or pressure) units given in the problem.

**Exercise:** A sample of gaseous N<sub>2</sub>O<sub>4</sub> with an initial partial pressure of 3.0 atm is prepared at a certain temperature and allowed to react as follows:

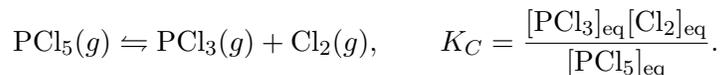


Once equilibrium is reached, it is found that the partial pressure of N<sub>2</sub>O<sub>4</sub> has dropped to 1.0 atm. Find the equilibrium partial pressure of NO<sub>2</sub>, then calculate  $K_P$  [Answer:  $P_{\text{NO}_2} = 4.0$  atm and  $K_P = 16$ .]

**5.6.2. Example 2.** Suppose that 1.50 mol PCl<sub>5</sub> (phosphorous pentachloride) is placed in a reaction vessel of volume 500 mL and allowed to reach equilibrium with its decomposition products phosphorous trichloride and chlorine at 250°C, when  $K_C = 1.80$ . What is the composition of the equilibrium mixture? All three substances are gases at 250°C.

*Strategy:* Write chemical equation and expression for equilibrium constant. Denote by  $x$  the change in molar concentration of the decomposing substance. Use reaction stoichiometry to express the molar concentrations of the decomposition products in terms of  $x$ . Calculate the molar concentrations by dividing the number of moles of each substance by the volume of the container.

The chemical equation is



The initial molar concentration of PCl<sub>5</sub> is

$$\text{Molar concentration of PCl}_5 = \frac{1.50}{0.500} = 3.00,$$

and we suppose that the change in its molar concentration is  $-x$  mol/L. Using the chemical equation above, we see that (with all concentrations in mol/L):

	PCl <sub>5</sub>	PCl <sub>3</sub>	Cl <sub>2</sub>
1. Initial molar concentration	3.00	0	0
2. Change in molar concentration	- $x$	+ $x$	+ $x$
3. Equilibrium molar concentration	3.00- $x$	$x$	$x$

Step 3: these values are the sums of the initial concentrations, step 1, and the changes in concentration brought about by reaction, step 2.

Step 2: the stoichiometry of the reaction implies that if the molar concentration of PCl<sub>5</sub> decreases by  $x$ , then the molar concentrations of PCl<sub>3</sub> and Cl<sub>2</sub> both increase by  $x$ .

Step 4: Substitution of these equilibrium values into the expression for the equilibrium constant gives:

$$K_C = \frac{[\text{PCl}_3]_{\text{eq}}[\text{Cl}_2]_{\text{eq}}}{[\text{PCl}_5]_{\text{eq}}} = \frac{x \times x}{3.00 - x},$$

and because we are told that  $K_C=1.80$ , the equation we have to solve is

$$1.80 = \frac{x^2}{3.00 - x}.$$

This expression rearranges to the quadratic equation:

$$x^2 + 1.80x - 5.40 = 0.$$

The solutions of this equation are:

$$x = \frac{-1.80 \pm \sqrt{(1.80)^2 - 4(1)(-5.40)}}{2} = 1.59 \text{ and } -3.39.$$

Because the concentrations must be positive and because (from step 3)  $x$  is the molar concentration of each of the products, we select 1.59 as the solution. It follows that at equilibrium

$$[\text{PCl}_5]_{\text{eq}} = 3.00 - x = 3.00 - 1.59 = 1.41,$$

$$[\text{PCl}_3]_{\text{eq}} = x = 1.59,$$

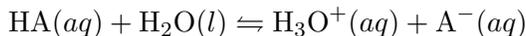
$$[\text{Cl}_2]_{\text{eq}} = x = 1.59,$$

that is, the equilibrium concentrations of PCl<sub>5</sub>, PCl<sub>3</sub> and Cl<sub>2</sub> are 1.41 mol/L, 1.59 mol/L and 1.59 mol/L, respectively.

**Exercise:** Bromine monochloride, BrCl, decomposes into bromine and chlorine and reaches the equilibrium  $2\text{BrCl}(g) \rightleftharpoons \text{Br}_2(g) + \text{Cl}_2(g)$ , for which  $K_C = 32$  at 500 K. If initially pure BrCl is present at a concentration of  $3.30 \times 10^{-3}$  mol/L, what is its molar concentration in the mixture at equilibrium? [Answer:  $3 \times 10^{-4}$  mol/L.]

## 5.7. Weak Acids and Bases

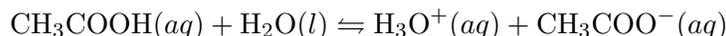
**5.7.1. Weak Acids.** A weak acid has a  $K_a$  smaller than 1. We write the reactions as bidirectional reactions:



Example (Oxtoby [1], Example 15.6):

*Question:* Acetic acid ( $\text{CH}_3\text{COOH}$ ) has  $K_a$  of  $1.76 \times 10^{-5}$  at  $25^\circ\text{C}$ . Suppose 1.000 mol is dissolved in enough water to give 1.000 L of solution. Calculate the pH and the fraction of acetic acid ionized at equilibrium.

*Solution:* The initial concentration is 1.000 M. Let's denote our "progress variable" as  $y$ . i.e.  $y$  can be taken to be the amount of acetic acid that ionizes. Then our "ICE table" looks like this:



	$[\text{CH}_3\text{COOH}]$	$[\text{H}_3\text{O}^+]$	$[\text{CH}_3\text{COO}^-]$
1. Initial concentration (M)	1.000	$\approx 0$	0
2. Change in molar concentration	$-y$	$+y$	$+y$
3. Equilibrium molar concentration	$1 - y$	$y$	$y$

Writing down the equation for the equilibrium constant:

$$K_a = 1.76 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}[\text{CH}_3\text{COO}^-]_{\text{eq}}}{[\text{CH}_3\text{COOH}]_{\text{eq}}} = \frac{y^2}{1 - y}$$

We can solve the quadratic equation or proceed by approximating  $1 - y \approx 1$  because we know  $y$  should be small (acetic acid is a weak acid, so only a small fraction should ionize at equilibrium).

$$1.76 \times 10^{-5} = \frac{y^2}{1 - y} \approx \frac{y^2}{1} \quad y = \sqrt{1.76 \times 10^{-5}} = 4.20 \times 10^{-3} \text{ M},$$

which is large compared to self-ionization of water ( $10^{-7}$  M). The pH is  $-\log_{10}(4.2 \times 10^{-3}) = 2.38$  and fraction ionized is  $y/1.000 = y = 4.2 \times 10^{-3}$ .

**Without approximation:** Suppose in the previous problem that instead of dissolving 1.000 mol we dissolve 0.001 mol. Then, we can no longer make this approximation in the denominator. Our equation is:

$$\frac{y^2}{0.001 - y} = 1.76 \times 10^{-5}$$

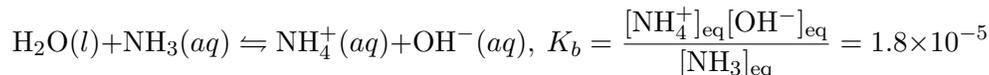
Because  $y$  is not small compared to 0.001 we should instead solve the quadratic equation:

$$y^2 + (1.76 \times 10^{-5})y - (1.76 \times 10^{-8}) = 0,$$

$$y = 1.24 \times 10^{-4} \text{ M} = [\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-],$$

which leads to  $\text{pH} = -\log_{10}(1.24 \times 10^{-4}) = 3.91$  and the percentage of acid that is ionized is  $(100\%) \times 1.24 \times 10^{-4} / 0.001 \text{ M} = 12.4\%$ .

**5.7.2. Weak Bases.** A weak base is only partially protonated in water and its  $K_b$  is less than 1:



Example (Oxtoby [1], Example 15.8):

*Question:* Calculate the pH of a solution made by dissolving 0.0100 mol of  $\text{NH}_3$  in enough water to give 1.000 L of solution at  $25^\circ\text{C}$ . The  $K_b$  for ammonia is  $1.8 \times 10^{-5}$ .

*Solution:* Setup an ICE table:

	$\text{H}_2\text{O}(l) + \text{NH}_3(aq)$	$\rightleftharpoons \text{NH}_4^+(aq)$	$+ \text{OH}^-(aq)$
1. Initial (M)	0.0100	$\approx 0$	0
2. Change	$-y$	$+y$	$+y$
3. Equilibrium	$0.0100 - y$	$y$	$y$

We get a quadratic equation, which we can solve to get:

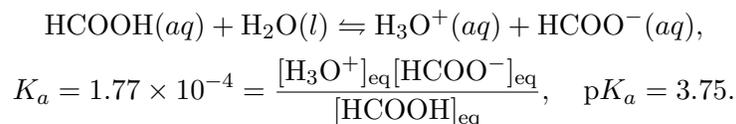
$$K_b = 1.8 \times 10^{-5} = \frac{y^2}{0.0100 - y}, \quad y = 4.15 \times 10^{-4} \text{ M} = [\text{OH}^-]_{\text{eq}}$$

$$[\text{H}_3\text{O}^+]_{\text{eq}} = \frac{K_w}{[\text{OH}^-]_{\text{eq}}} = \frac{1.0 \times 10^{-14}}{4.15 \times 10^{-4}} = 2.4 \times 10^{-11},$$

$$\text{pH} = -\log_{10}(2.4 \times 10^{-11}) = 10.64$$

## 5.8. Buffer Solutions

The goal of a buffer solution is to *maintain the pH approximately constant* with respect to small fluctuations of acids or bases. Biological systems require maintaining the pH within very narrow ranges.<sup>3</sup> A buffer is made from a weak acid or base. Consider a weak acid, formic acid (HCOOH), and its conjugate base, formate ion (HCOO<sup>-</sup>). Equilibrium is established:



The formate ion can also be obtained by dissolving a salt such as sodium formate (NaHCOO). To form a buffer, we also add salt for purposes of stabilizing the pH. This is the method used to create a buffer.

**5.8.1. Calculating the pH of a Buffer Solution.** Example (Oxtoby [1], Example 15.8):

*Question:* Suppose 1.00 mol of HCOOH and 0.500 mol of NaHCOO are added to water and diluted to 1.00 L. Calculate the pH of the solution.

*Solution:* As usual, we setup the ICE table:

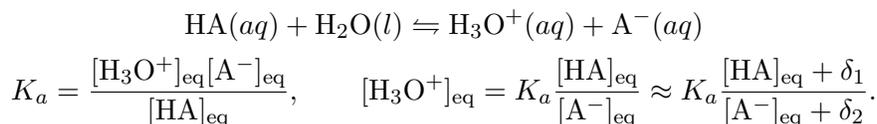
	HCOOH(aq) + H <sub>2</sub> O(l) ⇌	H <sub>3</sub> O <sup>+</sup> (aq)	+HCOO <sup>-</sup> (aq)
1. Initial (M)	1.00	≈0	0.500
2. Change	-y	+y	+y
3. Equilibrium	1.00-y	y	0.500+y

$$\frac{y(0.500 + y)}{1.00 - y} = K_a = 1.77 \times 10^{-4},$$

$y$  is small so we approximate  $0.500 + y \approx 0.500$  and  $1.00 - y \approx 1.00$ ,

$$\frac{y(0.500)}{1.00} \approx 1.77 \times 10^{-4}, \quad y \approx 3.54 \times 10^{-4} \text{ M} = [\text{H}_3\text{O}^+], \quad \text{pH} = 3.45.$$

5.8.1.1. *How a Buffer Works.* Consider the reaction for a weak acid HA:



This equation holds regardless of the concentration values involved.

<sup>3</sup>Lysosome pH is in the range 4.5-5.0; blood plasma, 7.4; average pH in typical muscle cells, 6.1; average pH in typical liver cells, 6.9; blood plasma, 7.4; mitochondria, 7.8; Golgi apparatus, 6.5; endoplasmic reticulum, 7.0; cytosol, 7.4.

If we make both concentrations  $[\text{HA}]$  and  $[\text{A}^-]$  very large, then small perturbations in each quantity ( $\delta_1, \delta_2$ ) produce little change in their ratio<sup>4</sup>. Thus,  $[\text{H}_3\text{O}^+]$  is relatively unaffected by these perturbations.

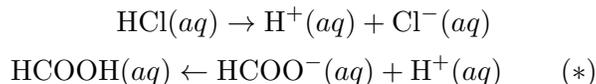
But if  $[\text{H}_3\text{O}^+]$  is unaffected, then the pH is unaffected. Thus, a buffer stabilizes the pH of the solution against perturbations.

If both  $[\text{HA}]$  and  $[\text{A}^-]$  very large, then their ratio approaches a constant, say 1. In that case, the  $\text{pH} \approx \text{p}K_a$ , according to the above equation. The buffer therefore attempts to keep the pH near the  $\text{p}K_a$  value. But other values of the pH are possible, by selecting different concentrations for  $[\text{HA}]$  and  $[\text{A}^-]$ . From a practical standpoint, it is easiest to prepare solutions for which  $[\text{HA}] \approx [\text{A}^-]$ , in which case, a buffer is prepared by selecting an acid whose  $\text{p}K_a$  value is close to the desired pH value and the concentrations  $[\text{HA}] \approx [\text{A}^-]$  are selected to “tweak” the pH to the desired value.

To make  $[\text{HA}]$  very large we simply dissolve a large amount of acid. To make  $[\text{A}^-]$  very large, we simply add salt that dissociates to yield the conjugate base. In the first example, we used sodium formate as the salt.

**5.8.2. pH Stability.** Adding Strong Acid to Buffer Solution: in previous problem suppose that we add 0.10 mole of a strong acid (e.g. HCl).

*Method 1:* HCl is a strong acid and will completely dissociate. The  $\text{H}^+$  ions can be assumed to react with formate ions to produce formic acid, i.e.,



For now, the reactions are assumed to proceed to completion (because HCl is a strong acid and  $\text{HCOO}^-$  is a “strong” base). Thus, the initial conditions are such that the amount of HCOOH is 1.0 mol (from the formic acid) plus 0.1 mol (from the HCl, which leads to the formation of HCOOH in the same amount). Thus, the initial amount of HCOOH is 1.1 mol.

Similarly, while we had 0.5 mol of  $\text{HCOO}^-$  from the sodium formate, now we have 0.4 mol of it, because 0.1 mol of it was used to form HCOOH due to the added HCl.

That being said, only the HCl reaction truly proceeds to completion since its  $K_a$  value is  $\sim 10^7$  (see Table 5.1). For the reaction (\*) the  $K_a$  value is  $1.77 \times 10^{-4}$ . Thus, the reaction (\*) is not complete (for the reaction to be complete, its value should be closer to  $\sim 10^{-7}$ ). Thus, our progress variable  $y > 0$  will describe a *decrease* in the amount of HCOOH from 1.10 mol in

<sup>4</sup>If  $[\text{HA}]$  and  $[\text{A}^-]$  are very large compared to  $\delta_1$  and  $\delta_2$ , respectively, then adding some perturbation  $\delta_i$  ( $i=1$  or  $2$ ) will have negligible effect on the ratio  $[\text{HA}]/[\text{A}^-] \approx ([\text{HA}] + \delta_1)/([\text{A}^-] + \delta_2)$ .  $\delta_1$  and  $\delta_2$  can be thought of as a perturbation to the system introduced by the addition or removal of substances that would normally alter the pH.

the ICE table below (since 1.10 mol is really an overestimate of the true amount of HCOOH that we have at equilibrium).

	HCOOH(aq) + H <sub>2</sub> O(l) ⇌ H <sub>3</sub> O <sup>+</sup> (aq) + HCOO <sup>-</sup> (aq)		
1. Initial (M)	1.10	≈0	0.40
2. Change	-y	+y	+y
3. Equilibrium	1.10-y	y	0.40+y

$$\frac{y(0.40 + y)}{1.10 - y} = K_a = 1.77 \times 10^{-4},$$

y is small so we approximate  $0.40 + y \approx 0.40$  and  $1.10 - y \approx 1.10$ ,

$$\frac{y(0.40)}{1.10} \approx 1.77 \times 10^{-4}, \quad y \approx 4.9 \times 10^{-4} \text{ M} = [\text{H}_3\text{O}^+], \quad \text{pH} = 3.31.$$

If these approximations are confusing, do not worry; just solve the full quadratic equation instead.

As you can see, the pH did not change by much (from 3.45 down to 3.31) even though 0.1 mol of a strong acid was added. Had this amount of acid been added to pure water, the pH would have dropped from 7 to 1.

*Method 2:* There is nothing special about assuming that the H<sup>+</sup> ions react with formate ions to produce formic acid. We could have assumed instead that HCl increases the number of H<sub>3</sub>O<sup>+</sup> ions and allowed y to describe the decrease in the number of such ions:

	HCOOH(aq) + H <sub>2</sub> O(l) ⇌ H <sub>3</sub> O <sup>+</sup> (aq) + HCOO <sup>-</sup> (aq)		
1. Initial (M)	1.00	≈0.10	0.50
2. Change	+y	-y	-y
3. Equilibrium	1.00+y	0.10-y	0.50-y

$$\frac{(0.1 - y)(0.5 - y)}{1 + y} = K_a = 1.77 \times 10^{-4},$$

Instead of making approximations, we solve the quadratic equation:

$$y^2 - (0.6 + 1.77 \times 10^{-4})y + 0.05 - 1.77 \times 10^{-4} = 0.$$

This yields the same end result as **Method 1** (as it should):

$$y = 0.099514, \quad [\text{H}_3\text{O}^+] = 0.1 - y = 4.9 \times 10^{-4} \text{ M}, \quad \text{pH} = 3.31.$$

(Recall that the  $\text{p}K_a$  of the buffer was 3.45.)

**5.8.3. Design of a Buffer.** The normal procedure is to choose an acid with  $\text{p}K_a$  as close as possible to the desired pH. Then we adjust the concentrations of acid and conjugate base to give exactly the desired pH. To see, this, note that since equilibrium concentrations of acid and base in the

buffers are close to the initial concentrations:

$$K_a = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}[\text{A}^-]_{\text{eq}}}{[\text{HA}]_{\text{eq}}} \approx \frac{[\text{H}_3\text{O}^+]_{\text{eq}}[\text{A}^-]_0}{[\text{HA}]_0}, \quad [\text{H}_3\text{O}^+]_{\text{eq}} \approx \frac{[\text{HA}]_0}{[\text{A}^-]_0} K_a.$$

Taking the logs of both sides of this equation yields:

$$\text{pH} \approx \text{p}K_a - \log_{10} \frac{[\text{HA}]_0}{[\text{A}^-]_0}.$$

This is called the Henderson-Hasselbach equation. It relates the desired pH to the  $\text{p}K_a$  of the weak acid (chosen as close a possible to the desired pH) and the ratio of concentrations of weak acid to conjugate base. This ratio is used to “tweak” the effects of the  $\text{p}K_a$  to bring it closer to the desired pH.

We also see from this equation that the buffer will be robust to changes in pH provided that the concentrations of weak acid to conjugate base are chosen large enough, so that small perturbation in their values does not affect the pH appreciably.

Let’s use this equation to design a buffer. We will need a table of  $\text{p}K_a$  values to enable us to pick the acid whose  $\text{p}K_a$  is close to the desired pH (see Table 5.1).

**Design a buffer with pH 4.60:**

$$\text{pH} \approx \text{p}K_a - \log_{10} \frac{[\text{HA}]_0}{[\text{A}^-]_0}.$$

The  $\text{p}K_a$  of acetic acid is 4.75, which is reasonably close to the desired value of 4.60, so we choose  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$  as the buffer system. We can fine-tune the pH from 4.75 down to 4.60 by adjusting the ratio of weak acid to conjugate base. First we write,

$$\text{pH} = 4.60 = \text{p}K_a - \log_{10} \frac{[\text{CH}_3\text{COOH}]_0}{[\text{CH}_3\text{COO}^-]_0}$$

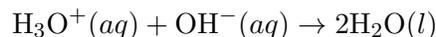
$$\log_{10} \frac{[\text{CH}_3\text{COOH}]_0}{[\text{CH}_3\text{COO}^-]_0} = \text{p}K_a - \text{pH} = 4.75 - 4.60 = 0.15$$

$$\frac{[\text{CH}_3\text{COOH}]_0}{[\text{CH}_3\text{COO}^-]_0} = 10^{0.15} = 1.4.$$

This can be obtained by dissolving 0.100 mol of sodium acetate ( $\text{NaCH}_3\text{COO}$ ) and 0.140 mol of acetic acid in water and diluting to 1.00 L. Other solutions are possible.

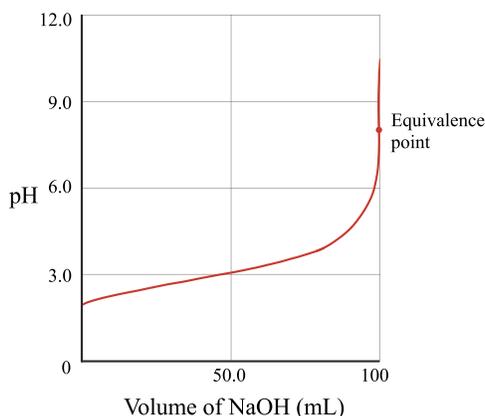
**Note:** While the ratio  $\frac{[\text{CH}_3\text{COOH}]_0}{[\text{CH}_3\text{COO}^-]_0}$  is important, the concentrations must be high enough. The higher the initial concentrations, the higher the ability of the buffer to resist changes in the pH.

**5.8.4. Titration of Strong Acid with Strong Base.** The simplest problem involves titrating a strong acid with a strong base. It simply involves counting number of moles to achieve neutralization:



*Question:* Suppose a solution of 100.0 mL (0.1000 L) of 0.1000 M HCl is titrated with 0.1000 M NaOH. What does the titration curve look like?

Figure 5.7 shows the titration curve for titration of strong acid by a strong base.



**Figure 5.8.** Titration curve (strong acid by a strong base).

This curve should be analyzed into 3 regions:

- **Below the equivalence point** we have acidic conditions. Adding base will neutralize the acid, up the point where  $n_{\text{base}} = n_{\text{acid}}$ , the equivalence point. Thus, below the equivalence point we have:

$$\begin{aligned} \text{pH} &= -\log_{10} [\text{H}_3\text{O}^+] = -\log_{10} \frac{n_{\text{H}_3\text{O}^+}}{V_{\text{tot}}} = -\log_{10} \frac{n_{\text{acid}} - n_{\text{base}}}{V_{\text{acid}} + V_{\text{base}}} \\ &= -\log_{10} \frac{c_{\text{acid}}V_{\text{acid}} - c_{\text{base}}V_{\text{base}}}{V_{\text{acid}} + V_{\text{base}}} \end{aligned}$$

which equals  $\text{pH}=1$  in the limit  $V_{\text{base}} \rightarrow 0$  since  $c_{\text{acid}}=0.1000$  M HCl.

**Note:** This function is of the form  $f(x) = -\log_{10}((1-x)/(1+x))$ . With a graphing calculator or a computer you can try plotting this function over the range  $x \in [0, 1]$  and compare with the shape of the titration curve before the equivalence point.

- **At the equivalence point** the number of moles of base added equals the number of moles of acid originally present. The concentrations of  $\text{OH}^-$

and  $\text{H}_3\text{O}^+$  must be equal and the pH is due solely to the auto-ionization of water. Thus, the pH is precisely 7.00.

- **Above the equivalence point** we have basic conditions. Adding more base makes it more basic. Thus, the only thing that matters is the moles of excess  $\text{OH}^-$  ions. The pH is obtained from the relation

$$\text{p}K_w = \text{pH} + \text{pOH}.$$

Because the base is a strong base, it is fully protonated. Thus, if we denote the concentration of *excess*  $\text{OH}^-$  ions by  $[\text{OH}^-]$ ,

$$[\text{OH}^-] = \frac{\text{moles of excess } \text{OH}^-}{\text{total volume}} = \frac{n_{\text{base}} - n_{\text{acid}}}{V_{\text{acid}} + V_{\text{base}}} = \frac{c_{\text{base}}V_{\text{base}} - c_{\text{acid}}V_{\text{acid}}}{V_{\text{acid}} + V_{\text{base}}}.$$

So,

$$\text{pH} = \text{p}K_w - \text{pOH} = 14.00 + \log_{10} \frac{c_{\text{base}}V_{\text{base}} - c_{\text{acid}}V_{\text{acid}}}{V_{\text{acid}} + V_{\text{base}}}.$$

**Note:** This function is of the form  $\log_{10}((x-1)/(1+x))$ . With a graphing calculator or a computer you can try plotting this function over the range  $x \in [1, 4]$  and compare with the shape of the titration curve after the equivalence point.

**5.8.5. Titration of Weak Acid with Strong Base.** Consider the titration of 100.0 mL of a 0.1000 M solution of acetic acid ( $\text{CH}_3\text{COOH}$ ) with 0.1000 M NaOH. So the concentrations are the same as in the previous problem, except that the acid is a weak acid instead of a strong acid. Because we have a weak acid, the  $\text{p}K_a$  should enter the picture. In what follows, we denote the acid as  $[\text{HA}]$  and its conjugate base as  $[\text{A}^-]$ .

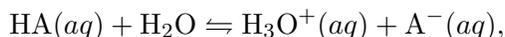
We note the following main differences:

- The titration curve (see Fig.5.9) begins at higher pH because the acid is not completely dissociated, leading to lower concentrations of  $\text{H}_3\text{O}^+$  ions compared to the case of HCl.
- A gradually rising portion of the curve, called the *buffer region*, appears before the steep rise to the equivalence point. At the midpoint, half of the original acid has reacted.
- The pH at equivalence point is greater than 7.00. When  $c_{\text{acid}}V_{\text{acid}} = c_{\text{base}}V_{\text{base}}$ , the solution will be more basic (there will be excess  $\text{OH}^-$ ) because we over-neutralize the acid, since the acid was not completely dissociated (weak acid).

Let us examine the main elements of this titration curve:

- **Initial point.** Before the base is added the weak acid is partially dissociated. The pH is obtained by setting up an ICE table for the dissociation

reaction



(let  $x = [\text{H}_3\text{O}^+]$ )

$$K_a = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}[\text{A}^-]_{\text{eq}}}{[\text{HA}]_{\text{eq}}} = \frac{x^2}{[\text{HA}]_0 - x} \approx \frac{x^2}{[\text{HA}]_0}, \quad x \approx \sqrt{K_a \cdot [\text{HA}]_0}.$$

- **Buffer region.** As soon as we add NaOH, it reacts with HA to form  $\text{A}^-$ . This means that up to the equivalence point we have a buffer over much of that interval. The pH is found from:

$$[\text{H}_3\text{O}^+]_{\text{eq}} = K_a \frac{[\text{HA}]_{\text{eq}}}{[\text{A}^-]_{\text{eq}}} \quad \text{or} \quad \text{pH} = \text{p}K_a - \log_{10} \frac{[\text{HA}]_{\text{eq}}}{[\text{A}^-]_{\text{eq}}}.$$

We note that at the midpoint of the buffer region, half the original HA has reacted, so  $[\text{HA}] = [\text{A}^-]$  or  $[\text{A}^-]/[\text{HA}] = 1$  and  $\text{pH} = \text{p}K_a$ . For the reaction at hand,  $\text{OH}^-$  is a stronger base than acetate ion, so it reacts almost completely with the acid originally present:



- **At equivalence point** the solution is more basic. You can setup an ICE table for the reverse reaction,  $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$ , to show that

$$[\text{OH}^-] \approx \sqrt{K_b \cdot [\text{A}^-]}, \quad [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}, \quad [\text{H}_3\text{O}^+] \approx \frac{K_w}{\sqrt{K_b \cdot [\text{A}^-]}}.$$

- **After the equivalence point** we have a basic solution. Its properties are calculated based on the quantity of excess  $\text{OH}^-$  ion.

See Fig. 5.9.

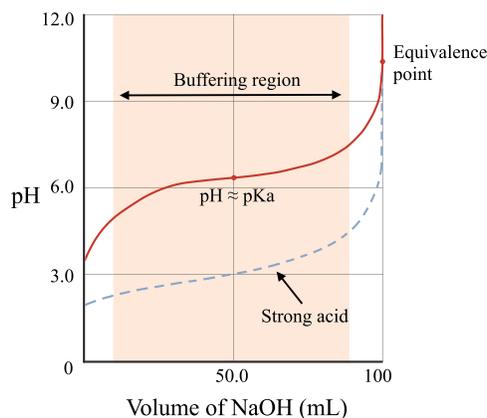
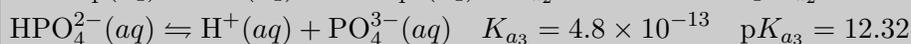
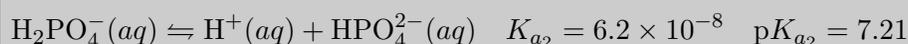
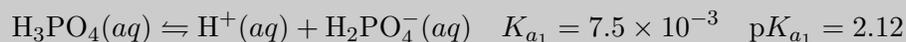


Figure 5.9. Buffering region.

**5.8.6. Phosphate Buffered Saline (PBS).** A commonly used buffer in biology is PBS (phosphate buffered saline). Let's look at ways to prepare a phosphate buffer.

*Question:* Prepare a "phosphate buffer" with pH of about 7.40.

*Solution:* From  $pK_a$  tables we find the following stages of ionization of phosphoric acid:



The most suitable of the three systems is  $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$ , because the  $pK_a$  of the acid  $\text{H}_2\text{PO}_4^-$  is closest to the desired pH. From the Henderson-Hasselbach equation we write

$$\text{pH} = pK_a + \log_{10} \frac{[\text{conjugate base}]}{[\text{acid}]}$$

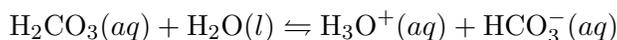
$$7.40 = 7.21 + \log_{10} \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

$$\log_{10} \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 0.19, \quad \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 1.5$$

One way to prepare this buffer with pH 7.40 is to dissolve disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) and sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) in a mole ratio of 1.5:1.0 in water. For example, we could dissolve 1.5 moles of  $\text{Na}_2\text{HPO}_4$  and 1.0 mole of  $\text{NaH}_2\text{PO}_4$  in enough water to make up a 1 L solution.

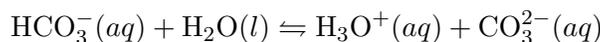
An actual PBS buffer is slightly different in composition. Instead of  $\text{NaH}_2\text{PO}_4$ , one dissolves  $\text{KH}_2\text{PO}_4$ . It also contains additional salts to provide physiological saline conditions.

**5.8.7. Polyprotic Acids.** Polyprotic acids can donate 2 or more protons. As an example, carbonic acid dissociates to form bicarbonate:



$$K_{a_1} = 4.3 \times 10^{-7} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}[\text{HCO}_3^-]_{\text{eq}}}{[\text{H}_2\text{CO}_3]_{\text{eq}}}$$

and



$$K_{a_2} = 4.8 \times 10^{-11} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}[\text{CO}_3^{2-}]_{\text{eq}}}{[\text{HCO}_3^-]_{\text{eq}}}$$

Two comments:

- $[\text{H}_3\text{O}^+]$  in the two ionization equilibria are the same. This follows from the equivalence relation ( $A \rightleftharpoons E$ ,  $E \rightleftharpoons B$  implies  $A \rightleftharpoons B$ ) at equilibrium, which follows from the principle of detailed balance. Here,  $E = [\text{H}_3\text{O}^+]$  and the equations are rearranged as needed.
- $K_{a_2}$  is less than  $K_{a_1}$  because the negative charge left behind by the loss of a hydrogen ion in the first ionization causes the second hydrogen ion to be more tightly bound.

The behavior of polyprotic acids is best described using a plot (Fig. 5.10). Take for example, the case of phosphoric acid ( $\text{H}_3\text{PO}_4$ ), which dissociates into the ions  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  and  $\text{H}_3\text{O}^+$  with acid dissociation equilibrium constants  $K_{a_1} = 7.1 \times 10^{-3}$ ,  $K_{a_2} = 6.3 \times 10^{-8}$  and  $K_{a_3} = 4.2 \times 10^{-13}$ .

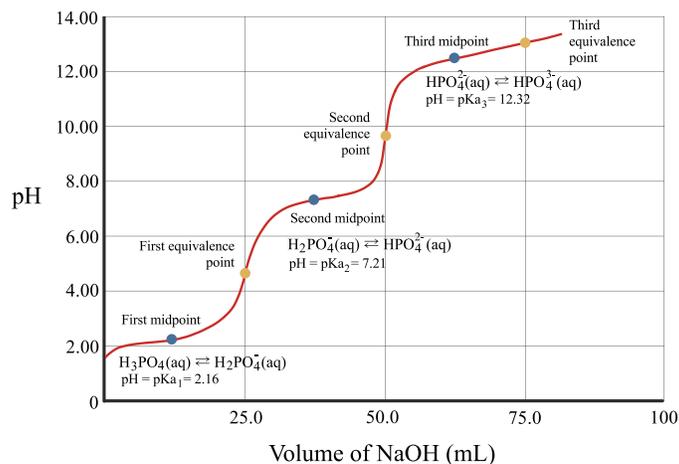
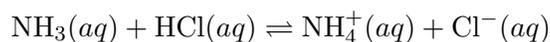


Figure 5.10. Titration curve for a polyprotic acid.

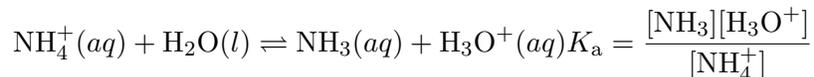
## 5.9. Problems

**Problem 64.** Ammonia ( $\text{NH}_3$ ) aqueous solution has a  $\text{p}K_a$  (9.25 at  $25^\circ\text{C}$ ) that is convenient for the control of pH. A buffer is prepared by mixing 0.10 mol of ammonia with 0.05 mol of  $\text{HCl}$  in a volume of 1.00 L aqueous solution. Compute the pH of the solution.

**Solution.** The addition of  $\text{HCl}$  converts some  $\text{NH}_3$  to its conjugate acid



The resulting solution is a mixture of a weak acid ( $\text{NH}_4^+$ ) and its conjugate base ( $\text{NH}_3$ ). It is a buffer by virtue of the reaction



Compute the concentrations of the  $\text{NH}_3$  and  $\text{NH}_4^+$  after complete reaction with the  $\text{HCl}$  but before the preceding equilibrium is established

$$[\text{NH}_3]_0 = \frac{(0.10 - 0.05 \text{ mol})}{1.00 \text{ L}} = 0.05 \text{ M} \quad \text{and} \quad [\text{NH}_4^+]_0 = \frac{0.05 \text{ mol}}{1.00 \text{ L}} = 0.05 \text{ M}$$

The equilibrium now reduces the concentration of the  $\text{NH}_4^+$  as it forms  $\text{H}_3\text{O}^+$  and  $\text{NH}_3$  in equal amounts. If  $x$  is the equilibrium concentration of  $\text{H}_3\text{O}^+(aq)$  ion, then

	$\text{NH}_4^+(aq)$	+	$\text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{NH}_3(aq)$	+	$\text{H}_3\text{O}^+(aq)$
Init. Conc. (M)	0.05		-		0.05		small
Change in Conc. (M)	$-x$		-		$+x$		$+x$
Equil. Conc. (M)	$0.05 - x$		-		$0.05 + x$		$x$

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{(0.05 + x)x}{(0.05 - x)}$$

Assume that  $x$  is small compared to 0.05. Then 0.05 in the numerator cancels out with that in the denominator

$$[\text{H}_3\text{O}^+] = K_a \text{ so that } \text{pH} = \text{p}K_a = 9.25$$

Clearly  $x$  is less than  $10^{-9}$ , so the assumption was justified.

Tip: The pH equals the  $\text{p}K_a$  of the weak acid. This is a general result in buffer solutions in which the acid and conjugate base concentrations are equal (and not extremely low). ■

**Problem 65.** A buffer solution is prepared from 100 mL of 0.1 M acetic acid and 25 mL of 0.1 M sodium hydroxide. The  $\text{p}K_a$  of acetic acid is 4.75 while the  $\text{p}K_b$  of sodium hydroxide is 0.2. What is the pH of the resulting solution? Is the acid-base reaction of  $\text{NaOH}$  a competing equilibrium that we must include in our calculation? Explain why it is or why it is not.

**Solution.** Total volume is 125 mL. We have 0.01 mol acetic acid (HA) and 0.0025 mol  $\text{NaOH}$ .  $\text{NaOH}$  reacts with acetic acid to yield acetate ( $\text{A}^-$ ), so the initial conditions are 0.0075 mol acetic acid and 0.0025 mol acetate

	HA	$\text{A}^-$	$\text{H}_3\text{O}^+$
I	0.060	0.020	0
C	$-x$	$+x$	$+x$
E	$0.060 - x$	$0.020 + x$	$+x$

which gives:

$$\frac{(0.020 + x)(x)}{0.060 - x} = K_a = 10^{-4.75}.$$

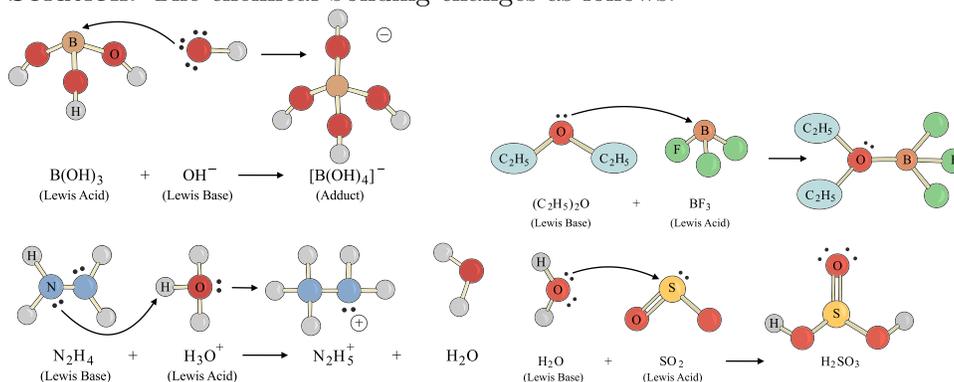
The quadratic equation,  $0 = x^2 + 0.02x - 1.1 \times 10^{-6}$ , is solved and we keep  $x = 5.3 \times 10^{-5}$ . Therefore,  $\text{pH} = -\log_{10}(5.3 \times 10^{-5}) = 4.3$ . The association

of NaOH does not compete with the dissociation of acetic acid, as NaOH is a strong base with a low  $pK_b$  of 0.2. This means that NaOH effectively dissociates entirely in our solution, so we do not need to consider the dissociation/association reaction in our calculation of the buffer solution pH. ■

**Problem 66.** For the following Lewis acid-base reactions below draw the Lewis structures (of each reactant and product), relevant chemical bonds, and indicate with arrows which bonds are formed or broken and which unpaired electrons are shared to form the adduct. (Note: when forming the adduct, bonds can be broken and formed apart from the sharing of electrons.) Identify the acid and the base:

- (a)  $B(OH)_3 + OH^- \rightarrow [B(OH)_4]^-$   
 (b)  $N_2H_4 + H_3O^+ \rightarrow N_2H_5^+ + H_2O$   
 (c)  $(C_2H_5)_2O + BF_3 \rightarrow (C_2H_5)_2OBF_3$   
 (d)  $H_2O + SO_2 \rightarrow H_2SO_3$

**Solution.** The chemical bonding changes as follows:



Lewis bases: (a)  $OH^-$ , (b)  $N_2H_4$ , (c)  $(C_2H_5)_2O$ . (d)  $H_2O$  ■

**Problem 67.** Consider the Lewis acid-base reaction:



- (a) Identify the acid and base among reactants.  
 (b) Many Lewis acid-base “titration reactions”, such as this one, result in the formation of complex (polyatomic) ions. The equilibrium constant for this reaction is called a formation constant of complexes ( $K_f$ ) (sometimes called a stability constant). Define the formation constant of  $[Ag(CN)_2]^-$ .  
 (c) Calculate the silver ion concentration,  $[Ag^+]$ , of a solution that initially is 0.10 M with respect to  $[Ag(CN)_2]^-$ . The formation constant of  $[Ag(CN)_2]^-$  is  $5.3 \times 10^{18}$  at room temperature.

**Solution.** (a) Lewis acid:  $Ag^+$ . Lewis base:  $CN^-$

$$(b) K_f = \frac{[[\text{Ag}(\text{CN})_2]^-]}{[\text{Ag}^+][\text{CN}^-]^2}$$

(c) The initial concentration of  $[\text{Ag}(\text{CN})_2]^-$  is 0.10 mol/L

	$\text{Ag}^+(aq)$	$+ 2 \text{CN}^-(aq)$	$\rightleftharpoons$	$[\text{Ag}(\text{CN})_2]^- (aq)$
I (M)	0	0		0.10
C (M)	$x$	$2x$		$-x$
E (M)	$x$	$2x$		$0.10-x$

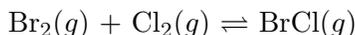
$$K_f = 5.3 \times 10^{18} = \frac{[[\text{Ag}(\text{CN})_2]^-]}{[\text{Ag}^+][\text{CN}^-]^2} = \frac{0.10 - x}{x \times (2x)^2}$$

Both  $Q$  and  $K_f$  are much larger than 1, so let us assume that the changes in concentrations needed to reach equilibrium are small. Thus  $0.10-x$  is approximated as 0.10:

$$x^3 = \frac{0.10}{4 \times 5.3 \times 10^{18}} = 4.717 \times 10^{-21}$$

$$x = [\text{Ag}^+] = 1.68 \times 10^{-7} \text{ mol/L} \quad \blacksquare$$

**Problem 68.** Consider the following reaction with an equilibrium constant of 322:



Determine the final partial pressure of each compound if a vessel of 0.0500 atm  $\text{Br}_2$  and 0.0400 atm  $\text{Cl}_2$  is left to achieve equilibrium.

**Solution.**  $\frac{(P_{\text{BrCl}})^2}{P_{\text{Br}_2} P_{\text{Cl}_2}} = K$

$$\frac{(2x \text{ atm})^2}{(0.0500 \text{ atm} - x \text{ atm})(0.0400 \text{ atm} - x \text{ atm})} = 322$$

$$318x^2 - 28.98x + 0.644 = 0$$

0.0768 atm BrCl  
 0.0116 atm  $\text{Br}_2$   
 0.0016 atm  $\text{Cl}_2$  ■

**Problem 69.** Take the solubility product of  $\text{CaF}_2$  to be  $4.0 \times 10^{-11}$  and use it to find the solubility of the compound. What can be said about trying to dissolve  $\text{CaF}_2$  in water?

**Solution.**  $\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-$

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2 = [\text{Ca}^{2+}][2\text{Ca}^{2+}]^2 = 4.0 \times 10^{-11}$$

$$[\text{Ca}^{2+}] = [\text{CaF}_2] = 0.000215 \text{ M}$$

$$[\text{F}^-] = 0.000430 \text{ M}$$

$$\frac{0.000215 \text{ mol}}{\text{L}} \times \frac{78.07 \text{ g}}{\text{mol}} = 0.0169 \text{ g}\cdot\text{L}^{-1}$$

Based on the value computed above, we would expect  $\text{CaF}_2$  to not be very soluble in water. ■

**Problem 70.** Describe how you would prepare 1 liter of a buffer at pH=9.0, using 1.0 moles  $\text{NH}_3$  and as much of any strong acid as needed.

**Solution.** We must look up the  $K_a$  for  $\text{NH}_4^+$

$$K_a = 5.67 \times 10^{-10} \quad \text{p}K_a = 9.25$$

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{NH}_3]}{[\text{NH}_4^+]}$$

	$\text{NH}_3 + \text{H}^+$	$\rightleftharpoons \text{NH}_4^+$
Initial (M)	1.0	0
Change (M)	$-x$	$+x$
Equilibrium (M)	$(1.0 - x)$	$+x$

$$\therefore 9.00 = 9.25 + \log_{10} \frac{(1.0 - x)}{x}$$

Solve for  $x = 0.64$  moles HCl added to a liter (M)

“moles HCl added = moles  $\text{NH}_4^+$ ” ■

**Problem 71.** A 40-ml sample of a 0.10 M solution of nitric acid is added to 20 ml of 0.30 M aqueous ammonia. What is the pH of the resulting solution?

**Solution.**

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log_{10} \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \\ &= 9.25 + \log_{10} \left[ \frac{(0.020 \text{ L})(0.30 \text{ M}) - (0.040 \text{ L})(0.10 \text{ M})}{(0.040 \text{ L})(0.10 \text{ M})} \right] \\ \text{pH} &= 9.25 + \log_{10}(0.50) = 9.25 - 0.30 = 8.95 \end{aligned}$$

Question: why did we not calculate the molarity of the conjugate base and weak acid in the  $\log_{10}(x)$  in the above equation? ■

**Problem 72.** Suppose you have a buffer at pH 5.0 that is 1.00 M in HX and 1.00 M in  $\text{X}^-$ , where HX is a weak acid with  $K_a = 1.0 \times 10^{-5}$  M. Calculate the effects of adding 50 ml of 1.0 M HCl to a 1-liter portion of this buffer and of adding 50 ml of 1.0 M NaOH to a separate 1-liter portion. What will the final pH be in each case?

**Solution.** 1st addition of the 50 mL of 1.0 M HCl

$$[\text{X}^-] = \frac{(1.0 \text{ M})(1 \text{ L}) - (1.0 \text{ M})(0.050 \text{ L})}{1.050 \text{ L}} = 0.90 \text{ M}$$

$$[\text{HX}] = \frac{(1.0 \text{ M})(1 \text{ L}) + (1.0 \text{ M})(0.050 \text{ L})}{1.050 \text{ L}} = 1.0 \text{ M}$$

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{X}^-]}{[\text{HA}]} = 5.00 + \log_{10} \frac{0.90}{1.0} = 4.95$$

2nd addition of the 50 mL of 1.0 M NaOH

$$[X^-] = \frac{(1.0 \text{ M})(1 \text{ L}) + (1.0 \text{ M})(0.050 \text{ L})}{1.050 \text{ L}} = 1.0 \text{ M}$$

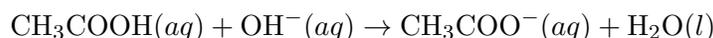
$$[HX] = \frac{(1.0 \text{ M})(1 \text{ L}) - (1.0 \text{ M})(0.050 \text{ L})}{1.050 \text{ L}} = 0.90 \text{ M}$$

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[X^-]}{[HA]} = 5.00 + \log_{10} \frac{1.0}{0.90} = 5.05$$

■

**Problem 73.** What volume of 1.0 M KOH must be added to 10 ml of 1.0 M acetic acid ( $\text{CH}_3\text{COOH}$ ) to give pH of 5.0? ( $K_a$  for acetic acid is  $1.8 \times 10^{-5}$  M). Is this mixture a good buffer? Why or why not?

**Solution.** The reaction is



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

$$\text{pH} = 5.0 \quad [\text{H}_3\text{O}^+] = 1.0 \times 10^{-5} \text{ M}$$

Let  $x$  = KOH added in "liters"

$$[\text{CH}_3\text{COO}^-] = \frac{(1.0 \text{ M})(x)}{0.010 \text{ L} + x}$$

$$[\text{CH}_3\text{COOH}] = \frac{(1.0 \text{ M})(0.010 \text{ L}) - (1.0 \text{ M})(x)}{0.010 \text{ L} + x}$$

$$K_a = 1.8 \times 10^{-5} = \frac{\frac{(1.0 \text{ M})(x)}{0.010 \text{ L} + x} (1 \times 10^{-5} \text{ M})}{\frac{(1.0 \text{ M})(0.010 \text{ L}) - (1.0 \text{ M})(x)}{(0.010 \text{ L} + x)}}$$

$$x = 6.4 \text{ mL of KOH}$$

$$\therefore [\text{CH}_3\text{COO}^-] = \frac{(1.0 \text{ M})(0.0064 \text{ L})}{(0.010 \text{ L} + 0.0064 \text{ L})} = \frac{0.0064 \text{ mol}}{0.0164 \text{ L}} = 0.39 \text{ M}$$

$$[\text{CH}_3\text{COOH}] = \frac{(1.0 \text{ M})(0.010 \text{ L}) - (1.0 \text{ M})(0.0064 \text{ L})}{(0.010 \text{ L} + 0.0064 \text{ L})} = 0.22 \text{ M}$$

This is a good buffer system since

$$[\text{CH}_3\text{COO}^-] \approx [\text{CH}_3\text{COOH}]$$

■

# Thermodynamics

Thermodynamics provides a framework to account for exchanges (transfers) of energy among different systems or subsets of a given system. Energy transfers can occur in the form of heat exchanges or different types of work. Thermodynamics is a topic that crosses many disciplines (physics, chemistry, engineering, life sciences, etc.). This chapter only provides a brief introduction to this vast topic. To learn more, the reader should consult the more authoritative treatises by Callen [15], Kittel [16], Moran & Shapiro [17], Atkins [14], McQuarrie & Simon [5], Ben-Amotz [18], Sonntag & Borgnakke [19] and Honig [20].

In thermodynamics the universe is divided into two parts: the system and its surroundings. We must then specify whether or not particles and heat are allowed to exchange between the system and its surroundings (Fig. 6.1).

## 6.1. Heat vs Work

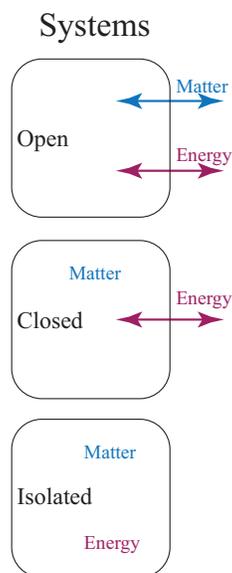
**Energy** is the capacity to do work. A change in energy can be thought of as the sum of heat and work (done, say, by the system on its surroundings, or vice-versa). **Heating** is the transfer of energy that makes use of *disorderly molecular motion*. See Fig. 6.2.

**Work** is the transfer of energy that makes use of *organized motion* (organized, as opposed to random molecular motions). See Fig. 6.3.

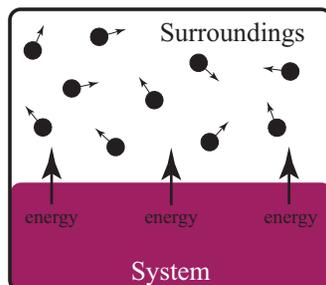
An **exothermic process** is one that releases energy as *heat* to the surroundings.<sup>1</sup> All combustion reactions are exothermic. An **endothermic process**

---

<sup>1</sup>Heat transfer is a process. Heat is not viewed as an entity. It is instead a process: the transfer of energy as a result of temperature difference. Similarly to a diffusion process which is a flux  $J_i$



**Figure 6.1.** If matter can be transferred to the system, it is called **open**, otherwise it is **closed**. An **isolated system** cannot exchange mass or heat with its surroundings. Walls of the system that allow transfer of heat are called **diathermic** whereas those that don't are called **adiabatic**. **Energy** is the capacity of a system to do **work**. Energy can also be transferred as **heat**.



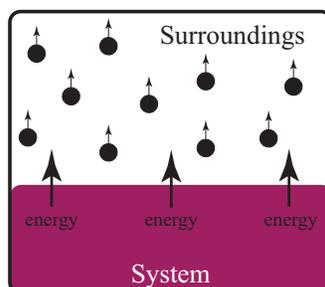
**Figure 6.2.** When energy is transferred to the surroundings as heat, the transfer stimulates random motion of the atoms in the surroundings. Transfer of energy from the surroundings to the system makes use of random motion (thermal motion) in the surroundings.

in the  $i$ -th chemical species driven by gradients in the chemical potential of that species,

$$J_i(\text{particle flux}) = -D \frac{d}{dx} \mu_i(x) \quad \text{Fick's law of diffusion}$$

( $D$  is a diffusion coefficient), heat transfer is a flux driven by gradients in temperature

$$q(\text{heat flux}) = -k \frac{d}{dx} T(x) \quad \text{Fourier's law}$$



**Figure 6.3.** When a system does work, it stimulates orderly motion in the surroundings. For instance, the atoms shown here may be part of a weight that is being raised. The ordered motion of the atoms in a falling weight does work on the system.

is a process in which energy is acquired from its surroundings as heat. An example is vaporization of water.

Heat occurs through random thermal motion. Heat transfer from a hot to a cold body occurs through random thermal motion, so heat should be thought of as a kind of disorderly motion. Suppose a system is in contact with its surroundings and heat flows into the system, the system's energy is increased as a result of the heat transfer. In contrast, work is a transfer of energy, but does not involve disorderly motion. Instead, it involves concerted motion of all particles. For example, a force can be used to lift an object. In this case, all of the molecules move together and in the same direction. This process does not involve disorderly motion.

Universe=System+Surroundings. We should always think of a thermodynamic system together with its surroundings. **Heating** is the energy transfer to the system making use of *thermal motion in the surroundings*. **Work** is the energy transfer to the system resulting from *concerted motion of atoms in the surroundings*.

## 6.2. Heat Capacity

Suppose we transfer some amount of heat  $\Delta Q$  to a system, its temperature will increase by an amount  $\Delta T$ . If you transfer double the heat  $2\Delta Q$ , the temperature will increase by double the amount,  $2\Delta T$ . The proportionality “constant” is the **heat capacity**,  $C(T)$ , which itself depends on temperature:

$$q \equiv \Delta Q = C(T)\Delta T.$$

---

where  $k$  is the coefficient of thermal conductivity (in general,  $k = k(T)$  is temperature dependent). At the interface between a hot and a cold body, the temperature gradient is large, causing a transfer of heat from the hot to the cold body. The direction hot  $\rightarrow$  cold is enforced by the minus sign.

Heat capacity is thus a kind of “resistance” or reluctance that a material shows towards raising its temperature in response to receiving heat from its surroundings. Suppose that we transfer 1 J of heat to the material. The smaller the heat capacity, the larger the temperature rise. The larger the heat capacity, the smaller the temperature rise. A closely related quantity is thermal conductivity; the latter is proportional to the heat capacity (see Section 6.2.1).

In thermodynamics we make the distinction between the heat capacity at constant pressure ( $C_P$ ) and at constant volume ( $C_V$ ) using a subscript  $P$  or  $V$ , respectively. This refers to the kind of experiment used to measure the heat capacity. As we will see later, those two values are different.

The **specific heat capacity** (not to be confused with concentration), denoted by a lowercase  $c$ , is the heat capacity per unit material.

- **Per unit mass:**  $c = C/m$ , where  $m$  is the mass of the body. SI Units: [J/kg.K]
- **Per mole:**  $c = C/n$ , where  $n$  is the number of moles. This is called the *molar heat capacity*. SI Units: [J/mol.K]

Why should we care about *specific* heat capacity? Because without it, heat capacity is an extensive property, i.e. it depends on the amount of material used.  $q = C\Delta T$  says that for a 1°C increase,  $q$  will double if the amount of material doubles (because a body twice as large requires twice the amount of heat transfer to cause this 1°C increase), therefore  $C$  should double. Because of this dependence, it is impossible to tabulate values of  $C$ . Dividing by the amount of material ( $n$  or  $m$ ) renders the heat capacity independent of the amount of material. It is then an intensive property which is intrinsic to the material type, not its quantity.

Another notation you may see for the definition of heat capacity is in terms of infinitesimal quantities:

$$C(T) = \frac{\delta q}{dT},$$

or the corresponding molar heat capacity

$$c(T) \equiv \frac{1}{n}C(T) = \frac{1}{n} \frac{\delta q}{dT}.$$

While this notation appears awkward, it is sometimes useful conceptually.

This notation appears to suggest that heat capacity is some type of derivative ( $\delta/dT$ ) of an extensive parameter (heat flow) with respect to an intensive property (temperature). These are, however, formal definitions. In practice, measured heat capacities are evaluated as derivatives with respect to temperature while holding some other variables constant ( $P$  or  $V$ ).

This is done as such, because the measured heat flow will depend on which parameters are held constant.  $C_V$  is the most convenient quantity for gases and theoreticians.  $C_P$  is the most common tabulated form.

**6.2.1. Thermal Conductivity.** If the temperature is non-uniform there will be a transfer of heat until a steady-state is reached. Similar to the case of particle diffusion, this transfer of heat acts to make the temperature more spatially uniform. The rate of heat loss per unit area ( $A$ ) is related to the temperature gradient according to:<sup>2</sup>

$$(6.1) \quad \frac{1}{A} \frac{\Delta Q}{\Delta t} = -\kappa \frac{\Delta T}{\Delta x},$$

where  $\kappa$  is the thermal conductivity.

For an ideal gas the heat transfer rate is proportional to the average molecular velocity ( $\bar{v}$ ), the mean free path ( $\lambda$ ) of the energy carrier (average distance traveled between consecutive scattering events, on the order of a few nm to  $\mu\text{m}$ ), and the specific (volume) heat capacity of the gas [ $c(T)$ ].

$$\kappa = \frac{1}{3} \bar{v} \lambda c(T).$$

A related quantity is the thermal diffusivity,  $\alpha$  (units:  $\text{m}^2/\text{s}$ ):

$$\alpha = \frac{\kappa}{c(T)}.$$

The units of  $c(T)$  are  $\text{J}/\text{m}^3\cdot\text{K}$ . Those of  $v$  are  $\text{m}/\text{s}$ . This implies that  $\kappa$  has units of  $\text{J}/\text{m}\cdot\text{s}\cdot\text{K}$  or  $\text{W}/\text{m}\cdot\text{K}$ . The unit  $\text{J}/\text{s}$  is also known as the Watt ( $\text{W}$ ). Inspection of Eq. (6.1) reveals that the units on the right hand side must be  $(\text{J}/\text{m}\cdot\text{s}\cdot\text{K}) \times (\text{K}/\text{m})$  or  $\text{W}/\text{m}^2$ . For equality to hold, these must also be the units of the left hand side. Indeed,  $Q$  has units of  $\text{J}$ , and therefore,  $\Delta Q/(A\Delta t)$  has units of  $\text{W}/\text{m}^2$ , as it should. This equation holds for each energy carrier (e.g. electron, phonon). For electrons,  $\bar{v}$  is on the order of  $10^6$   $\text{m}/\text{s}$ ; for phonons it is approximately  $10^3$   $\text{m}/\text{s}$ .

For solids, there are two contributions to the heat capacity: phonons and conduction electrons. (For non-metallic solids, only phonons contribute.) Atoms vibrating more energetically at one part of a solid transfer that energy to less energetic neighboring atoms. Phonons are propagating lattice waves that are quantized. For metals, the thermal conductivity is quite high,

<sup>2</sup>Using derivatives, this is:

$$\frac{1}{A} \frac{dQ}{dt} = -\kappa \frac{dT}{dx},$$

where the derivative on the left, of a function  $Q(x, t)$ , with respect to  $t$  holds  $x$  constant. Likewise, the derivative on the right hand side is with respect to  $x$  while holding  $t$  constant. This is normally denoted using partial derivatives:

$$\frac{1}{A} \frac{\partial Q}{\partial t} = -\kappa \frac{\partial T}{\partial x}.$$

and those metals which are the best electrical conductors are also the best thermal conductors.

**6.2.2. Heat Capacity of a Solid: Dulong-Petit Law.** In 1819, Dulong and Petit measured the specific heats<sup>3</sup> of several solids and found that the values for the various materials differed considerably. However, their heat capacity was close to 6 cal/K/mol (Table 6.1) or 25 J/mol.K.

Element	Atomic weight (g/mol)	Specific heat (cal/K/g)	Heat capacity (cal/K/mol)
Lithium	6.9	0.92	6.3
Beryllium	9.0	0.39	3.5
Magnesium	24.3	0.25	6.1
Carbon (diamond)	12.0	0.12	1.4
Aluminum	27.0	0.21	5.7
Iron	55.8	0.11	6.1
Silver	107.9	0.056	6.0
Lead	207.2	0.031	6.4
Mercury	200.6	0.033	6.6

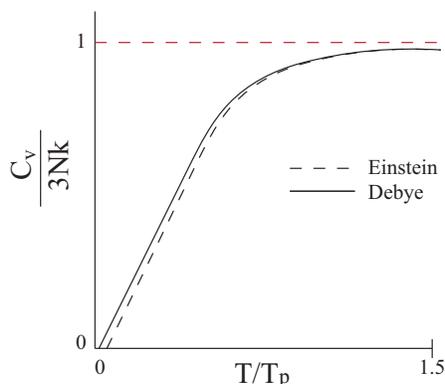
**Table 6.1.** Heat capacities of some solid elements. Dulong and Petit stated their law as: specific heat (cal/K.g)  $\times$  atomic weight (g/mol)  $\cong$  6 (cal/K.mol). 1 calorie equals 4.18 Joules. Source: [21]

Heat capacity arises because of the many different ways (degrees of freedom) in which molecules can absorb energy. The Law of Dulong and Petit is:

**Law of Dulong and Petit.** The molar specific heats of most solids at room temperature and above are nearly the same value. (This value is  $3R \approx 25$  J/mol.K.)

We note that the Dulong-Petit heat capacity is independent of temperature (in the high- $T$  limit only). See Fig. 6.4.

<sup>3</sup>Here, specific heat is the number of calories (or Joules) required to raise one gram (or kilogram) of material one degree celsius. The term *heat capacity* often refers to the heat required to raise *one mole* of material one degree celsius. In older chemistry books (e.g. [21]), “heat capacity” refers to “molar heat capacity”, whereas “specific heat capacity”, is also called “specific heat”, and that is the heat capacity per unit mass of a material. In modern chemistry textbooks (e.g. [1]), these two notions are called “specific heat capacity”, whereas “heat capacity” refers to the total heat capacity (of the entire volume of material). The latter, which is an extensive property, is less useful because such values cannot be tabulated for different materials, as the numerical value depends on the amount of material. In this section only, we use the old terminology.



**Figure 6.4.** The dimensionless heat capacity divided by three, as a function of temperature as predicted by the Debye and Einstein models. The horizontal axis is the temperature divided by the Debye temperature. The dimensionless heat capacity is zero at absolute zero, and rises to a value of three as the temperature becomes much larger than the Debye temperature. The red line corresponds to the classical limit of the Dulong-Petit law.

Units of heat transfer. The connection between heat transfer (SI units: Joule) and temperature change (units: Kelvin) should not be so unfamiliar to you at this point. We have seen in the case of gases that the average kinetic energy per molecule,  $K \equiv \frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T$ , established a connection between temperature and energy. Thus, a change in the kinetic energy  $\Delta K$  is proportional to a change in temperature  $\Delta T$ . The two quantities (energy and temperature) were related by the Boltzmann constant.  $k_B$  and  $C$  have the same SI units (J/K).

**6.2.3. Heat Capacity of Ideal Gas.** Consider an ideal monatomic gas held at constant volume  $V$ . The internal energy of an ideal monatomic gas is purely kinetic. There is no potential energy. From

$$K \equiv \frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T$$

or  $(3/2)RT$  for 1 mole, we can easily derive the heat capacity of an ideal gas by considering the change in temperature that accompanies an infinitesimal change in internal energy, which for an ideal gas is just the kinetic energy ( $U = K$ ).

The heat capacity is obtained by taking the derivative of energy with respect to temperature. For 1 mole of substance, the heat capacity is,

$$c_V = \frac{3}{2}R \quad \text{ideal gas}$$

Here,  $c_V$  denotes the specific (molar) heat capacity at constant volume. (The volume is constant because the gas is contained in a volume  $V$ .)

It can be shown that at constant pressure, the heat capacity of the ideal gas is:

$$c_P = \frac{5}{2}R. \quad \text{ideal gas}$$

**6.2.4. Internal Energy.** The internal energy of a system,  $U$ , is the sum of total kinetic and potential energy of the molecules in the system. Potential energy *includes the energy stored in the chemical bonds*. The internal energy is a **state function**, meaning that it depends only on the state of the system, not on the history or path taken to reach this state.

**State function:** To describe a system completely, we must indicate its temperature, pressure and amounts of substances present. When we have done this, we have specified the *state* of the system. Any property that has a unique value for a specified state of a system is said to be a *state function*. **Note:** Any function that depends on the *history* of the system — rather than its current state — is not a state function.

For a state function, we can express *changes* in the state function in terms of the final state minus the initial state,  $\Delta U = U_f - U_i$ , without any mention of the intermediate states taken to reach the final state from the initial state.

**Change in internal energy:** Because  $U$  is a state function, so is  $\Delta U = U_f - U_i$ . Suppose that a system goes from state 1 to state 2 and back to state 1. Its change of internal energy is  $U_2 - U_1$  followed by  $U_1 - U_2$ :

$$\Delta U = \Delta U_{1 \rightarrow 2} + \Delta U_{2 \rightarrow 1} = (U_2 - U_1) + (U_1 - U_2) = 0.$$

This says that the internal energy returns to its initial value, which it must do, since it is a function of state.

Internal energy is an **extensive property** of the system (i.e. if we double the size of the system, its internal energy doubles). The SI units of  $U$  are Joule (J). However, the internal energy per mole,  $U/n$ , is an **intensive property** of the system. The SI units of  $U/n$  are J/mol.

The change in internal energy  $U$  will contain terms which can be classified as heat transfer or work:

$$\Delta U \equiv \text{change in } U = (\text{heat}) + (\text{work}) \equiv q + w.$$

In general, we do not need to enumerate all contributions to the energy because thermodynamics is only concerned about *changes* in the energy

(e.g.  $\Delta U$  or  $dU$ ), in which case, only the terms that are involved in the change are needed.

In thermodynamics we are interested in  $dU$ , the total differential of the function  $U$ .  $dU$  is the sum of “infinitesimal” heat transfer,  $\delta Q$ , and “infinitesimal” work done on the system  $\delta W$ :

**$dU$  is the sum of infinitesimal heat transfer and work**

The change in internal energy is:

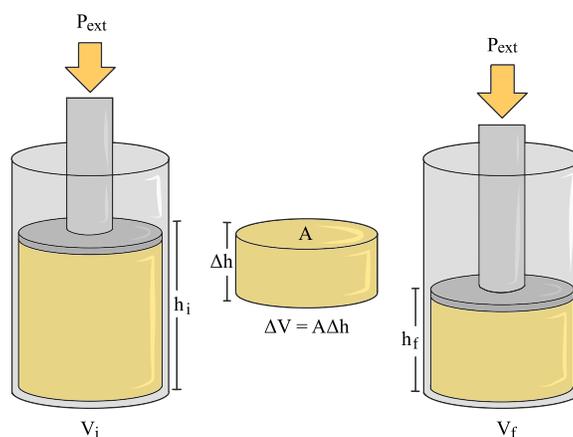
$$dU = \delta Q + \delta W$$

The total change in heat and work is obtained by integrating the infinitesimal expressions,  $q \equiv \Delta Q = \int \delta Q$  and  $w \equiv \Delta W = \int \delta W$ . For  $\Delta U$ , we have:

$$\Delta U = \int dU = \int \delta Q + \int \delta W = \Delta Q + \Delta W \equiv q + w.$$

Some books write  $q$  for heat transfer. We can write  $\Delta Q$  to emphasize that it is a change. We will see later that the first law of thermodynamics states that  $U$  is a state function, or equivalently, that  $dU$  is an exact differential. This implies that  $\Delta U = \int_i^f dU = U_f - U_i$  only depends on the state of the system (hence the name “state function”), not on the history of changes it undergoes between  $i$  and  $f$ . For more information about exact differentials, see Section A.9.

**6.2.5. Compression Work (Hydrostatic Pressure Work).** Suppose that we compress a gas using a piston by applying an external force (pressure), as shown in Fig. 6.5.



**Figure 6.5.** Work accomplished when compressing a gas using a piston.

The *system* is the gas inside the chamber. The *surroundings* is everything else external to it. The external pressure  $P_{ext}$  originates from the surroundings. The pressure is force per unit area:

$$P_{ext} = \frac{F_{ext}}{A}.$$

**6.2.6. Work Done by the Surroundings to the System is  $-P_{ext}\Delta V$ .** We also know that mechanical work,  $\Delta W$ , is obtained by integrating the force over distance (let  $z$  denote the vertical direction which corresponds to the direction of the displacement  $\Delta h$ ):

$$\Delta W = \int_{z_i}^{z_f} P_{ext} A dz = \int_{V_i}^{V_f} P_{ext} dV.$$

As a matter of convention in chemistry we put a negative sign to denote work done on the system by the surroundings. Engineers use the opposite convention (work done *by* the system). For example, if a gas is compressed (work done on the system),  $\Delta V < 0$ , leading to positive values of  $W$  in the definition below:

#### Compression work

$$\Delta W = - \int_{V_i}^{V_f} P_{ext} dV \quad \text{or} \quad \delta W = -P_{ext} dV$$

If  $P_{ext}$  remains constant during this change (as would be the case if the surroundings were atmospheric pressure, which remains essentially constant), we can pull it out of the integral and the work done on the system is the product of the external pressure and the change in the volume of the gas:

$$\Delta W = -P_{ext} \Delta V.$$

In general, depending on what you consider to be the surroundings,  $P_{ext}$  may not necessarily be constant, in which case you need to use  $\delta W = -P_{ext} dV$  and integrate  $\Delta W = \int \delta W$  along the path of the change.

**6.2.7. RECALL: Work = Force  $\times$  Distance.** In classical mechanics, we learn that force times distance is the mechanical work, i.e.

$$w = \int_i^f \vec{F} \cdot d\vec{x},$$

where  $i$  and  $f$  denote the initial and final points, respectively. If the force is in the  $x$  direction,  $\vec{F} = F\hat{x}$ , we have

$$w = \int_i^f F dx.$$

The integral is taken along some path with initial point  $i$  and final point  $f$ . The result is generally path-dependent, unless  $Fdx$  is the derivative of some function (say)  $g$ , i.e.  $Fdx = dg$ , in which case it only depends on the initial and final points since  $\int_i^f dg = g(f) - g(i)$  (fundamental theorem of calculus).

If  $F$  is constant along the path, then the work is simply  $F(x_f - x_i) = F\Delta x$ .

Now let's return to the example from the previous section, where a gas is compressed by a piston. Starting from  $P_{ext} = F_{ext}/A$ , substituting  $A = \Delta V/\Delta h$  yields  $P_{ext} = F_{ext}\Delta h/\Delta V$ . Thus,  $P_{ext}\Delta V = F_{ext}\Delta h$ . For infinitesimal changes,  $P_{ext}dV = F_{ext}dh$ . Since the work done by the surroundings on the system is  $-P_{ext}dV$ ,

$$-dw = P_{ext}dV = F_{ext}dh \quad P_{ext} \frac{dV}{dh} = F_{ext}.$$

The external force (force exerted on the system by its surroundings) is seen to be related to the spatial derivative of the work  $F_{ext} = -\frac{dw}{dh}$ . If  $h$  is the  $x$  direction:

$$F_{ext} = -\frac{dw}{dx}.$$

This is a general principle. The force is generally obtained by taking minus the gradient (spatial derivative) of the (potential) energy:

$$F_{ext} = -\frac{dU}{dx}.$$

(The kinetic energy does not appear because it rarely depends on position.)

### 6.3. Expansion ( $P - V$ ) Work

In chemistry,  $P - V$  work is important because it describes the behavior of gases and the work arising from a change in volume. This includes the work done by a gas as it expands and pushes against the atmosphere. Chemical reactions generate gases. The  $P - V$  work here is the work that must be done to make room for the gas it has produced.  $P - V$  work also describes compression (negative changes in volume).

**6.3.1. Free Expansion in Vacuum.** Suppose that a gas is allowed to expand in a vacuum. Since there is zero opposing force,  $P_{ext} = 0$  and the work is zero  $\Delta W = 0$ .

**6.3.2. Expansion Against Constant Pressure.** Suppose that a gas inside a piston expands, and the piston is pressing against the atmosphere. The latter corresponds to a constant pressure  $P_{ext}$ . Thus, it is constant and

we can take it outside the integral:

$$\Delta W = - \int_{V_i}^{V_f} P_{ext} dV = -P_{ext} \int_{V_i}^{V_f} dV = -P_{ext}(V_f - V_i) = -P_{ext}\Delta V.$$

**6.3.3. Reversible Process.** *Reversible* processes are important because they represent the most efficient processes. They are idealizations (no process in nature can be perfectly reversible) which enable us to do useful calculations. A process is fully reversible if both system and surroundings will return exactly to their initial states if the process is run in reverse. Less efficient processes do not have this property, and so are referred to as *irreversible*. A process is said to be *reversible* if it remains arbitrarily close to equilibrium with its surroundings at all times.

When a system is **arbitrarily close** to equilibrium with its surroundings, we mean close in the sense of infinitesimals. If  $T, P, \mu$  are the temperature, pressure and chemical potential of the *system* and  $T_{ext}, P_{ext}, \mu_{ext}$  are those of the surroundings, then arbitrarily close means that they are close in the sense of infinitesimals:

$$\begin{aligned} T_{ext} &= T + dT \\ P_{ext} &= P + dP \\ \mu_{ext} &= \mu + d\mu \end{aligned}$$

According to the rules of calculus, we can handle expressions containing infinitesimals such as  $dT$ ,  $dP$  and  $d\mu$ . However, second-order quantities such as  $(dT)^2$  or  $(dT)(dP)$  should be neglected because the square of an infinitesimally small quantity is so small that it is effectively zero.<sup>4</sup> If you don't want to deal with infinitesimals, it is usually safe to make the following substitutions (replace external pressure by internal pressure, etc.):

$$T_{ext} \approx T, \quad P_{ext} \approx P, \quad \mu_{ext} \approx \mu.$$

<sup>4</sup>From calculus, we know that

$$df = \frac{df}{dx} dx. \quad (1)$$

However, it is also the case that:

$$df(x) = f(x + dx) - f(x).$$

Taylor-expanding the first term,

$$df = \left[ \cancel{f(x)} + (dx) \frac{df}{dx} + \frac{(dx)^2}{2} \frac{d^2f}{dx^2} + O((dx)^3) \right] - \cancel{f(x)} \quad (2)$$

But for (1) and (2) to be equal we are "forced" to drop terms of order  $(dx)^2$  or higher. Thus, when handling differential expressions we keep terms of order  $O(dx)$  only. The higher order infinitesimal terms are negligible (too small).

**6.3.4. What Makes a Process Irreversible?** Irreversibility lead to a loss of energy. There are many different factors that make processes irreversible. The most common reasons are:

- **FRICITION.** When a system has energy which it converts into work, friction makes this conversion inefficient. Heat is lost to the surroundings. The dissipation of heat cannot be recovered.
- **UNRESTRAINED EXPANSION.** Suppose that at time  $t = 0$  a gas is compressed inside a volume with a piston. The surroundings are evacuated (vacuum). If we release the piston, the gas will expand. This process is irreversible because the gas will not spontaneously return to its initial compressed state. Work would be needed to re-compress the gas.
- **HEAT TRANSFER IN A TEMPERATURE GRADIENT.** Suppose we have a hot body connected to a cold body. Heat will be transferred from the hot body to the cold body. This process is spontaneous. Because heat will not spontaneously flow from the cold body to the hot body, this process is irreversible.
- **MIXING SUBSTANCES.** Suppose we have a volume  $V$  with two gases:  $H_2$  and  $O_2$ . The two gases are initially separated into two compartments by a wall. We then remove the wall and allow the gases to mix. This process is irreversible because the gases will never return to their original locations.
- **OTHER.** There are many other factors leading to irreversibility. Chemical reactions that move the initial concentrations towards equilibrium are irreversible. In fact, some reactions, such as combustion reactions, are unidirectional and obviously irreversible. Electrical current flowing in conductors of finite resistance lead to power dissipation. The power dissipated is proportional to the square of the current (Joule heating law).

**6.3.5. Reversible Compression.** If the mechanical compression work done by the surroundings on a system

$$\delta W = -P_{ext}dV$$

is reversible, this means we can write  $P_{ext} = P + dP$ ,

$$\delta W = -(P + dP)dV.$$

Noting that the product of infinitesimals  $dPdV$  is much smaller than the term  $PdV$ , we neglect  $dPdV$ :

$$\delta W = -PdV.$$

The reversible work done on the system is then:

$$\Delta W^{rev} = \int \delta W = - \int_{V_i}^{V_f} (P + dP)dV = - \int_{V_i}^{V_f} PdV.$$

What did we accomplish by changing  $\delta W = -P_{ext}dV$  to  $\delta W = -PdV$ ? The difference is significant because this allows us to replace  $P_{ext}$  by  $P$ . In many experiments  $P$  is known, because the gas mixture is known, and obtained from the equation of state, whereas  $P_{ext}$  is often unknown (e.g., the surroundings may be out of your control).

Indeed, when computing the work done on the gas,  $-\int F dx = -\int P_{ext} dV$ , the force  $F$  must be the gravitational force acting downward on all of the mass supported by the gas at pressure  $P$ . This mass includes that of the piston, the piston rod, the pan, any weight placed on the piston (to compress the gas), and the atmosphere above the piston. In the case of a reversible process this force  $F$  is never more than minutely out of balance with the force exerted upward on the piston face by the gas and given by the product of pressure and piston area. Thus, for all practical purposes,  $F = PA$  for the reversible process. The volume change of the gas (system) is  $dV = A dx$ ; thus  $dx = dV/A$  and the work done on the gas is

$$\Delta W = -\int F dx = -\int PA \frac{dV}{A} = -\int P dV.$$

For a reversible process, we replace  $P_{ext}$  by  $P$ , which in this equation means we set  $F = PA$ . This allows us to calculate the work using the properties of the system rather than its surroundings. It is generally difficult to know the exact properties of the surroundings in such calculations, especially when the gas expansion is rapid. In a reversible process, the forces are never more than differentially out of balance (e.g.  $P_{ext} = P + dP$ ).

For irreversible processes this substitution is not possible because we may not have thermal equilibrium. For example, suppose that gas expansion takes place: when a finite weight is removed from the piston in the processes described, the forces of gravity acting downward is overbalanced by the gas pressure acting upward by a finite amount (i.e.  $P_{ext} = P - \Delta P$ , where  $\Delta P$  is not an infinitesimal), and  $F$  does not equal  $PA$  again until a new equilibrium position of the piston is reached. (Similarly, for gas compression we have  $P_{ext} = P + \Delta P$ , and the internal gas pressure is overcome by the external pressure from the weight pressing downward.) Thus  $PA$  cannot be substituted in the integral  $\int F dx$ , and it is not possible to calculate the work from a knowledge of the properties of the system (the gas). The integral  $\int F dx$  is given by  $\int P dV$  only when the process is reversible; that is,

$$\Delta W^{rev} = -\int_{V_1}^{V_2} P dV$$

This work for an expansion process is the maximum work which the system can produce.

**6.3.6. Why are Reversible Processes Important?** The reversible process is unique, and important in thermodynamics, because it represents the *limit* of what is possible in the real world. We cannot imagine anything better than a reversible process. Such processes lend themselves to exact mathematical analysis, which is not the case for other processes. In thermodynamics, our choice is often to do calculations for reversible processes, or to do no calculations at all. The reasons for this is that reversible processes are those for which the forces causing change are almost exactly in balance. Thus the states through which the system passes during a reversible process are for all practical purposes equilibrium states, or more precisely are never removed more than differentially from equilibrium states (e.g.  $P_{ext} = P + dP$ ).

**6.3.7. Example: (Reversible Compression of an Ideal Gas).** To illustrate the application of this result, let's look at a specific example. The easiest case is an isothermal compression ( $T = const$ ) for an ideal gas ( $P = nRT/V$ ):

$$\begin{aligned}\Delta W^{rev} &= - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} \\ &= nRT \log(V_1/V_2).\end{aligned}$$

**6.3.8. Example: (Reversible Compression of VDW Gas).** A slightly more complicated example is the van der Waals gas. Suppose that  $n$  moles of gas are expanded from  $V_1$  to  $V_2$  reversibly and isothermally. Calculate  $\Delta W$  for a Van der Waals gas.

*Solution:*

$$\begin{aligned}P &= \frac{nRT}{V - nb} - \frac{n^2a}{V^2} \\ \Delta W^{rev} &= - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \frac{nRT}{V - nb} dV + \int_{V_1}^{V_2} \frac{n^2a}{V^2} dV \\ &= - nRT \int_{V_1}^{V_2} \frac{dV}{V - nb} + n^2a \int_{V_1}^{V_2} \frac{dV}{V^2} \\ &= - nRT \log \left| \frac{V_2 - nb}{V_1 - nb} \right| + n^2a \left( \frac{1}{V_1} - \frac{1}{V_2} \right).\end{aligned}$$

**6.3.9. Example:** (w/ numbers) Calculate the work done when 50 g of iron reacts with hydrochloric acid to produce  $\text{FeCl}_2(aq)$  and hydrogen in (a) a closed vessel of fixed volume, (b) an open beaker at  $25^\circ\text{C}$ .

*Solution:* For (a) the volume cannot change, so the expansion work done is zero ( $\Delta W = 0$ ). For (b) the gas pushes against the atmosphere,  $\Delta W = -P_{ext}\Delta V$ . After production of gas, the volume changed by  $\Delta V = V_f - V_i \approx$

$V_f = nRT/P_{ext}$  (the initial volume is so small compared to  $V_f$  that it can be neglected), where  $n$  is the amount of  $H_2$  produced. Therefore,

$$\Delta W = -P_{ext}\Delta V = -P_{ext}\frac{nRT}{P_{ext}} = -nRT.$$

Because the reaction is  $Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$ , we know that 1 mol  $H_2$  is generated when 1 mol  $Fe$  is consumed, and  $n$  can be taken as the amount of  $Fe$  atoms that react. The molar mass of  $Fe$  is 55.85 g/mol. Then,

$$\Delta W \approx -\frac{50 \text{ g}}{55.85 \text{ g/mol}} \times (8.3145 \text{ J/K.mol}) \times (298 \text{ K}) \approx -2.2 \text{ kJ}.$$

### 6.3.10. ENTROPY CHANGE during expansion of IDEAL GAS.

The ideal gas has  $PV = Nk_B T$  and  $U = \frac{3}{2}Nk_B T$ . Let's analyze the following 3 different expansion methods:

- **FREE EXPANSION:** Isolated system is a box with partition dividing it into two parts. The gas starts in one part with the other part evacuated. Partition is broken, allowing the gas to expand into the other part of the box. Energy of the system is constant. No work is done and no energy is lost/gained.
- **ISOTHERMAL EXPANSION:** Gas in a cylinder pushes piston doing work. Cylinder is in a bath with fixed temperature  $T$ .
- **ADIABATIC EXPANSION:** Cylinder with piston, so work is done, but system is isolated.

**FREE EXPANSION.** Since  $U = (3/2)Nk_B T$  and  $U$  is constant, so is  $T$ . Entropy must increase when  $V$  does, because

$$dU = TdS - PdV,$$

so

$$\Delta S = \int \frac{P}{T} dV = \frac{1}{T} \int PdV = Nk_B \int \frac{dV}{V} = Nk_B \log(V_{final}/V_{initial}).$$

Although the gas is *not* in equilibrium during a free expansion, we can still use our equilibrium thermodynamics to find out how much quantities like  $T$  and  $S$  change. That is because we have kept track of the total energy of the system as well as its volume. Since  $\Delta S$  depends on initial and final states only ( $S$  is a state function), we do not care what happens between initial and final states.

**ISOTHERMAL EXPANSION.**  $T$  is constant and so is  $U$ . Hence, entropy changes by the same amount as in the case of free expansion. However, work is done. The work comes not from the internal energy of the gas, which remains constant, but from the bath that is keeping  $T$  constant. In an isothermal expansion of an ideal gas, heat is extracted from the bath and

turned into work. The work done is given by

$$\Delta W = \int P dV = \int \frac{Nk_B T}{B} dV = Nk_B T \log(V_{final}/V_{initial}).$$

ADIABATIC EXPANSION. Work is also done in an adiabatic or isentropic expansion. In this case, however, there is no external source of heat, so the energy of the gas must decrease and so must its temperature. Isentropic process has  $dS = 0$  and (see Problem 77)

$$PV^\gamma = \text{constant},$$

where  $\gamma = c_P/c_V$ . During isothermal expansion we have  $PV = \text{constant}$  with a different constant (equal to  $Nk_B T$ ) for each temperature at which an expansion takes place. In an adiabatic expansion we have  $PV^\gamma = \text{constant}$  with a different constant for each entropy at which an expansion takes place. In the adiabatic case, the temperature is decreasing as the gas expands, causing  $P$  to fall faster than in the isothermal case as  $V$  increases. The difference is expressed in the exponent  $\gamma$ . For an atomic ideal gas  $\gamma = 5/3$ . For a diatomic gas,  $\gamma = 7/5$ .

**6.3.11. Path-Dependence of Work.** Work is *not* a state function, meaning that its numerical value depends on the *path* taken to go from one state to another. By path, we mean a curve (“sequence of steps”) in the  $P - V - T$  parameter space<sup>5</sup> (or more generally, involving any useful set of thermodynamic variables).

As an example, take a gas in a cylinder. The volume of the gas is allowed to expand, subject to changes in external pressure. Suppose we have 0.1 mol of gas at 300 K. The initial state has external pressure of 2 atm. The final state has pressure of 1 atm. Since at equilibrium, the external pressure equals the internal pressure, the initial volume is:

$$V_{initial} = \frac{nRT}{P_i} = \frac{(0.100 \text{ mol})(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(300 \text{ K})}{2 \text{ atm}} = 1.2315 \text{ L}.$$

The final volume is:

$$V_{final} = \frac{nRT}{P_f} = \frac{(0.100 \text{ mol})(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(300 \text{ K})}{1 \text{ atm}} = 2.463 \text{ L}.$$

The change in volume is:

$$\Delta V = V_{final} - V_{initial} = 2.463 \text{ L} - 1.2315 \text{ L} = 1.2315 \text{ L}.$$

<sup>5</sup>A curve  $\gamma(t)$  is a mapping  $\gamma : [0, 1] \rightarrow \mathbb{R}^3$ , where  $\gamma(t) = (P(t), V(t), T(t))$  and  $t$  is a parameter of the curve. A continuous curve is one where  $P(t)$ ,  $V(t)$  and  $T(t)$  are continuous functions of  $t$ .

An IRREVERSIBLE expansion<sup>6</sup> would yield

$$\begin{aligned}\Delta W &= -P_{ext}\Delta V = -(1 \text{ atm})(1.2315 \text{ L}) \\ &= -1.2315 \text{ L}\cdot\text{atm} \times \frac{101 \text{ J}}{1 \text{ L}\cdot\text{atm}} = -124.3815 \text{ J}\end{aligned}$$

A REVERSIBLE expansion would yield:

$$\begin{aligned}\Delta W &= -nRT \log(V_i/V_f) \\ &= -(0.100 \text{ mol})(8.31 \text{ J/mol/K})(300 \text{ K}) \log(1.2315/2.463) \\ &= -172.8 \text{ J}.\end{aligned}$$

Because of the negative sign, this is the work done by the system on its surroundings. We see that the work depends on the choice of path (here, irreversible vs reversible). The **reversible work is greater than the irreversible work**.

It is also interesting to carry out the irreversible expansion in  $N + 1$  discrete steps instead of a single step. At each step, we ramp down the pressure (from 2 atm down to 1 atm). The pressure at each step ( $i = 0, \dots, N$ ) is:

$$P_{ext,i} = (2 \text{ atm})(1 - i/N).$$

The change in volume at each step is:

$$\Delta V = (V_{final} - V_{initial})/(N + 1) = (1.2315 \text{ L})/(N + 1).$$

The total work is:

$$\Delta W = -\sum_{i=0}^N P_{ext,i}\Delta V = -\sum_{i=0}^N (2 \text{ atm})(1 - i/N) \frac{(1.2315 \text{ L})}{N + 1}.$$

Using the closed form expression,

$$\sum_{i=1}^n i = \sum_{i=0}^n i = \frac{n(n+1)}{2},$$

we perform the summation:

$$\begin{aligned}\Delta W &= -\frac{(2 \text{ atm})(1.2315 \text{ L})}{N + 1} \left( (N + 1) - \frac{1}{N} \frac{N(N + 1)}{2} \right) \\ &= -(2 \text{ atm})(1.2315 \text{ L}) \frac{1}{2} \times \frac{101 \text{ J}}{1 \text{ L}\cdot\text{atm}} \\ &= -124.3815 \text{ J}.\end{aligned}$$

This multi-step method makes absolutely no difference over the single-step method.

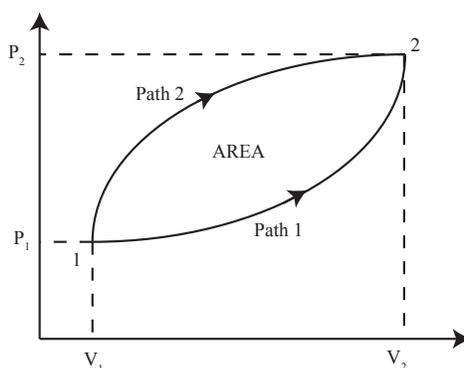
The path-dependence of work can be explained graphically by considering the area under the  $P - V$  graph. Consider a system which changes from state 1 ( $P_1, V_1$ ) to state 2 ( $P_2, V_2$ ). The work done on the system during the

<sup>6</sup>Isothermal expansion at constant pressure.

process is:

$$\Delta W = - \int_{V_1}^{V_2} P_{ext}(V) dV,$$

where  $P_{ext}(V)$  denotes the external pressure, which may be a function of volume.  $\Delta W$  is equal to the area under the  $P - V$  graph, as shown in Fig. 6.6. The magnitude of this area depends on the path taken when going from state 1 to state 2. The connecting curve shown on this graph is the path. On this figure, there are two paths shown: I and II. It is obvious that  $\Delta W_I - \Delta W_{II}$  is non-zero. This difference equals to the area labeled as 'A' on the graph. Only in the case where the two paths are identical will this area A be zero.



**Figure 6.6.** Work depends on path. Two paths are shown here (I and II) connecting the same start and end points (1, 2). However, the area under the curve (work) differs between the two paths. The difference equals to the area enclosed by paths I and II (area is labeled A).

**6.3.12. Why the Infinitesimals?** In the previous sections we have been writing down the work in terms of infinitesimal changes  $\delta W$ . The total work is obtained by integrating:

$$\Delta W = \int \delta W,$$

where  $\delta W$  represents infinitesimal work. For example, the  $P - V$  work term is

$$\delta W = -P_{ext} dV,$$

or

$$\delta W = -P dV,$$

in the case of reversible  $P - V$  work. The total work is

$$\Delta W = \int \delta W = - \int P(V) dV,$$

where  $P(V)$  denotes pressure expressed in term of volume, since the variable of integration is  $V$ . This is done using an equation of state.

You may ask, why are we working with infinitesimal expressions? This is because the intensive quantity (e.g., the pressure) may change along the path of integration. To get the total work  $\Delta W$ , we may need to express the intensive quantity in terms of the extensive quantity. This can be done using an equation of state, as we did in the above examples for the reversible compression of an ideal and VDW gas. The exact dependence of this intensive quantity is problem-dependent.

Working with infinitesimal expressions reminds us that integration is the process where infinitesimals are added along the path of integration. These infinitesimals are not necessarily constant along the path.

#### 6.4. Other Types of Work

Apart from P-V work (compressive mechanical work),  $\delta W = -P_{ext} dV$ , there exists several different other types of work corresponding to the various laws of physics available. Let us look at some examples.

**6.4.1. Work Done by Gravity.** Newton's law of gravitation is:

$$F = G \frac{m_1 m_2}{r^2} = \left( G \frac{m_1}{r^2} \right) m_2,$$

where  $F$  is the gravitational force acting between two objects of mass  $m_1$  and  $m_2$  whose centers-of-masses are separated by a distance  $r$ .  $G$  is the gravitational constant,

$$G = 6.674 \times 10^{-11} \text{ m}^3/\text{kg}/\text{s}^2.$$

If we take  $m_1$  to be the Earth's mass and consider displacements that are small compared to the Earth's radius, then  $r$  is essentially constant. Writing

$$g = \frac{Gm_1}{r^2},$$

where  $r$  is the radius of the Earth (6,357 km) and  $m_1$  is its mass ( $5.9722 \times 10^{24}$  kg). Then, the force can be written as (write  $m$  instead of  $m_2$ ):

$$F = mg.$$

The direction of  $F$  points towards the center of the Earth. The numerical value of  $g$  is approximately  $9.8 \text{ m}/\text{s}^2$ .

Suppose we lift an object of mass  $m$  from the surface of the earth ( $z = 0$ ) to a height ( $z = h$ ). The gravitational force  $F = mg$ , leads to a work term of the form  $\Delta W = \int_0^h F \cdot dz = F \int_0^h dz = mgh$ . Thus, elevating a body of mass  $m$  to a height  $h$  from the ground requires an amount of work  $mgh$ .

**6.4.2. Work Done by a Spring.** The linear restoring force  $F = kx$  (Hooke's law), where  $k$  is the spring constant and  $x$  is the extension of the spring from its rest position, leads to a term of the form  $\Delta W = \int F \cdot dx = \int kx dx = \frac{1}{2}kx^2$ .

**6.4.3. Electrostatic Work.** Suppose that we add an electric charge to an existing (static) system of charged particles  $\{(q_i, \mathbf{r}_i)\}_{i=1}^N$ . The charged particles distribution is described by an electric potential  $\phi$  or electromotive force,  $\mathcal{E}$ , which is additive (sum over all charges):

$$(6.2) \quad \phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \sum_{i=1}^N \frac{q_i}{|\mathbf{r} - \mathbf{r}_i|}.$$

This charge distribution gives rise to an electric field, which is obtained from the spatial derivative of  $\phi(\mathbf{r})$ :

$$\mathbf{E}(\mathbf{r}) = -\nabla\phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \sum_{i=1}^N q_i \frac{(\mathbf{r} - \mathbf{r}_i)}{|\mathbf{r} - \mathbf{r}_i|^3}.$$

Suppose that we place a charge  $q$  at  $\mathbf{r}$ . It will experience a force:

$$\mathbf{F} = q\mathbf{E}(\mathbf{r}).$$

The work is force over distance. The work done in moving a charge  $q$  from  $A$  to  $B$  is:

$$W = - \int_A^B \mathbf{F} \cdot d\mathbf{x} = -q \int_A^B \mathbf{E} \cdot d\mathbf{x}.$$

Here, the minus sign denotes the work done *on* the charge against the action of the field. Then, using  $\mathbf{E}(\mathbf{r}) = -\nabla\phi(\mathbf{r})$ ,

$$W = q \int_A^B \nabla\phi \cdot d\mathbf{x} = q \int_A^B d\phi = q(\phi_B - \phi_A).$$

We normally assume that a point charge is brought from infinity ( $A \rightarrow \infty$ ) to a point  $\mathbf{r}$  in a region of localized electric fields described by the potential  $\phi$  (which vanishes at infinity). Then,  $q\phi$  can be interpreted as the potential energy of the test charge  $q$  in the electrostatic field. The integral is a line integral along a curve  $C$  from  $A$  to  $B$ .  $d\mathbf{x}$  is an infinitesimal line element along the curve  $C$ .

Denote an infinitesimal charge added as  $dq$  and the associated work as  $\delta W$ . The work is  $\delta W = \mathcal{E}dq$  or

$$\boxed{\delta W = \phi dq},$$

depending on the notation used ( $\mathcal{E}$  vs  $\phi$ ).  $\mathcal{E}$  vs  $\phi$  are the same thing; some books will use  $\mathcal{E}$  whereas others will use  $\phi$ . The units of  $\mathcal{E}$  and  $\phi$  are volt (V), whereas those of  $dq$  are Coulomb (C). The total work is obtained by integrating  $\delta W$ . Note: the meaning of  $dq$  is clear if we write  $\rho(\mathbf{r})d^3\mathbf{r}$ , where  $\rho(\mathbf{r})$  is the charge density and  $d^3\mathbf{r}$  is a volume element centered on  $\mathbf{r}$ . Since

$\delta W$  is to be integrated, this integral is over all space:

$$\Delta W = \int \delta W = \int_{\Omega} \phi(\mathbf{r}) \underbrace{\rho(\mathbf{r}) d^3 \mathbf{r}}_{dq}.$$

where  $\Omega \in \mathbb{R}^3$  is a region of space. Suppose that a charge  $q$  is centered at the point  $\mathbf{r}_q$ . This means that  $\rho(\mathbf{r}) = q\delta(\mathbf{r} - \mathbf{r}_q)$ , where  $\delta$  is the Dirac delta function (see Section A.23). For the above-mentioned electrostatic charge distribution (Eq. 6.2), then:

$$\Delta W = \int_{\Omega} \phi(\mathbf{r}) q \delta(\mathbf{r} - \mathbf{r}_q) d^3 \mathbf{r} = \frac{q}{4\pi\epsilon_0} \sum_{i=1}^N \frac{q_i}{|\mathbf{r}_q - \mathbf{r}_i|}.$$

If the force depends on a single direction ( $x$ ), we may take:

$$\phi(x) = \frac{1}{4\pi\epsilon_0} \sum_{i=1}^N \frac{q_i}{|x - x_i|}, \quad E(x) = -\frac{d}{dx} \phi(x) = \frac{1}{4\pi\epsilon_0} \sum_{i=1}^N q_i \frac{x - x_i}{|x - x_i|^3},$$

$$\delta W = \phi(x) dq, \quad \Delta W = \frac{q}{4\pi\epsilon_0} \sum_{i=1}^N \frac{q_i}{|x_q - x_i|},$$

where  $|x - x_i| = \sqrt{(x - x_i)^2}$  and  $\frac{d}{dx} \frac{1}{|x - x_i|} = -\frac{(x - x_i)}{|x - x_i|^3}$ .

**6.4.4. Work Done by an Electric Field.** Suppose that we have an electric field  $\mathbf{E}$  and an object with an electric dipole moment  $\mathbf{p}$ . If this object is re-oriented in the presence of the electric field, work is required according to  $\delta W = \mathbf{E} \cdot d\mathbf{p}$ . The units of  $\mathbf{E}$  are V/m whereas those of  $\vec{p}$  are C·m, since a dipole  $\mathbf{p} = q\mathbf{d}$  consists of two point charges  $+q$  and  $-q$ , separated by a displacement vector  $\mathbf{d}$ . We recall from electrostatics that  $\mathbf{E} = -\nabla\phi$ , so you can see how these units also agree with the previous work  $\delta W = \phi dq$  (the units  $\nabla$  are  $\text{m}^{-1}$ ).

As an example, consider an *induced* dipole moment. Recall from Section 2.1.2 that  $\mathbf{p} = \epsilon_0 \alpha \mathbf{E}$  (where  $\epsilon_0$  was absorbed into the definition of  $\alpha$  when using the numbers from the table). In other words,  $\mathbf{p}$  is parallel to  $\mathbf{E}$  and is proportional to it. The infinitesimal work is then

$$\delta W = \mathbf{E} \cdot d\mathbf{p} = \alpha E dE = \alpha \frac{1}{2} dE^2.$$

Suppose we turn on the electric field (ramp it up from 0 to  $E$ ), the total work is then:

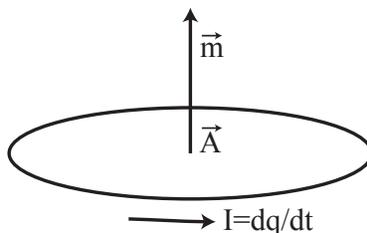
$$\Delta W = \int \delta W = \alpha \frac{1}{2} \int_0^{E^2} dE^2 = \frac{\alpha}{2} E^2.$$

Suppose we have argon, whose polarizability is 1.63 in units of  $1.11 \times 10^{-40} \text{ C}^2\text{m}^2/\text{J}$ , according to Table 2.5.

$$\Delta W = \frac{(1.63 \times 1.11 \times 10^{-40} \text{ C}^2\text{m}^2/\text{J}) E^2}{2}.$$

To get  $\Delta W = 1 \text{ J}$ , we need  $E = 1.05 \times 10^{20} \text{ V/m}$ . For  $\Delta W = 1 \text{ J}$ , we need  $E = 1.05 \times 10^{20} \text{ V/m}$ , which is enormous. Conversely, suppose we apply a laboratory-scale voltage, such as 100 V, across a distance of 1 cm, the term  $\delta W = \mathbf{E} \cdot d\mathbf{p}$  is so small (about  $\Delta W \approx 10^{-32} \text{ J}$ ) and its contribution does not matter compared to heats of reaction or even  $P - V$  work.

**6.4.5. Work Done by a Magnetic Field.** Suppose that we have a magnetic field  $\mathbf{B}$  and an object with a magnetic dipole moment  $\mathbf{m}$ . If this object is re-oriented in the presence of the magnetic field, work is required according to  $\delta W = \mathbf{B} \cdot d\mathbf{m}$ . The units of  $\mathbf{B}$  are Tesla (T) whereas those of  $\mathbf{m}$  are  $\text{J/T} = \text{A} \cdot \text{m}^2$  (Ampère-meter square), since a magnetic dipole  $\mathbf{m} = I\mathbf{A}$  can be described as a current  $I$  flowing around a loop whose area is  $A$  (area is a vector pointing normal to the surface). This is shown in Fig. 6.7.



**Figure 6.7.** Model for magnetic moment ( $\vec{m}$ ) as a current loop. The current,  $I$ , is the charge per unit time ( $dq/dt$ ). The loop has area  $A$ .  $\vec{A}$  is a vector pointing perpendicular to the loop surface area, in the direction given by the right-hand rule with respect to the current direction.

As in the previous section, we could illustrate the case of linear response (paramagnetism or diamagnetism), where the magnetization (magnetic moment per unit volume),  $\mathbf{M} = \mathbf{m}/V = (\chi/\mu_0)\mathbf{B}$ , where  $\chi$  is the magnetic susceptibility of the medium and  $\mu_0$  is the permeability of free space ( $\mu_0 = 1.257 \times 10^{-6} \text{ m.kg/s}^2/\text{A}^2$ ). We then get  $\delta W = \mathbf{B} \cdot d[(\chi/\mu_0)\mathbf{B}V] = V(\chi/\mu_0)\frac{1}{2}dB^2$ . Integration from  $B = 0$  to  $B = 1 \text{ T}$  gives  $\Delta W = (1/2)V(\chi/\mu_0) B^2$ . For water ( $\chi = -9 \times 10^{-6}$ ) in a 1 cc volume, we have  $\Delta W = -3.6 \times 10^{-6} \text{ J}$ , which is a small quantity. Note: this value of  $\delta W = \mathbf{B} \cdot d\mathbf{m}$  is larger than the value for  $\delta W = \mathbf{E} \cdot d\mathbf{p}$  calculated in the previous section. However, that's because we considered a 1 cc volume here instead of a single molecule, as was the case in the previous section. To do a fair comparison (over a 1 cc sample volume), suppose we had 1 cc of liquid argon, whose

density is 1.3954 g/cc, divided by its molar mass (39.9 g/mol), gives 0.035 mol/cc. In 1 cc of liquid argon polarized with a  $E=(100 \text{ V})/(1 \text{ cm})$  electric field,

$$\Delta W = (1 \text{ cc})(0.035 \text{ mol/cc})(6.022 \times 10^{23} \text{ mol}^{-1})(10^{-32} \text{ J}) = 2.11 \times 10^{-10} \text{ J}.$$

We conclude that energies associated with both electric and magnetic work are very small compared to enthalpies of reactions or  $P - V$  work (whose magnitudes are typically 1-1,000 J/mol).

Physically, magnetic moments in materials can arise from nuclear spins, unpaired electrons, or orbital moments. Let us write  $\boldsymbol{\mu}$  instead of  $\mathbf{m}$  to emphasize the atomic or molecular origin of the moment. Certain nuclei can have non-zero moments, depending on the configuration of its constituent protons and neutrons. For example, protons have spin  $I = 1/2$ ; hence, hydrogen nuclei have spin  $1/2$ . The spin angular momentum is  $\hbar\mathbf{I}$ , where  $|\mathbf{I}| = I$ . The corresponding magnetic moment is

$$\boldsymbol{\mu} = g\mu_N\mathbf{I},$$

where  $g$  is the proton  $g$ -factor ( $g = 5.5856947$ ),

$$\mu_N = \frac{e\hbar}{2m_p},$$

is the nuclear magneton.  $m_p$  is the mass of the proton,  $e$  is the elementary charge and  $\hbar$  is the Planck's constant divided by  $2\pi$  ( $\hbar = h/2\pi = 1.054 \times 10^{-34} \text{ J.s/rad}$ ). The numerical value of  $\boldsymbol{\mu}$  (for the proton) is:

$$\begin{aligned} \boldsymbol{\mu} = g\mu_N\mathbf{I} &= g\frac{e\hbar}{2m_p}\mathbf{I} = (5.585) \frac{(1.602 \times 10^{-19})(1.054 \times 10^{-34})}{2(1.672 \times 10^{-27})} \frac{1}{2} \\ &= 1.41 \times 10^{-26} \text{ A.m}^2 \end{aligned}$$

Note: since these formulas are in SI units, we do not need to explicitly work out or convert units as long as all the variables are stated in SI units, as was done here.

Let's calculate the work needed to bring this magnetic moment into a magnetic field of 1 T. The work is

$$\Delta W = \mathbf{B} \cdot \Delta\boldsymbol{\mu} = (1 \text{ T})(1.41 \times 10^{-26} \text{ A.m}^2) = 1.41 \times 10^{-26} \text{ J}.$$

Magnetic moments can come from electrons, in the form of spin or orbital angular momentum. The proton magnetic moment is  $1.521 \times 10^{-3}$  times that of the Bohr magneton. The Bohr magneton is a natural unit for expressing the magnetic moment of an electron:

$$\mu_B = \frac{e\hbar}{2m_e},$$

where  $m_e$  is the electron mass. Its numerical value is  $9.27401 \times 10^{-24}$  J/T. Electrons bound to atoms that occupy filled atomic or molecular orbitals pair up, according to the Pauli exclusion principle, as spin-up and spin-down ( $\uparrow\downarrow$ ), leaving zero net moment. However, unpaired electrons (spin-up or spin-down), have non-zero moment, leading to magnetic phenomena (paramagnetism, ferromagnetism, ferrimagnetism). An example is dioxygen, which is paramagnetic. The unpaired electrons in dioxygen are explained in terms of molecular orbital theory:

[https://en.wikipedia.org/wiki/Molecular\\_orbital\\_diagram#Dioxygen](https://en.wikipedia.org/wiki/Molecular_orbital_diagram#Dioxygen)

Non-zero orbital angular momentum of electrons gives rise to a magnetic moment:

$$\boldsymbol{\mu} = g\hbar \frac{(-e)}{2m_e} \mathbf{L} = -g\mu_B \mathbf{L},$$

where  $\hbar\mathbf{L}$  is the orbital angular momentum;  $|L| = \sqrt{l(l+1)}$ , where  $l = 0, 1, 2, \dots, n-1$  (corresponding to  $s, p, d, f, \dots$  orbitals).  $n$  is the principal quantum number. Electrons in  $s$  orbitals have  $L = 0$  and  $\mu = 0$ .

**6.4.6. Adding Molecules to a System.** It requires work to add a molecule to a system while keeping it at thermal equilibrium because at equilibrium the particle must have energy comparable to the average energy. Recall (see Section 1.3.3) that for a monatomic gas the average kinetic energy per molecule is related to temperature:

$$\frac{1}{2}mv^2 = \frac{3}{2}k_B T.$$

The new molecule or atom that we add must be imparted with this amount of energy otherwise the total energy (and consequently, the temperature  $T$ ) of the system will change. The energetic cost is given by the chemical potential:

$$\mu_i \approx \left( \frac{\Delta U}{\Delta N_i} \right)_{S,V,N_j \neq i}$$

where the subscript  $S, V, N_j \neq i$  indicates that other variables are being held constant. This definition holds in the limit of small  $\Delta N_i$ . For those familiar with partial derivatives (see Section A.5), the formal definition is:

$$\mu_i \equiv \left( \frac{\partial U}{\partial N_i} \right)_{S,V,N_j \neq i}.$$

$\mu_i$  is the energy required to add 1 particle to the system. You can think of it as the resistance to adding particles. The associated work is:

$$\delta W_i = \mu_i dN_i.$$

If there are  $N$  chemical species, the infinitesimal work is the sum:

$$\delta W = \sum_{i=1}^N \mu_i dN_i.$$

In chemistry, we normally work with molar quantities:

$$\mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S, V, n_j \neq i}, \quad \delta W = \sum_{i=1}^N \mu_i dn_i.$$

The units of  $\mu_i$  are the same (Joule) except that the amount of energy involved is that which involves adding a mole of substance to the system.

#### 6.4.7. The Infinitesimal Work Terms Follow a General Pattern.

We note that all types of works are of the form:

$$\delta W = (\text{intensive quantity}) \times d(\text{extensive quantity}).$$

In the above examples, our **intensive** and **extensive** quantities were:

Intensive variable	Corresp. Extensive variable	Type of work
$P$ (pressure)	$V$ (volume)	mechanical (e.g. $P - V$ ) work: when a system goes from high pressure $P_{ext}$ to lower pressure while changing its volume $V$ . The energy changes by $-P_{ext}dV$ .
$\phi$ (electrostatic potential) or $\mathcal{E}$ (electromotive force)	$q$ (electric charge)	electrical (e.g. electromotive force, emf): when a system goes from high emf $\mathcal{E}$ to low emf by transferring electric charges $q$ between the two electrodes. The energy changes by $\mathcal{E}.dq$ .
$\vec{E}$ (electric field)	$\vec{p}$ (electric dipole moment)	electrical polarization work: the force is defined by the surroundings' electric field strength and the "displacement" is change of the polarization of the medium (the sum of the electric dipole moments of the molecules).
$\vec{B}$ (magnetic field)	$\vec{m}$ (magnetic dipole moment)	magnetic work: here the force is defined by the surroundings' magnetic field strength and the "displacement" is the change of total magnetic dipole moment.
$mg$ (gravitational force)	$h$ (displacement)	gravitational work: the force is defined by the surroundings' gravitational field and the generalized displacement is change of the spatial distribution of the matter within the system. For example, the work involved when a point particle of mass $m$ is dropped from height $h_2$ to $h_1$ is $mg(h_2 - h_1)$ .
$kx$ (spring force)	$x$ (displacement)	(same as above)
$\mu$ (chemical potential)	$N$ (number of molecules) or $n$ (number of moles)	chemical: a system can go from high chemical potential $\mu_i$ to low potential by transferring particles $n_i$ . The energy change by $\mu_i dn_i$ .
$T$	$S$	thermal: a system equilibrates by going from high $T$ to low $T$ while transferring a quantity known as entropy $S$ . If $T$

		depends on position, heat will flow from regions of high $T$ to regions of low $T$ . The energy of the system changes by $TdS$ .
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## 6.5. Laws of Thermodynamics

**6.5.1. Classical thermodynamics describes systems close to equilibrium.** The laws of thermodynamics describe the behavior of systems which are in thermal equilibrium or approaching thermal equilibrium. *An equilibrium system is defined as one whose macroscopically observable properties do not change with time.*

Equilibrium implies the macroscopic properties are spatially homogeneous, i.e. there are no gradients (spatial derivatives) in the properties. For, if gradients were present, forces (fluxes) would be set into motion to restore the system to equilibrium conditions, eliminating the gradients.

Thermodynamics is capable of describing changes away from equilibrium, but only provided we are not too far from equilibrium. For example, it can predict the direction of a chemical reaction, heat flow or mass flux.

However, if the system is far from equilibrium, equilibrium thermodynamics will not predict its detailed behavior except to indicate the direction of change. What it does not do is provide information about the microscopic properties of the system. For that, we need *statistical mechanics*.

**6.5.2. The Four Classical Laws.** There are four classical laws of thermodynamics. The first and second laws introduce state functions,  $U$  and  $S$ . The zeroth law introduces the existence of temperature  $T$ , whereas the second law establishes the absolute temperature scale. The third law is statement regarding the properties of systems in equilibrium at absolute zero temperature.

<b>Zeroth Law</b> (Maxwell 1871, Carathéodory 1909)	If two systems are in thermal equilibrium with a third system, then they are in equilibrium with each other. In fact, there is a single system property (called temperature) that serves to indicate whether systems are in thermal equilibrium. Note: this law postulates the existence of a thermometer.
<b>First Law</b> (Hess 1841, Clausius & Rankine 1850)	There is a system property (i.e. state function) called energy, $U$ , that is conserved, but can take several different forms that can interconvert. Note: this law postulates the existence of a state function, $U$ .

<b>Second Law (Clausius 1854, Kelvin 1851, Carathéodory 1909, Carnot 1824)</b>	There is a system property (i.e. state function), $S$ , called entropy that, if the system is isolated from its environment, either increases or (in principle) remains constant during thermodynamic processes. Mathematically, $dS_{univ} \geq 0$ , where $S_{univ}$ is the entropy of the isolated system. Note: $S_{univ}$ can be taken to be the whole universe (system plus surroundings) because the universe is an isolated system. Note: this law postulates the existence of a state function, the entropy.
<b>Third Law (Nernst 1912)</b>	The entropy of a system is a universal constant (set to zero, for a perfect crystal) at the absolute zero of temperature. <sup>7</sup> Note: $S(T \rightarrow 0) = 0$ for a perfect crystal. The third law was first conjectured by Walther Nernst in 1912 and proved in 2017 by Lluís Masanes and Jonathan Oppenheim. <sup>8</sup>

## 6.6. Zeroth Law

The **Zeroth Law** of thermodynamics states that **thermal equilibrium is an equivalence relation**: *If  $A$  is in equilibrium with  $B$  and  $B$  is in equilibrium with  $C$  then  $A$  is in equilibrium with  $C$ .* What is an equivalence relation? A binary relation  $\sim$  on the set  $X = \{A, B, C, \dots\}$  is an *equivalence relation* if and only if it is reflexive, symmetric and transitive, i.e. for all  $A, B, C$  in  $X$ :

- $A \sim A$  (reflexivity)
- if  $A \sim B$  then  $B \sim A$  (symmetry)
- if  $A \sim B$  and  $B \sim C$  then  $A \sim C$  (transitivity)

Here,  $A \sim B$  denotes “ $A$  is in thermodynamic equilibrium with  $B$ ”.  $X$  denotes the set of all possible thermodynamical systems. In spite of its apparent simplicity, the zeroth law has the important consequence that it establishes any number of possible empirical temperature scales. Each thermodynamic system can be labeled with a temperature, similar to a real number system (systems with the same temperature are considered equivalent). The existence of an absolute temperature scale is then a consequence of the Second Law, which establishes the existence of the entropy. Other physical meanings of the zeroth law include: “All heat is of the same kind” (Maxwell) and “All diathermal walls are equivalent”.

<sup>7</sup>The entropy of degenerate systems tends to a nonzero value when  $T \rightarrow 0$ . This is why the Third Law is formulated in terms of “the entropy of a perfect crystal”. For perfect crystals, the ground state is non-degenerate.

<sup>8</sup>Masanes and Oppenheim, A general derivation and quantification of the third law of thermodynamics, *Nature Comm.* **8**, 14538 (2017) <https://www.nature.com/articles/ncomms14538>

## 6.7. First Law

The importance of *changes* is embedded in the statement of the First Law of thermodynamics,

**First Law of Thermodynamics** Statement 1: There is a system property (i.e. state function) called energy that is conserved, but can take several different forms that can interconvert.

Statement 2: For a system (open or closed), the change in internal energy is the sum of heat transfer and work done on the system:

$$dU = \delta Q + \delta W \quad \text{is an exact differential.}$$

For more information about exact differentials, see Section A.9.  $dU$  is the sum of “infinitesimal” heat transfer (from the surroundings to the system),  $\delta Q$ , and “infinitesimal” work done on the system  $\delta W$  by the surroundings. Here,  $q \equiv \Delta Q = \int \delta Q$  and  $w \equiv \Delta W = \int \delta W$ . Many textbooks write  $q$  for heat transfer. For an open system the work  $\delta W$  will contain a chemical term to describe the change in particle numbers. We shall see in Section 6.7.2 below that for an isolated system  $dU=0$ .

**6.7.1.  $U$  is a state function, meaning it is path independent.** If  $dU$  is an exact differential, its integral is independent of path,  $\Delta U = \int_i^f dU = U_f - U_i$  (according to the fundamental theorem of calculus), and only depends on the initial and final points. This is the definition of a state function. For more information about exact differentials, see Section A.9.

**First Law of Thermodynamics** (in integral form)

$$\Delta U = \Delta Q + \Delta W \quad \text{is independent of path.}$$

A function  $U$  which is independent of path is called a *state function* in the language of thermodynamics. This is because it only depends on the state of the system, not on the path taken to arrive at the final state.

Some textbooks (e.g. Oxtoby [1], p.529) use a slightly different notation ( $q \equiv \Delta Q$ ,  $w \equiv \Delta W$ ) which writes  $\Delta U = q + w$ . These definitions are equivalent. A state function implies that the change  $\Delta U$  can be written as the difference of final and initial states,  $U_f - U_i$ . Thus, internal energy is a state function. This is the same as saying that  $dU$  is an exact differential, which implies that  $\Delta U = \int_{U_i}^{U_f} dU = U_f - U_i$ . Obviously, this is independent of path (it only depends on initial and final states).

**6.7.2. First Law is a Statement on Conservation of Energy.** In this section we show that the First Law can be interpreted as a statement of

conservation of energy.

**Conservation of energy and energy transfer to the system or its surroundings.** In any process, the heat added to the system is removed from the surroundings ( $q = -q_{ext}$ ). The work done on the system is the work done by the surroundings ( $w = -w_{ext}$ ). Adding these two equations,

$$\begin{array}{r} q = -q_{ext} \\ + \quad w = -w_{ext} \\ \hline q + w = -(q_{ext} + w_{ext}), \end{array}$$

and invoking the first law ( $\Delta U = q + w$ ) on both sides gives:

$$\Delta U = -\Delta U_{ext} \quad \text{or} \quad \Delta U + \Delta U_{ext} = 0.$$

The total energy of the universe (system plus surroundings) is  $U_{univ} = U + U_{ext}$ . The change in  $U_{univ}$  is therefore always zero in any process:

$$\Delta U_{univ} = \Delta U + \Delta U_{ext} = 0.$$

Thus, energy is conserved (even in the presence of heat exchange and dissipation). It can only be *exchanged* between the system and its surroundings.

The statement  $\Delta U_{univ} = 0$  (“The energy of the universe is constant”) is another formulation of the First Law. In thermodynamics, the *universe* is another word for *isolated system*, this is equivalent to:

**The energy of an isolated system is constant. (1st Law)**

**6.7.3. Summary of First Law:**  $dU = \delta(\text{heat}) + \delta(\text{work})$ . The change in the internal energy for a *closed system*, by any process, is defined by the change in *external variables*:

$$dU = \delta Q + \delta W.$$

Since heat,  $Q$ , and work,  $W$ , are not state functions, many alternative paths can result in a given change  $dU$ .

As we will see in Section 6.8 below, there exists a state function  $S$  called entropy. For a reversible process, the heat transfer,  $\delta Q = TdS$ . Together with  $\delta W = -PdV$ ,  $dU$  can be expressed strictly in terms of internal variables:

$$dU = TdS - PdV,$$

where  $U$  is the internal energy of the system,  $T$  is the internal temperature (of the system),  $S$  is the system's entropy,  $P$  is the system's pressure and  $V$  is its volume. This follows from the definition of reversible process:  $P \approx P_{ext}$ ,  $T \approx T_{ext}$ . Here, the change in the internal energy is expressed in terms of state functions. The change in a state function is independent of the path and this last equation is valid, *regardless of which path the change in internal energy was brought about*. For a closed system,  $U$  is a function of  $S$  and  $V$ ; thus  $dU$  is a total *differential of internal variables*.

For an *open system*, the internal energy is, in addition, a function of the amount of matter, i.e.  $U$  is a function of  $S, V, \{n_i\}$ , where  $n_i$  is the amount (moles) of component  $i$ . The change in internal energy, expressed as the total differential of internal variables, will then be

$$dU(S, V, \{n_i\}) = TdS - PdV + \sum_i \mu_i dn_i,$$

where  $\mu_i$  denotes the chemical potential of component  $i$ :

$$\mu_i \approx \left( \frac{\Delta U}{\Delta n_i} \right)_{S, V, n_{j \neq i}} \quad \text{or} \quad \mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S, V, n_{j \neq i}}$$

The expression on the left is valid in the limit of small  $\Delta n_i$ . The summation is over all components. This latter expression for the differential  $dU$  contains only state functions.  $dU$  is a total differential of internal variables and the equation is generally valid for an open system. Chemical potentials have no absolute values; the value of  $U$  for an open system is at best given with respect to a reference state.

To summarize:

**FUNDAMENTAL EQUATION:** For a **closed system**, the First Law for a reversible process is:

$$dU(S, V) = TdS - PdV,$$

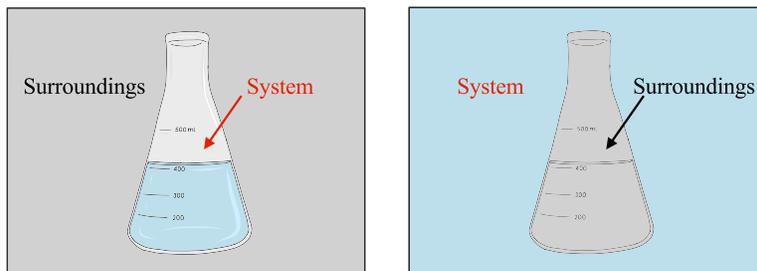
where  $U$  is the internal energy of the thermodynamic system. We note that  $T$  and  $P$  are internal variables, no external. For an **isolated system**, it is:

$$dU(S, V, \{n_i\}) = TdS - PdV + \sum_i \mu_i dn_i.$$

The summation runs over all chemical species present in our system. For example, if we have a two-component system (e.g. solvent and solute), there are two terms in this summation: one for the solvent and one for the solute.

**6.7.4. Choice of System vs Surroundings.** The differential  $dU$  used in the statement of the first law,  $dU = \delta(\text{heat}) + \delta(\text{work})$ , can refer to the system, its surroundings or the whole universe. It's up to us to decide

what we call the system and its surroundings. For example, when writing  $dU = \delta Q - P_{ext}dV$ , we could be referring to the circular region below, or its surroundings. See Fig. 6.8.



**Figure 6.8.** The universe is divided into a system and its surroundings. This division is largely arbitrary and a matter of convenience.

On the left, we have a system and its surroundings. The union of these two is the universe. On the right, we have the inverted situation: the system what used to be the surroundings, and the surroundings is what used to be the system. This inverted configuration is also possible. On the left,  $dU$  refers to the circular region,  $\delta Q$  is the heat transferred into it,  $dV$  refers to its volume change,  $P_{ext}$  refers to the external pressure acting on it from the surroundings. On the right,  $dU$  refers to the change in internal energy of the grey region,  $dV$  refers to the change in volume of the grey region and  $P_{ext}$  refers to the pressure exerted on the grey region by the colored region.

## 6.8. Second Law

If you take a cup of hot tea outside in cold weather, the tea will cool and heat will be transferred to the surroundings. Heat is transferred from the hot body (tea cup) to a cold body (surroundings). Energy is conserved: the heat lost by the cup is gained by its surroundings. Likewise, if heat were transferred to the cup from the surroundings, energy would be conserved as well. However, even though energy is conserved in both cases, the latter never happens: heat only flows from a hot body to a cold body, never the other way around. Thus, the First Law is not sufficient to describe thermodynamic processes. We need to introduce the idea of a *spontaneous* process, which is the subject of the Second Law. All spontaneous processes are irreversible. Most of the processes in nature are irreversible.

Natural processes are irreversible. They cannot be reversed without producing some change in the surroundings or in some other system. Examples of natural adiabatic processes are:

- Adiabatic transformation of work into internal energy of a system (Joule's experiment).

- Transfer of energy in the form of heat from a hotter to a colder body, both systems being enclosed in an adiabatic enclosure.
- Free expansion of a gas from one-half of an adiabatically enclosed system, to fill the entire system.
- Mixing of two dissimilar gases in an adiabatically enclosed system.
- Spontaneous phase change, or chemical reaction, occurring in an adiabatically isolated system.

These processes are irreversible: none of these processes taken in reverse violate the First Law. However, such reverse processes are never found in nature. Hence, the need for a state function that dictates the direction of natural processes.

There is an *extensive* thermodynamic state function called **entropy**,  $S$ , which can be used to indicate the direction in which systems may spontaneously evolve.  $S$  also dictates the maximum amount of work that can be obtained from a given chemical transformation or maximum efficiency for extracting work out of a heat engine.

To operate at maximum efficiency, a process must be fully *reversible*. Clausius defined change in entropy of a system<sup>9</sup>  $dS$  in terms of the quantity of heat  $\delta Q^{rev}$  that is *reversibly* added to the system at a given temperature  $T$ :

**Thermodynamic definition of entropy:** The infinitesimal change  $dS$  in entropy of a system  $S$  in terms of the quantity of heat  $\delta Q^{rev}$  that is *reversibly* added (to the system) at a given temperature  $T$ :

$$dS \equiv \frac{\delta Q^{rev}}{T}.$$

We comment on  $T$  in Remark 6.3 below. If heat  $\delta Q^{rev}$  is transferred from a reservoir (with temperature  $T_{ext}$ ) to a system, then the contribution to the entropy of the system is  $\delta Q^{rev}/T_{ext}$ . If a system dumps heat to another reservoir, then  $T$  refers to the temperature of that reservoir.

**Remark 6.1.** A process for which  $dS = 0$  is called *isentropic*. A process for which  $\delta Q = 0$  is called *adiabatic*. The two notions are equivalent when the process is reversible ( $\delta Q = \delta Q^{rev} = TdS$ ).

<sup>9</sup>In the definition of entropy,  $dS = \delta Q^{rev}/T$ , the  $1/T$  factor is an integrating factor. This integrating factor is analogous to integrating factors in the theory of differential equations, which are used to transform the differential equation into an exact differential equation. The reversible heat transfer,  $\delta Q^{rev}$ , by itself is not an exact differential. However, when multiplied by  $1/T$ , it is. Another way to say this is that while  $dS$  is exact differential, the product  $TdS$  is no longer exact. An example is the exact differential  $df = ydx + xdy$  (which we verified was exact using Euler's test). When multiplying by another function,  $df$  may no longer be exact. For example,  $w = ydf = y^2dx + xydy$  is no longer an exact differential even though  $df$  was exact.

**Remark 6.2.**  $S$  refers to the entropy of the system, not its surroundings.  $dS$  is a total differential which can be positive, zero or negative (since heat can be added or removed from the system).  $\delta Q^{rev}$  by itself is not an exact differential, but when multiplied by  $1/T$  it becomes exact. For more information about exact differentials, see Section A.9.

**Remark 6.3.**  $T$  is the **temperature at which the heat is supplied to the system**. Thus, to denote the temperature of the surroundings with our notation, we should write  $T_{ext}$ . Only when the source of heat is in thermal equilibrium with the system as a whole does it become the temperature of the system also (since  $T \approx T_{ext}$  for reversible process). When a system draws heat from a reservoir  $A$  and dumps heat into another reservoir  $B$ ,  $T_{ext}$  refers to  $T_A$  and  $T_B$ , which are the temperatures of reservoirs  $A$  and  $B$ , respectively.

**6.8.1. (System coupled to) HEAT BATH: Entropy of System vs Surroundings.** In thermodynamics, we often deal with a thermodynamic system coupled to a heat bath. The heat bath is much larger than the system. In the thermodynamic definition of entropy,  $dS = \delta Q^{rev}/T$ ,  $T$  is the temperature of the surroundings because the heat transferred to the system originates from the surroundings:

$$dS \equiv \frac{\delta Q^{rev}}{T_{ext}},$$

where  $T_{ext}$  is the temperature of the surroundings,  $S$  is the entropy of the system. Since the thermodynamic definition of the entropy invokes the notion of reversible heat transfer,  $T \approx T_{ext}$ .

The above discussion concerns the entropy of the system. What about the entropy change of the surroundings? Suppose that heat,  $\delta Q$ , is transferred to the surroundings. The surroundings, if much bigger than the system, is often called reservoir or heat bath. A reservoir has:

- Constant temperature ( $dT_{bath} = 0$ ),
- Constant volume ( $dV = 0$ ).

This means that

$$dU_{bath} = \delta Q_{bath} = T_{bath} dS_{bath}$$

since the  $PdV$  term is zero (constant volume). Since  $dU_{bath}$  is an exact differential, the total change in internal energy

$$\Delta U_{bath} = \int_i^f dU_{bath} = U_{bath,f} - U_{bath,i}$$

is independent of how the change is brought about and in particular, is *independent of whether the process is reversible or irreversible*. Our statements about  $dU_{bath}$  also apply to  $\delta Q_{bath}$ , to which it is equal. Therefore, we can

remove the constraint of reversibility:

$$dS_{bath} = \frac{\delta Q_{bath,rev}}{T_{bath}} = \frac{\delta Q_{bath}}{T_{bath}}.$$

Because the temperature of a bath is constant ( $dT_{bath} = 0$ ), we can integrate  $dS_{bath}$  while pulling  $T_{bath}$  outside the integral, leaving:

$$\Delta S_{bath} = \frac{\Delta Q_{bath}}{T_{bath}}.$$

This formula is important because it allows us to calculate the entropy change of the bath regardless of how the transfer takes place (reversibly vs irreversibly).

**Heat transfer from system to heat bath:** Suppose we have a chemical reaction taking place in a volume  $V$ . This is our system. 1.00 mol of  $\text{H}_2\text{O}(l)$  is formed from its elements under standard conditions at 298 K. The  $\Delta H$  of the reaction is -286 kJ/mol (reaction is exothermic). The energy released as heat is supplied to the surroundings, now regarded as being at constant pressure, so  $\delta Q_{bath} = +286$  kJ/mol. Therefore,

$$\Delta S_{bath} = \frac{2.86 \times 10^5 \text{ J}}{298 \text{ K}} = +960 \text{ J/K}.$$

This strongly exothermic reaction results in an increase in the entropy of the surroundings as energy is released as heat into them.

### 6.8.2. Total Entropy Change is the sum of Infinitesimal Changes.

Let  $S$  be the entropy of a system. To find the entropy change in the system, we need to find a reversible path and integrate or sum over the sequence of steps from initial to final state. (In practice, a reversible path is one that involves slow changes.) It will yield a state function which depends on initial and final point:

$$\Delta S = \int_i^f dS = S_f - S_i = \int_i^f \frac{\delta Q^{rev}}{T_{ext}} = \int_i^f \frac{\delta Q^{rev}}{T},$$

where in the last step, we have invoked the property  $T \approx T_{ext}$  of reversible processes.

The problem is further simplified if the process is *isothermal*, in which case temperature is a constant and can be taken out of the integral:

$$\Delta S = \frac{1}{T} \int_i^f \delta Q^{rev} \equiv \frac{\Delta Q^{rev}}{T}, \text{ where } \Delta Q^{rev} \equiv \int_i^f \delta Q^{rev}.$$

The total entropy is  $S_{univ} = S + S_{ext}$ . Its change is:

$$dS_{univ} = \underbrace{dS}_{\substack{\text{entropy change} \\ \text{in system}}} + \underbrace{dS_{ext}}_{\substack{\text{entropy change} \\ \text{in surroundings}}}.$$

The second law states that the total entropy change (of the universe) must be nonnegative:

**Second Law of Thermodynamics (Clausius inequality):**

The entropy of the universe is a nondecreasing function of time:

$$dS_{univ} = d(S + S_{ext}) = dS + dS_{ext} \geq 0.$$

Moreover,  $dS_{univ}$  is an exact differential. The entropy of the universe is

$$S_{univ} = S + S_{ext}.$$

The equality holds at thermal equilibrium when processes become reversible, in which case,  $dS = \delta Q^{rev}/T$ . This statement applies to an isolated system (“the entropy of an isolated system is nondecreasing”), not only the universe. The universe, of course, is an isolated system. We often use the terms “universe” and “isolated” (system) interchangeably.

**6.8.3. Internal vs External Entropy Change.** The entropy is an extensive property and the entropy of a system is the sum of the entropies of its parts. It is convenient to split  $dS$  into two contributions:

$$dS = d_e S + d_i S,$$

where  $dS$  is the increase of the entropy of the system,  $d_e S$  is the part of this increase due to interaction with the surroundings and  $d_i S$  denotes the part of this increase due to changes taking place inside the system.

The entropy increase  $d_e S$  due to interaction with the surroundings is related to the heat  $\delta Q$  absorbed by the system from its surroundings by

$$d_e S = \frac{\delta Q}{T_{ext}}$$

where  $T_{ext}$  is a positive quantity called the absolute temperature (of the bath).  $T_{ext}$  is the temperature at which the heat is supplied to the system: if the heat flows from the heat bath to the system, this is the temperature of the heat bath. Only when the source of heat is in thermal equilibrium with the system as a whole does it become the temperature of the system also.

The entropy increase  $d_i S$  due to changes taking place inside the system is positive for all natural changes (spontaneous and/or irreversible processes), is zero for all reversible changes and is never negative:

$$d_i S > 0 \quad (\text{spontaneous change})$$

$$d_i S = 0 \quad (\text{reversible change})$$

Thus, we get  $dS \geq \delta Q/T$ . This is another version of the **Second Law** of thermodynamics. For spontaneous changes:

$$dS > \frac{\delta Q}{T}$$

For reversible changes:

$$dS = \frac{\delta Q}{T}.$$

Note:  $S$  here is the entropy of a system, not the universe.

**6.8.4. Multi-Part Systems.** Systems consisting of multiple subsystems can be analyzed using the First and Second Laws as follows. The First Law is applied to each subsystem. The Second Law is then applied to the overall isolated system (all subsystems plus any surroundings, if applicable). This is illustrated in the example below for the case of two subsystems.

**System Consisting of Two Parts:** Consider a thermally insulated system consisting of two parts,  $A$  and  $B$  at uniform temperatures  $T_A$  and  $T_B$ , respectively. The volumes of subsystems  $A$  and  $B$  are fixed. The entropy  $S$  of the whole system is equal to the sum of  $S_A$  the entropy of  $A$  and  $S_B$  the entropy of  $B$ :

$$S = S_A + S_B.$$

Consider now the flow of an infinitesimal positive quantity  $\delta Q$  of heat from  $A$  to  $B$ . There are no chemical reactions and no internal entropy changes here ( $d_i S = 0$ ). Then, the reversible change can be expressed as:

$$d_e S_A = -\frac{\delta Q}{T_A}, \quad d_e S_B = \frac{\delta Q}{T_B}.$$

The increase in the entropy of the whole system due to this flow of heat is therefore

$$(6.3) \quad d_e S_A + d_e S_B = -\frac{\delta Q}{T_A} + \frac{\delta Q}{T_B} = \delta Q \left( \frac{1}{T_B} - \frac{1}{T_A} \right).$$

For a natural process, if positive heat  $\delta Q$  flows from  $A$  to  $B$ , this expression should be positive. This will be the case if

$$T_A > T_B.$$

Heat flows naturally from a higher to a lower absolute temperature.

**Remark 6.4.** If each of the phases  $A$  and  $B$  is in internal equilibrium then there are no changes in entropy other than that due to the flow of heat from  $A$  to  $B$ . If on the other hand, either phase, or both, is not in internal equilibrium there may be other entropy changes  $d_i S_A$  or  $d_i S_B$  in addition to the heat flow. These additional contributions can only be positive, so that the increase in entropy of the whole system will then be greater than

the expression (6.3). If  $T_A = T_B$  (zero temperature gradient), there is no entropy increase associated with heat flow, implying that the heat flow at thermal equilibrium is reversible.

**Remark 6.5.** The relations

$$d_e S_A = -\frac{\delta Q}{T_A}, \quad d_e S_B = \frac{\delta Q}{T_B},$$

follow from the fact that when the volumes are fixed ( $dV = 0$  and  $\delta W = 0$ ), the fundamental equation reads  $dU_A = \delta Q_A = T_A dS_A$  and  $dU_B = \delta Q_B = T_B dS_B$  for subsystems  $A$  and  $B$ , respectively. (Write the fundamental relation separately for  $A$  and  $B$ , and we get the above relations for  $d_e S_A$  and  $d_e S_B$ .)

**6.8.5. Clausius Inequality.** Heat added to the surroundings is opposite in sign to the heat added to the system

$$\delta Q_{ext}^{rev} = -\delta Q^{rev}.$$

For a reversible process,  $T \approx T_{ext}$ ,  $dS = \delta Q^{rev}/T$ ,

$$dS_{univ} = dS + dS_{ext} = \frac{\delta Q^{rev}}{T} + \frac{\delta Q_{ext}^{rev}}{T_{ext}} \approx \frac{\delta Q^{rev}}{T} - \frac{\delta Q^{rev}}{T} = 0.$$

This is the case  $dS_{univ} = 0$  (reversible process).

The remaining case is  $dS_{univ} > 0$  (irreversible process). First we note that the work done reversibly is always greater than the work done irreversibly, i.e.  $|\delta W^{rev}| \geq |\delta W|$ . This was shown in Section 6.3.11. Since  $\delta W$  and  $\delta W^{rev}$  are negative when energy leaves the system as work, this expression is the same as  $-\delta W^{rev} \geq -\delta W$ , and hence  $\delta W - \delta W^{rev} \geq 0$ . Because the internal energy is a state function, its change is the same for irreversible and reversible paths between the same two states, so we can also write:

$$dU = \delta Q + \delta W = \delta Q^{rev} + \delta W^{rev}.$$

It follows that

$$\delta Q^{rev} - \delta Q = \delta W - \delta W^{rev} \geq 0,$$

or

$$\delta Q^{rev} \geq \delta Q,$$

and therefore that

$$\frac{\delta Q^{rev}}{T} \geq \frac{\delta Q}{T}.$$

Using the thermodynamic definition of entropy ( $dS = \delta Q^{rev}/T$ ), we get the Clausius inequality:

$$dS \geq \frac{\delta Q}{T}.$$

Often we call the following expression the Clausius inequality:

$$\delta Q^{rev} \geq \delta Q.$$

In either case,  $\delta Q$  is the amount of heat absorbed by the system from its surroundings (in a process that can be irreversible), whereas  $\delta Q^{rev}$  is the heat added to the system in a reversible process. The equality holds in the reversible case.

**Remark 6.6.** There are many different formulations of the Clausius inequality. See, for example:

<http://www.eoht.info/page/Clausius+inequality>

Consider the transfer of energy as heat from one system (the hot source) at a temperature  $T_h$  to another system (cooler reservoir) at temperature  $T_c$ . This is illustrated in Fig. 6.9. When  $|\delta Q|$  leaves the hot source (so  $\delta Q_h < 0$ ), the Clausius inequality implies that  $dS \geq \delta Q_h/T_h$ . When  $|\delta Q|$  enters the cold sink, the Clausius inequality implies that  $dS \geq \delta Q_c/T_c$  (with  $\delta Q_c > 0$ ). Therefore, since  $S = S_{hot} + S_{cold}$  we have:

$$dS = d(S_{hot} + S_{cold}) = dS_{hot} + dS_{cold} \geq \frac{\delta Q_h}{T_h} + \frac{\delta Q_c}{T_c}$$

However,  $\delta Q_h = -\delta Q_c$ , so

$$(6.4) \quad dS \geq -\frac{\delta Q_c}{T_h} + \frac{\delta Q_c}{T_c} = \left( \frac{1}{T_c} - \frac{1}{T_h} \right) \delta Q_c$$

which is positive (because  $\delta Q_c > 0$  and  $T_h > T_c$ ). Hence, cooling (transfer of heat from hot to cold) is spontaneous. When you read Chapter 8, compare Eq. (6.4) to the first term in (8.6), the equation of entropy balance.

**6.8.6. Uncompensated Heat of Clausius.** We have seen in Section 6.8.3 that it is convenient to decomposed entropy change into a sum of two terms:

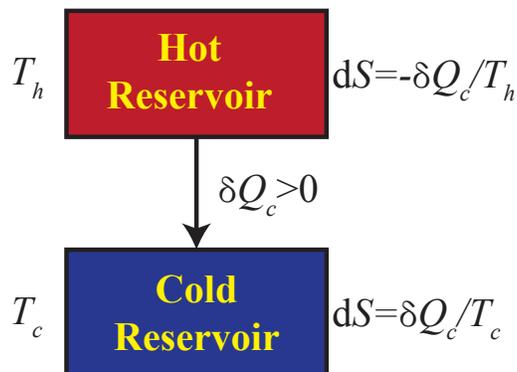
$$dS = d_e S + d_i S.$$

The term  $d_e S$ , also called the “entropy flow”, describes the entropy change due to exchange of matter and energy with the exterior. This quantity can be positive or negative. The term  $d_i S$  describes irreversible increases in entropy due to chemical reactions.

It is also convenient to distinguish the change in number of moles  $dn_k$  as the sum of two terms:

$$dn_k = d_i n_k + d_e n_k,$$

where  $d_i n_k$  is the change due to irreversible chemical reactions and  $d_e n_k$  is the change due to exchange of matter with the exterior.



**Figure 6.9.** Energy leaves the hot reservoir, decreasing its entropy. When the same quantity of energy enters the cool reservoir, the entropy increases by a larger amount. Overall, entropy increases and the process is spontaneous.

The Fundamental equation (also known as the “Gibbs equation”),

$$dU = TdS - PdV + \sum_k^N \mu_k dn_k,$$

describes *reversible* exchange of heat and matter. Because this corresponds to  $d_e S$ , we may use

$$d_e S = \frac{dU + PdV}{T} + (d_e S)_{matter} \quad \text{and} \quad d_i S \geq 0,$$

where  $(d_e S)_{matter}$  is the entropy change due to matter flow. We can then write

$$d_e S = \frac{dU + PdV}{T} - \frac{\sum_k^N \mu_k d_e n_k}{T}.$$

$d_e S$  can be positive or negative. If the change in number of moles  $dn_k$  were due to irreversible chemical reactions, then the resulting entropy production  $d_i S$  could be written as

$$d_i S = -\frac{\sum_k^N \mu_k d_i n_k}{T} > 0,$$

which is **always positive**. This is the “uncompensated heat” of Clausius for chemical reactions. Chemical reactions occur in such a way that  $d_i S$  is always positive in accordance with the Second Law.

**6.8.7. Clausius Theorem.** For a general irreversible process, the change in entropy of the system is:

$$\Delta S = \int_A^B dS = S_B - S_A = \int_A^B \underbrace{\frac{\delta Q^{rev}}{T}}_{dS \equiv \frac{\delta Q^{rev}}{T}} \geq \int_A^B \frac{\delta Q}{T}.$$

For any cyclic process (process which begins and ends at the same state)

$$S_B - S_A = 0$$

so that

$$\int_A^B \frac{\delta Q^{rev}}{T} \equiv \oint \frac{\delta Q^{rev}}{T} = 0.$$

Therefore,

$$\boxed{\oint \frac{\delta Q}{T} \leq 0.} \quad \text{Clausius' theorem (1854)}$$

The symbol  $\oint$  denotes that the process is carried out along a path that is cyclic (end point = start point).

The integral  $\oint \frac{\delta Q}{T}$  normally describes a system coupled to a large number of heat baths at carefully chosen temperature  $T_i$  ( $i = 1, 2, 3, \dots$ ):

$$\boxed{\oint \frac{\delta Q}{T} \approx \sum_{i=1}^N \frac{\delta Q_i}{T_i} \quad (= 0 \text{ if reversible})}$$

where  $N$  is the number of heat baths. For a reversible process, this summation equals zero. The integral is carried out along a full cycle. In the summation, the elementary isothermal processes are chosen to match the path of the arbitrary cycle as closely as possible. This equation makes no reference to the temperature of the system. It only describes the entropy changes due to heat transferred to/from the multiple heat baths.

To learn about the Carnot engine, see, e.g., Oxtoby [1], Section 13.4, “Carnot cycles, efficiency and entropy”.

**6.8.8. Applications of the Clausius Theorem.** REVERSIBLE PROCESS, PATH INDEPENDENCE. Let us start with a reversible process. Referring to the  $P - V$  diagram of Fig. 6.6, the integral  $\oint \delta Q/T$  along a closed path going from 1 to 2 (along path 1), then from 2 to 1 (along path 2) is:

$$\oint \frac{\delta Q}{T} = \int_{1, \text{ path 1}}^2 \frac{\delta Q}{T} + \int_{2, \text{ path 2}}^1 \frac{\delta Q}{T} = 0.$$

Since  $\int_1^2 \omega = -\int_2^1 \omega$  (along any path), the last equation reads:

$$\int_{1, \text{ path 1}}^2 \frac{\delta Q}{T} = \int_{1, \text{ path 2}}^2 \frac{\delta Q}{T}.$$

This tells us that the integral of  $\delta Q/T$  from state 1 to state 2 is independent of path. It depends only on the points 1 and 2.

**IRREVERSIBLE CYCLE.** In a less efficient (irreversible) cycle, a small fraction of  $\Delta Q_H$  (heat absorbed from a hot reservoir) is converted into work. This means the amount of heat delivered to the cold reservoir by an irreversible cycle,  $\Delta Q_L^{irr}$ , is greater than<sup>10</sup>  $\Delta Q_2$ . We therefore have

$$\frac{\Delta Q_1}{T_1} - \frac{\Delta Q_2^{irr}}{T_2} < 0.$$

Since the cycle engine returns to its initial state, whether it is reversible or irreversible, there is no change in its entropy. On the other hand, since heat transferred to the reservoirs and the irreversible engine have opposite sign, the *total change of entropy of the reservoirs is*

$$(6.5) \quad \frac{(-\Delta Q_1)}{T_1} - \frac{(-\Delta Q_2^{irr})}{T_2} > 0$$

if the reservoir temperatures can be assumed to be the same as the temperatures at which the engine operates. In fact, for heat to flow at a finite rate, the reservoir temperatures  $T'_1$  and  $T'_2$  must be such that  $T'_1 > T_1$  and  $T'_2 < T_2$ . In this case, the increase in entropy is even larger than (6.5).

**GENERALIZATION TO SYSTEM OR EXTERIOR.** We can generalize these identities for a system that goes through an arbitrary cycle, with the equalities holding for a reversible process, we have

$$\oint \frac{\delta Q}{T} \leq 0. \quad (\text{system})$$

For the “exterior” with which the system exchanges heat, since  $\delta Q$  has the opposite sign, we have

$$\oint \frac{\delta Q}{T} \geq 0. \quad (\text{exterior})$$

At the end of the cycle, be it reversible or irreversible, there is no change in the system’s entropy because it has returned to its original state. For irreversible cycles it means that the system expels more heat to the exterior. This is generally a conversion of mechanical energy into heat through irreversible processes. Consequently, the entropy of the exterior increases.

<sup>10</sup>Recall that the Clausius inequality,  $\delta Q^{rev} \geq \delta Q$ , where  $\delta Q$  is the amount of heat absorbed by the system from its surroundings (in a process that can be irreversible), whereas  $\delta Q^{rev}$  is the heat added to the system in a reversible process. On the other hand, if those quantities are negative, the sign changes:  $\delta Q^{rev} \leq \delta Q$ . Here,  $\delta Q$  is the heat delivered to the cold reservoir in an irreversible process.

This may be summarized as follows:

$$\begin{aligned} \text{Reversible cycle:} \quad dS &= \frac{\delta Q}{T} \oint dS = \oint \frac{\delta Q}{T} = 0 \\ \text{Irreversible cycle:} \quad dS &> \frac{\delta Q}{T} \oint dS = 0, \quad \oint \frac{\delta Q}{T} \leq 0. \end{aligned}$$

This statement can be made more precise by expressing the entropy change  $dS$  as a sum of two parts:

$$dS = d_e S + d_i S.$$

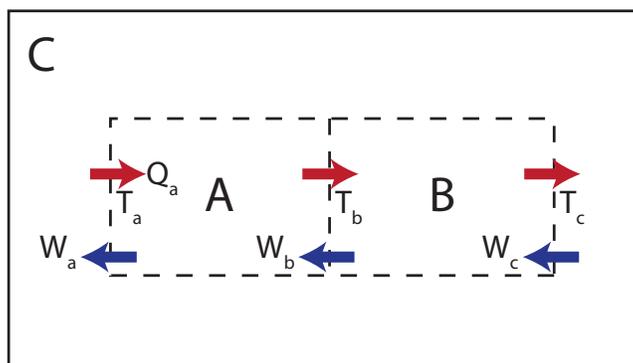
Here  $d_e S$  is the change of the system's entropy due to exchange of energy and matter and  $d_i S$  is the change in entropy due to irreversible processes within the system. For a closed system that does not exchange matter,  $d_e S = \delta Q/T$ . The quantity  $d_e S$  could be positive or negative, but  $d_i S$  can only be non-negative. In a cyclic process that returns the system to its initial state, since the net change in entropy must be zero, we have

$$\oint dS = \oint d_e S + \oint d_i S = 0.$$

Since  $d_i S \geq 0$ , we must have  $\oint d_e S \leq 0$ . For a closed system, we obtain the previous result:

$$\oint d_e S = \oint \frac{\delta Q}{T} \leq 0.$$

This means that, for the system to return to its initial state, the entropy  $\oint d_i S$  generated by the irreversible processes within the system has to be discarded through the expulsion of heat to the reservoir. There is no real system in nature that can go through a cycle of operations and return to its initial state without increasing the entropy of the exterior, or more generally, the universe. The increase in entropy distinguishes the future from the past.



**Figure 6.10.** Here, we partition the universe into 3 subsystems: A, B and C. C can be thought of as the surroundings. Heat and work is exchanged between  $A \leftrightarrow B$ ,  $B \leftrightarrow C$  and  $A \leftrightarrow C$ .

SETTING UP THE PROBLEM. When solving problems in thermodynamics, it is important to properly setup the equations. Those equations are the First and Second Laws, which need to be satisfied at all times we have thermal equilibrium. Let's take the universe and partition it into 3 different subsystems: A, B and C (Fig. 6.10). Let us simplify the notation here and write  $W_a$  for  $\Delta W_a$ ,  $Q_a$  for  $\Delta Q_a$ , etc. The system as a whole (A+B+C) is isolated ("universe"). However, heat and work can exchange between the subsystems. The internal energy of each subsystem changes as follows:

$$\Delta U_A \equiv (U_2 - U_1)_A = Q_a - W_a - Q_b + W_b$$

$$\Delta U_B \equiv (U_2 - U_1)_B = Q_b - W_b - Q_c + W_c$$

$$\Delta U_C \equiv (U_2 - U_1)_C = Q_c + W_a - Q_a - W_c$$

We can check that the First Law is fulfilled (energy of the universe is conserved):

$$\begin{aligned} \Delta U &= \Delta U_A + \Delta U_B + \Delta U_C = (U_2 - U_1)_A + (U_2 - U_1)_B + (U_2 - U_1)_C \\ &= Q_a - W_a - Q_b + W_b + Q_b - W_b - Q_c + W_c + Q_c + W_a - Q_a - W_c \\ &= 0. \end{aligned}$$

The Second Law should also be verified. First we write down the entropy change of each subsystems, applying the Clausius theorem to each subsystem. We must compute integrals of the form:

$$\int \frac{\delta Q_a}{T_a}, \text{ etc.}$$

However, if the heat transfer and temperature are constant during transfer, these types of integrals can be written as:  $\int \frac{\delta Q_a}{T_a} = (1/T_a) \int \delta Q_a \equiv \frac{\Delta Q_a}{T_a}$ , or in our abbreviated notation,  $\frac{Q_a}{T_a}$ , etc., where  $Q_a$  stands for  $\int \delta Q_a$ , the total heat transfer to subsystem A from C during a given step. In that case, we have:

$$\begin{aligned} \Delta S_A &\equiv (S_2 - S_1)_A \geq \frac{Q_a}{T_a} - \frac{Q_b}{T_b} \\ \Delta S_B &\equiv (S_2 - S_1)_B \geq \frac{Q_b}{T_b} - \frac{Q_c}{T_c} \\ \Delta S_C &\equiv (S_2 - S_1)_C \geq \frac{Q_c}{T_c} - \frac{Q_a}{T_a}. \end{aligned}$$

The inequality reminds us that the equal sign holds for reversible process, and in other cases the process is irreversible. Combining these (entropy is

additive) to get the entropy of the universe:

$$\begin{aligned}\Delta S &= \Delta S_A + \Delta S_B + \Delta S_C = (S_2 - S_1)_A + (S_2 - S_1)_B + (S_2 - S_1)_C \\ &\geq \frac{Q_a}{T_a} - \frac{Q_b}{T_b} + \frac{Q_b}{T_b} - \frac{Q_c}{T_c} + \frac{Q_c}{T_c} - \frac{Q_a}{T_a} = 0,\end{aligned}$$

since all the heat transfer terms cancel. Thus, we verified that  $\Delta S \geq 0$ , the Second Law is satisfied.

**6.8.9. Isentropic vs Adiabatic Process.** From the thermodynamic definition of entropy  $dS \equiv \frac{\delta Q^{rev}}{T}$ , we have that the heat transferred to the system in a reversible process is  $\delta Q^{rev} = TdS$ . A process for which  $dS = 0$  is called *isentropic*. A process for which  $\delta Q = 0$  is called *adiabatic*. The two notions are equivalent when the process is reversible ( $\delta Q = \delta Q^{rev} = TdS$ ).

**6.8.10. Reversible Process, Fundamental Equation of Thermodynamics.** For a reversible process the heat transferred is  $\delta Q^{rev} \equiv TdS$ . The infinitesimal change in energy is then

$$dU = TdS - PdV + \sum_i \mu_i dN_i$$

This equation is so important that it is called the *fundamental equation of thermodynamics*. It is valid for a reversible process. For the case of  $P - V$  work only,

$$dU \approx \left(\frac{\Delta U}{\Delta S}\right)_V dS + \left(\frac{\Delta U}{\Delta V}\right)_S dV$$

or, in the language of calculus,

$$dU \equiv \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV = TdS - PdV.$$

The differential element  $dU$ , and the two terms  $[(\cdot)dS$  and  $(\cdot)dV]$  giving rise to this infinitesimal change are plotted in Fig. 6.11. The last equation implies that:

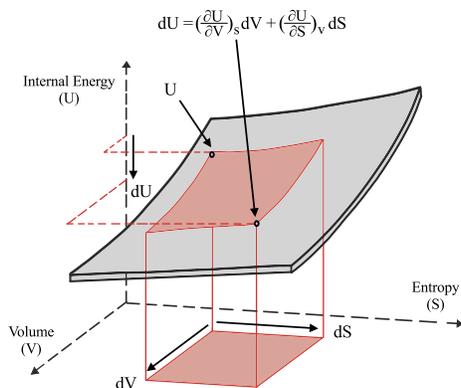
$$T = \left(\frac{\Delta U}{\Delta S}\right)_V, \quad P = -\left(\frac{\Delta U}{\Delta V}\right)_S,$$

in the limit of small  $\Delta S$  and  $\Delta V$ , respectively. Or,

$$T = \left(\frac{\partial U}{\partial S}\right)_V, \quad P = -\left(\frac{\partial U}{\partial V}\right)_S.$$

**6.8.11. Inequality for First Law, Irreversible Process.** For a general process we have  $\delta Q \leq TdS$ , according to the Clausius inequality

$$\delta Q^{rev} \geq \delta Q.$$



**Figure 6.11.** An overall change in  $U$ , which is denoted  $dU$ , arises when both  $V$  and  $S$  are allowed to change. If second-order infinitesimals are ignored, the overall change is the sum of changes for each variable separately.

Therefore, the Clausius inequality implies that

$$\boxed{dU \leq TdS - PdV + \sum_i \mu_i dN_i.} \quad (\text{First Law})$$

On the left hand side,  $dU$  refers to a general (not necessarily reversible) process. This inequality is true for a general process.

Note: we have not changed the First Law, which is still “ $dU = \delta Q + \delta W$  is an exact differential”. All we have done is express  $dU$  as an inequality because  $\delta Q \leq \delta Q^{rev} = TdS$ .

The equality  $\delta Q^{rev} = TdS$ , of course, follows from the thermodynamic *definition* of entropy  $dS = \delta Q^{rev}/T$ .

**6.8.12. Proof of Second Law.** A proof of the Second Law can be found in the articles [22, 23]. By examining the second law in the context of a finite system evolving over a short time period, the authors show from first principles that random fluctuations in the behavior of a non-equilibrium system can appear to violate the second law of thermodynamics over isolated periods of time, and that these local violations become more probable exponentially as we decrease either the size of the system or the time over which we measure the entropy. The mathematical form of this result is known as the fluctuation theorem. Remarkable, at the same time that the fluctuation theorem shows that the total entropy can decrease over very short periods of time in small systems, it also shows that in the limit of long times and

macroscopic systems the entropy must increase, providing a mathematical proof of the second law.

### 6.9. Third Law

The entropy,  $S(T)$ , is a function of temperature. According to the **Third Law** of thermodynamics (Nernst), the absolute entropy of a perfect crystal exists and the crystal's entropy equals zero at absolute zero:

$$\lim_{T \rightarrow 0} S(T) = 0.$$

Combining  $dS = \frac{\delta Q}{T}$ , with  $\delta Q = C_V dT$  (heating at constant volume),

$$S(T) = S_0 + \int_0^T \frac{C_V(T)}{T} dT.$$

$S_0$  is the entropy at absolute zero. An analogous formula exists at constant pressure:

$$S(T) = S_0 + \int_0^T \frac{C_P(T)}{T} dT.$$

Note that since the heat capacity is always positive, the entropy increases with increasing temperature.

If  $S_0$  is known, the absolute entropy  $S(T)$  can be obtained at any temperature  $T$  through measurements of the heat capacity versus temperature from 0 up to  $T$ .

Invoking the third law,  $S_0 = 0$ , and

$$S(T) = \int_0^T \frac{C_V(T)}{T} dT.$$

The heat capacity must be zero at zero temperature for this integral not to yield an infinite absolute entropy, which would violate the Third Law. The Debye theory of heat capacity gives the correct limit as absolute zero temperature is approached. For more information, see:

[https://en.wikipedia.org/wiki/Debye\\_model](https://en.wikipedia.org/wiki/Debye_model)

<http://vallance.chem.ox.ac.uk/pdfs/EinsteinDebye.pdf>

**6.9.1. Plausibility of the Third Law.** The plausibility of the Third Law can be appreciated from the Boltzmann entropy:<sup>11</sup>

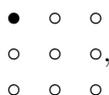
$$S = k_B \log \Omega,$$

where  $\Omega$  is the number of microstates (system configurations or degeneracy) consistent with a given total energy of the system. As an example, take a pure solvent frozen into a crystal. We are interested in the *ground state of the system* (the crystalline state). Its structure may look like this:

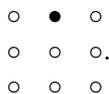


Here,  $\Omega = 1$  because there is only 1 such configuration. Any rearrangement of the solvent molecule correspond to the same configuration, as the molecules are indistinguishable from each other. Therefore, for a pure crystal (no solvent),  $\Omega = 1$  and  $S = 0$ , because at  $T = 0$  K (ground state) the system is in its unique ground state configuration. Although this is not a rigorous proof, it provides a kind of verification for the Third Law.

Recall that the Third Law is a statement about perfect crystals. An example where the Third Law is not applicable as stated above is a non-perfect crystal: replace a solute particle by 1 solvent particle. A configuration may look like:



or



<sup>11</sup>(Optional) A related concept is the Gibbs-Shannon entropy,

$$S = -k_B \sum_i p_i \log p_i.$$

Consider the case where there is only 1 possible configuration for the ground state. The index  $i$  labels all possible configurations in some parameter space. This situation corresponds to  $p_0 = 1$  (where 0 denotes the ground state, i.e. the only allowed configuration) and  $p_{i \neq 0} = 0$  (other configurations are not allowed). But this implies that  $S = 0$ . Even if the ground state is degenerate, their probability would be  $p_i = 1/N$  for each of these eigenstates of the ground state. Then,  $S = -k_B \sum_{i=1}^N \frac{1}{N} \log \frac{1}{N} = k_B \log N$ , where  $N$  denotes the number of states (not the number of particles). Suppose that the degeneracy is as large as Avogadro's number ( $6 \times 10^{23}$ ),  $k_B = 1.38 \times 10^{-23}$ , so  $S = (1.38 \times 10^{-23}) \log(6 \times 10^{23}) \approx (1.38 \times 10^{-23}) \cdot 55 \approx 10^{-21}$  J/K, which is vanishingly small (well below a measurable value of  $S$ ). Note: The Third Law is formulated in terms of "the entropy of a perfect crystal". This is because in a perfect crystal the ground state is unique and non-degenerate. When the ground state is degenerate, the entropy tends to a nonzero value when  $T \rightarrow 0$ .

In fact, there are  $N$  such possible configurations that correspond to the same total energy, where  $N$  is the number of lattice sites (allowed coordinates). If 3 solvent particles are replaced by 3 solute particles, there will be  $\binom{N}{3}$  such configurations and the degeneracy is  $\Omega = \binom{N}{3}$ . In general, the degeneracy is  $\Omega = \binom{N}{n}$ , where  $n$  is the number of solute particles replacing  $n$  solvent particles.

**6.9.2. Absolute Zero.** The third law is equivalent to the statement that “It is impossible by any procedure, no matter how idealized, to reduce the temperature of any system to zero temperature in a finite number of finite operations” (Guggenheim, 1967).

**6.9.3. Proof of Third Law.** A proof of the Third Law can be found in [24].

## 6.10. Thermodynamic Potentials

In classical thermodynamics, we often use thermodynamics potentials, such as  $U$ ,  $H$ ,  $A$  and  $G$ , depending on the experimental situation. They are all energies, and serve the same purpose of calculating *changes* in the energy of the system. Except that which one we should use depends on the experimental conditions.  $U$  depends on  $S, V, \{N_i\}$ . This may not be a convenient representation to use in many situations, because it may be difficult to keep  $S$  and  $V$  constant. It may be easier, for example, to keep  $T$  and  $P$  constant instead, as is the case for many chemistry experiments. In which case, we prefer to use  $G$ , the Gibbs free energy.

**6.10.1. Internal Energy.** The change in internal energy is

$$dU(S, V, \{N_i\}) = TdS - PdV + \sum_i \mu_i dN_i$$

if there is more than one chemical species. The differential form  $dU$  is exact, according to the First Law.

**6.10.2. Enthalpy.** The enthalpy is defined as:

$$H(S, P, \{N_i\}) = U + PV.$$

Differentiating:

$$dH(S, P, \{N_i\}) = dU + (PdV + VdP) = (TdS - PdV + \sum_i \mu_i dN_i) + (PdV + VdP).$$

This gives:

$$dH(S, P, \{N_i\}) = TdS + VdP + \sum_i \mu_i dN_i.$$

The enthalpy is useful for processes carried out at constant entropy and pressure, such as chemical reactions. Constant pressure because the reaction is often exposed to atmospheric pressure. The entropy is constant if there is no heat transferred to the system, since  $\delta Q^{rev} = TdS = 0$  (for a reversible process).

A calorimeter is a device that measures the heat flow during a process. They are the chief diagnostic tool in thermodynamics. Many calorimeters operate with the sample at fixed volume. We can design a calorimeter to maintain a constant temperature (using a suitable temperature control system, such as water bath or heating mantle) and constant pressure (by exposure to the atmosphere). Keeping certain variables fixed is important because it isolates the ones of interest. During a process, the enthalpy change is:

$$\Delta H = \int dH = \int (TdS + VdP).$$

If the pressure is fixed during a process ( $dP = 0$ ), then the enthalpy change is equal to the heat transferred:

$$(\Delta H)_P = \int TdS = \int \delta Q = \Delta Q.$$

The subscript  $P$  indicates that the pressure is held constant. The enthalpy was *invented* to make this relationship true.

**6.10.3. Helmholtz Free Energy.** The Helmholtz free energy is denoted as  $A$  or  $F$ , depending on the textbook. It is defined as:

$$A(T, V, \{N_i\}) = F = U - TS.$$

Applying the same ideas as above, you can verify that

$$dA(T, V, \{N_i\}) = -SdT - PdV + \sum_i \mu_i dN_i.$$

The differential form  $dA$  is also exact because it was obtained by differentiating  $A$ . The Helmholtz free energy is useful for processes carried out at constant temperature and volume (e.g., such as solids, whose volumes don't change).

Note: here,  $F$  denotes Helmholtz free energy, not force. In the section below, we will use  $F$  to denote force. While  $F$  is widely used in the literature to denote Helmholtz free energy, we will use  $A$  in these notes to avoid confusing the Helmholtz potential with the force  $F$ .

The definition  $A = U - TS$  shows that  $A$  is determined by a balance between internal energy and entropy. At low temperatures, the energy dominates. At high temperatures, the entropy dominates.

**6.10.4. Gibbs Free Energy.** The Gibbs Free energy is defined as:

$$G(T, P, \{N_i\}) = \underbrace{U + PV}_H - TS.$$

Similarly,

$$dG(T, P, \{N_i\}) = -SdT + VdP + \sum_i \mu_i dN_i.$$

The differential form  $dG$  is exact because it was obtained by differentiating  $G$ . The Gibbs free energy is useful in chemistry for processes carried out at constant temperature and pressure. Notice that  $H = U + PV$  and  $G = U + PV - TS$  are related by  $G = H - TS$ .

By integrating  $dG$  at constant temperature ( $dT = 0$ ) we have the famous formula:<sup>12</sup>

$$\Delta G = \Delta H - T\Delta S.$$

Notice that at constant  $T, P$  ( $dT = 0, dP = 0$ ), the Gibbs free energy is simply a measure of the energy exchanged through chemical transformation:

$$dG(T, P, \{N_i\}) = \sum_i \mu_i dN_i. \quad (\text{constant } T, P)$$

The Gibbs energy was *invented* with this experimental situation in mind. Many chemistry experiments are carried out at constant  $T, P$ .

By its construction,  $G = H - TS$ , the Gibbs free energy describes the balance between enthalpy and entropy (enthalpy dominates at low temperatures; entropy dominates at high temperatures). In a system held at constant  $P, T$ , the Gibbs energy will be at a minimum. The system can exchange energy with the surroundings by volume changes and heat transfer. Equilibrium is the state at which the entropy of the system plus surroundings is at a maximum. However, for the system itself, at constant  $P, T, N$ , equilibrium occurs when  $G$  is at a minimum.

**6.10.5. Landau Potential (Grand potential).** The grand potential is a quantity used in statistical mechanics, especially for irreversible processes in open systems. The grand potential is the characteristic state function for the grand canonical ensemble.

$$\Omega(T, V, \{\mu_i\}) = U - TS - \sum_i \mu_i N_i,$$

$$d\Omega(T, V, \{\mu_i\}) = -PdV - SdT - \sum_i N_i d\mu_i.$$

<sup>12</sup>Take  $G = H - TS$  and differentiate to get  $dG = dH - TdS - SdT = dH - TdS$  (since  $dT = 0$ ). Integrating gives  $\Delta G = \Delta H - T\Delta S$ , where  $\Delta G = \int dG$ ,  $\Delta H = \int dH$  and  $\Delta S = \int dS$ .

**6.10.6. Meaning of Free Energy.** The term “free energy” refers to any thermodynamic potential that has  $T$  as its independent variable instead of  $S$ . We know that the entropy of an isolated system can never decrease, however, an isolated system is of little experimental interest. We consider instead a system connected to a much larger system (heat bath) whose properties do not change significantly. For example, a bath may be chosen with  $T, P$  constant. Chemical reactions are rarely studied under conditions of constant entropy or constant energy. Usually, the chemist carries out reactions at constant temperature and pressure ( $T, P$ ), or constant volume and temperature ( $V, T$ ).

Examples of “free energies” include the Gibbs free energy,  $G \equiv G(T, P, \{N_i\})$ , and the Helmholtz free energy,  $A \equiv A(T, V, \{N_i\})$ . Per this definition, the Landau potential is also a type of free energy, since  $\Omega \equiv \Omega(T, V, \{\mu_i\})$ . On the other hand,  $H$  and  $U$  are not free energies, since they depend on  $S$  not  $T$ .

The free energies include:

$$\begin{aligned} A(T, V, \{N_i\}) &= U - TS, \\ G(T, P, \{N_i\}) &= H - TS, \\ \Omega(T, V, \{\mu_i\}) &= A - \sum_i \mu_i N_i. \end{aligned}$$

The thermodynamic potentials that are not free energies include:

$$U(S, V, \{N_i\}), S(U, V, \{N_i\}), H(S, P, \{N_i\}) = U + PV.$$

6.10.6.1. *Meaning of Free Energy.* First law,  $dU = \delta Q + \delta W$  and second law,  $dS \geq \delta Q/T$ , combined:  $TdS \geq dU - \delta W$ . (When changes are slow<sup>13</sup>, and the process is reversible, the equality holds,  $TdS = dU - \delta W$ .) Thus,  $\delta W \geq dU - TdS$ . Since  $A = U - TS$ , at constant temperature,  $dA = dU - TdS$ , we have that  $\delta W \geq dA$  or  $\Delta W \geq \Delta A$ . In a reversible process, the equality holds and the total work done is equal to the free energy change. For an irreversible process, the work done on the system by its surroundings is always greater than the increase in free energy. An equivalent formulation is obtained: *the work done by the system to the surroundings is always less than or equal to the decrease in its free energy.* Thus, the free energy of a system determines the maximum amount of work that the system can do.

**6.10.7. Any (“Create-Your-Own”) Potential.** There are situations where other choices of thermodynamic variables may be more convenient than the

<sup>13</sup>This relation holds for closed systems (closed to particle exchange). When particles can transfer,  $TdS = dU - \delta W - \mu dN$ .

ones given above. For example, consider the following potential:

$$\Phi(S, P, \{\mu_i\}) = U + PV - \sum_i \mu_i N_i$$

$$d\Phi(S, P, \{\mu_i\}) = TdS + VdP - \sum_i N_i d\mu_i$$

$d\Phi$  has the units of work. In classical mechanics infinitesimal work is of the form  $Fdx$ .<sup>14</sup>

Suppose that the variables  $S$ ,  $P$  and  $\mu_i$  are all spatially-dependent, i.e.  $S = S(x)$  [or  $S = S(\vec{x})$  in 3D]. Dividing through by  $dx$  gives the force:<sup>15</sup>

$$F = \frac{d\Phi}{dx} = \underbrace{T \frac{dS}{dx}}_{\text{entropic}} + \underbrace{V \frac{dP}{dx}}_{\text{mechanical}} - \underbrace{\sum_i N_i \frac{d\mu_i}{dx}}_{\text{chemical}}$$

where  $T \frac{dS}{dx}$  is interpreted as an *entropic force*.<sup>16</sup>

$$F_{\text{entropic}} = T \frac{dS}{dx}.$$

The three terms are:

- $T \frac{dS}{dx}$  is the entropic force. Entropic force is an emergent force that reflects a system's tendency to reach equilibrium by increasing entropy (in accordance with the Second Law).
- $V \frac{dP}{dx}$  is the force of  $P - V$  work originating from a pressure gradient (spatially non-uniform pressure). Pressure gradients drive flow.
- $N_i \frac{d\mu_i}{dx}$  is the force corresponding to the chemical work.

**6.10.8. Multi-Phase Systems.** Suppose that a system consists of multiple phases (e.g. gas, liquid, solid). Denoting the phase by  $\alpha$ , the fundamental

<sup>14</sup>(Optional)  $\vec{F} \cdot d\vec{x}$  in 3D.

<sup>15</sup>We are not really dividing through by  $dx$  but rather invoking the chain rule, i.e. since  $S = S(x)$ ,  $dS(x) = S'(x)dx = \frac{dS}{dx}dx$ .

<sup>16</sup>(Optional) In 3D, the analogous expression is:

$$\vec{F} \cdot d\vec{x} = \nabla\Phi \cdot d\vec{x} = T\nabla S \cdot d\vec{x} + V\nabla P \cdot d\vec{x} - \sum_i N_i \nabla\mu_i \cdot d\vec{x}.$$

where  $\nabla S = \frac{\partial S}{\partial x} \hat{x} + \frac{\partial S}{\partial y} \hat{y} + \frac{\partial S}{\partial z} \hat{z}$  is the gradient of  $S$ ,  $\nabla S \cdot d\vec{x}$  is the dot product of  $\nabla S$  and  $d\vec{x} = dx \hat{x} + dy \hat{y} + dz \hat{z}$ , i.e.  $\nabla S \cdot d\vec{x} = \frac{\partial S}{\partial x} dx + \frac{\partial S}{\partial y} dy + \frac{\partial S}{\partial z} dz$ , etc.

relations take the form:

$$\begin{aligned}dU &= \sum_{\alpha} T^{\alpha} dS^{\alpha} - \sum_{\alpha} P^{\alpha} dV^{\alpha} + \sum_{\alpha} \sum_i \mu_i^{\alpha} dn_i^{\alpha} \\dA &= - \sum_{\alpha} S^{\alpha} dT^{\alpha} - \sum_{\alpha} P^{\alpha} dV^{\alpha} + \sum_{\alpha} \sum_i \mu_i^{\alpha} dn_i^{\alpha} \\dH &= \sum_{\alpha} T^{\alpha} dS^{\alpha} + \sum_{\alpha} V^{\alpha} dP^{\alpha} + \sum_{\alpha} \sum_i \mu_i^{\alpha} dn_i^{\alpha} \\dG &= - \sum_{\alpha} S^{\alpha} dT^{\alpha} + \sum_{\alpha} V^{\alpha} dP^{\alpha} + \sum_{\alpha} \sum_i \mu_i^{\alpha} dn_i^{\alpha}\end{aligned}$$

where  $\sum_i$  denotes summation over the components and  $\sum_{\alpha}$  denotes summation over the phases. An example of multi-phase system is the example of phase equilibrium, discussed in Section 6.11.21.

**6.10.9. Entropy Representation, Fundamental Equation.** It is sometimes convenient to treat  $S$  (rather than  $U$ ) as the dependent variable, so that  $S(U, V, N_i)$  leads to the following *entropy representation* of the fundamental equation

$$dS(U, V, N_i) = \left(\frac{\partial S}{\partial U}\right)_{V, N_i} dU + \left(\frac{\partial S}{\partial V}\right)_{U, N_i} dV + \sum_i \left(\frac{\partial S}{\partial N_i}\right)_{U, V, N_j \neq N_i} dN_i,$$

whose coefficients can be read out from the Fundamental Equation by isolating  $dS$ :

**Entropy Representation of the Fundamental Equation:**

$$dS(U, V, N_i) = \left(\frac{1}{T}\right) dU + \left(\frac{P}{T}\right) dV - \sum_i \left(\frac{\mu_i}{T}\right) dN_i.$$

(reversible process,  $P = P_{ext}$ )

Matching the coefficients we get:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V, N_i}, \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U, N_i}, \quad \frac{\mu_i}{T} = - \left(\frac{\partial S}{\partial N_i}\right)_{U, V, N_j \neq N_i}.$$

The entropy representation gives a natural decomposition of the entropy as the sum of two terms: heat ( $dU/T$ ) + work (here,  $PV$  + chemical term). When  $dV = 0$ , we are left with heat transfer  $dU/T$  plus chemical terms. The chemical term can describe transport of chemical species in and out of the system, or it can describe spontaneous (irreversible) chemical transformations within the system. The heat term can be positive, zero or negative. It can describe reversible or irreversible heat transfer. Spontaneous chemical reactions are irreversible and lead to “entropy production”. The latter is nonnegative ( $\geq 0$ ).

**6.10.10. Gibbs Free Energy, Criteria for Spontaneity.** The criterion for spontaneity is given by the Second Law ( $dS_{univ} \geq 0$ ):

**Spontaneity Criterion (Entropy,  $dS_{univ} \geq 0$ ):**

$dS_{univ} > 0$	spontaneous (irreversible)
$dS_{univ} = 0$	reversible
$dS_{univ} < 0$	not spontaneous (“forbidden”)

In terms of the Gibbs energy  $G = H - TS$ , this becomes (fixed  $T$  and  $P$ ):

**Spontaneity Criterion (Gibbs energy,  $dG_{univ} \leq 0$ ):**

$dG_{univ} < 0$	spontaneous (irreversible)
$dG_{univ} = 0$	reversible
$dG_{univ} > 0$	not spontaneous (“forbidden”)

Thus, maximizing the entropy of the universe is equivalent to minimizing the Gibbs energy. Note that spontaneity does not imply that the reaction will necessarily occur at a detectable rate. See Chapter 7 for further details of reaction rates. The maximum principle is discussed in Section 6.11.12.

**6.10.11. Euler Relation.** Since  $U$  is extensive and is also a function of extensive variables  $S, V, N_i$ , if these variables are all multiplied by  $\lambda$ , then  $U$  will also change by the same factor:

$$U(\lambda S, \lambda V, \{\lambda N_i\}) = \lambda U(S, V, N_i).$$

Differentiating both sides with respect to  $\lambda$  gives:

$$\frac{d}{d\lambda} \lambda U(S, V, N_i) = U(S, V, N_i).$$

and

$$\begin{aligned} \left. \frac{d}{d\lambda} \right|_{\lambda=1} U(\lambda S, \lambda V, \{\lambda N_i\}) &= \frac{\partial U}{\partial S} \cdot \frac{d(\lambda S)}{d\lambda} + \frac{\partial U}{\partial V} \cdot \frac{d(\lambda V)}{d\lambda} + \sum_i \frac{\partial U}{\partial N_i} \cdot \frac{d(\lambda N_i)}{d\lambda} \\ &= \frac{\partial U}{\partial S} \cdot S + \frac{\partial U}{\partial V} \cdot V + \sum_i \frac{\partial U}{\partial N_i} \cdot N_i \end{aligned}$$

by the chain rule. Here,  $\left. \frac{d}{d\lambda} \right|_{\lambda=1}$  denotes the derivative with respect to  $\lambda$  evaluated at the point  $\lambda = 1$ .

Thus,  $U$  obeys

$$U = \underbrace{\left(\frac{\partial U}{\partial S}\right)}_T S + \underbrace{\left(\frac{\partial U}{\partial V}\right)}_{-P} V + \sum_i \underbrace{\left(\frac{\partial U}{\partial N_i}\right)}_{\mu_i} N_i.$$

Recall<sup>17</sup> that  $T \equiv (\partial U/\partial S)$ ,  $P \equiv -(\partial U/\partial V)$ ,  $\mu_i \equiv (\partial U/\partial N_i)$ . Then, we get the Euler relation:

$$U = TS - PV + \sum_i \mu_i N_i,$$

which can also be expressed in the *entropy representation* as:

$$S = \frac{U}{T} + \frac{PV}{T} - \sum_i \frac{\mu_i N_i}{T}.$$

**6.10.12. Gibbs-Duhem Relation.** Differentiating the Euler relation (reversible process,  $P = P_{ext}$ ):<sup>18</sup>

$$U = TS - PV + \sum_i \mu_i N_i,$$

we obtain

$$dU = TdS + SdT - PdV - VdP + \sum_i \mu_i dN_i + \sum_i N_i d\mu_i.$$

Comparing with the First Law:

$$dU = TdS - PdV + \sum_i \mu_i dN_i,$$

we see that for both to be correct we must have:

$$SdT - VdP + \sum_i N_i d\mu_i = 0. \quad (\text{Gibbs-Duhem})$$

Note: Writing the heat term as  $TdS$  implicitly assumes reversibility of the process. Therefore, we wrote  $P$  instead of  $P_{ext}$ . The Gibbs-Duhem equation shows that three intensive variables are not independent; if we know two of them, the value of the third can be determined from the Gibbs-Duhem equation.

<sup>17</sup>From  $dU = TdS - PdV + \mu dN$  we get  $T = \partial_S U$ ,  $P = -\partial_V U$  and  $\mu = \partial_N U$ .

<sup>18</sup>Reversibility is assumed because the expression for  $dU$  (First Law) makes use of  $\delta Q = TdS$ , which is true for a reversible process. For an irreversible process we have  $\delta Q \leq TdS$ . (See Clausius inequality below.) Incidentally, you can see that this Clausius inequality also implies that  $dU \leq TdS - PdV + \sum_i \mu_i dN_i$ .

**6.10.13. Application: (Chemical Potential of Ideal Gas).** Write down Gibbs-Duhem<sup>19</sup> for a single component system:<sup>20</sup>

$$d\mu = \left(\frac{V}{N}\right) dP - \left(\frac{S}{N}\right) dT.$$

If we assume that the temperature is constant ( $dT = 0$ ) and integrate:

$$\Delta\mu = \int d\mu = \mu(T, P) - \mu^\circ(T) = \int_{P_0}^P \left(\frac{V}{N}\right) dP.$$

Substituting  $V/N = k_B T/P$  from the ideal gas law:

$$\begin{aligned} \mu(T, P) &= \mu^\circ(T) + k_B T \log\left(\frac{P}{P_0}\right) = \mu^\circ(T) + k_B T \log\left(\frac{\rho}{\rho_0}\right) \\ (6.6) \quad &= \mu^\circ(T) + k_B T \log\left(\frac{[c]}{[c]_0}\right) \end{aligned}$$

where  $\rho = N/V$  and  $[c] = n/V = \rho/N_A$ .

## 6.11. Multi-Component Gas

Suppose we have a mixture of gases. Such an expression holds for each component:

$$\mu_i(T, P) = \mu_i^\circ(T) + k_B T \log\left(\frac{P_i}{P_0}\right)$$

For ideal gases, Dalton's law holds,  $P_i = X_i P$ , where  $P$  is the total pressure and  $X_i$  is the mole fraction of component  $i$ .  $P_0$  is a reference pressure, often taken to be 1 atm. Substituting Dalton's law and collecting the terms independent of composition into the square bracket:

$$\mu_i(T, P) = \underbrace{[\mu_i^\circ(T) + k_B T \log(P/P_0)]}_{\mu_i^*} + k_B T \log X_i$$

The term in square bracket (labeled  $\mu_i^*$ ) is the chemical potential of the *pure substance* under some reference conditions ( $P, T$ ).  $P_0$  can be regarded as the unit of pressure used. When  $X_i = 1$  (pure substance of type  $i$ ), the log term is zero and only the square bracket remains. If our pure substance were an ideal gas,  $U = \frac{3}{2} N k_B T$ . Taking the derivative with respect to  $N$  gives  $\frac{3}{2} k_B T$ , which is the energy cost of adding a molecule to a gas at temperature  $T$ .

### 6.11.1. Gibbs Free Energy (Integrated Form, using Euler's Formula).

<sup>19</sup>An easy trick to remember this equation is to start from the First Law for a reversible chemical process,  $dU = TdS - PdV + \sum_i \mu_i dN_i$ , and reverse the roles of the intensive and extensive variables, then set  $dU = 0$ .

<sup>20</sup>Gibbs-Duhem assumes reversibility because its derivation involved a  $TdS$  term; hence we may write  $P = P_{ext}$ .

Definition of Gibbs energy. The Gibbs energy is defined as<sup>21</sup>

$$G(P, T, \{N_i\}) = \underbrace{U + PV}_H - TS,$$

where the transformation from  $U$  swaps the roles of  $V$  in favor of  $P$  and  $S$  in favor of  $T$ . In chemistry it is common to work at constant  $T$  and  $P$ . With  $dU = TdS - PdV + \sum_i \mu_i dN_i$  (for a reversible process,  $\delta Q = TdS$ ),

$$dG = -SdT + VdP + \sum_i \mu_i dN_i.$$

Constant  $T, P$ . At constant  $T, P$  ( $dT = 0, dP = 0$ )

$$dG = \sum_i \mu_i dN_i.$$

6.11.1.1. *Integrated Form.* Combining  $G = U - TS + PV$  with the Euler formula<sup>22</sup>  $U = TS - PV + \sum_i \mu_i N_i$

$$G = \sum_i \mu_i N_i.$$

Thus, the *Gibbs free energy is equal to the sum of all the chemical potentials of the molecules in any system*, regardless of any assumptions of constant  $T$  or  $P$ . (Here we did not impose any restrictions such as constant temperature or pressure<sup>23</sup>.)

6.11.1.2. *Single-Component, Ideal Gas.* For a single component<sup>24</sup>,  $G = \mu N$  and substituting Eq. (6.6) yields:

$$G = G^\circ + k_B T N \log \left( \frac{P}{P_0} \right) = G^\circ + k_B T N \log \left( \frac{\rho}{\rho_0} \right) = G^\circ + k_B T N \log \left( \frac{[c]}{[c]_0} \right).$$

or in terms of *molar Gibbs energy*  $G/n$ ,

$$\frac{G}{n} = \mu^\circ + RT \log \left( \frac{P}{P_0} \right) = \mu^\circ + RT \log \left( \frac{\rho}{\rho_0} \right) = \mu^\circ + RT \log \left( \frac{[c]}{[c]_0} \right).$$

**6.11.2. At Equilibrium,  $dG = 0$ .** For a chemical reaction (usually,  $T, P$  are constant),  $dG = \sum_i \mu_i dN_i$ . The second law states that  $dG = 0$  at

<sup>21</sup>Note: we have assumed reversibility because of the presence of the  $TdS$  term. In this case, we write  $P$  in place of  $P_{ext}$ .

<sup>22</sup>An easy way to remember the Euler formula is to start with the First Law for a reversible chemical process,  $dU = TdS - PdV + \sum_i \mu_i dN_i$ , and remove the 'd' in the differentials.

<sup>23</sup>The only two elements that were used to derive this formula were the definition of the Gibbs energy and the Euler relation. The latter was derived using the extensively property of the thermodynamic variables. Thus, the result was obtained without assuming constant  $P$  or  $T$ .

<sup>24</sup>We often write  $P, \rho$  and  $[c]$  instead of  $P/P_0, \rho/\rho_0$  and  $[c]/[c]_0$ , where  $P, \rho$  and  $[c]$  are expressed in units of  $P_0, \rho_0$  and  $[c]_0$ , respectively.

equilibrium. Thus,  $\sum_i \mu_i dN_i = 0$ . Integration of  $dG$  gives:

$$\Delta G = \int_{react.}^{prod.} dG = G(prod.) - G(react.) = \sum_i \mu_i \int dN_i = \sum_i \mu_i \Delta N_i.$$

We built up  $\Delta G$  by starting with an elementary mass  $\{dN_i\}$  and adding to it elementary masses of the same pressure, temperature and composition as the first. By adding infinitesimal values of  $G$  we build a finite value of  $\Delta G$ . Since the chemical potentials are intensive properties and the intensive state is fixed by pressure, temperature and relative composition of substances, the values of  $\mu_i$  remain constant throughout the process of accretion.

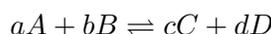
We therefore have the equilibrium condition ( $\Delta G = 0$ ) is equivalent to

$$\sum_i \mu_i \Delta N_i = 0.$$

However,  $\Delta N_i$  (and also  $dN_i$ ) is proportional to the stoichiometric coefficient  $\nu_i$ . Thus, the equilibrium condition is

$$\boxed{\sum_i \mu_i \nu_i = 0.}$$

There is a sign convention that we must follow for the stoichiometric coefficients: the products are positive, the reactants are negative. Let's look at a simple example:



is written in the more general form

$$0 = \sum_i \nu_i A_i,$$

where  $A_i$  denotes the  $i$ -th chemical species and  $\nu_i$  is the associated stoichiometric coefficient (taken negative for a reactant species or positive for a product species) in the balanced chemical equation. For this reaction, we have:  $\nu_1 = -a$ ,  $\nu_2 = -b$ ,  $\nu_3 = c$ ,  $\nu_4 = d$  and  $A_1 = A$ ,  $A_2 = B$ ,  $A_3 = C$  and  $A_4 = D$ .

**6.11.3. Chemical Potential, Activity.** Activities are used as a way to account for non-idealities of solutions. Chemical potentials can be written in terms of activities ( $a_i$ ), as follows:

$$\mu_i = \mu_i^\circ + RT \log a_i.$$

This can be taken as the definition of activity:

$$a_i \equiv \exp\left(\frac{\mu_i - \mu_i^\circ}{RT}\right).$$

The equilibrium condition  $\sum_i \mu_i \nu_i = 0$  becomes

$$0 = \sum_i \mu_i^\circ \nu_i + RT \sum_i \nu_i \log a_{i,\text{eq.}}$$

The values  $\mu_i^\circ$  can be found tabulated for different (pure) chemical species  $i$  and some standard conditions. The above definition of activity is not intuitive. The newcomer may instead want to consider the simpler description:

$$a_i = \gamma_{X,i} X_i \quad a_i = \gamma_{c,i} \frac{c_i}{c_0} \quad a_i = \gamma_{P,i} \frac{P_i}{P_0},$$

where the  $\gamma$ 's are "activity coefficients" (equal to 1 for an ideal substance),  $X_i$  is mole fraction of  $i$ ,  $c_i$  is concentration of  $i$  and  $P_i$  is the partial pressure of  $i$ .  $c_0$  is a reference concentration (e.g. 1 M) and  $P_0$  is a reference pressure (e.g. 1 atm).

Thus, for ideal substances, you can think of  $a_i$  as either:

$$a_i = X_i \quad \text{or} \quad \frac{c_i}{c_0} \quad \text{or} \quad \frac{P_i}{P_0},$$

where  $c_0$  and  $P_0$  are reference concentrations and pressures, respectively. Typically, we choose  $c_0 = 1$  M and  $P_0 = 1$  atm.

**6.11.4. Gibbs Free Energy of Reaction.** To recap what we have done, we just calculated  $\Delta G$  of the reaction, by integrating  $dG$  from reactants to products. Let's use a subscript "rxn" to emphasize this:

$$\begin{aligned} \Delta G_{\text{rxn}} &= \int_{\text{react.}}^{\text{prod.}} dG = G(\text{prod.}) - G(\text{react.}) \\ &= \sum_i \mu_i \nu_i = \underbrace{\sum_i \mu_i^\circ \nu_i}_{\Delta G_{\text{rxn}}^\circ} + RT \sum_i \nu_i \log a_i. \end{aligned}$$

At equilibrium  $\Delta G_{\text{rxn}} = 0$ . (Obviously, this is only valid at constant  $T, P$ .)

**6.11.5. Standard Gibbs Free Energy of Reaction.** The first term is a collection of constants describing an energy change going from reactants to products:

$$\sum_i \mu_i^\circ \nu_i = G_{\text{prod.}}^\circ - G_{\text{react.}}^\circ = \Delta G_{\text{rxn}}^\circ$$

which depends only on the properties of the unmixed species. The quantity  $\Delta G_{\text{rxn}}^\circ$  is known as the *standard Gibbs free energy* of the reaction. Its value can be obtained from tables.

The second term is rewritten as

$$RT \sum_i \nu_i \log a_i = RT \sum_i \log a_i^{\nu_i} = RT \log \left[ \prod_i a_i^{\nu_i} \right].$$

Then we have, at equilibrium,

$$\Delta G_{rxn}^{\circ} + RT \log \left[ \prod_i a_{i,\text{eq}}^{\nu_i} \right] = 0.$$

The quantity in the brackets can be identified as the *reactant quotient*,  $Q$ , the ratio of product and reactant activities, each raised to its stoichiometric power. For example, for the symbolic reaction:

$$aA + bB \rightleftharpoons cC + dD$$

$$Q = \prod_i a_i^{\nu_i} = \frac{\text{products}}{\text{reactants}} = \frac{a_C^c a_D^d}{a_A^a a_B^b}.$$

I will not be using activity here. Thus, we replace activity by concentrations (in units of 1 M) and pressures (in units of 1 atm):

$$\Delta G_{rxn}^{\circ} = -RT \log K = -RT \log \left[ \prod_i ([c_i]_{\text{eq}})^{\nu_i} \right] \quad \text{or} \quad -RT \log \left[ \prod_i (P_{i,\text{eq}})^{\nu_i} \right].$$

**6.11.6. Reaction Constant.** At equilibrium  $\Delta G_{rxn}^{\circ}$  and  $T$  are constants,  $Q = K$  and we have the central equation of chemical equilibrium theory:

$$\Delta G_{rxn}^{\circ} = -RT \log K$$

where  $K = \frac{a_C^c a_D^d}{a_A^a a_B^b}$  (activities are equilibrium values). When dealing with solutions,  $K_C = \frac{[C]_{\text{eq}}^c [D]_{\text{eq}}^d}{[A]_{\text{eq}}^a [B]_{\text{eq}}^b}$ . Here, the concentrations are equilibrium values. Note that  $a_i \propto [A_i] = n_i/V$  and the proportionality constants have been absorbed into the definition of  $K_C$ . Similarly, for gaseous mixtures,  $a_i \propto P_i$  and  $K_P = \frac{P_{C,\text{eq}}^c P_{D,\text{eq}}^d}{P_{A,\text{eq}}^a P_{B,\text{eq}}^b}$ .

**6.11.7. What is the Meaning of the Standard Gibbs Free Energy?**

We saw that chemical reactions can be written in the general form,

$$\sum_i \nu_i A_i = 0,$$

where  $A_i$  denotes the  $i$ -th chemical species and  $\nu_i$  is the associated stoichiometric coefficient (taken negative for a reactant species or positive for a product species) in the balanced chemical equation. For example, with the reaction



we have that  $\nu_1 = -a$ ,  $\nu_2 = -b$ ,  $\nu_3 = c$ ,  $\nu_4 = d$  and  $A_1 = A$ ,  $A_2 = B$ ,  $A_3 = C$  and  $A_4 = D$ . At chemical equilibrium we have that  $dG = 0$  (constant  $T, P$ ),

where  $dG = \sum_i \mu_i dn_i$ . Integrating from reactants to products gives

$$\Delta G_{rxn} = G(\text{prod.}) - G(\text{react.}) = \sum_i \mu_i \nu_i,$$

since

$$\int_{\text{react.}}^{\text{prod.}} dn_i = \Delta n_i = \nu_i$$

(with the above sign convention). Thus,  $\sum_i \mu_i \nu_i = 0$ . Finally, we note that the combination of  $G = U - TS + PV$  and the Euler formula,

$$U = TS - PV + \sum_i \mu_i n_i,$$

leads to  $G = \sum_i \mu_i n_i$ , which implies that  $G_i/n_i = \mu_i$  ( $\mu_i$ , the chemical potential, is also the molar Gibbs energy). We have seen that substitution of the ideal gas expression for  $\mu_i$  into  $\sum_i \mu_i \nu_i = 0$  leads to

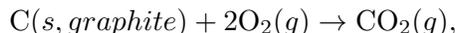
$$\Delta G_{rxn} = \Delta G_{rxn}^0 + RT \log Q,$$

where  $\Delta G_{rxn}^0 = \sum_i \mu_i^\circ \nu_i$ . It is important to note that  $\Delta G_{rxn}$  and  $\Delta G_{rxn}^0$  are two different things.

$\Delta G_{rxn}^0$  is computed as follows:

$$\Delta G_{rxn}^0 = \sum_i \nu_i (\Delta G_f^\circ)_i,$$

where  $\nu_i$  are the stoichiometric coefficients of species  $i$  in the reaction (products are positive, reactants are negative) and  $\Delta G_f^\circ$  are standard Gibbs energies of formation ( $i$  denotes the  $i$ -th chemical species in the reaction). These values are found in tables. The symbol  $^\circ$  attached to  $\Delta G_{rxn}^0$  means “standard” Gibbs energy, which has a single value for a particular reaction at a given temperature and pressure. We can obtain the value of  $\Delta G_{rxn}^0$  from tables (such as Appendix D of Oxtoby [1]). It corresponds to the free energy change for a process that never really happens: the *complete transformation* of pure reactants into pure products at a constant pressure of 1 atm (or whatever the reference conditions happen to be; but usually 1 atm). In the case of the reaction:

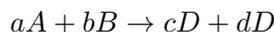


$\Delta G_{rxn}^0$  is the free energy change for the complete transformation of pure graphite and  $\text{O}_2$  into pure  $\text{CO}_2$  at a constant pressure of 1 atm.

In contrast to  $\Delta G_{rxn}^0$ , which is a *constant* for a given reaction,  $\Delta G_{rxn}$  varies continuously as the composition changes, finally reaching zero at equilibrium.  $\Delta G_{rxn}$  is the “distance” (in free energy) from the equilibrium state of a given reaction. The two are related by:

$$\Delta G_{rxn} = \Delta G_{rxn}^0 + RT \log Q,$$

where  $Q$  is the reaction quotient, which would be, for a reaction



$Q = P_C^c P_D^d / (P_A^a P_B^b)$  or  $Q = [C]^c [D]^d / ([A]^a [B]^b)$ . At equilibrium we have  $\Delta G_{rxn} = 0$  and the above equation gives  $\Delta G_{rxn}^0 = -RT \log K$  (because  $Q = K$  at equilibrium).

The change in standard Gibbs free energy *for the above reaction* is the sum of standard Gibbs energies of formation:

$$\Delta G_{rxn}^{\circ} = c(\Delta G_f^{\circ})_C + d(\Delta G_f^{\circ})_D - a(\Delta G_f^{\circ})_A - b(\Delta G_f^{\circ})_B.$$

The equation,  $\Delta G_{rxn}^0 = -RT \log K$ , is important because it relates the equilibrium composition of a chemical reaction system to measurable physical properties of the reactants and products. If you know the entropies ( $S^{\circ}$ ) and the enthalpies ( $\Delta H_f^{\circ}$ ) of formation of a set of substances, you can predict (since  $\Delta G_{rxn}^{\circ} = \Delta H_{rxn}^{\circ} - T\Delta S_{rxn}^{\circ}$  at constant temperature) the equilibrium constant of any reaction involving these substances without the need to know anything about the mechanism of the reaction. We may find tables of  $\Delta G_f^{\circ}$ ,  $S^{\circ}$  and  $\Delta H_f^{\circ}$  for different substances in chemistry handbooks (e.g., [12]) or textbooks (e.g., [1]).

The standard enthalpy of formation or standard heat of formation of a compound is the change of enthalpy during the formation of 1 mole of the substance from its constituent elements, with all substances in their standard states, and at a pressure of 1 atm. There is no standard temperature. It is usually denoted  $\Delta H_f^{\circ}$ . The superscript  $^{\circ}$  on this symbol indicates that the process has occurred under standard conditions at the specified temperature (usually 25°C).

The standard Gibbs free energy of formation of a compound is the change of Gibbs free energy that accompanies the formation of 1 mole of a substance in its standard state from its constituent elements in their standard states (the most stable form of the element at 1 atm of pressure and the specified temperature, usually 25°C).

**6.11.8. Where to Find Values for  $\Delta H_f^{\circ}$ ,  $\Delta G_f^{\circ}$  and  $S^{\circ}$ .** Values of  $\Delta H_f^{\circ}$ ,  $S^{\circ}$  and  $\Delta G_f^{\circ}$  can be found tabulated in most chemistry textbooks (usually, in appendices), and on the internet. In chemistry books, we do not find  $\Delta G_{rxn}^{\circ}$  values for all possible chemical reactions, because it would be impossible to list all possible chemical reactions (there are too many of them). Instead, we will find tables of the energy of formation of various compounds, which may be involved in your reaction. Textbooks often denote these energies of formation as  $\Delta G_f^{\circ}$ .

Standard enthalpies of formation can be found at  
[https://en.wikipedia.org/wiki/Standard\\_enthalpy\\_of\\_formation](https://en.wikipedia.org/wiki/Standard_enthalpy_of_formation)

Standard Gibbs free energies of formation can be found at  
[https://en.wikipedia.org/wiki/Standard\\_Gibbs\\_free\\_energy\\_of\\_formation](https://en.wikipedia.org/wiki/Standard_Gibbs_free_energy_of_formation)

Appendix D of Oxtoby [1], entitled “Standard Chemical Thermodynamic Properties”, contains tabulated values for enthalpies, entropies and Gibbs energies of formation. Please note that Oxtoby [1] writes  $S^\circ$  and not  $\Delta S_f^\circ$ . This is because the Third Law guarantees the existence of an absolute entropy scale. So what is being tabulated here is the absolute entropy  $S^\circ$  for each substance. On the other hand, there exists no absolute scale for  $\Delta H_f^\circ$  and  $\Delta G_f^\circ$ , hence the  $\Delta$  notation.

Table 6.4 is an excerpt from page 1 of the Appendix D of Oxtoby [1]. Oxtoby [1] prefaces the table as follows: “This table lists standard enthalpies of formation  $\Delta H_f^\circ$ , standard third-law entropies  $S^\circ$ , standard free energies of formation  $\Delta G_f^\circ$ , and molar heat capacities at constant pressure,  $c_P$ , for a variety of substances, all at 25°C (298.15 K) and 1 atm. [...] Note that the solution-phase entropies are not absolute entropies but are measured relative to the arbitrary standard  $S^\circ(\text{H}^+(\text{aq})) = 0$ . Consequently, some of them (as well as some of the heat capacities) are negative.”

**Table 6.4.** Excerpt from Appendix D of Oxtoby [1].

Substance	$\Delta H_f^\circ(25^\circ\text{C})$	$S^\circ(25^\circ\text{C})$	$\Delta G_f^\circ(25^\circ\text{C})$	$c_P(25^\circ\text{C})$
units	kJ/mol	J/K/mol	kJ/mol	J/K/mol
H(g)	217.96	114.60	203.26	20.78
H <sub>2</sub> (g)	0	130.57	0	28.82
H <sup>+</sup> (aq)	0	0	0	0
H <sub>3</sub> O <sup>+</sup> (aq)	-285.83	69.91	-237.18	75.29
Li(s)	0	29.12	0	24.77
Li(g)	159.37	138.66	126.69	20.79
Li <sup>+</sup> (aq)	-278.49	13.4	-293.31	68.6
LiH(s)	-90.54	20.01	-68.37	27.87
Li <sub>2</sub> O(s)	-597.94	37.57	-561.20	54.10
LiF(s)	-615.97	35.65	-587.73	41.59
LiCl(s)	-408.61	59.33	-384.39	47.99
LiBr(s)	-351.21	74.27	-342.00	—
LiI(s)	-270.41	86.78	-270.29	51.04
Na(s)	0	51.21	0	28.24
Na(g)	107.32	153.60	76.79	20.79
Na <sup>+</sup> (aq)	-240.12	59.0	-261.90	46.4
Na <sub>2</sub> O(s)	-414.22	75.06	-375.48	69.12

NaOH( <i>s</i> )	-425.61	64.46	-379.53	59.54
NaF( <i>s</i> )	-573.65	51.46	-543.51	48.86
NaCl( <i>s</i> )	-411.15	72.13	-384.15	50.50

**6.11.9. The Standard States.** When writing  $\Delta G_f^\circ$ , the  $^\circ$  indicates that all components (reactants and products) are in their standard states. This concept of standard states is especially important in the case of the free energy. For most practical purposes, the following definitions are used (see [https://en.wikipedia.org/wiki/Standard\\_enthalpy\\_of\\_formation](https://en.wikipedia.org/wiki/Standard_enthalpy_of_formation))

- Gases: 1 atm partial pressure (i.e., the hypothetical state it would have assuming it obeyed the ideal gas equation at a pressure of 1 atm).
- Pure liquids: for a solute present in an ideal solution, a concentration of exactly 1 M at a pressure of 1 atm.
- Solutes: an effective concentration of 1 mol/L. (“Effective” concentrations approach real concentrations as the latter approach zero; for practical purposes, these can be considered identical at real concentrations smaller than about  $10^{-4}$  molar.)
- Solids: for a pure substance or a solvent in a condensed state (a liquid or a solid), the standard state is the pure liquid or solid under a pressure of 1 atm.
- For an element: the form in which the element is most stable under 1 atm of pressure. One exception is phosphorus, for which the most stable form at 1 atm is black phosphorus, but white phosphorus is chosen as the standard reference state for zero enthalpy of formation.
- All elements in their standard states (oxygen gas, hydrogen gas, nitrogen gas, solid carbon in the form of graphite, etc.) have a standard enthalpy of formation ( $\Delta H^\circ$ ) of zero, as there is no change involved in their formation.
- There is no “standard temperature” in thermodynamics, but one often uses  $25^\circ$ . (Thermodynamic standard state is different from STP used in gas law calculations.)
- Some texts will use 1 atm as the reference pressure; others may use 1 bar.

**6.11.10. Example Calculation.** Find the standard Gibbs energy change for the reaction



where the following values of standard Gibbs energies of formation are found from tables:  $\text{CaCO}_3(s)$ : -1128 kJ/mol,  $\text{CaO}(s)$ : -603.5 kJ/mol,  $\text{CO}_2(g)$ : -137.2 kJ/mol.

*Solution:* Substitute these values into the equation for  $\Delta G_{rxn}^\circ$ , we find:

$$\Delta G_{rxn}^\circ = [(-603.5 - 137.2) - (-1128)] \text{ kJ/mol} = +387.3 \text{ kJ/mol}.$$

A positive value for  $\Delta G_{rxn}^\circ$  means that the process is not spontaneous (under standard conditions), i.e. solid calcium carbonate will not form solid calcium oxide and  $\text{CO}_2$  at 1 atm at  $25^\circ$ . Note: This reaction is carried out on a large scale to manufacture cement, so obviously the process can be spontaneous under different conditions.

Recall the relationship between  $K$  and  $\Delta G_{rxn}^\circ$ :

$$K = \exp\left(-\frac{\Delta G_{rxn}^\circ}{RT}\right).$$

Here, since  $\Delta G_{rxn}^\circ$  is positive,  $K < 1$ , meaning the equilibrium favors the reactants, meaning that  $\text{CaCO}_3$  wants to remain in its solid form.

The practical importance of the Gibbs energy is that it allows us to make predictions based on the properties ( $\Delta G_{rxn}^\circ$  values) of the reactants and products themselves, eliminating the need for experiment.

**6.11.11. What about Mechanical Work?** So far we have only discussed energies stored in a chemical bond in the context of enthalpy. When we think of a chemical reaction, we want to know the energies involved when forming products or reactants. This helps determine the reaction conditions that favor a given process.

If a reaction is carried out in a fixed volume vessel, the change in internal energy equals the heat of the reaction. If the volume is allowed to expand, we also have a  $PdV$  term to worry about in the expression for the internal energy change. Does this term matter in practice?

Consider the following reaction:



From the data of Table 6.4, we find for  $\Delta H$ :

$$\begin{aligned}\Delta H &= \Delta H_{\text{H}(g)} + \Delta H_{\text{Li}(g)} - \Delta H_{\text{LiH}(s)} = (217.96 + 159.37 - (-90.54)) \text{ kJ/mol} \\ &= 467.87 \text{ kJ/mol}.\end{aligned}$$

Thus, the reaction is endothermic and requires about half a megaJoule per mole of energy to move forward. To carry out this reaction on a mole of substance, we supply this energy. The stoichiometry shows that 2 moles of gas are produced (1 mol of  $\text{H}(g)$  and 1 mol of  $\text{Li}(g)$ ) for each mole of  $\text{LiH}(s)$  consumed. If the volume is allowed to expand, the work carried out on its surroundings is:

$$\begin{aligned}w &= -P\Delta V = -(\Delta n)RT = -(2 \text{ mol})(8.31 \text{ J/K/mol})(300 \text{ K}) \\ &= -4.986 \text{ kJ/mol}.\end{aligned}$$

This energy related to mechanical work is about 1% of the energy of the reaction. Thus, it can be safely neglected in calculations. Moreover we note that at 300 K, the value of  $RT$  (molar thermal energy) is 2.5 kJ/mol. This

says that the thermal energy (molecular fluctuations) is comparable to, and therefore nearly indistinguishable from, the mechanical work.

**6.11.12. Maximum Principle, Reaction Analysis w/ Helmholtz Free Energy.** The maximum principle refers to the entropy that reaches a maximum at equilibrium ( $dS = 0$ ). When entropy reaches a maximum, the energies reach a minimum. Depending on the conditions of your experiment, analysis of chemical equilibrium can be done using any thermodynamic potential:

$$\begin{aligned}dU &= TdS - PdV + \sum_i \mu_i dn_i \\dS &= \frac{1}{T}dU + \frac{P}{T}dV - \frac{1}{T} \sum_i \mu_i dn_i \\dH &= TdS + VdP + \sum_i \mu_i dn_i \\dA &= -SdT - PdV + \sum_i \mu_i dn_i \\dG &= -SdT + VdP + \sum_i \mu_i dn_i\end{aligned}$$

At equilibrium, these differentials are zero:

$$dU = 0, \quad dS = 0, \quad dH = 0, \quad dA = 0, \quad dG = 0,$$

or in integrated form

$$\Delta U = 0, \quad \Delta S = 0, \quad \Delta H = 0, \quad \Delta A = 0, \quad \Delta G = 0.$$

Entropy is “concave down” meaning that spontaneous processes drive it towards a maximum:

$$dS > 0 \quad (\text{spontaneous process, away from equilibrium}).$$

By that we mean that if  $A$  is an equilibrium state and  $B$  is another state away from equilibrium, we should always have  $S(B) \geq S(A)$ . The system goes from state  $B$  to state  $A$ ;  $S$  will continue to increase until it can’t get any bigger, at which point equilibrium has been reached.

Conversely, energies are all “concave up” functions, meaning that spontaneous processes drive them towards a minimum:

$$\begin{aligned}dU < 0 & \quad (\text{spontaneous process, away from equilibrium}) \\dH < 0 & \quad (\text{spontaneous process, away from equilibrium}) \\dA < 0 & \quad (\text{spontaneous process, away from equilibrium}) \\dG < 0 & \quad (\text{spontaneous process, away from equilibrium}).\end{aligned}$$

This is justified by the Second Law and the definitions of the thermodynamic potentials. For example, the First and Second Laws combined give

$$(6.7) \quad dU \leq TdS - PdV + \sum_i \mu_i dn_i.$$

Suppose that we have a mixture of substances in a box. First, we consider the case where  $S, V, \{n_i\}$  are fixed. Equation (6.7) gives:

$$dU \leq 0, \quad \text{where } S, V, \{n_i\} \text{ constant.}$$

Or in integrated form,

$$\boxed{(\Delta U)_{S,V,\{n_i\}} \leq 0.}$$

Next we assume that  $T, V, \{n_i\}$  are fixed. Then,  $dU \leq TdS$  or  $d(U - TS) \leq 0$ . Since  $A = U - TS$ , this translates to

$$dA \leq 0, \quad \text{where } T, V, \{n_i\} \text{ constant.}$$

Or in integrated form,

$$\boxed{(\Delta A)_{T,V,\{n_i\}} \leq 0.}$$

Thus,  $A$  must be a minimum at equilibrium.

Suppose that instead of  $T, V, \{n_i\}$  fixed, we have  $T, P, \{n_i\}$  constant. Then Eq. (6.7) becomes

$$d(U - TS + PV) \leq 0$$

or, in other words,

$$dG \leq 0, \quad \text{where } T, P, \{n_i\} \text{ constant.}$$

In integrated form:

$$\boxed{(\Delta G)_{T,P,\{n_i\}} \leq 0.}$$

Therefore, under these conditions,  $G$  must be a minimum.

Finally, suppose that  $S, P, \{n_i\}$  are constant. Equation (6.7) becomes  $d(U + PV) \leq 0$ . Since  $H = U + PV$ , this means:

$$dH \leq 0, \quad \text{where } S, P, \{n_i\} \text{ constant.}$$

In integrated form:

$$\boxed{(\Delta H)_{S,P,\{n_i\}} \leq 0.}$$

Any of these thermodynamic potentials can be used to analyze chemical reactions. Which one to use depends on the conditions of the reactions. Chemists often use the Gibbs energy because most chemical reactions are carried out at constant  $T, P$ . There are, however, circumstances where other variables are held constant. For example, gas-phase reactions done in a container of fixed volume (e.g. gas cylinder) are more appropriately described

using the Helmholtz energy:

$$dA = -SdT - PdV + \sum_i \mu_i dn_i.$$

At constant  $T, V$ , this becomes:

$$dA = \sum_i \mu_i dn_i. \quad (\text{constant } T, V)$$

The condition for equilibrium is  $dA = 0$ , which yields the same condition for equilibrium as that given by the Gibbs energy:

$$0 = \sum_i \mu_i dn_i. \quad \text{or} \quad 0 = \sum_i \mu_i \nu_i. \quad (\text{constant } T, V)$$

The same chemical reaction analysis can be carried out with  $A$  instead of  $G$ .

**6.11.13. Heat Transfer at Constant Volume and Pressure.** For a closed system ( $dN_i = 0$ ) under constant volume,

$$dU = \delta Q - \underbrace{P_{ext} dV}_{dV=0} = \delta Q_V = C_V(T)dT,$$

which implies that

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

If the temperature dependence of  $C_V$  over some temperature range of interest is negligible,  $C_V(T) = C_V$ , the expression for  $dU$  can be integrated to give:

$$\Delta U = C_V \Delta T.$$

For a closed system at constant pressure,

$$dH = \delta Q + \underbrace{V dP_{ext}}_{dP_{ext}=0} = \delta Q_P = C_P(T)dT,$$

which implies that

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P.$$

If  $C_P$  is independent of temperature we can integrate  $dH$  to get:

$$\Delta H = C_P \Delta T.$$

**6.11.14. Relationship Between Specific Heats.** Take the derivative of

$$H = U + PV \quad (\text{definition of enthalpy})$$

with respect to temperature:

$$\underbrace{\frac{\partial H}{\partial T}}_{C_P} = \frac{\partial(U + PV)}{\partial T} = \underbrace{\frac{\partial U}{\partial T}}_{C_V} + \frac{\partial(PV)}{\partial T}$$

$$\boxed{C_P = C_V + \frac{\partial(PV)}{\partial T}}$$

For an ideal gas,  $PV = nRT$ , so the second term equals  $nR$ , and we obtain:

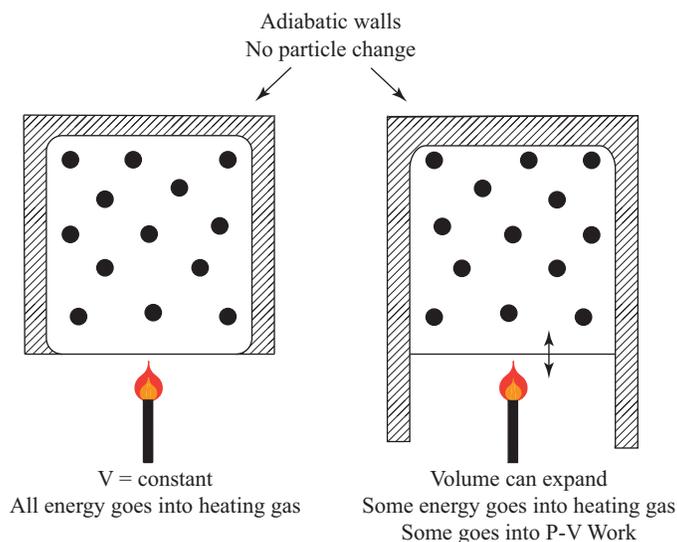
$$C_P = C_V + nR.$$

Dividing through by  $n$  we get a relationship between the specific heats:

$$\boxed{c_P = c_V + R.} \quad (\text{Mayer's relation})$$

A look at the term  $\frac{\partial(PV)}{\partial T}$  reveals that it is always positive because as temperature increases,  $PV$  also increases. Thus,  $C_P > C_V$ .

The situation is illustrated in Fig. 6.11.



**Figure 6.12.** Difference between heating at constant pressure vs volume.

Thus,

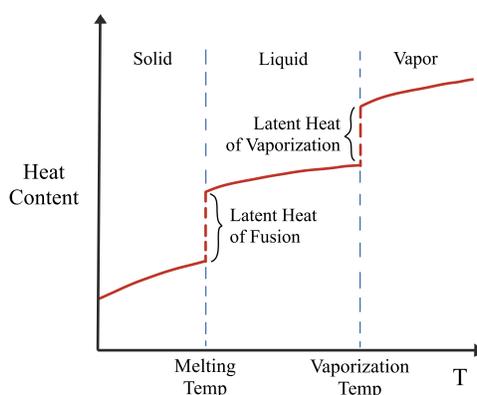
$$\left(\frac{\partial U}{\partial T}\right)_V \equiv \boxed{C_V < C_P} \equiv \left(\frac{\partial H}{\partial T}\right)_P.$$

The enthalpy accounts for energy transfer to the environment through the expansion of the system.

**6.11.15. Latent Heat.** Latent heats are associated with phase transitions, such as the melting of solids or vaporization of liquids and solids. It is the

heat absorbed or released by a thermodynamic system as it undergoes a phase transition.

At the microscopic level, this heat serves to break or form bonds. Such heats are also called heat of fusion (melting), heat of vaporization, etc. There are entropy changes associated with such phase transitions, namely, the entropy of fusion, entropy of vaporization, etc. Entropy changes because there is a spatial rearrangement of the molecules in the system (e.g. from ordered crystal to disorder in a liquid). See Fig. 6.13.



**Figure 6.13.** Difference between heating at constant pressure vs volume.

For a reversible process,

$$dS = \frac{\delta Q^{rev}}{T}$$

Consider a small temperature interval  $[T_C - \epsilon, T_C + \epsilon]$  centered on  $T_C$  (critical temperature), with  $\epsilon$  so small that the temperature is essentially constant. The system undergoes a phase transition at  $T_C$ . The latent heat associated with this transition is

$$\delta Q_{lat} = T_C dS_{lat}, \quad \text{or} \quad \Delta Q_{lat} = T_C \Delta S_{lat},$$

where  $\Delta S_{lat}$  is called the *entropy of fusion or vaporization*, if the process is one of melting or evaporation, respectively.

We can also express it in terms of the enthalpy change  $dH = TdS + VdP$  at constant pressure ( $dP = 0$ ) gives

$$\Delta S = \int_{T_C - \epsilon}^{T_C + \epsilon} \frac{dH}{T}$$

across the phase transition (see Fig. 6.14).

and

$$\boxed{\Delta S_{lat} = \frac{\Delta H_{lat}}{T_C}},$$

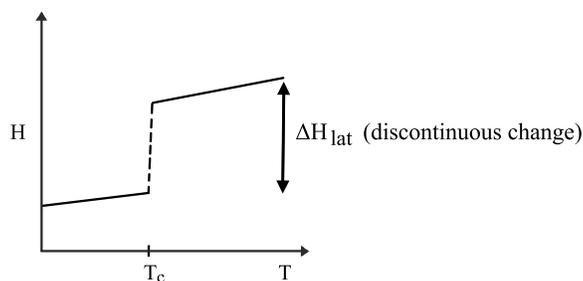


Figure 6.14. Latent heat.

where  $T_C$  is the phase transition temperature (critical temperature) and  $\Delta H_{lat}$  is the latent heat. Since we assumed constant  $P$ ,  $\Delta H_{lat}$  is the same as  $\Delta Q_{lat}$ . This formula gives the entropy change  $\Delta S_{lat}$  corresponding to latent heat  $\Delta H_{lat}$  of a phase transition at constant  $P$ .

Remarks:

- $\Delta S_{lat}$  and  $\Delta H_{lat}$  represent discontinuous changes between two phases of the same substance occurring at the transition temperature  $T_C$ .
- Latent heats are tabulated as *specific latent heats*,  $L$ , which is an intensive property:  $L \equiv \Delta Q_{lat}/m$ , where  $m$  is the mass of the substance. The common units are kJ/kg.

**6.11.16. Application of First and Second Laws: Equilibrium Establishes a Common Temperature.** Suppose that  $A$  denotes the system and  $B$  denotes the surroundings (see Fig. 6.15) and that  $A$  and  $B$  are separated by a thermally conductive wall. Assume that the volumes of  $A$  and  $B$  do not change. The combined system is the *universe* and it is isolated. Because entropy is an *extensive* property,  $S_A$  and  $S_B$  added yields the entropy of the universe:

$$S = S_A + S_B.$$

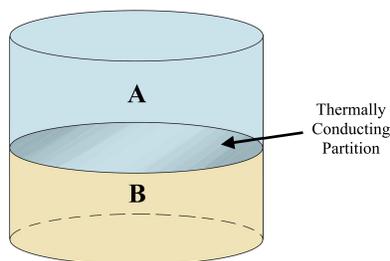


Figure 6.15. Two closed, constant-volume, sub-systems are separated by a thermally conducting partition. The second law requires that at thermal equilibrium the temperatures of the two subsystems will necessarily become equal ( $T_A = T_B$ ).

First, we rewrite the fundamental equation

$$dU = TdS - PdV + \sum_i \mu_i dn_i$$

in the entropy representation:

$$dS = \left(\frac{1}{T}\right) dU + \left(\frac{P}{T}\right) dV - \sum_i \left(\frac{\mu_i}{T}\right) dn_i.$$

The entropy of the isolated system (“universe”) is the sum of entropies of  $A$  and  $B$ ,  $S = S_A + S_B$  (entropy is additive). Then, we invoke the fundamental equation in the entropy representation (with  $dV = 0$  and  $dN_i = 0$ ),

$$dS = dS_A + dS_B = \left(\frac{1}{T_A}\right) dU_A + \left(\frac{1}{T_B}\right) dU_B$$

where we have invoked the First Law twice, once for  $S_A$  and once for  $S_B$ . Since energy is conserved ( $A + B$  is an isolated system)  $dU_A = -dU_B$ :

$$dS = \left[ \left(\frac{1}{T_A}\right) - \left(\frac{1}{T_B}\right) \right] dU_A.$$

Since  $V_A, V_B, N_A, N_B$  are all constant, there can be no mechanical or chemical work exchanged between the system and its surroundings and so  $dU_A = \delta Q$ .

$$(6.8) \quad dS = \left[ \left(\frac{1}{T_A}\right) - \left(\frac{1}{T_B}\right) \right] \delta Q$$

where  $\delta Q$  is the heat transferred to the system (or to the surroundings if  $\delta Q < 0$ ). At thermal equilibrium, entropy of the system is maximized  $dS = 0$ . So a nonzero infinitesimal heat exchange  $\delta Q \neq 0$  implies that the temperatures of  $A$  and  $B$  must be equal:

$$\boxed{T_A = T_B.} \quad (A \text{ and } B \text{ in thermal equilibrium})$$

**Note:** Suppose that  $T_A$  (the system) is higher than  $T_B$ . Then we expect heat to flow from the system into the surroundings. The second law  $dS \geq 0$  and Eq. (6.8) imply that  $dU_A = \delta Q < 0$  and indeed heat flows out of the system. So the Second Law correctly predicts the direction of the heat exchange.

**6.11.17. When is Heat Transfer Reversible?** We have previously seen that reversibility is defined as a process for which the surroundings have intensive variables that are arbitrarily close to those of the system, i.e.  $P = P_{ext} + dT$ ,  $P = P_{ext} + dP$ ,  $\mu = \mu_{ext} + d\mu$ . We’ve also seen that  $dS = 0$  when a process is reversible. Let us check that these two conditions imply each other. Using the notation from the previous section, we would expect that if  $T_A$  is vastly different than  $T_B$ , the process would not be reversible. Let  $T_B = T$  and  $T_A = T - dT$  so that the process is truly

reversible. Then,

$$dS = \left[ \left( \frac{1}{T - dT} \right) - \left( \frac{1}{T} \right) \right] \delta Q$$

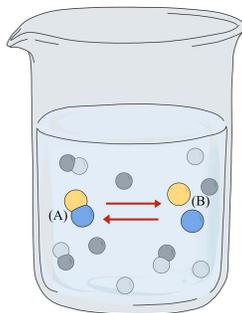
Factoring out  $1/T$  and invoking the geometric series,  $1/(1 - r) = 1 + r + r^2 + \dots$  with  $r = dT/T$ , we have:

$$dS = \left[ \left( 1 + \frac{dT}{T} + \frac{dT^2}{T^2} + \dots \right) - 1 \right] \frac{\delta Q}{T} \approx \frac{\delta Q dT}{T^2} \approx 0,$$

since  $\delta Q dT$  is an infinitesimal of the second order. Thus, the entropy change  $dS$  is zero when the process is reversible.

**6.11.18. Can we Have Isothermal Heat Transfer?** Isothermal means  $dT = 0$  or  $T = \text{constant}$ . From  $dS = \delta Q^{rev}/T$ , a heat transfer  $\delta Q^{rev}$  to the system corresponds to a change in its energy in the amount of  $TdS$ . Thus, it describes a change in entropy, i.e. given  $\Delta Q^{rev} > 0$ , we must have  $\Delta S > 0$ . This can happen, for example, during the course of a phase transition. Some amount of heat (latent heat) is transferred to the system at constant temperature while the entropy changes.

**6.11.19. Application of First and Second Laws: Chemical Equilibria.** In a similar way, we can use the Second Law to predict that at thermal equilibrium the chemical potentials of the reactant and product species should be equal to each other. Consider a chemical a system in which one chemical component ( $A$ ) may react to form another component ( $B$ ). For example,  $A$  and  $B$  could be the gauche and trans conformational isomers of  $n$ -butane, or they could be the native and denatured states of a protein. See Fig. 6.16.



**Figure 6.16.** A closed, insulated, constant-volume, system contains molecules that can inter-convert between two different chemical states ( $A$  and  $B$ ). The second law requires that the chemical potentials of the two compounds must become equal ( $A = B$ ) at equilibrium.

We will also assume that the container which holds the system is insulated and sealed (so neither heat nor matter can enter or leave), and that the volume of the container is constant. Thus, no work or heat exchange can take place between the system and its surroundings (so it is isolated).

Now imagine that we initially put some amounts of  $A$  and  $B$  into the system which are not equal to their equilibrium concentrations. The entropy representation of the fundamental equation implies that the total entropy change is

$$dS(U, V, N_i) = \left(\frac{1}{T}\right) dU + \left(\frac{P}{T}\right) dV - \sum_i \left(\frac{\mu_i}{T}\right) dN_i,$$

and since energy and volume are constant  $dU = dV = 0$ ,

$$dS = -\left(\frac{\mu_A}{T_A}\right) dN_A - \left(\frac{\mu_B}{T_B}\right) dN_B.$$

At thermal equilibrium  $T_A = T_B = T$ . Moreover, stoichiometric balance requires that  $dN_B = -dN_A$ ,

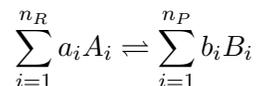
$$dS = -\left[\left(\frac{\mu_A}{T}\right) - \left(\frac{\mu_B}{T}\right)\right] dN_A.$$

At equilibrium  $dS = 0$  and (provided  $dN_A \neq 0$ ),

$$\mu_A = \mu_B.$$

Away from equilibrium  $dS > 0$ , so if  $\mu_A > \mu_B$  then we must have  $dN_A < 0$  (reactants are consumed), as would be expected. Thus, the Second Law correctly predicts the direction of change in a chemical reaction.

**6.11.20. Generalization to Arbitrary Reactions.** The above result may be extended to chemical reactions involving more complex stoichiometry,



where  $a_i$  and  $b_i$  are stoichiometric coefficients for the reactant  $A_i$  and product  $B_i$  species, respectively.  $n_R$  is the number of reactants.  $n_P$  is the number of products.

The chemical reaction can be written as an equation, where  $\{A_i\}$  denote the set of all reactants and products,  $\{\nu_i\}$ , the set of stoichiometric coefficients with the convention that  $\nu_i$  are positive numbers for the reactants ( $\nu_i = a_i$ ) and negative numbers for the products ( $\nu_i = -b_i$ ),

$$\sum_{i=1}^{n_S} \nu_i A_i = 0,$$

with  $n_S = n_R + n_P$ .

For any such reaction one may use the following equation to express the relationship between the chemical potentials of the reacting species at equilibrium:

**Chemical Equilibrium:**

$$\sum_{i=1}^{n_S} \nu_i \mu_i = 0 \quad \text{at equilibrium.}$$

This result follows from the same analysis as in the previous section. There, we would also have that at thermal equilibrium, all temperatures are the same,  $T_i = T$  for all  $i$ .

The  $dN_i$  are parametrized by a new variable  $t$ , i.e. so that  $dN_i(t) = N'_i(t)dt$ , where  $t \in [0, 1]$  is a variable that denotes the “extent of the reaction”. Then  $t = 0$  the reaction begins and when  $t = 1$ , it ends.  $N'_i(t)$  is the speed at which species  $i$  is produced or depleted; it is proportional to the stoichiometric coefficient  $\nu_i$ , so we write  $N'_i(t) = \alpha \nu_i$ , where  $\alpha$  is a constant.<sup>25</sup>

Under those conditions, the chemical term in  $dS$  reads:

$$dS = - \left[ \sum_{i=1}^{n_S} \left( \frac{\mu_i}{T_i} \right) \alpha \nu_i \right] dt = - \frac{\alpha}{T} \left[ \sum_{i=1}^{n_S} \mu_i \nu_i \right] dt.$$

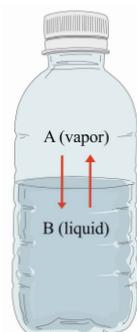
At equilibrium,  $dS = 0$  (provided  $dt \neq 0$ ), from which it follows that the coefficient of  $dt$  must vanish, i.e.  $\sum_{i=1}^{n_S} \nu_i \mu_i = 0$ .

**6.11.21. Application of First and Second Laws: Phase Equilibrium.** In thermodynamics, phases are treated as separate components. Consider a system composed of two sub-systems whose boundary allows the exchange of molecules, as well as heat and mechanical work. For example, one sub-system could be a vapor phase A and the other a liquid phase B, as shown in Fig. 6.17. In such a situation, we may again invoke the Second Law to obtain general relations between all of the intensive variables of the two sub-systems at equilibrium.

For simplicity we will assume there is only one chemical component in the system (such as water). We assume that the number of water molecules in the vapor phase is  $N_A$  and in the liquid phase is  $N_B$ .

Note that when molecules are exchanged between the two phases the volumes  $V_A$  and  $V_B$ , as well as the energies  $U_A$  and  $U_B$ , of each phase will also change. We further assume that both phases are enclosed by a sealed and insulated container of fixed total volume (so the entire system is isolated from its surroundings).

<sup>25</sup>If  $t$  is time, then  $dN_i$  denotes the change in number of molecules of species  $i$  whereas  $N'_i(t)dt$  denotes the rate of change in  $N_i$  times  $dt$ .



**Figure 6.17.** A closed, insulated, constant-volume, system contains two phases ( $A$  and  $B$ ). The second law requires that at equilibrium the temperature, pressure and chemical potentials of the two phases will necessarily become equal ( $T_A = T_B$ ,  $P_A = P_B$  and  $\mu_A = \mu_B$ ).

When we apply the fundamental equation to each phase we obtain the following expressions.

$$\begin{aligned} dS_A &= \left(\frac{1}{T_A}\right) dU_A + \left(\frac{P_A}{T_A}\right) dV_A - \left(\frac{\mu_A}{T_A}\right) dN_A \\ dS_B &= \left(\frac{1}{T_B}\right) dU_B + \left(\frac{P_B}{T_B}\right) dV_B - \left(\frac{\mu_B}{T_B}\right) dN_B. \end{aligned}$$

The entropy change of the entire system is again  $dS = dS_A + dS_B$ . Since the total energy, volume and number of molecules are all conserved, we may equate  $dU_A = -dU_B = dU$ ,  $dV_A = -dV_B = dV$ , and  $dN_A = -dN_B = dN$ . Thus, an infinitesimal entropy change of the whole system, resulting from the transfer of some molecules between phase  $A$  and phase  $B$ , may be expressed as follows.

$$dS = \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right) dV - \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right) dN.$$

At equilibrium  $dS = 0$  when  $dU \neq 0$  and  $dV \neq 0$  and  $dN \neq 0$ , so all three quantities in parentheses must equal to zero. Thus implies that all three of the following intensive variables of the two phases must be equal at equilibrium:

$$\boxed{T_A = T_B, \quad P_A = P_B, \quad \mu_A = \mu_B.}$$

In fact, you can check that

$$\boxed{T_A = T_B + dT, \quad P_A = P_B + dP, \quad \mu_A = \mu_B + d\mu,}$$

leads to equilibrium ( $dS = 0$ ).

In any two phase equilibrium all of the intensive variables of the two phases – temperatures, pressures and chemical potentials – must be in perfect balance with each other.

If the system contained more than one chemical species then similar expressions would hold for each chemical species. Moreover, if the system contained molecules that can chemically react with each other, then  $\sum_i \nu_i \mu_i = 0$  would impose an additional equilibrium condition which must hold for any such reactive species.

### 6.11.22. Application of Chemical Potential, Various Equilibria.

Gibbs energy of mixing. Suppose that we have two perfect gases,  $A$  and  $B$ , in two containers, in the amounts  $n_A$  and  $n_B$ , respectively. Both are at temperature  $T$  and pressure  $P$ . The chemical potentials of the two gases have their “pure” values,

$$\mu(T, P) = \mu^\circ(T) + RT \log(P/P_0)$$

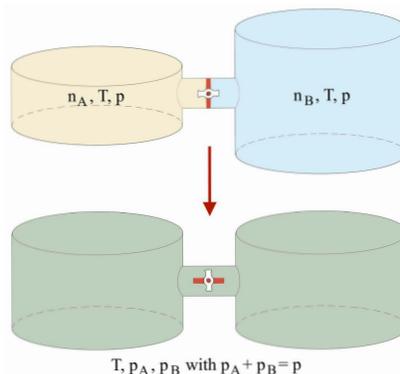
where  $\mu^\circ$  is the *standard chemical potential* (standard conditions for a gas often means pure gas at 1 bar). See Fig. 6.18. We can take  $P_0$  to be 1 bar and take  $P$  to be the pressure in units of 1 atm. For substance  $A$  we have:

$$\mu_A = \mu_A^\circ + RT \log(P).$$

For  $B$  we have:

$$\mu_B = \mu_B^\circ + RT \log(P).$$

Setting  $P = 1$  atm in those expressions (pure gas at 1 atm) leads to  $\mu_A = \mu_A^\circ$  and  $\mu_B = \mu_B^\circ$  (in each respective container), as it should.



**Figure 6.18.** Arrangement for calculating the thermodynamic functions of mixing of two perfect gases.

Gibbs energy of the total system is (before mixing):

$$G_i = n_A \mu_A + n_B \mu_B = n_A(\mu_A^\circ + RT \log P) + n_B(\mu_B^\circ + RT \log P).$$

After mixing, the partial pressures are  $P_A$  and  $P_B$  ( $P_A + P_B = P$ ). The total Gibbs energy changes to:

$$G_f = n_A(\mu_A^\circ + RT \log P_A) + n_B(\mu_B^\circ + RT \log P_B)$$

The difference,  $G_f - G_i$ , the Gibbs energy of mixing,  $\Delta G_{mix}$ , is therefore

$$\Delta G = G_f - G_i = n_A RT \log(P_A/P) + n_B RT \log(P_B/P).$$

Replacing  $n_A$  by  $X_A n$ , where  $n$  is the total number of moles of  $A$  and  $B$ , and using Dalton's law,  $P_A = X_A \cdot P$ , we have:

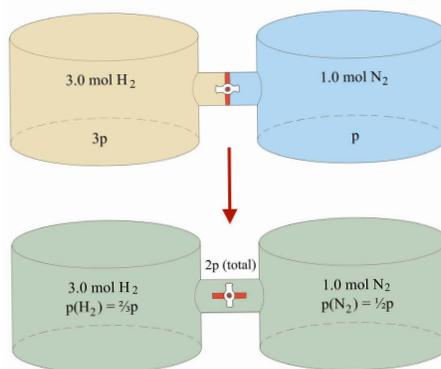
$$\Delta G_{mix} = nRT(X_A \log X_A + X_B \log X_B).$$

Because  $0 \leq X_A, X_B \leq 1$ , the logs are negative and  $\Delta G_{mix} < 0$ . Thus, perfect gases mix spontaneously in all proportions. And from  $dG = -SdT + VdP$ ,  $S = -(\partial G/\partial T)$ , the entropy of mixing is:

$$\Delta S_{mix} = -nR\{X_A \log X_A + X_B \log X_B\}.$$

Note: since  $\Delta G = \Delta H - T\Delta S$ , it follows that  $\Delta H_{mix} = 0$ . This is expected for a system in which there are no interactions between the molecules forming the gaseous mixture. It follows that the driving force for mixing comes from the increase in entropy of the system because the entropy of the surroundings is unchanged.

6.11.22.1. *Example: (Gibbs energy of mixing).* A container is divided into two equal compartments (Fig. 6.19). One contains 3.0 mol  $\text{H}_2(\text{g})$  at  $25^\circ\text{C}$ . The other contains 1.0 mol  $\text{N}_2(\text{g})$  at  $25^\circ\text{C}$ . Calculate the Gibbs energy of mixing when the partition is removed. Assume perfect behavior.



**Figure 6.19.** The initial and final states considered in the calculation of the Gibbs energy of mixing of gases at different initial pressures.

*Solution:* The formula from the previous section cannot be used directly because the initial gas pressures are different. Given that the pressure of nitrogen is  $P$  and the pressure of hydrogen is  $3P$ , the initial Gibbs energy is

$$G_i = (3.0 \text{ mol})\{\mu^\circ(\text{H}_2) + RT \log 3P\} + (1.0 \text{ mol})\{\mu^\circ(\text{N}_2) + RT \log P\}$$

When the partition is removed and each gas occupies twice the original volume, the partial pressure of nitrogen falls to  $\frac{1}{2}P$  and that of hydrogen

falls to  $\frac{3}{2}P$ . Therefore, the Gibbs energy changes to

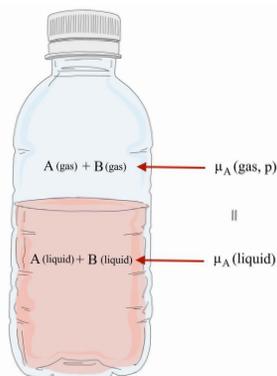
$$G_f = (3.0 \text{ mol})\{\mu^\circ(\text{H}_2) + RT \log \frac{3}{2}P\} + (1.0 \text{ mol})\{\mu^\circ(\text{N}_2) + RT \log \frac{1}{2}P\}$$

Taking the difference gives the Gibbs energy of mixing:

$$\begin{aligned} \Delta G_{mix} = G_f - G_i &= (3.0 \text{ mol})RT \log \left( \frac{\frac{3}{2}P}{3P} \right) + (1.0 \text{ mol})RT \log \left( \frac{\frac{1}{2}P}{P} \right) \\ &= - (3.0 \text{ mol})RT \log 2 - (1.0 \text{ mol})RT \log 2 \\ &= - (4.0 \text{ mol})RT \log 2 = -6.9 \text{ kJ} \end{aligned}$$

Here,  $\Delta G_{mix} < 0$ , however, the negative sign does not necessarily indicate spontaneity.  $dG < 0$  indicates spontaneity only at constant temperature and pressure. (Here, the pressure dropped from  $4P$  to  $2P$  when opening the partition.)

**Problem.** Suppose that 2.0 mol  $\text{H}_2$  at 2.0 atm and  $25^\circ\text{C}$  and 4.0 mol  $\text{N}_2$  at 3.0 atm and  $25^\circ\text{C}$  are mixed at constant volume. Calculate  $\Delta G_{mix}$ . What would be the value of  $\Delta G_{mix}$  had the pressures been identical initially? [-9.7 kJ, -9.5 kJ]



**Figure 6.20.** At equilibrium, the chemical potential of the gaseous form of a substance  $A$  is equal to the chemical potential of its condensed phase. The equality is preserved if a solute is also present. Because the chemical potential of  $A$  in the vapor depends on its partial vapor pressure, it follows that the chemical potential of liquid  $A$  can be related to its partial vapor pressure.

**6.11.23. Ideal Solutions & Raoult's Law.** Suppose we have an ideal solution made up of two components,  $A$  and  $B$  (Fig. 6.20). Let us denote with a  $*$  the quantities relating to pure substances. Let  $\mu_A^*(l)$  denote the chemical potential of pure  $A$  (liquid). Vapor pressure of the pure liquid is  $P_A^*$ . Chemical potential in the vapor is  $\mu_A^\circ + RT \log P_A^*$ . These two chemical

potentials are equal at equilibrium:

$$\underbrace{\mu_A^*(l)}_{\text{liquid}} = \underbrace{\mu_A^\circ + RT \log P_A^*}_{\text{gas}} \quad (\text{pure A})$$

If another substance, a solute, is also present in the liquid, the chemical potential of  $A$  in the liquid is changed to  $\mu_A(l)$  and its vapor pressure is changed to  $P_A$ . The vapor and solvent are still in equilibrium, so we can write

$$\mu_A(l) = \mu_A^\circ + RT \log P_A. \quad (\text{add some B})$$

Next, we combine these two equations to eliminate the standard chemical potential of the gas. To do so, we solve for  $\mu_A^\circ$  in both equations and equate the two results to obtain

$$\mu_A(l) = \mu_A^*(l) - RT \log P_A^* + RT \log P_A = \mu_A^*(l) + RT \log(P_A/P_A^*).$$

Substituting Raoult's law,  $P_A = X_A \cdot P_A^*$ , we get:

$$\boxed{\mu_A(l) = \mu_A^*(l) + RT \log X_A.}$$

This important equation can be used as the definition of an ideal solution (so that it implies Raoult's law rather than stemming from it) and is better, because it does not assume that the vapor is a perfect gas.

**6.11.24. Liquid Mixtures: Ideal Solutions.** Suppose that we mix two liquids  $A$  and  $B$ . Before mixing, we have:

$$G_i = n_A \mu_A^* + n_B \mu_B^*.$$

When they are mixed, the individual chemical potentials are modified, and the total Gibbs energy is,

$$G_f = n_A \{\mu_A^* + RT \log X_A\} + n_B \{\mu_B^* + RT \log X_B\}.$$

Consequently, the Gibbs energy of mixing,  $G_f - G_i$  is

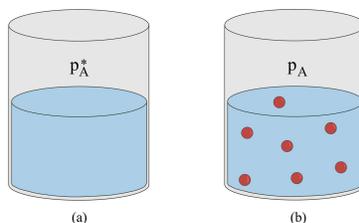
$$\Delta G_{mix} = nRT \{X_A \log X_A + X_B \log X_B\}.$$

And from  $dG = -SdT + VdP$ ,  $S = -(\partial G/\partial T)$ , the entropy of mixing is:

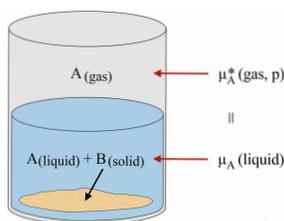
$$\Delta S_{mix} = -nR \{X_A \log X_A + X_B \log X_B\}.$$

**6.11.25. Elevation of Boiling Point.** The vapor pressure of a pure liquid represents a balance between the increase in disorder arising from vaporization and the decrease in disorder of the surroundings. See Figs. 6.21 and 6.22.

The heterogeneous equilibrium of interest when considering boiling is between the solvent vapor and the solvent in solution at 1 atm. We denote the solvent by  $A$  and the solute by  $B$ . The equilibrium is established at a



**Figure 6.21.** (a) Liquid is represented by the blue space. (b) When solute (red circles) is present, the disorder of the condensed phase is increased, and there is decreased tendency to acquire the disorder of the vapor.



**Figure 6.22.** The heterogeneous equilibrium involved in the calculation of the elevation of boiling point is between  $A$  in the pure vapor and  $A$  in the mixture,  $A$  being the solvent and  $B$  a non-volatile solute.

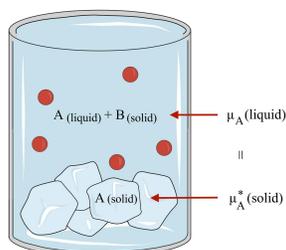
temperature for which

$$\mu_A^*(g) = \mu_A^*(l) + RT \log X_A.$$

(The pressure of 1 atm is the same throughout and is not written explicitly.) This equation implies<sup>26</sup> that the presence of a solute at a mole fraction  $X_B$  causes an increase in normal boiling point from  $T^*$  to  $T^* + \Delta T$ , where

$$\Delta T = K \cdot X_B, \quad K = \frac{RT^{*2}}{\Delta_{vap}H}.$$

<sup>26</sup>From Atkins [14]: Rearranging the equation to  $\log X_A = \frac{\mu_A^*(g) - \mu_A^*(l)}{RT} = \frac{\Delta_{vap}G}{RT}$ , where  $\Delta_{vap}G$  is the Gibbs energy of vaporization of the pure solvent ( $A$ ). Differentiating both sides with respect to  $T$  gives:  $\frac{d \log X_A}{dT} = \frac{1}{R} \frac{d(\Delta_{vap}G/T)}{dT} = -\frac{\Delta_{vap}H}{RT^2}$ , where use was made of the Gibbs-Helmholtz equation,  $(\partial(G/T)/\partial T)_P = -H/T^2$ . Multiplying both sides by  $dT$  and integrating from  $X_A = 1$  (boiling point  $T = T^*$  of pure solvent) to  $X_A$  (boiling point  $T$ ),  $\int_0^{\log X_A} d \log X_A = -\frac{1}{R} \int_{T^*}^T \frac{\Delta_{vap}H}{T^2} dT$ . The left hand side integrates to  $\log X_A = \log(1 - X_B)$ . For constant enthalpy of vaporization,  $\log(1 - X_B) = -\frac{\Delta_{vap}H}{R} \int_{T^*}^T \frac{1}{T^2} dT$ , and therefore,  $\log(1 - X_B) = \frac{\Delta_{vap}H}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right)$ . We now suppose that the amount of solute present is so small that  $X_B \ll 1$ . We can write  $\log(1 - X_B) \approx -X_B$  and obtain  $X_B = \frac{\Delta_{vap}H}{R} \left( \frac{1}{T^*} - \frac{1}{T} \right)$ . Finally, because  $T \approx T^*$ , it follows that  $\frac{1}{T^*} - \frac{1}{T} = \frac{T - T^*}{T T^*} \approx \frac{\Delta T}{T^{*2}}$ , with  $\Delta T = T - T^*$ . PROOF of Gibbs-Helmholtz: on one hand,  $-S = (\partial G/\partial T)_P = (G - H)/T$ , on the other hand,  $\left( \frac{\partial(G/T)}{\partial T} \right)_P = \frac{1}{T} \left( \frac{\partial G}{\partial T} \right)_P + G \frac{d(1/T)}{dT} = \frac{1}{T} \left( \frac{\partial G}{\partial T} \right)_P - \frac{G}{T^2} = \frac{1}{T} \left\{ \left( \frac{\partial G}{\partial T} \right)_P - \frac{G}{T} \right\}$ . In the curly bracket, we substitute  $\left( \frac{\partial G}{\partial T} \right)_P - \frac{G}{T} = \frac{G - H}{T} - \frac{G}{T} = -\frac{H}{T}$ . Gibbs-Helmholtz follows.



**Figure 6.23.** Heterogeneous equilibrium involved in the calculation of the lowering of freezing point is between  $A$  in the pure solid and  $A$  in the mixture,  $A$  being the solvent and  $B$  a solute that is insoluble in solid  $A$ .

**6.11.26. Depression of Freezing Point.** The heterogeneous equilibrium now of interest is between pure solid solvent  $A$  and the solution with solute present at a mole fraction  $X_B$  (Fig. 6.23). At the freezing point, the chemical potentials of  $A$  in the two phases are equal:

$$\mu_A^*(s) = \mu_A^*(l) + RT \log X_A$$

The calculation is the same as in the previous section, and the result is

$$\Delta T = K' \cdot X_B, \quad K' = \frac{RT^{*2}}{\Delta_{fus}H},$$

where  $\Delta T$  is the freezing point depression,  $T^* - T$ , and  $\Delta_{fus}H$  is the enthalpy of fusion of the solvent. Larger depressions are observed in solvents with low enthalpies of fusion at high melting points. When the solution is dilute, the mole fraction is proportional to the molality of the solute,  $b$ , and it is common to write the last equation as

$$\Delta T = K_f \cdot b.$$

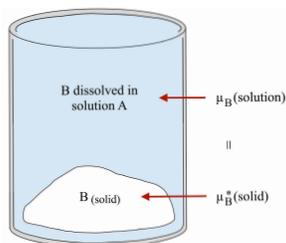
where  $K_f$  is the empirical freezing-point constant.

**6.11.27. Solubility.** When a solid solute is left in contact with a solvent, it dissolves until the solution is saturated. Saturation is a state of equilibrium, with the undissolved solute in equilibrium with the dissolved solute. Therefore, in a saturated solution the chemical potential of the pure solid solute,  $\mu_B^*(s)$ , and the chemical potential of  $B$  in solution,  $\mu_B$ , are equal (Fig. 6.24).

Because the latter is  $\mu_B = \mu_B^*(l) + RT \log X_B$ , we can write

$$\mu_B^*(s) = \mu_B^*(l) + RT \log X_B.$$

This expression is the same as the starting expression in the last section, except that the quantities refer to the solute  $B$ , not the solvent  $A$ . It leads



**Figure 6.24.** Heterogeneous equilibrium involved in the calculation of the solubility is between pure solid  $B$  and  $B$  in the mixture.

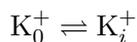
to:

$$\log X_B = \frac{\Delta_{fus}H}{R} \left( \frac{1}{T_f} - \frac{1}{T} \right).$$

**6.11.28. Example: (Ion transport Across Cell Membrane).** There are ions (e.g.  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , etc.) found in the intra and extra-cellular spaces at different concentrations. Cell membrane proteins participate in the transport of such ions. As an example, let us analyze the chemical equilibrium of  $\text{K}^+$  ions using the first two laws of thermodynamics. Recall that for a chemical reaction:

$$\Delta G_{rxn} = \Delta G_{rxn}^\circ + RT \log Q$$

where  $\Delta G_{rxn}^\circ = -RT \log K_{eq}$ . This is valid when a chemical reaction is the only “work” done. However, there may be other terms in the expression for  $\Delta G$  that need to be accounted for. Consider the “chemical reaction” where a potassium ion is shuttled in and out of the cell cytoplasm:



Chemical reaction equilibrium alone would state that

$$\mu_i - \mu_0 = RT \log \left( \frac{[\text{K}^+]_i}{[\text{K}^+]_o} \right)$$

Where  $[\text{K}^+]_i$  is the potassium ion concentration inside the cell and  $[\text{K}^+]_o$  is its concentration found outside (in the extracellular matrix). The difference  $\mu_i - \mu_0$  represents gradient (difference) in the chemical potential across the cell membrane. This chemical potential gradient acts as a driving force to shuttle ions in and out of the cell (depending on whether  $[\text{K}^+]_i > [\text{K}^+]_o$  or  $[\text{K}^+]_i < [\text{K}^+]_o$ ). See Fig. 6.25.

However, this cannot be the only force because if we shuttle all ions out of the cell (for instance), the electrostatic repulsion among potassium ions in the extracellular matrix will be large enough to drive some of these ions to re-enter the cytoplasm. Thus, we must include electrostatic repulsions.

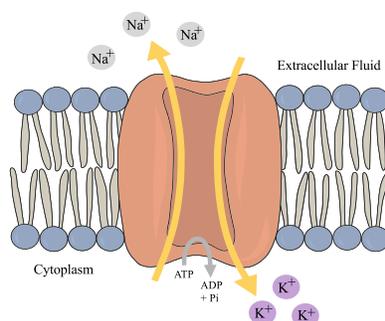


Figure 6.25. Potassium pump.

Electrostatic repulsions can be accounted for by adding electrostatic work. Recall that the electrostatic work is of the form  $\delta W_{el.} = \phi dq$  where  $dq$  is the charge added or removed, and  $\phi$  is the local electrostatic potential. Here we write  $\phi_o$  for the electrostatic potential in the extracellular matrix and  $\phi_i$  for the potential inside the cytoplasm. The total work is obtained by integrating from reactants to products. As far as the integral  $\Delta W_{el.} = \int_{reactants}^{products} \phi dq$  is concerned, going from reactants to products means we *subtract* a charge  $Q$  from the extracellular space (work =  $-Q\phi_o$ ) and *add* it to the intracellular space (work =  $+Q\phi_i$ ).

The total integral along this path yields the sum of these two terms: one from the extracellular matrix, and one for the cytoplasm:

$$\Delta W_{el.} = Q(\phi_i - \phi_o),$$

where  $\phi_o$  acquires a negative sign because we are removing an ion of charge  $Q$  from the extracellular matrix (and add it to the cytoplasm). The difference  $\phi_i - \phi_o$  is the potential difference across the cell membrane (units: volts). When the electrostatic force balances out the chemical force,  $\Delta G = 0$  and these two terms are equal:

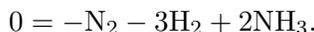
$$\Delta\phi \equiv \phi_i - \phi_o = \frac{RT}{Q} \log \left( \frac{[K^+]_i}{[K^+]_o} \right).$$

This potential difference,  $\Delta\phi \equiv \phi_i - \phi_o$  (in volts), is called the *Nernst potential*. Inspection of this equation shows that  $Q$  must be specified in units of Coulomb per mole;  $Q$  in these units is often called the Faraday's constant,  $F \equiv 9.65 \times 10^4$  C/mol. (Otherwise, replace  $RT$  by  $k_B T$  and  $Q$  is then specified in units of Coulomb.)

Please note that the above analysis is valid in thermal equilibrium (steady state) and does not describe dynamics, such as those observed in cardiac tissues or neuronal networks.

There are ways to directly measure ion concentrations and voltages. For a discussion of  $\text{Ca}^{2+}$  and voltage sensing via specially-designed fluorophores, see the paper [25].

**6.11.29. Affinity of Reaction and Reaction Enthalpy.** General chemical reactions are represented by an equation,  $\sum_i \nu_i A_i = 0$ , where the stoichiometric coefficients  $\nu_i$  are negative for reactants and positive for products. For example:



The *extent of reaction*  $\xi$  is defined by:

$$\xi = \frac{n_i(\xi) - n_i(0)}{\nu_i},$$

where  $n_i(\xi)$  is the amount of substance  $A_i$  present when the extent of reaction is  $\xi$ .  $n_i(0)$  is the amount of  $A_i$  present when  $\xi = 0$ , corresponding to the specified initial conditions. The units of  $\xi$  are moles. For example, if 1 mol of  $\text{N}_2$  and 3 mol of  $\text{H}_2$  are converted completely into 2 mol of  $\text{NH}_3$

$$\xi = \frac{n_{\text{NH}_3}(\xi) - n_{\text{NH}_3}(0)}{\nu_{\text{NH}_3}} = \frac{2 \text{ mol} - 0 \text{ mol}}{2} = 1 \text{ mol}$$

$$\xi = \frac{n_{\text{N}_2}(\xi) - n_{\text{N}_2}(0)}{\nu_{\text{N}_2}} = \frac{0 \text{ mol} - 1 \text{ mol}}{-1} = 1 \text{ mol}$$

$$\xi = \frac{n_{\text{H}_2}(\xi) - n_{\text{H}_2}(0)}{\nu_{\text{H}_2}} = \frac{0 \text{ mol} - 3 \text{ mol}}{-3} = 1 \text{ mol}$$

$\xi$  is independent of which chemical is used to compute it. Note also that

$$\boxed{d\xi = \frac{dn_i}{\nu_i}.}$$

Using this notation, the fundamental equation

$$dG = -SdT + VdP + \sum_i \mu_i dn_i,$$

becomes:

$$dG = -SdT + VdP + \sum_i \mu_i \nu_i d\xi.$$

If we define the *reaction affinity* by:

$$\boxed{\mathcal{A} = - \sum_i \mu_i \nu_i.}$$

Then  $dG$  is written:

$$\boxed{dG = -SdT + VdP - \mathcal{A}d\xi.}$$

From this, we see that

$$\mathcal{A} = - \left( \frac{\partial G}{\partial \xi} \right)_{T,P}.$$

For the special case of constant  $T, P$ , we see that  $dG = -\mathcal{A}d\xi$ . Since  $G$  is a state function, integrating from  $\xi = 0$  to  $\xi = 1$  mol yields:

$$\mathcal{A} = -\Delta G_{rxn} = - \sum_i \nu_i \mu_i \geq 0.$$

(This assumes that  $\mathcal{A}$  is independent of  $\xi$ .)

In a similar manner, the fundamental equations for the thermodynamic potentials  $U, S, H, A$ :

$$\begin{aligned} dU &= TdS - PdV + \sum_i \mu_i dn_i & \rightarrow & \quad dU = TdS - PdV - \mathcal{A}d\xi \\ dS &= \frac{1}{T}dU + \frac{P}{T}dV - \frac{1}{T} \sum_i \mu_i dn_i & \rightarrow & \quad dS = \frac{1}{T}dU + \frac{P}{T}dV + \frac{\mathcal{A}}{T}d\xi \\ dH &= TdS + VdP + \sum_i \mu_i dn_i & \rightarrow & \quad dH = TdS + VdP - \mathcal{A}d\xi \\ dA &= -SdT - PdV + \sum_i \mu_i dn_i & \rightarrow & \quad dA = -SdT - PdV - \mathcal{A}d\xi \\ dG &= -SdT + VdP + \sum_i \mu_i dn_i & \rightarrow & \quad dG = -SdT + VdP - \mathcal{A}d\xi \end{aligned}$$

**6.11.30. Enthalpy is the “Heat Content”.** Recall the second law,  $dS_{univ} = dS + dS_{ext} \geq 0$ , where  $S$  is the system and  $S_{ext}$  is the surroundings. Now consider the system  $S$ ; the total entropy production for this system can be decomposed into two terms:

$$dS = d_e S + d_i S.$$

The first term,  $d_e S$ , is the entropy produced by the interaction of the system with its surroundings, e.g.

$$d_e S = \frac{\delta Q}{T}. \quad (\text{if process is reversible})$$

The second term,  $d_i S$ , is the entropy produced by irreversible processes going on inside the system (for example, chemical reactions). **When the only interaction with a system’s surroundings is the absorption of heat  $\delta Q$** , and the only irreversible process going on within the system is a chemical reaction, we can write explicit expressions for  $d_e S$  and  $d_i S$ :

The fundamental equation for  $dS$  reduces to:

$$dS = \underbrace{\frac{\delta Q}{T}}_{d_e S} + \underbrace{\frac{\mathcal{A}}{T}d\xi}_{d_i S}.$$

Thus,

$$\boxed{d_e S = \frac{\delta Q}{T}, \quad d_i S = \frac{\mathcal{A}d\xi}{T}.}$$

These two contributions describe the measurable heat transfer and the irreversible heat (absorbed or released) of the reaction. *We note that the term  $d_i S$  can describe a bona fide chemical reaction or the transfer of matter to another subsystem* (essentially, any process that can be described using chemical potentials). When matter is transported, this causes a transfer of heat.

Consider the complete transformation of stoichiometric amounts of reactants at  $T, P$  into products at  $T, P$ , so that  $\Delta\xi = 1$  mol. Because  $H$  is a function of the state of the system, the enthalpy change due to the reaction

$$\Delta H_{rxn}^\circ = (\Delta Q)_P$$

is equal to the heat absorbed at constant pressure. This quantity was formerly called the *heat of reaction at constant pressure*, but is now called the *reaction enthalpy*. Another historic name for enthalpy is *heat content*. The superscript  $^\circ$  denotes its value under standard conditions (typically, 1 atm, 1 M, 25 $^\circ$ ) The subscript *rxn* tells us that this is the enthalpy change during the reaction.  $\Delta H_{rxn}^\circ$  is the change in an extensive property, but numerical data always refer to  $\Delta\xi = 1$  mol so that the units of  $\Delta H_{rxn}^\circ$  are J/mol, or more commonly kJ/mol.

The idea that enthalpy is the heat transfer at constant pressure is illustrated by the fundamental equation for  $H$ :

$$(dH)_P = TdS + \mathcal{V}dP - \mathcal{A}d\xi = TdS - \mathcal{A}d\xi$$

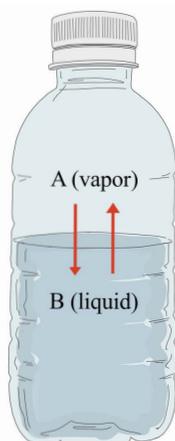
which, at constant pressure, features two terms,  $TdS$ , the measurable heat transfer and  $-\mathcal{A}d\xi$ , the enthalpy associated with mass transport or irreversible chemical reaction. It is because of this property that enthalpy is called *heat content*.

**6.11.31. Forces and Fluxes.** The fundamental equation in the entropy representation is particularly important because of its special structure:

$$dS = \left(\frac{1}{T}\right) dU + \left(\frac{P}{T}\right) dV - \sum_i \left(\frac{\mu_i}{T}\right) dn_i.$$

It has the structure of a sum of terms, each of which represents a force times a flux. The forces are:

- $\frac{1}{T}$ : tendency for heat flow
- $\frac{P}{T}$ : tendency for volume change
- $\frac{\mu}{T}$ : tendency for particle exchange



**Figure 6.26.** A closed, insulated, constant-volume, system contains two phases ( $A$  and  $B$ ). The second law requires that at equilibrium the temperature, pressure and chemical potentials of the two phases will necessarily become equal ( $T_A = T_B$ ,  $P_A = P_B$  and  $\mu_A = \mu_B$ ).

Recall our previous analysis of phase equilibrium (Fig. 6.26), which begins by writing down the First Law for each subsystem  $dS = dS_A + dS_B$  in the entropy representation ( $A + B$  is a closed system, so that  $dU = dU_A = -dU_B$ ,  $dV = dV_A = -dV_B$ ,  $dn = dn_A = -dn_B$ ):

$$dS = \left( \frac{1}{T_A} - \frac{1}{T_B} \right) dU + \left( \frac{P_A}{T_A} - \frac{P_B}{T_B} \right) dV - \left( \frac{\mu_A}{T_A} - \frac{\mu_B}{T_B} \right) dn.$$

$dS$  is called the dissipation function because  $dS > 0$  indicates an irreversible process where energy is dissipated (cannot be converted into useful work).

Notice that all the terms in the expression for  $dS$  are of the form of a gradient in intensive property ( $1/T$ ,  $P/T$ ,  $\mu/T$ ) times the differential of an extensive property ( $U$ ,  $V$ ,  $n$ ). The former is called a *force*; the latter is called a *flux*:

$$\boxed{\text{dissipation function} = \text{force} \times \text{flux} = X \cdot J}$$

**6.11.32. Internal vs External Variables: Heat Transfer Only.** A system with only heat transfer can be exemplified as consisting of two pieces of metal at different absolute temperatures,  $T_1$  and  $T_2$ , where  $T_1 > T_2$ . A small quantity of heat,  $\delta Q$ , is allowed to pass from subsystem 1 to subsystem 2 in course of a short time interval,  $dt$  (Fig. 6.27).

The quantity of heat is so small that changes in the temperatures of the subsystems can be disregarded: Since there is no transfer of matter, each subsystem behaves as a closed system. The transfer of  $\delta Q$  leads to the following changes in the subsystems:

$$dU_1 = T_1 dS_1 - P_1 dV_1 \quad dU_2 = T_2 dS_2 - P_2 dV_2,$$

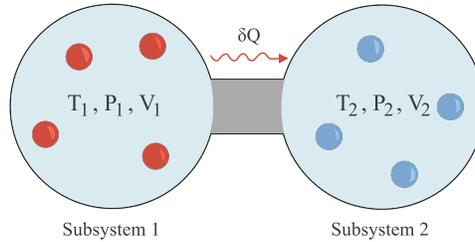


Figure 6.27. Only heat can transfer.

or with the equations solved with respect to entropy change:

$$dS_1 = \frac{dU_1}{T_1} + \left(\frac{P_1}{T_1}\right) dV_1 \quad dS_2 = \frac{dU_2}{T_2} + \left(\frac{P_2}{T_2}\right) dV_2.$$

When  $P$ – $V$  work is the only work carried out,  $dU_1$  and  $dU_2$  can be expressed by the external variables, which are measurable quantities,

$$dU_1 = \delta Q_1 - P_1 dV_1 \quad dU_2 = \delta Q_2 - P_2 dV_2.$$

The total system is adiabatic,

$$\delta Q = -\delta Q_1 = \delta Q_2,$$

so that

$$dU_1 + dU_2 = -P_1 dV_1 - P_2 dV_2.$$

Total entropy production is:

$$dS = dS_1 + dS_2 = -\frac{\delta Q}{T_1} + \frac{\delta Q}{T_2} = \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \delta Q = \Delta(1/T) \delta Q,$$

or

$$\frac{dS}{dt} = \Delta(1/T) \frac{\delta Q}{dt}.$$

Multiplying by  $T_2$  gives the dissipated energy

$$T_2 \frac{dS}{dt} = T_2 \Delta(1/T) \frac{\delta Q}{dt},$$

where  $\delta Q/dt$  is the rate of transport of heat. The units of  $T_2 \frac{dS}{dt}$  and  $\delta Q/dt$  are Watts (1 W=1 J/s).

**6.11.33. Internal vs External Variables: Heat Transfer + Matter Transport.** A system with transfer of heat and matter can be exemplified by two gas containers at different absolute temperatures,  $T_1$  and  $T_2$ , where  $T_1 > T_2$  (Fig. 6.28).

A small quantity of heat,  $\delta\Phi$ , and small quantities of the different gas components,  $dn_i$ , are allowed to pass from subsystem 1 to subsystem 2 in course of the time  $dt$ . The total heat transferred,  $\delta\Phi$ , is composed of a measurable heat and the *enthalpy of the transferred matter*. Since the total system is adiabatic, the total heat removed from subsystem 1 is equal to the total

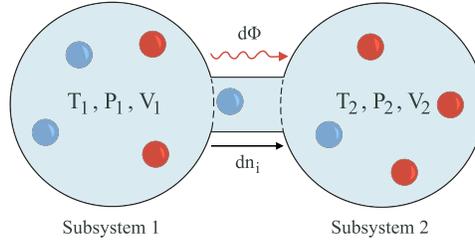


Figure 6.28. Both heat and matter can transfer.

heat received by subsystem 2. The enthalpy of the transferred matter, however, may be different in the two subsystems, and thus the measurable heat change will be different in the two subsystems.

The changes in the subsystems are:

$$\delta\Phi = \delta\Phi_2 = -\delta\Phi_1.$$

In terms of internal variables,

$$dU_1 = T_1 dS_1 - P_1 dV_1 + \sum_i \mu_{i,1} dn_{i,1} \quad dU_2 = T_2 dS_2 - P_2 dV_2 + \sum_i \mu_{i,2} dn_{i,2}.$$

Solving for  $dS$ ,

$$(6.9) \quad dS_1 = \frac{dU_1}{T_1} + \frac{P_1}{T_1} dV_1 - \frac{1}{T_1} \sum_i \mu_{i,1} dn_{i,1}, \quad dS_2 = \frac{dU_2}{T_2} + \frac{P_2}{T_2} dV_2 - \frac{1}{T_2} \sum_i \mu_{i,2} dn_{i,2}.$$

In terms of external variables, when we only have  $P - V$  work:

$$(6.10) \quad dU_1 = \delta\Phi_1 - P_1 dV_1 \quad dU_2 = \delta\Phi_2 - P_2 dV_2, \\ dU_1 + dU_2 = -\delta\Phi_1 - P_2 dV_2.$$

Since  $\delta\Phi = \delta\Phi_2 = -\delta\Phi_1$ . Then, plugging Eq. (6.10) into (6.9),

$$(6.11) \quad dS_1 = -\frac{\delta\Phi}{T_1} + \frac{1}{T_1} \sum_i \mu_{i,1} dn_i, \quad dS_2 = \frac{d\Phi}{T_2} - \frac{1}{T_2} \sum_i \mu_{i,2} dn_i.$$

The production of entropy in the total system is  $dS = dS_1 + dS_2$  and therefore

$$dS = \left( \frac{1}{T_2} - \frac{1}{T_1} \right) d\Phi + \sum_i \left( \frac{\mu_{i,2}}{T_2} - \frac{\mu_{i,1}}{T_1} \right) dn_i, \\ (6.12) \quad dS = \Delta(1/T) \delta\Phi - \sum_i \Delta(\mu_i/T) dn_i.$$

Multiplying by  $T_2$  and dividing by time ( $dt$ ), we have the dissipated energy (J/s)

$$\boxed{T_2 \frac{dS}{dt} = T_2 \Delta(1/T) \frac{\delta\Phi}{dt} - T_2 \sum_i \Delta(\mu_i/T) \frac{dn_i}{dt}.$$

It is possible to develop Eq. (6.12) further and put it in a more useful form (see Section 6.11.34):

$$dS = \Delta(1/T)\delta Q_1 - \frac{1}{T} \sum_i \Delta\mu_{i,T} dn_i.$$

**6.11.34. Algebraic Details.** Starting from Eq. (6.11),

$$dS_1 = -\frac{\delta\Phi}{T_1} + \frac{1}{T_1} \sum_i \mu_{i,1} dn_i, \quad dS_2 = \frac{\delta\Phi}{T_2} - \frac{1}{T_2} \sum_i \mu_{i,2} dn_i,$$

and solving for  $\delta\Phi$ , we have:

$$\delta\Phi = -T_1 dS_1 + \sum_i \mu_{i,1} dn_{i,1} = T_2 dS_2 + \sum_i \mu_{i,2} dn_{i,2}.$$

The entropy of an open system can be expressed as a function of temperature, pressure and amounts of substances,  $S = S(T, P, \{n_i\})$ . The experiment can be arranged such that the pressure within each subsystem is kept constant. The change in entropy with temperature and amounts of substances for subsystem 1 can be written,

$$\begin{aligned} dS_1 &= \left(\frac{\partial S_1}{\partial T}\right)_{P, n_i} dT + \sum_i \left(\frac{\partial S_1}{\partial n_{i,1}}\right)_{P, T, n_{j \neq i}} dn_{i,1} \\ &= (C_{P,1}/T_1) dT + \sum_i S_{i,1} dn_{i,1}, \end{aligned}$$

and in a similar way for subsystem 2. The heat capacity of the system multiplied by the change in temperature is equal to the measurable heat absorbed by the system,  $C_{P,1} dT = -\delta Q_1$  where  $\delta Q_1$  is the heat removed from subsystem 1. Here it is assumed that  $dT$  is so small that changes in  $C_{P,1}$  can be neglected. When the amounts of substances transferred from subsystem 1 to subsystem 2 are small, the change in partial molar entropy,  $S_{i,1}$  can be neglected. Thus, for subsystem 1,

$$dS_1 = -\delta Q_1/T_1 - \sum_i S_{i,1} dn_i.$$

This equation combines with Eq. (6.11) for  $dS_1$  to give

$$\delta\Phi = \delta Q + \sum_i (\mu_{i,1} + T_1 S_{i,1}) dn_i,$$

or, since  $G = H - TS$ , the partial molar quantity at constant  $T$  is:

$$G_i \equiv \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_T = \left(\frac{\partial H}{\partial n_i}\right)_T - T \left(\frac{\partial S}{\partial n_i}\right)_T \equiv H_i - TS_i.$$

Or  $H_i = \mu_i + TS_i$ ,

$$(6.13) \quad \delta\Phi = \delta Q_1 + \sum_i H_{i,1} dn_i.$$

In a similar way, we can express  $d\Phi$  by the heat *absorbed* by subsystem 2,  $\delta Q_2$ , and the enthalpy added to subsystem 2 by the transfer of  $dn_i$  moles of substance:

$$(6.14) \quad d\Phi = \delta Q_2 + \sum_i H_{i,2} dn_i.$$

Comparing Eq. (6.13) and (6.14) we see that the difference in  $\delta Q$  values corresponds to a difference in the  $H$  values:

$$\delta Q_2 - \delta Q_1 = \sum_i (H_{i,1} - H_{i,2}) dn_i.$$

For gases,  $H_{i,1} - H_{i,2} \approx 0$ .

The enthalpies,  $H_i$ , do not have absolute values, and therefore  $\delta\Phi$  does not have an absolute value. We shall choose subsystem 1 as the reference state, and replace  $\delta\Phi$  in Eq. (6.12) by the expression given in Eq. (6.13). The second term in Eq. (6.12),  $\sum_i \Delta(\mu_i/T) dn_i$ , can also be referred to subsystem 1 as the reference state. The chemical potentials are functions of temperature, pressure and composition, and for small differences in these parameters between the two subsystems, we have by the rules of derivation

$$\Delta(\mu_i/T) = \Delta(1/T)\mu_{i,1} + \frac{1}{T_1}(\partial\mu_{i,1}/\partial T)_{P,n_i}\Delta T + \frac{1}{T_1}\Delta\mu_{i,T},$$

where  $\Delta\mu_{i,T}$  gives the variation in  $\mu_i$  with changes in composition and pressure.

Since (from  $H_i = \mu_i + TS_i$ )

$$(\partial\mu_{i,1}/\partial T)_{P,n_i} = -S_{i,1},$$

and

$$\Delta(1/T) = \left( \frac{1}{T + \Delta T} - \frac{1}{T} \right) \approx -\frac{\Delta T}{T^2},$$

and

$$T_1 \approx T.$$

Therefore,

$$(6.15) \quad \sum_i \Delta(\mu_i/T) dn_i = \Delta(1/T) \sum_i (\mu_{i,1} + TS_{i,1}) dn_i + \frac{1}{T} \sum_i \Delta\mu_{i,T} dn_i.$$

Introducing Eq. (6.13) and (6.15) into (6.12) we obtain

$$dS = \Delta(1/T)\delta Q_1 - \frac{1}{T} \sum_i \Delta\mu_{i,T} dn_i.$$

This form may be better because it explicitly separates the two contributions to the entropy production originating from heat transfer and particle transport.

**6.11.35. Gibbs Free Energy: Ideal Gas Equilibria.** We have seen that the progress of a chemical reaction  $\sum_i \nu_i A_i = 0$  can be described using the *extent of the reaction*,  $\xi = \frac{n_i(\xi) - n_i(0)}{\nu_i}$ . From this,  $d\xi = dn_i/\nu_i$  or  $d\xi/dt = (1/\nu_i)dn_i/dt$ . The fundamental equation,  $dG = -SdT + VdP + \sum_i \mu_i dn_i$ , can be rewritten as  $dG = -SdT + VdP + \sum_i \nu_i \mu_i d\xi$ , or  $dG = -SdT + VdP - \mathcal{A}d\xi$ , where  $\mathcal{A} = -\sum_i \mu_i \nu_i$  or  $\mathcal{A} = -\left(\frac{\partial G}{\partial \xi}\right)_{T,P}$ . Finally,  $\mathcal{A} = -\Delta G_{rxn} = -\sum_i \nu_i \mu_i$ .

Consider a gas-phase reaction  $A \rightleftharpoons B$ . If the pressures are low enough, the gases can be considered ideal gases. Recall that for ideal gases, the chemical potentials are:

$$\mu_A(T, P) = \mu_A^\circ(T) + RT \log(P_A/1 \text{ atm})$$

$$\mu_B(T, P) = \mu_B^\circ(T) + RT \log(P_B/1 \text{ atm})$$

where  $P_A$  and  $P_B$  are partial pressures in units of 1 atm.

Inserting these expressions into the expression for  $\left(\frac{\partial G}{\partial \xi}\right)$  gives:

$$\left(\frac{\partial G}{\partial \xi}\right) = \mu_B - \mu_A = (\mu_B^\circ + RT \log P_B) - (\mu_A^\circ + RT \log P_A) = \Delta G_{rxn}^\circ + RT \log \frac{P_B}{P_A},$$

where  $\Delta G_{rxn}^\circ = \mu_B^\circ - \mu_A^\circ$ . Writing  $Q = P_B/P_A$ , this is

$$\Delta G_{rxn} = \Delta G_{rxn}^\circ + RT \log Q.$$

At equilibrium  $\Delta G_{rxn} = 0$ ,  $Q$  is denoted by  $K$ , and we have:

$$\Delta G_{rxn} = -RT \log K + RT \log Q = RT \log(Q/K).$$

This expression, together with the second law  $\Delta G_{rxn} \leq 0$ , allows us to study the direction of a reaction.

For a general chemical reaction of the form  $\sum_i \nu_i A_i = 0$ , the quantity  $\Delta G_{rxn} \equiv \left(\frac{\partial G}{\partial \xi}\right) = \sum_i \mu_i \nu_i$ , is the Gibbs free energy change of the reaction. Then,

$$\begin{aligned} \left(\frac{\partial G}{\partial \xi}\right) &= \Delta G_{rxn} = \sum_i \left[ \mu_i^0 + RT \log(P_i/P^\circ) \right] \nu_i \\ &= \Delta G_{rxn}^0 + RT \sum_i \nu_i \log(P_i/P^\circ), \end{aligned}$$

where  $P^\circ$  is a reference pressure (usually 1 atm or 1 bar). Then,

$$\boxed{\Delta G_{rxn} = RT \log(Q/K)},$$

where

$$Q = \prod_i (P_i/P^\circ)^{\nu_i}, \quad K = \prod_i (P_{i,eq}/P^\circ)^{\nu_i}, \quad \Delta G_{rxn}^0 = \sum_i \nu_i \mu_i^0 = -RT \log(K).$$

Recall that although  $Q$  has the *form* of an equilibrium constant, the pressures are not necessarily at equilibrium.

The quantity  $\Delta G_{rxn}^\circ(T)$  is the change in standard Gibbs energy for the reaction between unmixed reactants in their standard states at temperature  $T$  and a pressure of one bar to form unmixed products in their standard states at the same temperature  $T$  and a pressure of  $P_0$  (usually, taken to be 1 atm or 1 bar). If all pressures are referenced to 1 bar (or 1 atm),  $Q$  is unitless.

From the previous equation,

$$\Delta G_{rxn}(T) = -RT \log(K) + RT \log(Q) = RT \log(Q/K).$$

We see that:

- At equilibrium,  $Q = K$ .
- If  $Q < K$  then  $Q$  must increase as the system moves toward equilibrium. Partial pressures of the products must increase and those of reactants must decrease. The reaction proceeds from left to right. In terms of  $\Delta G_{rxn}$ , if  $Q < K$ , then  $\Delta G_{rxn} < 0$ , indicating that the reaction is spontaneous from left to right as written.
- If  $Q > K$ , then  $Q$  must decrease as the reaction proceeds to equilibrium. Pressures of products must decrease and those of reactants must increase. Equivalently, if  $Q > K$  then  $\Delta G_{rxn} > 0$ , indicating that the reaction is spontaneous from right to left as written.

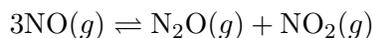
**6.11.36. Enthalpy and Entropy Contribute to  $\Delta G_{rxn}^\circ$ .** We know that at constant temperature we have:

$$\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T\Delta S_{rxn}^\circ.$$

Consequently, we may express the equilibrium constant as a product of two contributions, one from enthalpy and one from entropy:

$$(6.16) \quad K = \exp\left(-\frac{\Delta G_{rxn}^\circ}{RT}\right) = \exp\left(-\frac{\Delta H_{rxn}^\circ}{RT}\right) \exp\left(\frac{\Delta S_{rxn}^\circ}{R}\right).$$

**6.11.37. Example 1: Three Components Reaction.** The above formula states that the change in standard Gibbs energy for a reaction is related to the equilibrium constant. But the latter depends on equilibrium partial pressures. For example,



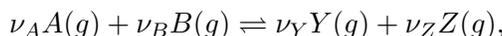
has

$$K = \frac{(P_{\text{N}_2\text{O}})_{\text{eq}} \cdot (P_{\text{NO}_2})_{\text{eq}}}{(P_{\text{NO}})_{\text{eq}}^3}$$

so (taking  $P_0=1$  atm and expressing pressures in units of  $P_0$ ),

$$\Delta G_{rxn}^\circ = -RT \log \frac{(P_{N_2O})_{eq}(P_{NO_2})_{eq}}{(P_{NO})_{eq}^3}.$$

**6.11.38. Example 2: Four Components Reaction.** For a reaction of the type:



we have:

$$\begin{aligned} \Delta G_{rxn} &= \nu_Y \mu_Y + \nu_Z \mu_Z - \nu_A \mu_A - \nu_B \mu_B \\ &= \nu_Y \mu_Y^\circ(T) + \nu_Z \mu_Z^\circ(T) - \nu_A \mu_A^\circ(T) - \nu_B \mu_B^\circ(T) \\ &\quad + RT \left( \nu_Y \log \frac{P_Y}{P_0} + \nu_Z \log \frac{P_Z}{P_0} - \nu_A \log \frac{P_A}{P_0} - \nu_B \log \frac{P_B}{P_0} \right), \end{aligned}$$

which can be written in the form:

$$\Delta G_{rxn}(T) = \Delta G_{rxn}^\circ(T) + RT \log Q,$$

where

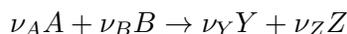
$$\Delta G_{rxn}^\circ(T) = \nu_Y \mu_Y^\circ(T) + \nu_Z \mu_Z^\circ(T) - \nu_A \mu_A^\circ(T) - \nu_B \mu_B^\circ(T),$$

and

$$Q = \frac{(P_Y/P_0)^{\nu_Y} (P_Z/P_0)^{\nu_Z}}{(P_A/P_0)^{\nu_A} (P_B/P_0)^{\nu_B}}.$$

**6.11.39. Standard Gibbs Energies of Reactions (Using Tabulated Values).** Standard entropies ( $\Delta S_{rxn}^\circ$ ) and enthalpies ( $\Delta H_{rxn}^\circ$ ) of reactions can be combined to obtain the standard Gibbs energy of a reaction,  $\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T\Delta S_{rxn}^\circ$  (valid for constant temperature). The standard Gibbs energy of a reaction is the difference in standard molar Gibbs energies of the products and reactants in their standard states at the temperature specified for the reaction as written.

In Oxtoby [1], what we denote here as  $\mu_i^0$  is called standard Gibbs energy of formation and denoted  $\Delta G_f^\circ$ . Appendix D of your book can be used to calculate equilibrium constants; e.g.



has

$$\Delta G_{rxn}^\circ = \nu_Y \Delta G_f^\circ[Y] + \nu_Z \Delta G_f^\circ[Z] - \nu_A \Delta G_f^\circ[A] - \nu_B \Delta G_f^\circ[B].$$

where the values for the  $\Delta G_f^\circ[Y]$  can be looked up in tables.

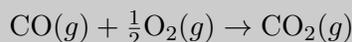
The **standard Gibbs energy of formation** of a compound is the change of Gibbs free energy that accompanies the formation of 1 mole of a substance in its standard state from its constituent elements in their standard states (the most stable form of the element at 1 bar of pressure and the

specified temperature, usually 298.15 K or 25°C). Standard Gibbs energies of formation are tabulated. See Appendix D of Oxtoby [1] for such a list.

In terms of the **standard Gibbs energies of formation**,  $\Delta G_f^\circ$ :

$$\Delta G_{rxn}^\circ = \sum_{I \in \text{prod.}} \nu_I (\Delta G_f^\circ)_I - \sum_{J \in \text{react.}} \nu_J (\Delta G_f^\circ)_J.$$

**Example:** To calculate the standard Gibbs energy of the reaction



at 25°C. Looking up tabulated values for each substance in Appendix D, we write:

$$\begin{aligned} \Delta G_{rxn}^\circ &= \Delta G_f^\circ(\text{CO}_2, g) - \left\{ \Delta G_f^\circ(\text{CO}, g) + \frac{1}{2} \Delta G_f^\circ(\text{O}_2, g) \right\} \\ &= -394.4 \text{ kJ/mol} - \left\{ (-137.2) + \frac{1}{2}(0) \right\} \text{ kJ/mol} \\ &= -257.2 \text{ kJ/mol} \end{aligned}$$

**6.11.40. Adiabatic Decompression.** The process of adiabatic decompression is used for cooling gases. The principle is illustrated in Fig. 6.29. In the equations below, ‘1’ refers to the ‘initial’ state and ‘2’ refers to the ‘final’ state. Step 1 uses the law for isothermal compression (see Section 6.3.7):

$$\Delta W = -nRT \log \left( \frac{V_2}{V_1} \right)$$

with  $\Delta U = 0$  for an ideal gas (isothermal process), so that  $\Delta Q = \Delta W$ . The second step uses the law for adiabatic expansion:

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1},$$

where  $\gamma$  is a constant ( $\gamma = c_P/c_V$ ). Equivalently,  $TV^{\gamma-1} = \text{constant}$ .

*Problem:* Derive the above law for reversible adiabatic expansion of an ideal gas. (See Problem 77 for solution.)

*Problem:* Show that this is equivalent to  $PV^\gamma = \text{constant}$ .

*Problem:* Explain how this leads to cooling.

## 6.12. Electric and Magnetic Work

Can electric and magnetic fields generate work? In this section we look at the case of electrical charges subjected to the influence of electric and magnetic fields. This material is standard and can be found in most textbooks of electrodynamics, e.g. see Griffith [26] or Jackson [27]. In electrodynamics, the electric field is denoted  $\mathbf{E}$ . There is an associated quantity called the *electric displacements*, denoted  $\mathbf{D}$ . An applied electric field gives rise to a

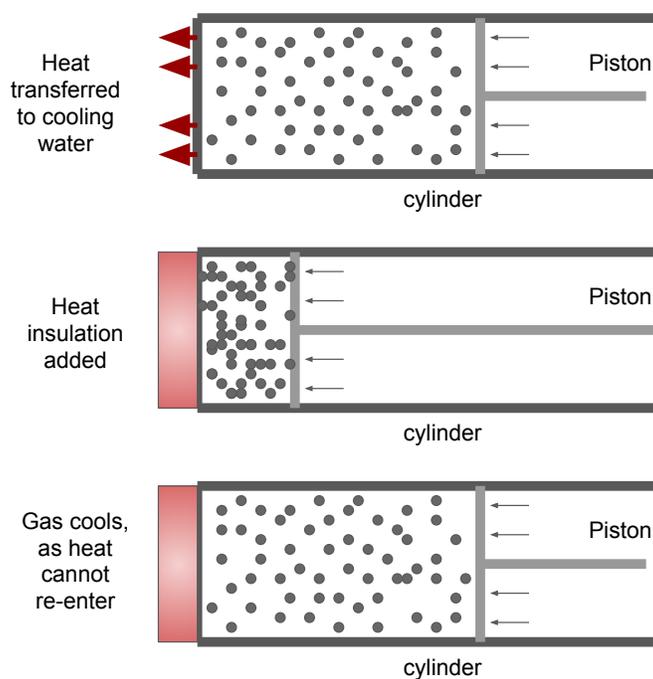


Figure 6.29. Adiabatic decompression leads to cooling of gas.

polarization  $\mathbf{P}$  (molecules develop an induced dipole moment). These three fields are related by:

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}.$$

In linear media,  $\mathbf{D} = \epsilon \mathbf{E}$ , where  $\epsilon$  is the dielectric constant of the linear medium. The corresponding magnetic quantities are  $\mathbf{B}$  (magnetic induction),  $\mathbf{H}$  (magnetic field) and  $\mathbf{M}$  magnetic polarization or magnetization. Magnetic polarization is magnetic moment ( $\vec{m}$ ) per unit volume:  $\vec{m} = \text{vol} \cdot \mathbf{M}$ . Similarly,  $\vec{p} = \text{vol} \cdot \mathbf{P}$  for the electric dipole moment. The magnetic moments align when an external magnetic field is applied. These three fields are related by:

$$\mathbf{H} = \frac{1}{\mu_0} \mathbf{B} - \mathbf{M}.$$

In linear media, we have  $\mathbf{H} = \frac{1}{\mu} \mathbf{B}$ , where  $\mu$  is the magnetic permeability of the medium.  $\mathbf{E}$  and  $\mathbf{B}$  are the fundamental fields because they determine the force on electric charges according to the Lorentz force law:

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}).$$

$\mathbf{H}$  and  $\mathbf{D}$  are called *auxiliary fields*.

**6.12.1. Derivation.** Upon first reading, you may skip this section, which is provided for completeness and whose details are not essential to the development of thermodynamical relations. We start with the Lorentz force,

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}).$$

Take the dot product<sup>27</sup> with  $d\mathbf{l}$ , an element of length:

$$\mathbf{F} \cdot d\mathbf{l} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \cdot d\mathbf{l}.$$

We replace  $d\mathbf{l}$  by  $\mathbf{v}dt$ , where  $\mathbf{v}$  is the velocity of electric charges, then divide by  $dt$  to get  $dW/dt$ , the rate of change in the work (why we use the rate of change will be clear later, as the Poynting vector emerges). Also, because electric charge is possibly distributed elsewhere in space, we really should replace  $q$  by a charge density,  $\rho$ , and integrate over volume to get the total work (and use  $\mathbf{J} = \rho\mathbf{v}$ ):

$$(6.17) \quad \frac{dW}{dt} = - \int_{vol} \rho(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \cdot \mathbf{v} d^3\mathbf{r} = - \int_{vol} \rho\mathbf{E} \cdot \mathbf{v} d^3\mathbf{r} = - \int_{vol} \mathbf{E} \cdot \mathbf{J} d^3\mathbf{r}.$$

The negative sign appears because we are calculating the work done *on the charge* against the action of the field (see Jackson [27], Chapter 1).

The magnetic force term dropped out because the triple product<sup>28</sup>  $(\mathbf{v} \times \mathbf{B}) \cdot \mathbf{v}$  vanishes, as two of its vectors are parallel. However, this does not mean that the magnetic field does not play a role. Let us look at the current density,  $\mathbf{J}$ . We can obtain an expression for  $\mathbf{E} \cdot \mathbf{J}$  by invoking Ampère's law:

$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}.$$

Take the dot product with  $\mathbf{E}$ :

$$(6.18) \quad \mathbf{E} \cdot \mathbf{J} = \mathbf{E} \cdot (\nabla \times \mathbf{H}) - \mathbf{E} \cdot \frac{\partial \mathbf{D}}{\partial t}.$$

Next, we use the identity,<sup>29</sup>

$$\mathbf{H} \cdot (\nabla \times \mathbf{E}) - \mathbf{E} \cdot (\nabla \times \mathbf{H}) = \nabla \cdot (\mathbf{E} \times \mathbf{H}),$$

in which we substitute Faraday's law

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t},$$

<sup>27</sup>The dot product is defined in Section A.3.

<sup>28</sup>A triple product,  $(\mathbf{A} \times \mathbf{B}) \cdot \mathbf{C}$ , is a scalar (number) which equals to the volume generated by the three vectors  $\mathbf{A}, \mathbf{B}, \mathbf{C}$ . When any two vectors are parallel, the volume is zero.

<sup>29</sup>This can be verified as follows:

$\nabla \cdot (\mathbf{E} \times \mathbf{H}) = \partial_i(\epsilon_{inm} E_n H_m) = \epsilon_{inm}(\partial_i E_n) H_m + \epsilon_{inm} E_n (\partial_i H_m) = \mathbf{H} \cdot (\nabla \times \mathbf{E}) - \mathbf{E} \cdot (\nabla \times \mathbf{H})$ , where in the second term we have used  $\epsilon_{inm} = \epsilon_{nmi} = -\epsilon_{nim}$ .

to get

$$(6.19) \quad -\mathbf{H} \cdot \frac{\partial \mathbf{B}}{\partial t} - \mathbf{E} \cdot (\nabla \times \mathbf{H}) = \nabla \cdot (\mathbf{E} \times \mathbf{H}).$$

In Eq. (6.18), we replace  $\mathbf{E} \cdot (\nabla \times \mathbf{H})$  by Eq. (6.19), to get:

$$\mathbf{E} \cdot \mathbf{J} = -\mathbf{H} \cdot \frac{\partial \mathbf{B}}{\partial t} - \nabla \cdot (\mathbf{E} \times \mathbf{H}) - \mathbf{E} \cdot \frac{\partial \mathbf{D}}{\partial t}.$$

Substituting this expression into Eq. (6.17), we get:

$$(6.20) \quad \frac{dW}{dt} = - \int_{vol} \left( -\mathbf{H} \cdot \frac{\partial \mathbf{B}}{\partial t} - \nabla \cdot (\mathbf{E} \times \mathbf{H}) - \mathbf{E} \cdot \frac{\partial \mathbf{D}}{\partial t} \right) d^3\mathbf{r}.$$

The middle term can be converted to a surface integral using the Gauss divergence theorem:

$$(6.21) \quad \frac{dW}{dt} = \int_{vol} \left( \mathbf{H} \cdot \frac{\partial \mathbf{B}}{\partial t} + \mathbf{E} \cdot \frac{\partial \mathbf{D}}{\partial t} \right) d^3\mathbf{r} + \int_{\partial vol} (\mathbf{E} \times \mathbf{H}) \cdot d\mathbf{s}.$$

In linear media,  $\mathbf{B} = \mu\mathbf{H}$  and  $\mathbf{D} = \epsilon\mathbf{E}$ , and we can write this as:

$$(6.22) \quad \boxed{\frac{dW}{dt} = \frac{d}{dt} \int_{vol} \frac{1}{2} (\mathbf{H} \cdot \mathbf{B} + \mathbf{E} \cdot \mathbf{D}) d^3\mathbf{r} + \int_{\partial vol} (\mathbf{E} \times \mathbf{H}) \cdot d\mathbf{s}.}$$

The first integral is the total energy stored in the electromagnetic fields. The first term represents the rate of change in the total energy stored. The quantity

$$\boxed{W_{EH} = \frac{1}{2} (\mathbf{H} \cdot \mathbf{B} + \mathbf{E} \cdot \mathbf{D})}$$

is the energy density of the electromagnetic field. The second term describes the transport of energy in and out of the volume ( $vol$ ), through the surface  $\partial vol$ . The vector  $\mathbf{S} \equiv \mathbf{E} \times \mathbf{H}$  is called the *Poynting vector*. The Poynting vector is relevant in cases where electromagnetic radiation is present.

The first term in Eq. (6.22) can also be written as (for *linear media*):

$$(6.23) \quad dW = \int_{vol} d \frac{1}{2} (B^2/\mu + \epsilon E^2) d^3\mathbf{r} = \int_{vol} \frac{1}{2} (\mu^{-1} \mathbf{B} \cdot d\mathbf{B} + \epsilon \mathbf{E} \cdot d\mathbf{E}) d^3\mathbf{r}.$$

If the fields  $\mathbf{E}$  and  $\mathbf{B}$  are spatially uniform (over the volume  $vol$ ), integration over the volume yields a factor  $vol$ . Then, the total energy differential is:

$$dW = vol (\mu^{-1} \mathbf{B} \cdot d\mathbf{B} + \epsilon \mathbf{E} \cdot d\mathbf{E}).$$

This is often written as:

$$(6.24) \quad \boxed{dW = vol (\mathbf{H} \cdot d\mathbf{B} + \mathbf{E} \cdot d\mathbf{D}).}$$

Note: some authors go directly from Eq. (6.21) to

$$dW = \int_{vol} (\mathbf{H} \cdot d\mathbf{B} + \mathbf{E} \cdot d\mathbf{D}) d^3\mathbf{r} + dt \int_{\partial vol} (\mathbf{E} \times \mathbf{H}) \cdot d\mathbf{s}.$$

This implies elimination of the time parametrization

$$(6.25) \quad \frac{\partial \mathbf{B}}{\partial t} dt \rightarrow d\mathbf{B}, \quad \frac{\partial \mathbf{D}}{\partial t} dt \rightarrow d\mathbf{D}.$$

Since  $\mathbf{B}$  and  $\mathbf{D}$  are functions of position and time, their total derivatives are:

$$d\mathbf{B} = \frac{\partial \mathbf{B}}{\partial \mathbf{r}} \cdot d\mathbf{r} + \frac{\partial \mathbf{B}}{\partial t} dt, \quad d\mathbf{D} = \frac{\partial \mathbf{D}}{\partial \mathbf{r}} \cdot d\mathbf{r} + \frac{\partial \mathbf{D}}{\partial t} dt.$$

Thus, the substitution (6.25) can only be justified if spatial variations of  $\mathbf{B}$  and  $\mathbf{D}$  are small (i.e.  $\frac{\partial \mathbf{B}}{\partial \mathbf{r}} \approx 0$  and  $\frac{\partial \mathbf{D}}{\partial \mathbf{r}} \approx 0$ ) or if  $vol$  is sufficiently large so that edge effects (spatial non-uniformities) contribute negligibly to the volume integral.

**6.12.2. Magnetic and Electric Polarizations.** In Eq. (6.24), namely  $dW = vol (\mathbf{H} \cdot d\mathbf{B} + \mathbf{E} \cdot d\mathbf{D})$ , only the fields  $\mathbf{E}, \mathbf{D}, \mathbf{B}, \mathbf{H}$  appear. When we derived Eq. (6.24), we could have just as easily written instead (reader should check this):<sup>30</sup>

$$dW = vol (\mathbf{B} \cdot d\mathbf{H} + \mathbf{D} \cdot d\mathbf{E}).$$

It would be desirable to decompose the contributions of the external and internal fields. Since  $\mathbf{B} = \mu_0 \mathbf{H} + \mathbf{M}$  and  $\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}$ , we have:

$$\begin{aligned} dW &= vol ((\mu_0 \mathbf{H} + \mathbf{M}) \cdot d\mathbf{H} + (\epsilon_0 \mathbf{E} + \mathbf{P}) \cdot d\mathbf{E}) \\ &= vol [(\mu_0 \mathbf{H} \cdot d\mathbf{H} + \epsilon_0 \mathbf{E} \cdot d\mathbf{E}) + \mathbf{M} \cdot d\mathbf{H} + \mathbf{P} \cdot d\mathbf{E}] \end{aligned}$$

A useful approximation can be obtained by decomposing the fields  $\mathbf{E}, \mathbf{H}$  as the sum of externally applied fields (subscript 0) and any additional fields (subscript  $dm$ )<sup>31</sup> arising after introduction of the sample in the external field:

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_{dm}, \quad \mathbf{E} = \mathbf{E}_0 + \mathbf{E}_{dm}.$$

The  $dm$  fields are usually very small compared to the externally applied fields:  $\|\mathbf{H}_{dm}\| \ll \|\mathbf{H}_0\|$  and  $\|\mathbf{E}_{dm}\| \ll \|\mathbf{E}_0\|$ . In this approximation the

<sup>30</sup>Check also that substituting,  $\mathbf{B} = \mu_0 \mathbf{H} + \mathbf{M}$  and  $\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}$  into  $dW = vol (\mathbf{H} \cdot d\mathbf{B} + \mathbf{E} \cdot d\mathbf{D})$  yields:

$$\begin{aligned} dW &= vol (\mathbf{H} \cdot d(\mu_0 \mathbf{H} + \mathbf{M}) + \mathbf{E} \cdot d(\epsilon_0 \mathbf{E} + \mathbf{P})) \\ &= vol [(\mu_0 \mathbf{H} \cdot d\mathbf{H} + \epsilon_0 \mathbf{E} \cdot d\mathbf{E}) + \mathbf{H} \cdot d\mathbf{M} + \mathbf{E} \cdot d\mathbf{P}] \\ &= vol \left[ \frac{1}{2} d(\mu_0 H^2 + \epsilon_0 E^2) + \mathbf{H} \cdot d\mathbf{M} + \mathbf{E} \cdot d\mathbf{P} \right] \end{aligned}$$

It's a matter of convenience which set of independent variables one uses. However,  $\vec{m} = vol \cdot \mathbf{M}$  and  $\vec{p} = vol \cdot \mathbf{P}$  are extensive variables whereas  $\mathbf{H}$  and  $\mathbf{E}$  are intensive. We recall from Section 6.4.7 that work differentials are of the form  $\delta W = (\text{intensive quantity}) \times d(\text{extensive quantity})$ . Thus, the correct form is:

$$dW = vol \left[ \frac{1}{2} d(\mu_0 H^2 + \epsilon_0 E^2) \right] + \mathbf{H} \cdot d\vec{m} + \mathbf{E} \cdot d\vec{p}.$$

<sup>31</sup>An example of field perturbation is the *demagnetizing field* associated with magnets.

expression for work reduces to:<sup>32</sup>

$$(6.26) \quad dW = vol \left[ \frac{1}{2} d \left( \mu_0 H_0^2 + \epsilon_0 E_0^2 \right) + \mathbf{M} \cdot d\mathbf{H}_0 + \mathbf{P} \cdot d\mathbf{E}_0 \right].$$

The advantages of this expression are two-fold:

- (1) The terms are broken down into two parts: the energy required to create<sup>33</sup> the external field (the  $\mu_0 H_0^2 + \epsilon_0 E_0^2$  term), and the energy required to realign the external fields (the  $\mathbf{M} \cdot d\mathbf{H}_0 + \mathbf{P} \cdot d\mathbf{E}_0$  term).
- (2) For the  $\mathbf{M} \cdot d\mathbf{H}_0 + \mathbf{P} \cdot d\mathbf{E}_0$ , we see that the external fields ( $\mathbf{H}_0$  and  $\mathbf{E}_0$ ) are the control parameters. This is better representative of real experimental conditions, where the experimentalist controls the external fields rather than the polarization fields inside the material.

**6.12.3. Linear Media, Curie's Law.** The internal energy differential with electromagnetic work, Eq. (6.26), reads:

$$dU = \delta Q + vol \left[ \frac{1}{2} d \left( \mu_0 H_0^2 + \epsilon_0 E_0^2 \right) + \mathbf{M} \cdot d\mathbf{H}_0 + \mathbf{P} \cdot d\mathbf{E}_0 \right].$$

In paramagnetic materials, the Curie-Weiss law holds,

$$\mathbf{M} = \chi \mathbf{H}, \quad \chi = \frac{C}{T},$$

where  $C$  is a material-dependent constant. In dielectric materials a similar law often holds,

$$\mathbf{P} = \chi_e \epsilon_0 \mathbf{E} = \alpha \mathbf{E},$$

where  $\alpha$  is a material-dependent constant called the polarizability (see Section 2.1.2 and Table 2.5). Under these circumstances<sup>34</sup>, we have:

$$\begin{aligned} dU &= \delta Q + vol \left[ \frac{1}{2} d \left( \mu_0 H_0^2 + \epsilon_0 E_0^2 \right) + \frac{1}{2} d \left( \frac{C}{T} H_0^2 + \alpha E_0^2 \right) \right] \\ &= \delta Q + \frac{vol}{2} d \left[ \left( \mu_0 + \frac{C}{T} \right) H_0^2 + (\epsilon_0 + \alpha) E_0^2 \right] \end{aligned}$$

The term  $C/T$  is much larger than  $\mu_0$ ;<sup>35</sup> thus, we neglect the  $\mu_0$  term.

<sup>32</sup>The factor of  $\frac{1}{2}$  arises because we used  $HdH = \frac{1}{2}dH^2$ .

<sup>33</sup>Energy is required to bring the charges and currents required to create the fields.

<sup>34</sup>The conditions include: Curie law, linear media, and approximating  $\mathbf{H} \approx \mathbf{H}_0$  and  $\mathbf{E} \approx \mathbf{E}_0$ .

<sup>35</sup>For those interested in a justification of this approximation: The Curie constant is given by  $\frac{\mu_0 \mu_B^2}{3k_B} N g^2 J(J+1)$ , where  $J$  is the total angular momentum quantum number of the paramagnetic atoms,  $g$  is the Landé factor,  $g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$  ( $S$ : spin,  $L$ : orbital,  $J$ : total angular momenta). For an electron spin,  $g \approx 2$ .  $N$  is the density of magnetic atoms ( $10\text{-}100 \times 10^{27}$  atoms/m<sup>3</sup> for solids).  $\mu_B$  is the Bohr magneton ( $9.274 \times 10^{-24}$  J/T). Plugging these typical values at room temperature gives  $C/T \approx 10^3 \mu_0$ , which is much larger than  $\mu_0$ . In adiabatic demagnetization experiments, the temperature is typically much lower (liquid helium), so the approximation is well justified.

**6.12.4. Adiabatic Demagnetization.** Adiabatic demagnetization (W.F. Giaque) can be used for cooling (Fig. 6.30) in a process that is analogous to adiabatic decompression (Section 6.11.40) but instead involves the spin degrees of freedom of paramagnetic salts.<sup>36</sup> Adiabatic demagnetization<sup>37</sup> of a paramagnetic salt is a two-steps sequence that enables cooling below 1 K. Temperatures around 1 mK have been reached. The steps are: (1) isothermal magnetization followed by (2) adiabatic demagnetization (Fig. 6.30):

- (1) **Isothermal magnetization** (thermal contact with cold He gas). At time zero, spins in the paramagnetic salt are randomly oriented (disordered state). The system undergoes isothermal demagnetization in the presence of a strong magnetic field. The entropy of the spin system decreases, as the spins align with the magnetic field (ordered state). While the final temperature is unchanged, heat is lost to the surroundings in order to dissipate the entropy. (Lowering the temperature would also lead to alignment of the spins.)
- (2) **Adiabatic demagnetization** (He gas pumped away; no thermal contact with He). Next, heat transfer is stopped (paramagnetic salt is insulated) and the external field is turned off, leading the spins to randomly reorient. However, the temperature has decreased. While heat transfer outside the system is not allowed, heat can be transferred between spin and lattice. However, the lattice entropy is much lower than the spin entropy. The total entropy of the isolated system (paramagnetic salt) has not changed much, since heat was not allowed to transfer ( $dS = \delta Q/T \approx 0$ ).

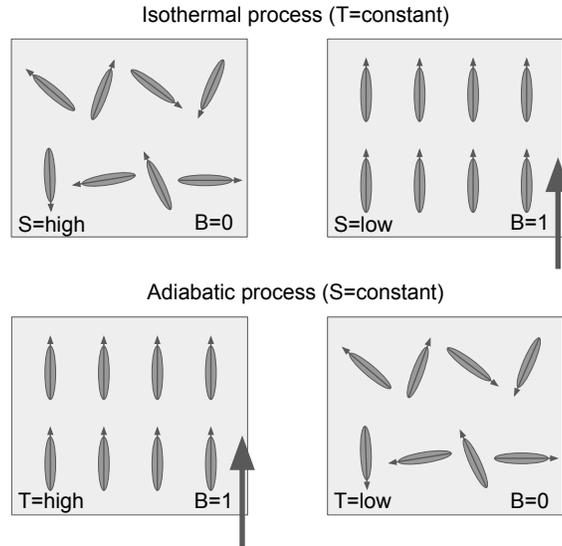
Let us see how this two-step process could possibly work (Fig. 6.31). Our starting point is Eq. (6.26). Let us take the “system” as the paramagnetic salt plus electromagnetic coils as well as the surrounding helium (liquid helium bath plus helium gas in contact with the salt). This forms an isolated system. For isolated systems, the change in internal energy is zero ( $dU = 0$ ). During isothermal magnetization, heat is allowed to exchange between the helium and the salt in order to maintain the salt temperature constant:

$$\delta Q_{\text{He}} = -\delta Q_{\text{salt}}.$$

<sup>36</sup>The isothermal compression of a gas (we apply pressure and the entropy decreases) is analogous to the isothermal magnetization of a paramagnet or a soft ferromagnet: we apply an external magnetic field and the magnetic entropy decreases. The subsequent adiabatic expansion of a gas (we lower pressure at constant entropy and temperature decreases) is equivalent to adiabatic demagnetization (we remove the external field, the total entropy remains constant and temperature decreases since the magnetic entropy increases).

<sup>37</sup>Giaque Nobel prize lecture:

[http://www.nobelprize.org/nobel\\_prizes/chemistry/laureates/1949/giaque-lecture.pdf](http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1949/giaque-lecture.pdf)



**Figure 6.30.** Adiabatic demagnetization. The first step involves turning on a magnetic field at constant temperature. The spins align with the magnetic field, reducing the entropy. In the second step, the entropy is held constant while the field is turned off. Since the entropy remains constant, the only possible outcome left to compensate for the loss of magnetic field is for the temperature to decrease.

If the process is reversible and isothermal,

$$T_{\text{He}} dS_{\text{He}} = -T_{\text{salt}} dS_{\text{salt}},$$

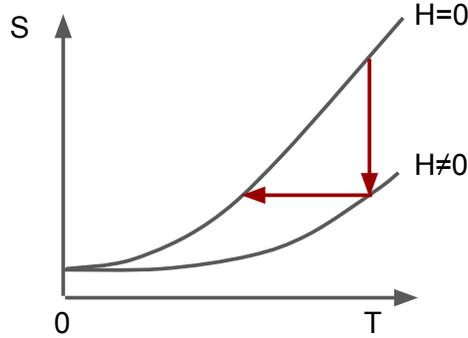
we have  $T_{\text{He}} = T_{\text{salt}} \equiv T$  and  $dS_{\text{He}} = -dS_{\text{salt}}$ . The entropy in the context of heat transfer is the lattice entropy (random atomic motions). The paramagnetic salt also has spin entropy, which does not exchange with the helium in any way because no exchange mechanism exists<sup>38</sup>.

The total salt entropy should be viewed as the sum of lattice ( $L$ ) and spin ( $S$ ) contributions:

$$dS_{\text{salt}} = dS_{\text{salt}}^L + dS_{\text{salt}}^S.$$

Our previous statement  $\delta Q_{\text{He}} = -\delta Q_{\text{salt}}$  refers to the lattice contributions because heat can only be transferred via lattice motions. We are left with a non-vanishing  $TdS_{\text{salt}}^S$  term describing changes in the spin entropy. ( $TdS_{\text{He}}^S = 0$  because helium is not magnetic.) The physical origin of  $dS_{\text{salt}}^S$  is the alignment of the magnetic moments of the paramagnetic salt due to the ramping up of the magnetic field.

<sup>38</sup>For spin entropy to exchange, we would need a spin-spin coupling mechanism, which does not exist here.



**Figure 6.31.** Process of adiabatic demagnetization. During isothermal magnetization, the entropy of the spins is lowered. During adiabatic demagnetization, entropy remains constant but temperature decreases.

The first law then reads (with  $E_0 = 0$  and neglecting the  $\mu_0$  term):

$$dU = 0 = TdS_{salt}^S + \frac{vol}{2}d\left[\frac{C}{T}H_0^2\right].$$

During isothermal magnetization, the field is ramped up from 0 to some value  $H$ . The spin entropy decreases by an amount proportional to  $(H/T)^2$ :

$$\Delta S_{salt}^S = \int dS_{salt}^S = S_{salt}^S(H) - S_{salt}^S(0) = -\frac{vol}{2}C\left(\frac{H}{T}\right)^2.$$

During adiabatic demagnetization, the entropy remains constant since  $\delta Q = TdS = 0$ . The field is ramped down from  $H$  to  $H_{int}$ , where  $H_{int}$  is the internal magnetic field due to coupling to neighboring magnetic moments. If the entropy is proportional to  $(H/T)^2$ , the condition of the initial entropy to equal the final entropy:

$$S_{salt}^S(initial) = const \times \left(\frac{H}{T_i}\right)^2 = S_{salt}^S(final) = const \times \left(\frac{H_{int}}{T_f}\right)^2,$$

leads to:

$$T_f = T_i \left(\frac{H_{int}}{H}\right).$$

The internal field is typically on the order of a few Gauss ( $10^{-4}$  T). The external field ( $H$ ) is on the order of a Tesla. Therefore, cooling by 3-4 orders of magnitude is possible.

### 6.13. Problems

**Problem 74.** Write down an expression for the absolute entropy of a substance at constant temperature, constant number of moles, with temperature-dependent heat capacity,  $c_P \equiv c_P(T)$ , at any temperature. (You may assume a reversible process or any other reasonable assumptions.)

**Solution.** Absolute entropy begins at  $T = 0$ . Let us choose the enthalpy because heats of fusion and vaporization are tabulated as enthalpies. The differential element of  $H$  is:

$$dH = TdS + VdP + \sum_i \mu_i dn_i.$$

At constant pressure and number of moles, the last 2 terms vanish. We are left with  $dH = TdS$ . Moreover, we know that for a reversible process,  $(dH)_P = TdS = (\delta Q)_P = nc_P dT$ . Let us work with molar entropy, so we divide by  $n$  (or equivalently, take  $n = 1$  mol). Thus,  $dS = c_P dT/T$ . Integration from 0 to  $T$  gives:

$$S(T) = S(0) + \int_0^{T_f} \frac{c_P(T)}{T} dT + \frac{\Delta_{fus}H}{T_f} + \int_{T_i}^{T_f} \frac{c_P(T)}{T} dT + \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^T \frac{c_P(T)}{T} dT.$$

Here,  $\Delta_{fus}H$  and  $\Delta_{vap}H$  denote the enthalpies of fusion and vaporization, respectively.  $T_b$  and  $T_f$  are the boiling and freezing points, respectively. ■

**Problem 75.** The specific heat of a monatomic ideal gas per mole is  $c_V = 3R/2$ . Find its Helmholtz free energy  $A$  as a function of number of moles  $n$ , volume  $V$  and temperature  $T$ . (You can assume a reversible process, or any other reasonable assumptions.)

**Solution.** Let's assume that we have a fixed number of moles  $n$ . For an ideal gas we have

$$dU = nc_V dT$$

and

$$U = nc_V T + U_0$$

where  $U_0$  is the internal energy of the system when  $T = 0$ . Now, we need an expression for  $S$  as function of  $n$ ,  $V$  and  $T$ . Thus, we view  $S \equiv S(n, V, T)$ :

$$dS(n, V, T) = \left( \frac{\Delta S}{\Delta n} \right)_{V,T} dn + \left( \frac{\Delta S}{\Delta V} \right)_{n,T} dV + \left( \frac{\Delta S}{\Delta T} \right)_{V,n} dT.$$

The first term is zero because  $n$  is fixed ( $dn = 0$ ). The second term is  $(P/T)dV$ , as is known from the Fundamental Equation. The last term, the change in entropy with respect to temperature can be obtained from  $\delta Q^{rev} = TdS = nc_V dT$ , which, after rearrangement gives  $dS = nc_V dT/T$ . Thus, the

change in entropy with respect to temperature is  $nc_V/T$ . Therefore,

$$dS = \frac{nc_V}{T}dT + \frac{P}{T}dV.$$

For the ideal gas,  $c_V = (3/2)R$  and  $P/T = nR/V$ . Integrate from  $(V_0, T_0)$  to  $(V, T)$ :

$$S = \frac{3nR}{2} \log(T/T_0) + nR \log(V/V_0) + S_0,$$

where  $S_0$  is an integration constant. Then,

$$A = U - TS = \frac{3nRT}{2} - \left( \frac{3nRT}{2} \log(T/T_0) - nRT \log(V/V_0) \right) + F_0$$

where

$$F_0 = U_0 - T_0 S_0.$$

■

**Problem 76.** The VDW eq. of state for 1 mol of gas is:

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT$$

The gas undergoes an isothermal expansion from volume  $V_1$  to  $V_2$ . Calculate the change in the Helmholtz free energy.

**Solution.** The eq. of state is rearranged as:

$$P = \frac{RT}{(V - b)} - \frac{a}{V^2}.$$

Recall that

$$dA = -SdT - PdV + \sum_i \mu_i dn_i.$$

During an isothermal process,

$$\begin{aligned} \Delta A &= - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \left( \frac{RT}{V - b} - \frac{a}{V^2} \right) dV \\ &= - RT \log \left| \frac{V_2 - b}{V_1 - b} \right| + a \left( \frac{1}{V_1} - \frac{1}{V_2} \right) \end{aligned}$$

■

**Problem 77.** Show that the pressure of an ideal gas undergoing reversible adiabatic expansion from volume  $V_i$  to volume  $V_f$  is related to its initial pressure by

$$P_f = V_f^\gamma = P_i V_i^\gamma,$$

where  $\gamma = c_P/c_V$ , the ratio of molar specific heats at constant pressure and volume. Another way to write this result is  $PV^\gamma = \text{constant}$ .

**Solution.** For a reversible process,  $P_{ext} \approx P$ . The expansion work is then  $\delta W = -PdV$ . We also have that for an ideal gas  $dU = C_V dT$ . On the other

hand, for an adiabatic process,  $\delta Q = 0$  and  $dU = \delta W$ . This gives:

$$C_V dT = -PdV.$$

For an ideal gas, we can replace  $P$  by  $nRT/V$ :

$$\frac{C_V dT}{T} = -\frac{nR dV}{V}.$$

Integrate from initial to final state, assuming that  $C_V$  is independent of temperature:

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}.$$

Integration gives:

$$C_V \log \frac{T_f}{T_i} = -nR \log \frac{V_f}{V_i} = nR \log(V_i/V_f).$$

Writing  $c = C_V/nR = c_V/R$ , we get:

$$\log(T_f/T_i)^c = \log(V_i/V_f),$$

which implies that  $(T_f/T_i)^c = (V_i/V_f)$  and

$$\frac{T_i}{T_f} = \left(\frac{V_f}{V_i}\right)^{1/c} = \left(\frac{V_f}{V_i}\right)^{\gamma-1},$$

where  $\gamma = c_P/c_V$  and  $c_P - c_V = R$ . From the ideal gas law,  $\frac{P_i V_i}{P_f V_f} = \frac{T_i}{T_f}$  and this becomes:

$$\frac{P_i}{P_f} = \frac{V_f}{V_i} \times \left(\frac{V_f}{V_i}\right)^{\gamma-1} = \left(\frac{V_f}{V_i}\right)^{\gamma},$$

which gives  $P_i V_i^\gamma = P_f V_f^\gamma$ , the sought expression. ■

**Problem 78.** We have seen that the standard Gibbs free energy of a reaction,  $\Delta G_{rxn}^\circ$ , is given as a sum of standard Gibbs energy of formation, for each reactant and products (with reactants taken as negative):

$$\Delta G_{rxn}^\circ = \sum_i \nu_i (\Delta G_f^\circ)_i$$

where the sum  $i$  runs over all reactants and products. (a) Prove that this formula follows from the fact that  $dG$  is an exact differential. (b) Using only the formula from (a) and the relationship between  $G$ ,  $H$  and  $S$ , prove also that:

$$\Delta H_{rxn}^\circ = \sum_i \nu_i (\Delta H_f^\circ)_i, \quad \Delta S_{rxn}^\circ = \sum_i \nu_i S_i^\circ$$

where  $S_i^\circ$  and  $(\Delta H_f^\circ)_i$  are the entropies (absolute) and enthalpies of formation for species  $i$ , respectively.  $\Delta H_{rxn}^\circ$  and  $\Delta S_{rxn}^\circ$  are the standard enthalpy and entropy changes for the reaction.

**Solution.** (a)  $\Delta G_{rxn}^\circ = \sum_i \nu_i (\Delta G_f^\circ)_i$  follows from the fact that  $G$  is a state function, i.e.  $\Delta G = \int_{\text{reactants}}^{\text{products}} dG$ . Integrate along the following path: Destroy all reactants one by one (order is unimportant) and Form all the products one by one (order is unimportant). Each molecule destroyed and formed contributes a term in the summation (with appropriate sign).

(b) First we have the basic relationship from thermodynamics (constant  $T$ ),  $\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T\Delta S_{rxn}^\circ$ . Each term in the summation  $\Delta G_{rxn}^\circ = \sum_i \nu_i (\Delta G_f^\circ)_i$ , we view  $(\Delta G_f^\circ)_i$  as a small increment  $dG_i$  that contributes to the integral, for which we apply the following decomposition  $dG_i = dH_i - TdS_i$ . Let's write  $dH_i \equiv (\Delta H_f^\circ)_i$  and  $dS_i \equiv S_i^\circ$ . This gives the decomposition

$$\Delta G_{rxn}^\circ = \sum_i \nu_i (\Delta G_f^\circ)_i = \sum_i \nu_i (\Delta H_f^\circ)_i - T \sum_i \nu_i S_i^\circ.$$

And since  $\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T\Delta S_{rxn}^\circ$ , in the limit  $T \rightarrow 0$ , the second term vanishes, we have  $\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ$  and  $\Delta G_{rxn}^\circ = \sum_i \nu_i (\Delta H_f^\circ)_i$ . Therefore,

$$\Delta H_{rxn}^\circ = \sum_i \nu_i (\Delta H_f^\circ)_i.$$

Taking the limit  $T \rightarrow \infty$ , the first term is negligible compared to the second term, leaving only  $\Delta G_{rxn}^\circ = -T\Delta S_{rxn}^\circ$  and  $\Delta G_{rxn}^\circ = -T \sum_i \nu_i S_i^\circ$ . It follows that:

$$\Delta S_{rxn}^\circ = \sum_i \nu_i S_i^\circ.$$

■

**Problem 79.** Hess's law states that *the total enthalpy change during the complete course of a reaction is the same whether the reaction is made in one step or in several steps*. Mathematically, the statement of Hess's law, as pertains to the *net or overall reaction*, is:

$$\Delta H_{rxn}^\circ = \sum_{I \in \text{products}} \nu_I (\Delta H_f^\circ)_I - \sum_{J \in \text{reactants}} \nu_J (\Delta H_f^\circ)_J,$$

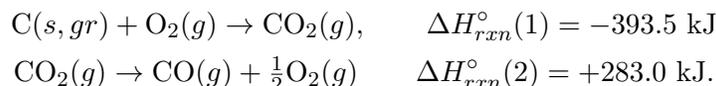
where the reaction is the *net reaction*. The summation is over all reactants (products) in the *net equation*.  $(\Delta H_f^\circ)_I$  is called *enthalpy of formation* (of species  $I$ ) and  $\nu_I$  is the stoichiometric coefficient of species  $I$ . (Here,  $\nu_I$  and  $\nu_J$  are all positive.) When the conditions are standard, the enthalpy of formation is denoted as  $(\Delta H_f^\circ)_I$  (standard enthalpy of formation).

(a) Prove that Hess's law is a consequence of the fact that  $H$  is a state function ( $dH$  is an exact differential), i.e. it does not depend on the path taken to get from the reactants to the products. Prove that the above statement for the *net reaction* is entirely equivalent to summing up reaction

enthalpies from individual reactions:

$$\Delta H_{rxn}^{\circ} = \sum_{i \in \text{reactions}} \Delta H_{rxn}^{\circ}(i),$$

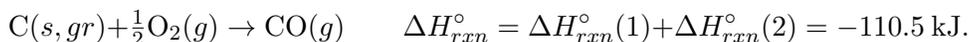
where  $\Delta H_{rxn}^{\circ}(i)$  denotes the net (overall) reaction enthalpy of the  $i$ -th reaction. The sum runs over all reactions that make up the net reaction. Suppose that we have two concurrent reactions taking place:



(b) Apply Hess's law to obtain  $\Delta H_{rxn}^{\circ}$  for the net reaction.

**Solution.** (a) Hess's law follows from  $\Delta H_{rxn}^{\circ} = \int_{\text{reactants}}^{\text{products}} dH_{rxn}^{\circ}$  and choosing a path in the net reaction that destroys all reactant molecules regardless of order (destruction implies a negative sign) and creates all product molecules (without regards to order). This is equivalent to summing over all reactions: because  $H$  is a state function, the value of  $\Delta H_{rxn}^{\circ}$  is the same, regardless of the choice of path. Here, we choose a different path, which takes us through all reactions one by one. This is entirely equivalent, because the chemical reaction is treated as an equation; multiple reactions are added to give the net reaction. The integral is a linear operator, hence, it is applied to each term in the summation (and the summation is identical whether we look at the net reaction or the sum of individual reactions).

(b) The net reaction (and net enthalpy change) is the sum:



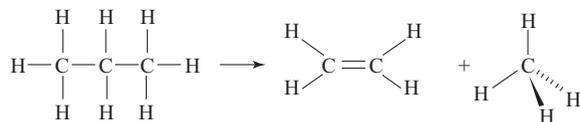
■

**Problem 80. METHOD OF BOND ENTHALPIES.** In chemical reactions, bonds are broken and new ones are formed. Think about reactants: one way to consume reactants is to destroy all the chemical bonds of all reactants, until atoms are separate. On the products side: to form the product molecules, we assemble the atoms together and create a number of chemical bonds. There is an energy associated with breaking and forming these bonds. It is possible to use this information to estimate the enthalpy change  $\Delta H_{rxn}^{\circ}$  of a reaction, which can be calculated from:

$$\Delta H_{rxn}^{\circ} = \sum_{\substack{I \in \text{bonds} \\ \text{broken}}} \Delta H_I^{\circ} - \sum_{\substack{J \in \text{bonds} \\ \text{formed}}} \Delta H_J^{\circ},$$

where  $\Delta H_I^{\circ}$  is the energy absorbed when a particular bond is broken and  $\Delta H_J^{\circ}$  is the energy released when a bond is formed. (a) Prove that this restatement of Hess's law is entirely equivalent to the one in Problems 1

and 2. (b) Prove also that this new statement follows from the fact that  $H$  is a state function (and  $dH$  is an exact differential). (c) Consider the following example on cracking of propane (thermal decomposition,  $\Delta H_{rxn}^\circ > 0$  endothermic) to make ethene (Fig. 6.32).



**Figure 6.32.** Method of bond enthalpy illustrated.

Here is some data on average bond enthalpy (units are kJ/mol)

C – H bond: +415

C – C bond: +345

C = C bond: +611

Add up all the energies of the broken bonds; add up all the energies of the bonds that are reformed and subtract one from the other. Show that  $\Delta H_{rxn}^\circ = 4,010 - 3,931 = 79$  kJ/mol. (Hint: 10 bonds must be broken on the reactants side to consume the reactants, whereas 9 bonds must be formed on the products side to synthesize the needed products.)

**Solution.** (a) This reformulation of Hess's law is justified by the choice of path, which here involves destroying molecules or forming them, one chemical bond at a time. (This is longer, and involves more steps, but the end result is the same, i.e. the value of  $\Delta H_{rxn}^\circ$  is identical.)

(b) This follows from the fact that  $dH$  is an exact differential because the original Hess's law is also based on this fact. And since the two are equivalent, the proof follows.

(c) We have, for the left hand side (bonds broken):

$$2 \text{ C} - \text{C} \quad 2 \times 345 = 690 \text{ kJ/mol}$$

$$8 \text{ C} - \text{H} \quad 8 \times 415 = 3,320 \text{ kJ/mol}$$

These energies add up to a total of 4,010 kJ/mol.

For the right hand side (bonds formed),

$$1 \text{ C} = \text{C} \quad 1 \times 611 = 611 \text{ kJ/mol}$$

$$8 \text{ C} - \text{H} \quad 8 \times 415 = 3,320 \text{ kJ/mol}$$

for a total of 3,931 kJ/mol. The net difference between reactant bonds destroyed and product bonds formed is:

$$\Delta H_{rxn}^{\circ} = 4,010 - 3,931 = 79 \text{ kJ/mol.}$$

■

**Problem 81.** METHOD OF BOND ENTHALPIES. In Problem 80, is it really necessary to completely break down all bonds and reform them or can you find a short-cut to computing  $\Delta H$  of the reaction without having to completely take apart all molecules and reform them (including reforming the same bonds that were broken!)? Reformulate the statement for the method of bond enthalpies with this short-cut in mind.

**Solution.** No, it is not necessary to break ALL the bonds and reform them. When we break a bond and reform it, there is no net change in this particular bond, so why bother breaking and reforming it? Such pairs of events can be discounted because they cancel each other out. In other words, for a given reaction (reactants + products), the initial conditions (reactants) and final conditions (products) are fixed regardless of the path (from reactants to products) we choose. Instead of the “long path” (that involves breaking ALL bonds), we can instead choose a shorter path that does not involve destroying ALL bonds. Instead we may limit the breaking and forming of bonds to the bare minimum necessary. In real reactions, not all bonds in all reactants are broken; only a small number of bonds are broken. ■

**Problem 82.** Prove the following formula

$$d(\Delta G) = (\Delta V)dP - (\Delta S)dT,$$

which allows us to calculate how  $\Delta G$  varies with temperature and pressure.  $\Delta G = \int dG$  denotes a change in  $G$ , for example,  $\Delta G = G(\text{products}) - G(\text{reactants})$  being one possible application.

**Solution.** Apply the fundamental equation,  $dG = VdP - SdT$ , twice, once to all the reaction products collectively,  $G(\text{products})$ , and once to all the reactants collectively,  $G(\text{reactants})$ :

$$dG_{\text{prod}} = V_{\text{prod}}dP - S_{\text{prod}}dT, \quad dG_{\text{react}} = V_{\text{react}}dP - S_{\text{react}}dT$$

$$\begin{aligned} dG_{\text{prod}} - dG_{\text{react}} &= d(G_{\text{prod}} - G_{\text{react}}) = d(\Delta G) \\ &= (V_{\text{prod}} - V_{\text{react}})dP - (S_{\text{prod}} - S_{\text{react}})dT \\ &= (\Delta V)dP - (\Delta S)dT. \end{aligned}$$

■

**Problem 83.** Consider the reaction  $\text{CuBr}_2(s) \rightleftharpoons \text{CuBr}(s) + \frac{1}{2} \text{Br}_2(g, 1 \text{ atm})$ . In what direction does this reaction proceed at 300 K and 1 atm pressure?

At 300 K, 1 atm, the following data is available from tables:

	$\Delta H_f^\circ$ kcal/mol	$S_{300\text{ K}}^\circ$ cal/mol/K
CuBr <sub>2</sub> (s)	-33.2	30.1
CuBr(s)	-25.1	21.9
Br <sub>2</sub> (g, 1 atm)	+7.34	58.64

**Solution.** The favored direction of reaction will be indicated by the sign of  $\Delta G_{300}^\circ$ , to calculate which we need only determine  $\Delta H_{300}^\circ$  and  $\Delta S_{300}^\circ$  for the reaction.

$$\begin{aligned}\Delta H_{300}^\circ &= (\Delta H_f^\circ)_{\text{CuBr}} + \frac{1}{2}(\Delta H_f^\circ)_{\text{Br}_2} - (\Delta H_f^\circ)_{\text{CuBr}_2} \\ &= -25.1 + 3.67 - (-33.2) = +11.8 \text{ kcal/mol.}\end{aligned}$$

$$\begin{aligned}\Delta S_{300}^\circ &= (S_{300}^\circ)_{\text{CuBr}} + \frac{1}{2}(S_{300}^\circ)_{\text{Br}_2} - (S_{300}^\circ)_{\text{CuBr}_2} \\ &= +21.9 + 29.32 - 30.1 = +21.1 \text{ cal/mol.}\end{aligned}$$

$$\begin{aligned}\Delta G_{300}^\circ &= \Delta H_{300}^\circ - T\Delta S_{300}^\circ = 11,800 - (298)(21.1) \\ &= 5,500 \text{ cal/mol} = 5.5 \text{ kcal/mol.}\end{aligned}$$

Not rightward, but rather, leftward progress of the reaction is thus strongly favored at 300 K, and will reduce the Br<sub>2</sub> pressure far below 1 atm. Recall that the equilibrium constant  $K = RT \exp(-\Delta G_{rxn}^\circ/RT)$ . A positive value of  $\Delta G_{rxn}^\circ$  means that  $K < 1$  and the equilibrium is towards reactants. ■

**Problem 84.** For the reaction of Problem 83, at what temperature will the three substances coexist at equilibrium under a pressure of 1 atm?

**Solution.** At whatever temperature ( $T$ ) the three substances coexist at 1 atm pressure, we will have  $\Delta H_T^\circ - T\Delta S_T^\circ = \Delta G_T^\circ = 0$ . Noting that  $\Delta H^\circ$  and  $\Delta S^\circ$  are the same in sign, we essay the approximation in which the two terms are treated as substantially constant over the temperature range concerned. In that case,

$$\Delta H_T^\circ \approx \Delta H_{300}^\circ = 11.8 \text{ kcal/mol}$$

$$\Delta S_T^\circ \approx \Delta S_{300}^\circ = 21.1 \text{ cal/mol.K}$$

and then

$$11,800 - T(21.1) = \Delta G_T^\circ = 0, \quad T = 11,800/21.1 = 560^\circ \text{ K.}$$

■

**Problem 85.** (a) Which is the more stable form of carbon at 300 K and 1 atm pressure, diamond or graphite? (b) At 300 K, what pressure would be required to form diamond (density, 3.5 g/ml) from graphite (density, 2.25 g/ml)? (c) How can you be confident of the soundness of this entire mode of analysis? Some relevant data are as follows:

Heat capacity data yield for diamond (300 K),  $\bar{S}_{300}^{\circ} = 0.58$  cal/mol.K, where  $\bar{S} = -(\mathrm{d}\bar{G}/\mathrm{d}T)_P$  and  $\bar{G}$  is the *molar* Gibbs free energy.

Heat capacity data yield for graphite (300 K),  $\bar{S}_{300}^{\circ} = 1.37$  cal/mol.K

For C(graphite)  $\rightarrow$  C(diamond),  $\Delta\bar{S}_{300}^{\circ} = -0.79$  cal/mol.K

On combustion: C(graphite) + O<sub>2</sub>  $\rightleftharpoons$  CO<sub>2</sub>,  $\Delta\bar{H}_{300}^{\circ} = -94.03$  kcal.

On combustion: C(diamond) + O<sub>2</sub>  $\rightleftharpoons$  CO<sub>2</sub>,  $\Delta\bar{H}_{300}^{\circ} = -94.48$  kcal.

For C(graphite)  $\rightarrow$  C(diamond):  $\Delta\bar{H}_{300}^{\circ} = +450$  cal/mol.

And the given densities imply:

For diamond: gram-atomic volume =  $12/3.5 = 3.4$  ml/gr-atom. (Note: Gram atomic mass is another term for the mass, in grams, of one mole of atoms of that element. "Gram atom" is a former term for a mole of substance (expressed in grams). Example: gram atomic mass of Hydrogen is mass of 1 mole atoms = 1.008 grams.)

For graphite: gram-atomic volume =  $12/2.25 = 5.3$  ml/gr-atom.

For C(graphite)  $\rightarrow$  C(diamond):  $\Delta\bar{V}_{300} = -1.9$  ml/gr-atom, where  $\bar{V} = (\mathrm{d}\bar{G}/\mathrm{d}t)_T$ .

**Solution.** (a) For the reaction C(graphite)  $\rightarrow$  C(diamond),

$$\Delta\bar{G}_{300}^{\circ} = \Delta\bar{H}_{300}^{\circ} - T\Delta\bar{S}_{300}^{\circ} = 450 - 300(-0.79) = +685 \text{ cal/mol}$$

At room temperature and atmospheric pressure, the favored direction of reaction is thus the inverse change of diamond into graphite. Under ordinary conditions diamond is therefore a thermodynamically unstable species, which exists only because of the extreme slowness of its conversion into the more stable graphite.

(b) At atmospheric pressure the reaction C(graphite)  $\rightarrow$  C(diamond) is characterized by  $\Delta\bar{G}_{300}^{\circ} > 0$ . But with  $\Delta\bar{V} < 0$  in this reaction, a sufficient rise of pressure should change the sign of  $\Delta\bar{G}$  and, hence, the favored direction of reaction at 300 K. For consider that the effect of a change of pressure at constant temperature will be given by the following reduced form

$$\mathrm{d}(\Delta\bar{G}) = \Delta\bar{V}\mathrm{d}P.$$

If we approximate by treating  $\Delta\bar{V}$  as constant ( $= -0.0019$  lit) over the entire pressure range involved, the last equation can easily be integrated. For the upper limit we choose that pressure ( $P^*$ ) at which  $\Delta\bar{G}_{300}^{\circ} = 0$ , i.e. the pressure under which diamond and graphite stand in equilibrium with each other at 300 K. For the lower limit we use the standard pressure of 1 atm, at which we have just found  $\Delta\bar{G}_{300}^{\circ} = +685$  cal/mol. However, with  $\Delta\bar{V}$  in liters and pressure in atmospheres, the appropriate unit for  $\Delta\bar{G}$  is not calories but lit-atm (1 lit-atm = 101.325 J). Multiplication by

the factor 0.0413 converts a-figure in calories to one in lit-atm, so that  $\Delta\bar{G}_{300}^{\circ} = 0.0413(685) = 28.3$  lit atm. We have then,

$$\int_{28.3}^0 d(\Delta\bar{G}) = -0.0019 \int_1^{P^*} dP,$$

$$0 - 28.3 = -0.0019(P^* - 1),$$

$$P^* \approx 15,000 \text{ atm.}$$

At 25°C diamond and graphite would stand in equilibrium under a pressure of 15,000 atm. At still higher pressures graphite becomes thermodynamically unstable, and its conversion into diamond is then possible in principle, though so slow in practice as to be wholly undetectable.

(c) Since at room temperature no equilibrium of graphite with diamond ever is attained in practice, there remains room for skepticism that we have correctly calculated what would be the equilibrium condition. But, given expressions for  $\Delta\bar{H}$  and  $\Delta\bar{V}$  as functions of temperature and pressure, by integration of equation  $d(\Delta\bar{G}) = \Delta\bar{V}dP$ , we can calculate that the equilibrium pressure is of the order of 75,000 atm at 1500°K. And here the soundness of our calculation is attested by an unmistakable production of diamond from graphite at pressures that exceed the equilibrium pressure. ■

**Problem 86.** Iron has a heat capacity of  $25.1 \text{ J K}^{-1} \text{ mol}^{-1}$ , approximately independent of temperature between 0°C and 100°C.

(a) Calculate the enthalpy and entropy change of 1.00 mol iron as it is cooled at atmospheric pressure from 100°C to 0°C.

(b) A piece of iron weighing 55.85 g and at 100°C is placed in a large reservoir of water held at 0°C. It cools irreversibly until its temperature equals that of the water. Assuming the water reservoir is large enough that its temperature remains close to 0°C, calculate the entropy changes for the iron and the water and the total entropy change in this process.

**Solution.** a)

$$\Delta H_{\text{Fe}} = n c_p \Delta T = (1.00 \text{ mol})(25.1 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 - 373.15 \text{ K})$$

$$= -2510 \text{ J} = -2.51 \times 10^3 \text{ J}$$

$$\Delta S_{\text{Fe}} = n c_p \log \frac{T_f}{T_i} = (1.00 \text{ mol})(25.1 \text{ J K}^{-1} \text{ mol}^{-1}) \log \frac{273.15}{373.15} = -7.83 \text{ J K}^{-1}$$

b) The entropy  $S$  is a function of state, and the initial and final states of the piece of iron are the same as in part a). Therefore,  $\Delta S_{\text{Fe}} = -7.83 \text{ J K}^{-1}$ . The reservoir of water gains the 2510 J of heat from the piece of iron at a constant temperature of 273.15 K. Therefore  $\Delta S_{\text{water}} = 2510 \text{ J}/273.15 \text{ K} =$

+9.19 J K<sup>-1</sup>.

$$\Delta S_{\text{total}} = \Delta S_{\text{Fe}} + \Delta S_{\text{water}} = 1.36 \text{ J K}^{-1}$$

■

**Problem 87.** (a) Use data from Appendix D from Oxtoby [1] to calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  at 25 °C for the reaction



(b) Calculate  $\Delta G^\circ$  at 590 K, assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature.

(c) Careful high-temperature measurements show that when this reaction is performed at 590 K,  $\Delta H_{590}^\circ$  is 158.36 kJ and  $\Delta S_{590}^\circ$  is 177.74 J K<sup>-1</sup>. Use these facts to compute an improved value of  $\Delta G_{590}^\circ$  for this reaction. Determine the percentage error in  $\Delta H_{590}^\circ$  that comes from using the 298-K values in place of the 590-K values in this case.

**Solution.** a) The reaction of interest is



Appendix D supplies  $\Delta H_f^\circ$  and  $S^\circ$  values at 298 K for the computation of  $\Delta H_{298}^\circ$  and  $\Delta S_{298}^\circ$

$$\Delta H_{298}^\circ = 2(-137.2) + 1(0) - 2(-220.1) = 165.8 \text{ kJ}$$

$$\Delta S_{298}^\circ = 2(86.2) + 1(222.96) - 2(108.07) = 179.2 \text{ J K}^{-1}$$

b)

$$\Delta G_{590} \approx \Delta H_{590}^\circ - T\Delta S_{590}^\circ = 165.8 \text{ kJ} - (590 \text{ K})(0.1792 \text{ kJ K}^{-1}) = 60.1 \text{ kJ}$$

c) Use the experimental values at 590 K instead of the values at 298.15 K

$$\Delta G_{590} = \Delta H_{590}^\circ - T\Delta S_{590}^\circ = 158.36 \text{ kJ} - (590 \text{ K})(0.17774 \text{ kJ K}^{-1}) = 53.5 \text{ kJ}$$

The answer using  $\Delta H_{298}^\circ$  and  $\Delta S_{298}^\circ$  is about 12 % larger than the actual  $\Delta G_{590}$ . Tip. The temperature dependence of  $\Delta H^\circ$  and  $\Delta S^\circ$  should not always be neglected. Taking it into consideration becomes important when the temperature differs a lot from 298.15 K. ■

**Problem 88.** Find the Gibbs free energy and the entropy associated with mixing 10 g of liquid water, 5 g of liquid ethanol, and 1 g of liquid methanol at 298 K?

**Solution.**

$$G_i = n_{\text{H}_2\text{O}}\mu_{\text{H}_2\text{O}}^* + n_{\text{EtOH}}\mu_{\text{EtOH}}^* + n_{\text{MeOH}}\mu_{\text{MeOH}}^*$$

$$G_f = n_{\text{H}_2\text{O}}(\mu_{\text{H}_2\text{O}}^* + RT \log(X_{\text{H}_2\text{O}})) + n_{\text{EtOH}}(\mu_{\text{EtOH}}^* + RT \log(X_{\text{EtOH}})) \\ + n_{\text{MeOH}}(\mu_{\text{MeOH}}^* + RT \log(X_{\text{MeOH}}))$$

$$G_{mix} = G_f - G_i = nRT(X_{\text{H}_2\text{O}} \log(X_{\text{H}_2\text{O}}) + X_{\text{EtOH}} \log(X_{\text{EtOH}}) + X_{\text{MeOH}} \log(X_{\text{MeOH}}))$$

$$S_{mix} = -nR(X_{\text{H}_2\text{O}} \log(X_{\text{H}_2\text{O}}) + X_{\text{EtOH}} \log(X_{\text{EtOH}}) + X_{\text{MeOH}} \log(X_{\text{MeOH}}))$$

$$n_{\text{H}_2\text{O}} = 0.555 \text{ mol}, n_{\text{EtOH}} = 0.108 \text{ mol}, n_{\text{MeOH}} = 0.0312 \text{ mol}, n = 0.694 \text{ mol}$$

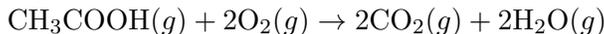
$$X_{\text{H}_2\text{O}} = 0.800, X_{\text{EtOH}} = 0.156, X_{\text{MeOH}} = 0.0450$$

$$G_{mix} = -454 \text{ J}$$

$$S_{mix} = 1.52 \text{ J/K}$$

■

**Problem 89.** Find the reaction affinity at constant pressure and temperature for the following reaction going to completion:



Data:  $G_f^\circ(\text{CO}_2(g)) = -394.36 \text{ kJ/mol}$ ,  $G_f^\circ(\text{H}_2\text{O}(g)) = -228.59 \text{ kJ/mol}$ ,  $G_f^\circ(\text{CH}_3\text{COOH}(g)) = -374.1 \text{ kJ/mol}$

**Solution.**  $\Delta G_{rxn} = G_f(\text{products}) - G_f(\text{reactants}) = 2 \times G_f^\circ(\text{CO}_2(g)) + 2 \times G_f^\circ(\text{H}_2\text{O}(g)) - G_f^\circ(\text{CH}_3\text{COOH}(g)) = -871.8 \text{ kJ/mol}$

$$\text{Affinity} = -\left(\frac{\partial G}{\partial \xi}\right)_{T,P}$$

$$\text{Affinity} = -\Delta G_{rxn} = -871.8 \text{ kJ/mol}$$

■

**Problem 90.** For the reaction  $2 \text{Ca}(s) + \text{O}_2(g) \rightarrow 2 \text{CaO}(s)$  find the equilibrium constant at 300 K given that  $\mu_{\text{CaO}}^\circ = -604.17 \text{ kJ mol}^{-1}$  at that temperature. What can you conclude about the reaction based on the magnitude of the equilibrium constant?

**Solution.**  $\Delta\mu^\circ = \mu_{\text{CaO}}^\circ(2) - \mu_{\text{O}_2}^\circ(1) - \mu_{\text{Ca}}^\circ(2) = -1208.34 \text{ kJ mol}^{-1}$

$$\Delta\mu^\circ = -RT \log K$$

$$K = \exp\left[\frac{-\Delta\mu^\circ}{RT}\right]$$

$$K = 2.5 \times 10^{210}$$

■

**Problem 91.** Assume the reaction  $\text{N}_2(g) + 3 \text{H}_2(g) \rightarrow 2 \text{NH}_3(g)$  has taken place in a 2 L container and has reached equilibrium. There are 0.1 mole of  $\text{H}_2(g)$ , 0.15 mole of  $\text{N}_2(g)$ , and 1.5 moles of  $\text{NH}_3(g)$  present at a temperature of 500 K. Find the change in chemical potential for the reaction if the equilibrium constant is 0.1744 under the stated conditions.

**Solution.**

$$\mu_i = \mu_i^\circ + RT \log(P_i)$$

$$\Delta\mu = \mu_{\text{NH}_3}^\circ(2) - \mu_{\text{H}_2}^\circ(3) - \mu_{\text{N}_2}^\circ(1) + RT \log\left(\frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3 P_{\text{N}_2}}\right)$$

Let

$$\Delta\mu^\circ = \mu_{\text{NH}_3}^\circ(2) - \mu_{\text{H}_2}^\circ(3) - \mu_{\text{N}_2}^\circ(1)$$

$$\Delta\mu^\circ = -RT \log(K) = 7260 \text{ J.mol}^{-1}$$

If we treat the gases as ideal then we have:

$$P_{\text{H}_2} = nRT/V = (0.1 \text{ mol})(0.08312 \text{ L.bar.mol}^{-1}\text{K}^{-1})(500 \text{ K})/(2 \text{ L}) = 2.0786 \text{ bar}$$

$$P_{\text{N}_2} = 3.1179 \text{ bar}$$

$$P_{\text{NH}_3} = 31.179 \text{ bar}$$

$$RT \log\left(\frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^2 P_{\text{N}_2}}\right) = (4157.24 \text{ J.mol}^{-1})(3.55) = 14758 \text{ J.mol}^{-1}$$

$$\Delta\mu = 22018 \text{ J.mol}^{-1}$$

■

**Problem 92.** Suppose we have an ideal gas. We double the gas volume by an isothermal expansion that proceeds (1) reversibly and (2) irreversibly into a vacuum. What is the change in entropy during this process (1 and 2)?

**Solution.** (1) For the reversible expansion

$$\Delta S = nR \log(V_2/V_1) = (2.30)(1)(1.99) \log 2 = +1.38 \text{ cal/mol.K.}$$

(2) For the irreversible expansion to the same final state, the entropy change in the gas must again be +1.38 cal/mol.K. ■

**Problem 93.** What is the change in entropy of the surroundings when the volume of an ideal gas is doubled by an isothermal expansion that proceeds (1) reversibly or (2) irreversibly?

**Problem 94.** When the volume of an ideal gas is reduced two-fold by a reversible isothermal compression, what is the change of entropy of (1) the gas and (2) the surroundings?

**Problem 95.** Under 1 atm pressure at 279 K, the reversible crystallization of benzene from its melt is accompanied by an entropy change of -8.53 cal/mol.K. What is the molar heat of fusion of benzene at its melting point?

**Problem 96.** The heat capacity at constant pressure ( $c_P$ ) for carbon monoxide is 7.0 cal/mol.K (ignore temperature dependences). What is the entropy change when a mole of CO is (1) heated from 100 K to 200 K, or (2) cooled from 1500 K to 750 K?

**Problem 97.** At 1000 K,  $4.49 \times 10^{-2}$  as many molecules in a sample of carbon monoxide (CO) are in the first excited vibrational-energy state as in the ground state. How far above the ground state is the first excited state, in kJ/mol?

**Solution.** Given  $T = 1000 \text{ K}$ , molecule=CO (carbon monoxide) and  $N_1/N_0 = 4.49 \times 10^{-2}$  (vibrational energy). Let  $x$ =number of molecules in the ground

state (vibrational) and  $4.49 \times 10^{-2}x$  = number of molecules in the 1st excited vibrational state. Using the equation

$$\frac{N_i}{N_j} e^{-(\epsilon_i - \epsilon_j)/k_B T} = e^{-\Delta\epsilon/k_B T}$$

$$\frac{N_1}{N_0} = \frac{4.49 \times 10^{-2}x}{x} = e^{-\Delta\epsilon/(1.38 \times 10^{-23} \text{ J/K})(1000 \text{ K})}$$

$$\log(4.49 \times 10^{-2}) = \frac{-\Delta\epsilon}{1.38 \times 10^{-20} \text{ J}}$$

$$(-3.10)(1.38 \times 10^{-20} \text{ J}) = -\Delta\epsilon$$

$$\Delta\epsilon = 4.28 \times 10^{-20} \text{ J}$$

Now, to convert to the final units of kJ/mol.

$$(4.28 \times 10^{-20} \text{ J}) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) \left( \frac{6.022 \times 10^{23}}{1 \text{ mol}} \right) = 25.8 \text{ kJ/mol}$$

■

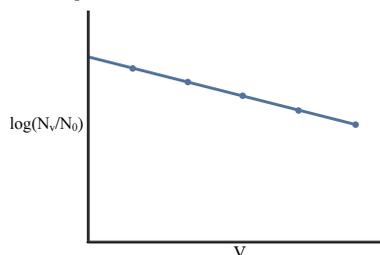
**Problem 98.** Molecular nitrogen has a vibrational energy  $h\nu = 2230 \text{ cm}^{-1}$ . A sample of nitrogen is heated in an electric arc. Spectroscopic methods are used to determine the relative populations of excited vibrational levels. The results are presented in the table below

Vibrational level ( $v$ )	0	1	2	3	4	...
$N_v/N_0$	1.000	0.200	0.040	0.008	0.002	...

Use these results in combination with the information about the spacing of vibrational energy levels to determine whether the nitrogen is in thermodynamic equilibrium with respect to vibrational energy. In other words, does the vibrational population obey the Maxwell-Boltzmann distribution law? If so, what is the vibrational temperature of the gas? Is this value necessarily the same as the translational temperature of the gas? Why or why not? Hint: try to rearrange the Maxwell-Boltzmann equation appropriate for this problem so that there is a linear relationship between  $v$  and some function of  $N_V/N_0$ . Then plot the data and calculate the slope.

**Solution.** We are given: molecule is  $\text{N}_2(g)$  and  $h\nu = 2230 \text{ cm}^{-1}$ . Relative populations of the first four excited state to the ground state. One way to approach this problem is to rearrange the Maxwell-Boltzmann distribution (equation) to look like a linear function, graph the function and calculate  $T$  from the slope. We are looking at vibrational energy, so we use:  $\epsilon_v = (v + 1/2)h\nu$  and  $N_v/N_0 = e^{-(\epsilon_v - \epsilon_0)/k_B T} = e^{-((v+1/2)h\nu - (1/2)h\nu)/k_B T}$ , where the second term in the exponent is from  $\epsilon_0 = (0 + 1/2)h\nu$ . Therefore,  $N_V/N_0 = e^{-vh\nu/k_B T}$  Linearize this equation by taking the log of both sides:

$\log(N_v/N_0) = -nk\nu/k_B T$  or  $\log(N_V/N_0) = -v(h\nu/k_B T)$  which is of the form  $y = mx$ .



The slope of this line is  $m = -1.5649 = -k\nu/k_B T$ . Note: depending on your program and graphing the data, the slope value may differ from mine. Solving for  $T$ , we get:  $T = 2050K$ , which becomes  $T = 2000 K$  (1 sig. fig.). The  $T_v$  is usually the same as  $T_{translational}$  but doesn't have to be under certain conditions. ■

**Problem 99.** In thermodynamics, the partial derivatives of physical quantities are related to one another by application of the commutativity property of partial derivatives,  $\partial_x \partial_y f(x, y) = \partial_y \partial_x f(x, y)$ , which follows from the equality of mixed partial derivatives for sufficiently smooth functions. For example, if the internal energy is expressed as

$$dU = TdS + \mu dN$$

it follows that

$$T = \left. \frac{\partial U}{\partial S} \right|_N \quad \text{and} \quad \mu = \left. \frac{\partial U}{\partial N} \right|_S$$

The joint second derivative of  $U$  is then given by

$$\frac{\partial^2 U}{\partial S \partial N} = \frac{\partial^2 U}{\partial N \partial S} = \left. \frac{\partial T}{\partial N} \right|_S = \left. \frac{\partial \mu}{\partial S} \right|_N$$

Since  $(\partial y / \partial x) = (\partial x / \partial y)^{-1}$ , the above equation can be inverted to give

$$\left. \frac{\partial S}{\partial \mu} \right|_N = \left. \frac{\partial N}{\partial T} \right|_S.$$

Similar identities can be obtained from the variations of other state functions. Show that:

$$\begin{aligned} + \left( \frac{\partial T}{\partial V} \right)_S &= - \left( \frac{\partial P}{\partial S} \right)_V = \frac{\partial^2 U}{\partial S \partial V} \\ + \left( \frac{\partial T}{\partial P} \right)_S &= + \left( \frac{\partial V}{\partial S} \right)_P = \frac{\partial^2 H}{\partial S \partial P} \\ + \left( \frac{\partial S}{\partial V} \right)_T &= + \left( \frac{\partial P}{\partial T} \right)_V = - \frac{\partial^2 A}{\partial T \partial V} \\ - \left( \frac{\partial S}{\partial P} \right)_T &= + \left( \frac{\partial V}{\partial T} \right)_P = \frac{\partial^2 G}{\partial T \partial P} \end{aligned}$$

Recall that  $U = U(S, V)$ ,  $H = H(S, P)$ ,  $A = A(T, V)$  and  $G = G(T, P)$ .

**Solution.** These “Maxwell relations” are all derived the same way. Take the third one, for example,  $A(T, V) = U - TS$  and  $dA = -SdT - pdV$  lead to

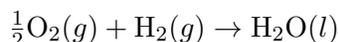
$$S = - \left. \frac{\partial A}{\partial T} \right|_V \quad \text{and} \quad P = - \left. \frac{\partial A}{\partial V} \right|_T$$

Equating the second partial derivatives ( $\partial^2 A / \partial T \partial V$ ) we get

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial P}{\partial T} \right|_V$$

similarly for all other relations. ■

**Problem 100.** The reaction



is used to produce an electrical current. The details of the production of electrical current are not important for solving this problem; we only need to assume that the free energy can be converted into current (electrical work) through some process.

From tables of thermodynamic data, we find the following information in J/mol.K for the standard entropies of formation ( $\Delta S_f^\circ$ ):  $\text{O}_2(g)$ : 205.0,  $\text{H}_2(g)$ : 130.6,  $\text{H}_2\text{O}(l)$ : 70.0. Standard enthalpy of formation for water,  $\Delta H_f^\circ = -285.9$  kJ/mol; those for  $\text{H}_2$  and  $\text{O}_2$  are zero.

Use this information to find:

- The amount of heat released if the reaction were to take place by direct combustion (of oxygen and hydrogen)
- The amount of electrical work the same reaction can perform when carried out in a fuel cell at 298K under reversible conditions
- The amount of heat released under the same conditions (when electrical current is produced)

**Solution.** First, we need to find  $\Delta H_{rxn}^\circ$  and  $\Delta S_{rxn}^\circ$  for the process. Recalling that the standard enthalpy of formation of the elements is zero,  $\Delta H_{rxn}^\circ = H_f^\circ(\text{products}) - H_f^\circ(\text{reactants}) = -285.9 \text{ kJ mol}^{-1} - 0 = -285.9 \text{ kJ mol}^{-1}$ . Similarly,  $\Delta S_{rxn}^\circ = S_f^\circ(\text{products}) - S_f^\circ(\text{reactants}) = (70.0) - (\frac{1}{2} \times 205.0 + 130.6) = -163 \text{ JK}^{-1}\text{mol}^{-1}$ .

a) When the hydrogen and oxygen are combined directly, the heat released will be  $\Delta H_{rxn}^\circ = -285.9 \text{ kJ mol}^{-1}$ .

b) The maximum electrical work the fuel cell can perform is given by  $\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T\Delta S_{rxn}^\circ = -285.9 \text{ kJ mol}^{-1} - (298 \text{ K})(-163 \text{ JK}^{-1} \text{ mol}^{-1}) = -237.2 \text{ kJ mol}^{-1}$ .

c) The heat released in the reaction is the difference between the enthalpy change (the total energy available) and the reversible work that was expended:  $\Delta H_{rxn}^\circ - \Delta G_{rxn}^\circ = T\Delta S_{rxn}^\circ = (298 \text{ K})(-163 \text{ J.K}^{-1}\text{mol}^{-1}) = -48800 \text{ J mol}^{-1} = -48.8 \text{ kJ mol}^{-1}$ . ■

**Problem 101.** Two ideal gases at constant temperature and pressure are separated by a partition. There are 0.07 mol of gas A and 0.12 mol of gas B. Find the entropy change of the system after the partition is released and the two gases are allowed to mix. It is useful to know that entropy is a state function and that the entropy of a system is given by  $S = k_B \log \Omega$  where  $\Omega$  is the number of accessible microstates to the system and  $\log$  is the natural logarithm. For an ideal gas,  $\Omega \propto V^N$  where  $V$  is the volume of the gas and  $N$  is the number of gas particles. Since  $S$  depends on  $N$  through  $\Omega$ ,  $S$  is an extensive property. To find the entropy change, you will want to consider the system as two subsystems, one consisting of gas A and the other consisting of gas B, and then calculate the entropy of the system before and after the gases mix. The change is equal to the difference between pre- and post-mixing.

**Solution.** Since entropy is a state function, the entropy change is equal to the entropy of the mixture subtracted by the entropy of the two gases prior to mixing.

$$\begin{aligned}\Delta S &= S_{mixture} - S_A - S_B \\ S_{mixture} &= k_B \log(C(V_A + V_B)^{N_A + N_B})\end{aligned}$$

where  $C$  is some constant of proportionality.

$$\begin{aligned}S_{mixture} - S_A - S_B &= k_B(N_A + N_B) \log(C(V_A + V_B)) - k_B N_A \log(CV_A) \\ &\quad - k_B N_B \log(CV_B) \\ &= k_B N_A \log\left(\frac{V_A + V_B}{V_A}\right) + k_B N_B \log\left(\frac{V_A + V_B}{V_B}\right)\end{aligned}$$

Since we are dealing with ideal gases, we can relate the volumes to moles.

$$\frac{V_A + V_B}{V_A} = \frac{n_A + n_B}{n_B}$$

Next we insert  $k_B = R/N_{Avogadro}$  and  $X_A = \frac{n_A + n_B}{n_A}$ .

$$\begin{aligned} \Delta S &= R(n_A \log X_A + n_B \log X_B) \\ &= 8.314 \text{ J K}^{-1} \left[ 0.07 \log \left( \frac{0.19}{0.07} \right) + 0.12 \log \left( \frac{0.19}{0.12} \right) \right] = 1.04 \text{ J K}^{-1} \end{aligned}$$

■

**Problem 102.** A non-uniform chemical potential ( $d\mu/dx \neq 0$ ) leads to a mass flux from regions of high concentration to regions of low concentration. Let's see how we can relate this gradient (slope,  $d\mu/dx$ ) to the diffusion of particles. We know that the chemical potential for an ideal gas is of the form

$$\mu = \mu_0 + k_B T \log(c/c_0)$$

where  $\mu_0$  is a reference chemical potential (only depends on  $T$ , but otherwise a constant),  $c(x, t)$  is the concentration ( $[M]$ ) of a chemical species of interest at position  $x$  and time  $t$ , and  $c_0$  is a reference concentration (say,  $1 \text{ M}$ ).

Let's first establish the principle of "conservation of mass". Let us consider a 1D flow of particles along the  $x$  direction and a "volume element" of length  $dx$  centered at  $\frac{x+dx}{2}$ . Since we are working in 1D we may take the concentration  $c(x, t)$  to have units of particles per unit length. The flow of particles can be described in terms of the particle flux,  $J = c(x, t)v$ , where  $v$  is the velocity of particles.  $J$  has units of particles per unit time. Of course,  $J$  represents a *net flux*, meaning that  $J = 0$  describes equal number of particles moving to the left as to the right. Thus, when  $J = 0$ , there is no change in the number of particles in the volume element  $dx$ . Therefore, its rate of change is zero:  $\partial c/\partial t = 0$ . Moreover, even when  $J = \text{constant}$ , we still have  $\partial c/\partial t = 0$  because even though there may be a net flux of particles, the number of particles that enter  $dx$  equals the number that leaves  $dx$  during some time interval  $dt$ . The only way that  $\partial c/\partial t$  can be nonzero is if  $J$  is not spatially uniform. If there is a slope in  $J$ , there will be a change in  $c$  over time.

In a time interval  $dt$ , the increase in concentration with time,  $\partial c/\partial t$ , will equal the excess of molecules diffusing into the region at position  $x$  over those diffusing out at position  $x + dx$ , divided by the volume ( $dx$ ):

$$\frac{\partial c}{\partial t} = \frac{1}{dx} [J(x) - J(x + dx)]$$

(a) Show that  $\partial c/\partial t = -\partial J/\partial x$ . This is a statement of the conservation of mass. Explain why/how this equation amounts to mass conservation.<sup>39</sup>

Next we must deal with the particle flux  $J = c(x, t)v$ . What should  $v$  be? It turns out that according to *linear response theory*, systems near equilibrium have currents proportional to the first derivative (gradient) of their properties. The examples given in class are Fourier's law,  $J = k(\partial T/\partial x)$  (heat flow proportional to temperature gradient), and Fick's law,  $J = -D(\partial\mu/\partial x)$  (particle flux proportional to the chemical potential gradient). Other examples include Ohm's law (electrical current proportional to the gradient of the electromagnetic potential) and in viscous fluids, where the shear rate is proportional to the shear stress.

Thus, we set  $v = -\gamma(\partial\mu/\partial x)$ , where  $\gamma$  is a coefficient of mobility. This gives  $J \propto \partial\mu/\partial x$ . Namely,  $J = -\gamma c(x, t)\partial\mu/\partial x$ .

b) Insert the ideal gas expression for  $\mu$  into  $J = -\gamma c(x, t)\partial\mu/\partial x$  to find  $J = -\gamma k_B T \partial c/\partial x$ . Then use the expression found in part (a) to arrive at a diffusion equation where  $D = \gamma k_B T$ . Confirm that this diffusion equation is identical to the one derived in class using Einstein's method.

(c) Consider two solutes,  $A$  and  $B$ , dissolved in solution. Write an expression to describe the diffusion of the sum of  $A$  and  $B$  and call  $c_{AB}(x, t) = c_A(x, t) + c_B(x, t)$ . (Hint: no work is needed here, just borrow the result you derived in the previous question.)

**Solution.** a) Taylor expansion of  $J(x + dx)$  gives

$$J(x + dx) = J(x) + dx \left( \frac{\partial J}{\partial x} \right) + \mathcal{O}(dx^2)$$

where  $\mathcal{O}(dx^2)$  are terms of order equal to or higher than  $dx^2$ . Hence, in the limit  $dx \rightarrow 0$ :

$$\frac{\partial c}{\partial t} = \frac{1}{dx} \left[ \cancel{J(x)} - \cancel{J(x)} - dx \left( \frac{\partial J}{\partial x} \right) + \mathcal{O}(dx^2) \right] = -\frac{\partial J}{\partial x}$$

b) Inserting the expression for  $\mu$  for the ideal gas, we find:

$$\begin{aligned} J &= -\gamma c(x, t) \frac{\partial \mu}{\partial x} = -\gamma c(x, t) \frac{\partial (k_B T \log(c(x, t)/c_0))}{\partial x} \\ &= -\gamma c(x, t) \frac{k_B T}{c} \frac{\partial c}{\partial x} = -\gamma k_B T \frac{\partial c}{\partial x} \end{aligned}$$

<sup>39</sup>Hint: Taylor expand  $J(x + dx)$ . Recall from calculus that the Taylor expansion of  $f(x)$  at  $x$  is the series  $\sum_{i=0}^{\infty} \frac{f^{(i)}(a)}{i!} (x - a)^i$ , where  $f^{(i)}$  denotes the  $i$ -th derivative of  $f$  evaluated at the point  $a$ . In practice (i.e. in the physical sciences), only the lowest order terms are needed when  $x$  is close to  $a$ . In that case, we only need Taylor's theorem,  $f(x) = f(a) + f'(a)(x - a) + \mathcal{O}((x - a)^2)$ , where  $\mathcal{O}((x - a)^2)$  is a term that tends to zero as  $(x - a)$  goes to zero.

and thus the rate of change of  $c(x, t)$  is given by the diffusion equation

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} = \gamma k_B T \frac{\partial^2 c}{\partial x^2}$$

where  $D = \gamma k_B T$ .

c) The above treatment is for ideal solutions by choice of  $\mu = \mu_0 + k_B T \log(c/c_0)$ . Thus, solutes  $A$  and  $B$  are non-interacting and the diffusion of the sum,  $c_{AB}(x, t)$ , is the sum of the parts,  $c_A(x, t)$  and  $c_B(x, t)$ .

$$c_{AB}(x, t) = c_A(x, t) + c_B(x, t)$$

$$\frac{\partial c_{AB}}{\partial t} = \frac{\partial c_A}{\partial t} + \frac{\partial c_B}{\partial t} = \gamma_A k_B T \frac{\partial^2 c_A}{\partial x^2} + \gamma_B k_B T \frac{\partial^2 c_B}{\partial x^2}$$

■

**Problem 103.** Thermodynamic relationships can be used to accurately describe the slopes of phase diagram coexistence curves. Specifically, the Clapeyron equation can be used to characterize the discontinuous phase transition of a single material.

a) Show that at constant temperature  $T$  and pressure  $P$ , the infinitesimal change in Gibbs free energy can be written as

$$dG = (\mu^g - \mu^l)dn^g$$

Note that for a liquid-gas phase change,  $dn^l = -dn^g$ , the Gibbs free energy of a liquid-gas mixture is given by  $G = G^l + G^g$ , and the chemical potential  $\mu$  can be defined as

$$\mu = \left( \frac{\partial G}{\partial n} \right)_{P, T}$$

b) Derive the Clapeyron equation (subscript  $t$ =phase transition),

$$\frac{dP}{dT} = \frac{\Delta_t \bar{H}}{T \Delta_t \bar{V}}$$

by taking the total derivative\* of both sides of the following expression

$$\mu^\alpha(T, P) = \mu^\beta(T, P)$$

where  $\alpha$  and  $\beta$  represent two states of a phase transition at equilibrium. You may find the following relationships useful, where the overline indicates the intensive molar quantity

$$\left( \frac{\partial \mu}{\partial P} \right)_T = \left( \frac{\partial \bar{G}}{\partial P} \right)_T = \bar{V} \quad \text{and} \quad \left( \frac{\partial \mu}{\partial T} \right)_P = \left( \frac{\partial \bar{G}}{\partial T} \right)_P = -\bar{S}$$

$$\Delta_t \bar{S} = \frac{\Delta_t \bar{H}}{T}$$

\*The total derivative  $df$  is best explained by an example: consider a function  $f(x, y)$ . Its total derivative is

$$df = \left(\frac{\partial f}{\partial y}\right)_x dy + \left(\frac{\partial f}{\partial x}\right)_y dx.$$

c) How much does the melting point of benzene increase per atmosphere of pressure (within the vicinity of 1 atm)? Take  $\Delta_{\text{fus}}\bar{H}$  (at 278.7 K) to be 9.95 kJ mol<sup>-1</sup> and  $\Delta_{\text{fus}}\bar{V}$  (at 278.7 K) to be 10.3 cm<sup>3</sup> mol<sup>-1</sup>.

**Solution.** a) Take the derivative of  $G = G^l + G^g$  with respect to  $n$  at constant  $T$  and  $P$ .

$$dG = \left(\frac{\partial G^g}{\partial n^g}\right)_{P,T} dn^g + \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T} dn^l$$

Since  $dn^l = -dn^g$ ,

$$dG = \left[\left(\frac{\partial G^g}{\partial n^g}\right)_{P,T} - \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T}\right] dn^g$$

$$dG = (\mu^g - \mu^l) dn^g \quad (\text{constant } T \text{ and } P)$$

b) Take the total derivative

$$\left(\frac{\partial \mu^\alpha}{\partial P}\right)_T dP + \left(\frac{\partial \mu^\alpha}{\partial T}\right)_P dT = \left(\frac{\partial \mu^\beta}{\partial P}\right)_T dP + \left(\frac{\partial \mu^\beta}{\partial T}\right)_P dT$$

Evoking the relationships

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V} \quad \text{and} \quad \left(\frac{\partial \mu}{\partial T}\right)_P = \left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S}$$

results in

$$\bar{V}^\alpha dP - \bar{S}^\alpha dT = \bar{V}^\beta dP - \bar{S}^\beta dT$$

Since this expression is in equilibrium, it is appropriate to evoke

$$\Delta_t \bar{S} = \frac{\Delta_t \bar{H}}{T}$$

where it follows that

$$\frac{dP}{dT} = \frac{\Delta_t \bar{H}}{T \Delta_t \bar{V}}$$

c)  $\frac{dP}{dT}$  evaluates to:

$$\frac{9950 \text{ J mol}^{-1}}{(278.68 \text{ K})(10.3 \text{ cm}^3 \text{ mol}^{-1})} \left(\frac{10 \text{ cm}}{1 \text{ dm}}\right)^3 \left(\frac{0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}}\right) = 34.2 \text{ atm K}^{-1}$$

Taking the reciprocal

$$\frac{dT}{dP} = 0.0292 \text{ K atm}^{-1}$$

■

**Problem 104.** A chemical reaction is at equilibrium, according to its equilibrium constant,  $K$ . It is possible to estimate the equilibrium constant at temperatures other than standard conditions by using the enthalpy of reaction  $\Delta H_{\text{rxn}}^\circ$  and the van't Hoff equation.

a) First, show that the expression

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^\circ + RT \log(Q)$$

follows from the definition

$$dG = \sum_J \mu_J dn_J$$

Recall that  $\mu_J = \mu_J^\circ + RT \log(a_J)$  where  $\mu_J$  and  $a_J$  are the chemical potential and activity of species J, respectively. Furthermore, the extent of reaction  $\xi$  can be defined by the expression  $dn_J = \nu_J d\xi$  where  $\nu_J$  is the stoichiometric number of species J.

b) Derive the van't Hoff equation

$$\frac{d(\log K)}{d(1/T)} = -\frac{\Delta H_{\text{rxn}}^\circ}{R}$$

by taking the derivative with respect to temperature of  $\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^\circ + RT \log Q$  at equilibrium standard conditions. Use the Gibbs-Helmholtz equation

$$\frac{d(\Delta G_{\text{rxn}}^\circ/T)}{dT} = -\frac{\Delta H_{\text{rxn}}^\circ}{T^2}$$

in your derivation.

c) Consider the synthesis of ammonia at 298 K



and using the van't Hoff equation, estimate the equilibrium constant at 500 K. Take  $\Delta H_{\text{rxn}}^\circ = -92.2 \text{ kJ mol}^{-1}$  and assume it is constant over this temperature range.

**Solution.** a) Express the infinitesimal change in Gibbs free energy in terms of extent of reaction  $\xi$

$$dG = \sum_J \mu_J dn_J = \left( \sum_J \nu_J \mu_J \right) d\xi$$

It follows that

$$\Delta G_{\text{rxn}} = \left( \frac{\partial G}{\partial \xi} \right)_{P,T} = \sum_{\text{J}} \nu_{\text{J}} \mu_{\text{J}}$$

Substituting the chemical potential of species J

$$\Delta G_{\text{rxn}} = \sum_{\text{J}} \nu_{\text{J}} \mu_{\text{J}}^{\circ} + RT \sum_{\text{J}} \nu_{\text{J}} \log(a_{\text{J}}) = \Delta G_{\text{rxn}}^{\circ} + RT \sum_{\text{J}} \log(a_{\text{J}}^{\nu_{\text{J}}})$$

where the identity  $a \log x = \log x^a$  has been used. Finally, evoking the identity  $\log x + \log y + \dots = \log(xy \dots)$  results in

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^{\circ} + RT \prod_{\text{J}} a_{\text{J}}^{\nu_{\text{J}}} = \Delta G_{\text{rxn}}^{\circ} + RT \log(Q)$$

where

$$Q = \prod_{\text{J}} a_{\text{J}}^{\nu_{\text{J}}}$$

b) Taking the derivative with respect to  $T$  of the following

$$\log K = -\frac{\Delta G_{\text{rxn}}^{\circ}}{RT}$$

which results in

$$\frac{d \log K}{dT} = -\frac{1}{R} \frac{d(\Delta G_{\text{rxn}}^{\circ}/T)}{dT}$$

Substitute the Gibbs-Helmholtz equation

$$\frac{d \log K}{dT} = \frac{\Delta H_{\text{rxn}}^{\circ}}{RT^2}$$

The required form of the van't Hoff equation can be obtained by substituting the following identity

$$\frac{d(1/T)}{dT} = -\frac{1}{T^2} \quad \text{so} \quad dT = -T^2 d(1/T)$$

c) Integrate the result of part (b) assuming constant standard enthalpy of reaction

$$\log K_2 - \log K_1 = -\frac{1}{R} \int_{1/T_1}^{1/T_2} \Delta H_{\text{rxn}}^{\circ} d(1/T) = -\frac{\Delta H_{\text{rxn}}^{\circ}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

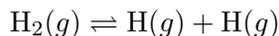
$$\log K_2 = \log(6.1 \times 10^5) - \frac{(-92.2 \times 10^3 \text{ J mol}^{-1})}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{500 \text{ K}} - \frac{1}{298 \text{ K}} \right) = -1.71$$

Thus

$$K_2 = 0.18$$

■

**Problem 105.** Consider the chemical equilibrium reaction under standard conditions



By what factor is the rate of the reverse reaction greater than that of the forward? Take the chemical potential of monatomic hydrogen gas  $\mu_{\text{H}}^{\circ}$  to be 203.26 kJ/mol.

**Solution.**

$$\begin{aligned}\Delta G_{rxn}(T, P) &= \sum_{\text{J}} \nu_{\text{J}} \mu_{\text{J}} \\ 2(203.26 \text{ kJ/mol}) - 1(0) &= 406.52 \text{ kJ/mol} \\ \Delta G_{rxn}^{\circ}(T, P) &= -RT \log K_{\text{eq}} = 406.52 \times 10^3 \text{ kJ/mol} \\ K_{\text{eq}} &= \frac{K_{+}}{K_{-}} = 5.5 \times 10^{-72}\end{aligned}$$

The reverse reaction occurs at a rate on the order of  $10^{72}$  times faster (under standard conditions). ■

**Problem 106.** Consider the following situation: (a) Let  $K = \exp\left(\frac{-\Delta G_{rxn}^{\circ}}{k_B T}\right)$ . If  $K_w = 10^{-14}$  at RT, will  $K_w$  be greater or less than  $10^{-14}$  at  $T = 0^{\circ}\text{C}$ ? (b) At a different temperature  $K_w = 6.3 \times 10^{-13}$ . Find pH of neutral water at this temperature. (c) Relate pH and pOH using the value of  $K_w$  given in the previous step.

**Solution.** (a)  $K \propto \frac{1}{e^x}$ , so it will be lower since the argument of the exponential will be larger.

$$\begin{aligned}\text{(b) } K_w &= [\text{H}^+][\text{OH}^-] = [\text{H}^+]^2 \\ \text{pH} &= -\log[\sqrt{6.3 \times 10^{-13}}] = 6.10 \\ \text{(c) } \text{pH} + \text{pOH} &= 12.2\end{aligned}$$

**Problem 107.** Liquid helium and liquid argon are both cryogenic fluids; He(*l*) boils at 4.21 K, and Ar(*l*) boils at 90.2 K. The specific heat of liquid helium near its boiling point is  $4.25 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ , and the specific heat of liquid argon near its boiling point is  $1.12 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ . The enthalpy of vaporization of He(*l*) is  $25.1 \text{ J}\cdot\text{g}^{-1}$ , and the enthalpy of vaporization of Ar(*l*) is  $161.1 \text{ J}\cdot\text{g}^{-1}$ . Discuss which is a better coolant near its boiling point and which is better at its boiling point.

**Solution.** Near the boiling point, the larger the specific heat the better the coolant. It takes more energy from whatever is cooled in order to raise its temperature, thus better cooling the other substance. Thus, He is the better coolant near its boiling point.

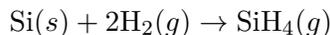
At the boiling point, the larger the enthalpy of vaporization the better the coolant as it takes more energy from whatever is cooled for it to vaporize. Therefore, Ar is the better coolant at its boiling point. ■

**Problem 108.** Find the  $\Delta H_f^{\circ}$  and  $\Delta U_f^{\circ}$  for SiH<sub>4</sub>(*g*) from its elements at 298 K, if 0.17 L of the compound at 298 K and  $P=0.981$  bar is burned in a

constant-volume calorimeter in an excess of oxygen and causes the evolution of 9.757 kJ of heat. The reaction is:



and the formation of silane from its elements is:



**Solution.**

$$n = \frac{PV}{RT} = \frac{(0.968 \text{ atm}) \cdot (0.17\text{L})}{(0.082057 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(298 \text{ K})} = 0.00673 \text{ mol}$$

$$9.757 \text{ kJ} / 0.00673 \text{ mol} = 1450 \text{ kJ/mol} = \Delta H_C^\circ$$

$$\begin{aligned} \Delta H_C^\circ &= 2\Delta H_f^\circ(\text{H}_2\text{O}(l)) + \Delta H_f^\circ(\text{SiO}_2(s, \text{quartz})) - \Delta H_f^\circ(\text{SiH}_4(g)) \\ \Delta H_f^\circ(\text{SiH}_4(g)) &= (2 \times -285.83 \text{ kJ/mol}) + (-910.94 \text{ kJ/mol}) - (-1450 \text{ kJ/mol}) \\ \Delta H_f^\circ(\text{SiH}_4(g)) &= -32.8 \text{ kJ/mol} \\ \Delta H_f^\circ &= \Delta U_f^\circ + \Delta n_f RT, \quad \Delta n_f = 1 - 2 = -1 \\ \Delta U_f^\circ &= \Delta H_f^\circ - \Delta n_f RT = -32.8 \text{ kJ/mol} - (-1 \times 8.314 \text{ J/mol}\cdot\text{K} \times 298 \text{ K} \times \\ & (1 \text{ kJ}/1000 \text{ J})) = -30.3 \text{ kJ/mol} \quad \blacksquare \end{aligned}$$

**Problem 109.** A container with 3 moles of ideal gas initially has a pressure and temperature of 5 atm and 300 K, respectively. Through an isothermal irreversible expansion against a constant pressure of 1 atm its final volume becomes 62 L. (a) Find the work done in the process. (b) Find the work done if the expansion had been done reversibly. (c) Why are (a) and (b) different?

**Solution.** We start with  $dw = -P_{ext}dV$ . For a reversible process,  $P_{ext} = P$

(a)

$$w_{irrev} = -P_{ext}\Delta V = -(1 \text{ atm})(62 \text{ L} - 14.8 \text{ L}) = -47.2 \text{ atm}\cdot\text{L}$$

(b)

$$w_{rev} = -nRT \log(V_2/V_1) = -105.8 \text{ atm}\cdot\text{L}$$

(c) Work is not a state function. The reversible work will always be greater.  $\blacksquare$

**Problem 110.** (a) If an ideal gas is reversibly heated in such a way that its volume is exponentially dependent on the temperature ( $V = [1.3 \text{ L}]e^{(0.01 \text{ K}^{-1})T}$ ), what is the relationship between pressure and temperature? Find the work done by the system during an isothermal expansion from  $V_1$  to  $V_2$ . (b) What is the change in the internal energy of a system with 3 moles that is heated from 100 K to 250 K? Would it be different or equal if the heating had been done through a non-reversible process?

**Solution.** (a)

$$P = \frac{nRT}{V} = nRT \frac{1}{[1.3 \text{ L}]e^{(0.01 \text{ K}^{-1})T}} = \frac{nRT}{1.3} e^{-(0.01 \text{ K}^{-1})T}.$$

In this case,  $dT = 0$  implies  $dV = 0$  so the expansion work is zero.

(b)

$$dU = C_v dT = (3/2)nRTdT,$$

$$\Delta U = \int_{100}^{250} (3/2)(3)RTdT = (9/2)R(250 \text{ K} - 100 \text{ K}) = 5612.3 \text{ J}.$$

The change in  $U$  would be the same for both paths. ■

**Problem 111.** Calculate  $\Delta H^\circ$  and  $\Delta G^\circ$  at  $25^\circ\text{C}$  for the reaction:



Which of the two oxides is more stable at  $25^\circ\text{C}$  and  $P_{\text{O}_2}=1 \text{ atm}$ ?

**Solution.**

$$K_p = (P_{\text{O}_2})^{1/2}$$

$$\begin{aligned} \Delta G^\circ & \left[ \left( \frac{1}{2} \text{ mol} \right) (0) + (2 \text{ mol}) (-1014.2 \text{ kJ/mol}) \right] - [(3 \text{ mol}) (-741.0 \text{ kJ/mol})] \\ & = 195 \text{ kJ} > 0 \end{aligned}$$

The process is not spontaneous as written. Therefore,  $\text{Fe}_2\text{O}_3(s)$  is the more "stable" of the two iron oxides. ■

**Problem 112.** The molar enthalpy of fusion of ice at  $0^\circ\text{C}$  is  $6.02 \text{ kJ/mol}$ . The molar heat capacity of supercooled water is  $75.3 \text{ J/mol/K}$ . One mole of supercooled water at  $-10^\circ\text{C}$  is induced to crystallize in a heat-insulated vessel. The result is a mixture of ice and water at  $0^\circ\text{C}$ . What fraction of this mixture is ice? What is  $\Delta S$  for the system?

**Solution.** The freezing of metastable supercooled water is certainly a spontaneous and irreversible process. The transformation can be thought of as two separate reversible processes.

1.  $l(-10^\circ\text{C}) \rightarrow l(0^\circ\text{C})$  "heat is required"
2.  $l(0^\circ\text{C}) \rightarrow s(0^\circ\text{C})$  "heat is evolved"

Because the system is thermally isolated from the surroundings,  $Q = 0$ . Therefore, the heat required to raise the temperature of the liquid from  $-10^\circ\text{C}$  to  $0^\circ\text{C}$  equals the heat evolved from the fusion of the ice. i.e.  $q_1 = -q_2$ . Therefore,

$$q_1 = n\tilde{C}_p\Delta T = (1.00 \text{ mol})(75.3 \text{ J/K}\cdot\text{mol})(10 \text{ K}) = 733 \text{ J}$$

$$q_2 = n\Delta\tilde{H}_{fus}$$

but the magnitude of  $q_1$  and  $q_2$  are equal. So,

$$n = \frac{q_2}{\Delta\tilde{H}_{fus}} = \frac{753 \text{ J}}{6.02 \times 10^3 \text{ J/mol}} = 1.25 \times 10^{-1} \text{ mol}$$

(amount of ice formed)

$$\%ICE = \frac{1.25 \times 10^{-1} \text{ mol frozen}}{1.00 \text{ mol total}} \times 100 = 13\%$$

$$\Delta S_1 = n\tilde{C}_p \log \frac{T_f}{T_i} = (1.00 \text{ mol})(75.3 \text{ J/mol}) \log \left( \frac{273}{263} \right) = 2.81 \text{ J/K}$$

$$\begin{aligned} \Delta S_2 &= \frac{-(n)\Delta\tilde{H}_{fus}}{T_{fus}} = \frac{-(1.25 \times 10^{-1} \text{ mol})(6.02 \times 10^3 \text{ J/K}\cdot\text{mol})}{273 \text{ K}} \\ &= -2.76 \text{ J/K} \end{aligned}$$

$$\Delta S_{total} = 2.81 \text{ J/K} + (-2.76 \text{ J/K}) = 5 \times 10^{-2} \text{ J/K}$$

Small, but still greater than zero. ■

**Problem 113.** At 1200 K and in the presence of solid carbon, an equilibrium mixture of CO and CO<sub>2</sub> contains 98.3 mol percent CO and 1.69 mol percent CO<sub>2</sub> with the total pressure at 1 atm. What are  $P_{CO}$  and  $P_{CO_2}$ , what is the equilibrium constant, and what is  $\Delta G^\circ$  associated with the reaction  $CO_2(g) + C(\text{graphite}) \rightleftharpoons 2CO(g)$  at 1200 K?

**Solution.**

$$K_p = \frac{P_{CO}^2}{P_{CO_2}} = \frac{(0.983 \text{ atm})^2}{(1.69 \times 10^{-2} \text{ atm})} = 57.2 \text{ atm}$$

$$\begin{aligned} \Delta G^\circ &= -RT \log K_p = -(8.315)(1200) \log(57.2) \text{ J/mol} = 40,376 \text{ J/mol} \\ &= 40.4 \text{ kJ/mol} \end{aligned}$$

■

**Problem 114.** Part (1): Calculate the standard free-energy change and the equilibrium constant for dimerization of NO<sub>2</sub> to N<sub>2</sub>O<sub>4</sub> at 25° C.

Part (2): Calculate  $\Delta G$  for this reaction at 25° C when the pressure of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> are each held at 0.01 atm. Which way will the reaction tend to proceed?

**Solution.** Part (1):

$$\begin{aligned} \Delta G^\circ &= [(1 \text{ mol})(98.3 \text{ kJ/mol}^{-1})] - [(2.00 \text{ mol})(51.8 \text{ kJ/mol})] \\ &= -5.3 \text{ kJ/mol of N}_2\text{O}_4 \end{aligned}$$

$$K_p = e^{-\Delta G^\circ/RT} = e^{-(5.3 \text{ kJ/mol})(1000 \text{ J/kJ})/(8.315 \text{ J/K}\cdot\text{mol})(298 \text{ K})} = 8.50$$

Part (2):

$$Q = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} = \frac{(0.01 \text{ atm})}{(0.01 \text{ atm})^2} = 100 \text{ atm}^{-1}$$

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \log \frac{Q}{1 \text{ atm}} = -5.3 \times 10^3 \text{ J/mol} + (8.315)(298) \log(100) \\ &= 6.1 \text{ kJ/mol} > 0 \end{aligned}$$

not spontaneous! Reaction shifts back toward reactants. ■



# Chemical Kinetics

Chemical reactions proceed at different rates, depending on the chemical species reacting together and on the conditions of the reaction. The study of chemical kinetics involves the construction of models of chemical reactions and the validation of such models against experiments. A model for a chemical reaction consists of the following parts:

- A mechanism. This is a set of elementary chemical reactions to describe how reactants form intermediates, intermediates combine with one another and reactants, and ultimately products are produced.
- A set of rate equations. These are differential equations corresponding to the reaction mechanism and giving the rates of change of all reactants, intermediates, and products.
- A set of integrated rate equations. These show the concentrations as functions of time for reactants, intermediates, and products. They are obtained by integrating the rate (differential) equations.

The criterion for an acceptable theoretical model is that it agrees with experimental observations of measured time varying concentrations. When a theoretical chemist finds an acceptable model he says he “understands” the reaction.

If we know the reaction mechanism (i.e. the elementary steps of a reaction) we can write down the rate law. Otherwise, we may not have the reaction mechanism but instead only a net reaction; in this case, the rate law must be determined experimentally.

### 7.1. Order of Reaction

Many chemical reactions you will encounter are *net* reactions. For example,  $5\text{Fe}^{2+}(\text{aq}) + \text{MnO}_4^{-}(\text{aq}) + 8\text{H}_3\text{O}^{+}(\text{aq}) \rightarrow 5\text{Fe}^{3+}(\text{aq}) + 12\text{H}_2\text{O}(\text{l}) + \text{Mn}^{2+}(\text{aq})$  is a net reaction because the left hand side appears to imply that 5 ions  $\text{Fe}^{2+}$  collide with 1 ion  $\text{MnO}_4^{-}$  simultaneously to form the stated products. This is not possible. Usually, collisions are binary. Many-body collisions are rarely observed due to their unlikely occurrence<sup>1</sup>; at most, 3-body collisions are observed experimentally. Reactions involving only 1 body are possible in the case of a decomposition reaction or radioactive decay.

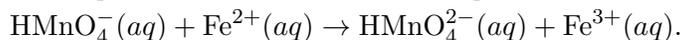
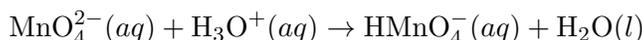
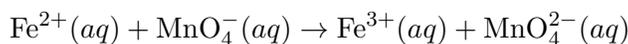
From knowledge of a *net reaction* we cannot determine the order of the reaction by inspection of the balanced equation. Instead, experiments must be carried out to determine its order. The rate of the reaction will be proportional to

$$\text{rate of forward reaction} \propto [\text{Fe}^{2+}]^{\alpha}[\text{MnO}_4^{-}]^{\beta}[\text{H}_3\text{O}^{+}]^{\delta},$$

$$\text{rate of backward reaction} \propto [\text{Fe}^{3+}]^{\gamma}[\text{Mn}^{2+}]^{\zeta}[\text{H}_2\text{O}]^{\xi},$$

where  $\alpha, \beta, \delta, \gamma, \zeta, \xi$  are non-negative constants (not necessarily integers) which are determined from experimental data. The *order of the reaction* is the sum  $\alpha + \beta + \delta$  or  $\gamma + \zeta + \xi$ . Sometimes we speak of the order with respect to a particular species. For example, the reaction is of order  $\alpha$  with respect to  $[\text{Fe}^{2+}]$ .

The above reaction instead proceeds through a series of *elementary steps* (path) involving binary collisions (sometimes elementary steps can involve 3-body collisions). Some of these steps include (this list is not complete):



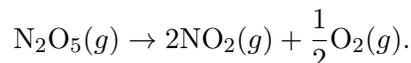
A series of elementary steps is called the *reaction mechanism*. It is generally quite challenging to determine the nature of the reaction mechanism because these involve reaction intermediates that are produced and consumed immediately. In the above reaction mechanism the ions  $\text{MnO}_4^{2-}$  and  $\text{HMnO}_4^{-}$  are reaction intermediates. The short-lived nature of reaction intermediates poses a problem from the standpoint of experimental techniques. Currently, chemists employ a combination of experimental techniques together with results from *ab initio* calculations to provide insights into reaction mechanisms.

<sup>1</sup>Such reactions are unlikely because they required the simultaneous collision of many different molecules, which is much less likely to occur than binary collisions.

## 7.2. Reaction Order from Experiments

The order of the reaction can be determined from experiments by plotting reaction rate vs concentration of reactants or products. If a reaction is known to be an elementary step, then its order can be read off from the stoichiometric coefficients by writing down these coefficients as exponentials (similarly to the procedure we use for writing down equilibrium constants).

Some decomposition reactions are *first order*:



It is found from experiments that the rate of the forward reaction is  $k[\text{N}_2\text{O}_5]$ , where  $k$  (the *rate constant*) is determined from the slope of a reaction rate vs concentration plot, so it is first order. The rate constant,  $k$ , is a quantity that depends on temperature, as we will see in the next lecture.

In general, a reaction that depends on a single reactant,  $aA \rightarrow \text{products}$ , has a rate proportional to the reactant concentration raised to a power  $n$ :

$$\text{rate} = k[\text{A}]^n,$$

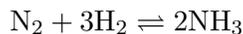
where  $n$  may be different from  $a$ .  $n$  must be determined from experiments. For example, the rate of  $\text{C}_2\text{H}_6(g) \rightarrow 2\text{CH}_3(g)$  is found to be  $k[\text{C}_2\text{H}_6]^2$  from experiments. This is a *second order reaction*. Some reactions are independent of reactant concentrations (rate= $k$ ). Fractional order is also possible. An example is the decomposition of  $\text{CH}_3\text{CHO}$  which is found from experiments to be of order  $3/2$ , i.e., rate= $k[\text{CH}_3\text{CHO}]^{3/2}$ .

**Reaction Order is Derived from Experimental Data:** In the simplest cases (e.g. reaction rate depends on only 1 reactant), it is easy to determine the reaction order from a small number of data points. See, for example, Oxtoby [1], Example 18.1. In the general case, you need to fit the reaction rate expression as function of concentration for each reactant (or product) concentration. The measurement of reaction rates involves measuring reactants as function of time. The “rate”  $d[\text{A}]/dT$  is the time derivative of the concentration of  $[\text{A}]$  and is obtained from a plot of  $[\text{A}]$  vs time.

If there is more than 1 chemical species involved, such as  $aA + bB \rightarrow \text{products}$ , the rate depends on more than one exponent, namely  $\text{rate} = -(1/a)d[\text{A}]/dt = k[\text{A}]^m[\text{B}]^n$ , where  $m, n$  are exponents to be determined experimentally. The overall order of the reaction is  $m + n$ .

### 7.3. The Reaction Rate

Suppose we have a reaction of the type  $\sum_i \nu_i A_i = 0$ , where  $\nu_i$  are the stoichiometric coefficients (negative on the reactant side, and positive on the products side) and  $A_i$  are the chemical species. IUPAC defines the “rate of reaction” as  $\dot{\xi} \equiv \frac{d\xi}{dt} = \frac{1}{\nu_i} \frac{dn_i}{dt}$ , where  $n_i$  is the number of moles of species  $A_i$  and  $\xi$  is called the “extent of the reaction”. For example,



The reaction rate is:

$$\dot{\xi} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt}.$$

**7.3.1. First order reaction: example.** A first order reaction is a reaction whose rate law is of the form:

$$-\frac{d[\text{A}]}{dt} = k[\text{A}]$$

where  $k$  is a rate coefficient.

For example, the following reaction



has a rate law that is found to be:

$$-\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5]$$

The rate law can be integrated if we rewrite it in the form (constants such as ‘2’ can be absorbed in the definition of  $k$ ):

$$\frac{d[\text{A}]}{[\text{A}]} = -k dt$$

to get

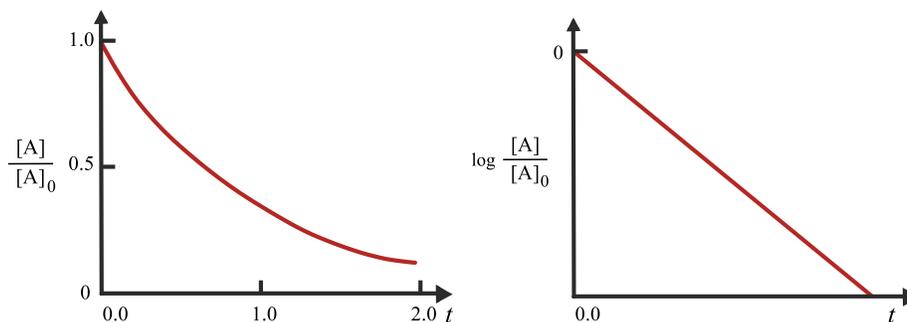
$$\begin{aligned} \int_{[\text{A}]_0}^{[\text{A}](t)} \frac{d[\text{A}]}{[\text{A}]} &= -k \int_0^t dt \quad \Rightarrow \quad \log[\text{A}](t) - \log[\text{A}]_0 = -kt \\ \Rightarrow \quad \log\left(\frac{[\text{A}](t)}{[\text{A}]_0}\right) &= -kt \quad \Rightarrow \quad [\text{A}](t) = [\text{A}]_0 e^{-kt} \end{aligned}$$

In Fig. 7.1, the concentration as function of time (left) and log concentration vs time (right) are shown. On a semilog plot,

$$\boxed{\log[\text{A}](t) = \log[\text{A}]_0 - kt}$$

the graph of  $\log[\text{A}](t)$  vs  $t$  is a straight line with slope  $-k$  and intercept  $\log[\text{A}]_0$ .

Thus, an experimental measurement of  $[A](t)$  vs time will yield the initial concentration  $[A]_0$  by extrapolating to  $t = 0$  and the rate constant  $k$  from the slope. The rate constant is a basic property of every chemical reaction.



**Figure 7.1.** A first order reaction leads to exponential decay of initial reactant concentrations with time (left). On a semi-log plot (right), the exponential decay appears as a straight line.

The *half-life* is defined by the time  $t$  for which  $[A](t)/[A]_0 = \frac{1}{2}$ . That is,  $1/2 = e^{-kt}$ , or

$$t_{1/2} = \log(2)/k.$$

**7.3.2. Second Order Reaction: Examples.** An example of a second-order reaction is



which is found experimentally to obey the rate law:

$$-\frac{d[\text{ClO}^-]}{dt} = k[\text{ClO}^-]^2.$$

This is an equation of the form:

$$-\frac{d[A]}{dt} = k[A]^2, \quad \text{or} \quad -\frac{d[A]}{[A]^2} = k dt.$$

Integrating,

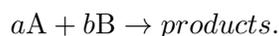
$$-\int_{[A]_0}^{[A](t)} \frac{d[A]}{[A]^2} = k \int_0^t dt.$$

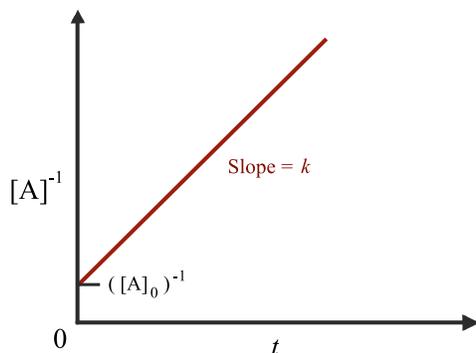
which gives:

$$\frac{1}{[A](t)} = \frac{1}{[A]_0} + kt.$$

Plotting  $\frac{1}{[A](t)}$  vs time gives a straight line with slope  $k$  and intercept  $\frac{1}{[A]_0}$ , as shown in Fig. 7.2.

Another type of second-order reaction is a reaction





**Figure 7.2.** For second order reactions, the inverse of  $[A](t)$  decays linearly with time from some initial concentration  $[A]_0$ .

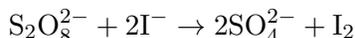
whose rate is of the form

$$rate = k[A][B]$$

i.e.

$$-\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = k[A][B].$$

For example,



whose rate law is found experimentally to be:

$$\frac{d[S_2O_8^{2-}]}{dt} = -k[S_2O_8^{2-}][I^-]$$

#### 7.4. Measurement Methods

In order to study reaction kinetics we need analytical techniques that will report on concentrations of different chemical species as function of time. In general, we may not know what the stoichiometry of the overall reaction is (which is the sum of all the steps in the reaction mechanism). When the stoichiometry is known, we can write down the equilibrium constant. Sometimes, we don't know what all the products are.

Chemical analysis can be done using gravimetric or volumetric techniques, which can be made specific to one or more reactants or products. Chemical analysis is generally slow and can perturb the reaction itself, as it involves withdrawing a physical sample from the system. Separation of chemicals can be done via chromatography, gel electrophoresis, or capillary electrophoresis, followed by analysis of the separated species.

Physical methods, such as pressure or volume measurements (without sample extraction and analysis), can be much more rapid than chemical methods. Suppose that a reaction is carried out in a vessel of fixed volume:



The reaction (in the forward direction) produces two moles of product for every mole of reactant, leading to an increase in the pressure inside the vessel. If the gas mixture is ideal, we may invoke the ideal gas law to relate the concentration of chemical species to the pressure inside the vessel:

$$\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{V} \frac{dn_{total}}{dt} = \frac{1}{RT} \frac{dP}{dt}.$$

The last equality follows from the ideal gas law. The previous equality follows from:

$$n_{total} = n_{\text{O}_2} + n_{\text{NO}} + n_{\text{NO}_2},$$

stoichiometry

$$\Delta n_{\text{NO}_2} = -\frac{1}{2}\Delta n_{\text{O}_2} \quad \text{and} \quad \Delta n_{\text{NO}} = \frac{1}{2}\Delta n_{\text{O}_2},$$

and

$$\frac{dn_{total}}{dt} = \frac{dn_{\text{O}_2}}{dt} + \frac{dn_{\text{NO}}}{dt} + \frac{dn_{\text{NO}_2}}{dt} = \frac{dn_{\text{O}_2}}{dt} \left(1 + \frac{1}{2} - \frac{1}{2}\right) = \frac{dn_{\text{O}_2}}{dt}.$$

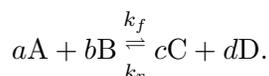
Pressure measurements (e.g., with strain gauges) take on the order of a millisecond, so while the method is faster than chemical methods, it is slower than optical methods. We can also work at constant pressure by allowed the gas in a vessel expand through a piston and monitor volume changes. The total volume is the sum of the partial volumes of the species present.

Electrochemical methods can also be used to monitor the course of a reaction. For example, the electrical conductivity of the following solution will vary as the reaction proceeds:



Finally, spectroscopic methods are commonly used to monitor reactions: electron spin resonance (ESR), nuclear magnetic resonance (NMR), mass spectrometry, and optical spectroscopy (ultraviolet, IR and visible). Other methods such as light scattering, optical rotation, flash photolysis, pulse radiolysis and relaxation have been used. Spectroscopic methods are chemically selective and report on the various chemical species. ESR, NMR and optical methods rely on the absorption of radiation (microwave, radiofrequency, optical photons) at different wavelengths to probe various chemical groups. Optical methods are generally the fastest ones (down to picoseconds and femtoseconds).

**7.4.1. Steady State, Elementary Reactions of the Type  $aA + bB \rightleftharpoons cC + dD$ .** In general, “steady state” and “equilibrium” are not equivalent. The term steady state means that time derivatives of observable quantities are zero. Steady state often implies equilibrium. However, some steady states are not equilibrium states. For example, a fluid flowing at constant velocity is by no means an equilibrium state. However, it is a steady state because the velocity, an observable quantity, is constant. Equilibrium refers to thermal equilibrium, which is the point where the differential of  $G$  is zero. Let’s look at an example of a steady state. Suppose we have the elementary reaction



Its rate is the sum of two terms. The first term describes the rate of depletion of A while the second term describes the rate of production of A:

$$-\dot{\xi} = \frac{1}{a} \frac{d[A]}{dt} = \frac{1}{b} \frac{d[B]}{dt} = -\frac{1}{c} \frac{d[C]}{dt} = -\frac{1}{d} \frac{d[D]}{dt} = -k_f[A]^a[B]^b + k_r[C]^c[D]^d.$$

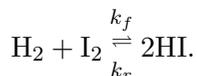
At steady-state ( $\dot{\xi}=0$ ), the rates of the forward and backward reactions are equal:

$$k_f[A]_{\text{eq}}^a[B]_{\text{eq}}^b = k_r[C]_{\text{eq}}^c[D]_{\text{eq}}^d.$$

This is also known as the principle of detailed balance. And since  $K \equiv k_f/k_r$ ,

$$K \equiv \frac{k_f}{k_r} = \frac{[C]_{\text{eq}}^c[D]_{\text{eq}}^d}{[A]_{\text{eq}}^a[B]_{\text{eq}}^b}.$$

An example of such an elementary reaction is:



Its rate is:

$$-\dot{\xi} = \frac{d[\text{I}_2]}{dt} = -k_f[\text{H}_2][\text{I}_2] + k_r[\text{HI}]^2.$$

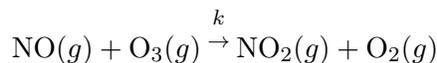
At equilibrium,  $d/dt=0$ , the steady-state gives the equilibrium constant:

$$K \equiv \frac{k_f}{k_r} = \left( \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \right)_{\text{eq}}.$$

**7.4.2. Reaction Order, From Elementary Reactions.** If the elementary steps are known, then the reaction order is known. For example, the elementary step



is first order (asterisk denotes an excited state) and its rate is  $k[\text{N}_2\text{O}_5^*]^1$ . Likewise, the elementary step

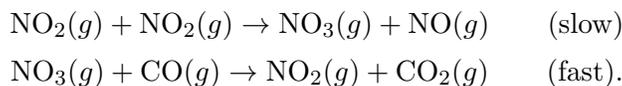


yields a second order reaction whose rate is  $k[\text{NO}]^1[\text{O}_3]^1$ . It is second order because the exponents add up to  $1 + 1 = 2$ .

**7.4.3. Net Reactions vs Reaction Mechanism: Example 1.** As a reminder, the reactions we usually write are *net reaction*, e.g.,

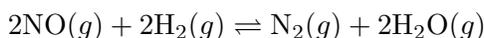


whose order is unknown without data from experiments. However, if the elementary steps are known, we can determine the order. In this particular case, the reaction mechanism is known. It involves the following steps:

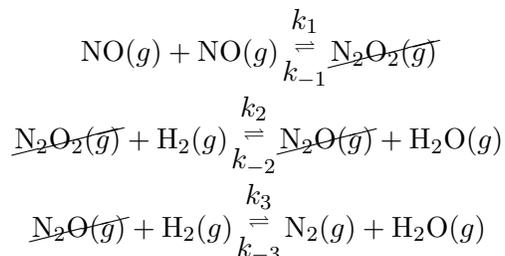


You can check that adding these two reactions yields the net reaction (\*).  $\text{NO}_3$  is a reaction intermediate because it is produced then consumed in the subsequent step and does not show up in the net reaction.

**7.4.4. Net Reactions vs Reaction Mechanism: Example 2.** Suppose we have an overall reaction:



whose elementary steps describe a series of binary collisions shown below. You can check that adding these 3 equations together yields the overall reaction (we indicate which terms cancel out - those are the reaction intermediates).



At equilibrium, we take the rate laws and set  $\dot{\xi} = 0$ . This results in detailed balance:

$$\begin{aligned} k_1[\text{NO}]_{\text{eq}}^2 &= k_{-1}[\text{N}_2\text{O}_2]_{\text{eq}} \\ k_2[\text{N}_2\text{O}_2]_{\text{eq}}[\text{H}_2]_{\text{eq}} &= k_{-2}[\text{N}_2\text{O}]_{\text{eq}}[\text{H}_2\text{O}]_{\text{eq}} \\ k_3[\text{N}_2\text{O}]_{\text{eq}}[\text{H}_2]_{\text{eq}} &= k_{-3}[\text{N}_2]_{\text{eq}}[\text{H}_2\text{O}]_{\text{eq}} \end{aligned}$$

We also know that the equilibrium constants are equal to the ratio of the forward and reverse reaction rate constants:

$$K_1 = \frac{[\text{N}_2\text{O}_2]_{\text{eq}}}{[\text{NO}]_{\text{eq}}^2} = \frac{k_1}{k_{-1}}, \quad K_2 = \frac{[\text{N}_2\text{O}]_{\text{eq}}[\text{H}_2\text{O}]_{\text{eq}}}{[\text{N}_2\text{O}_2]_{\text{eq}}[\text{H}_2]_{\text{eq}}} = \frac{k_2}{k_{-2}},$$

$$K_3 = \frac{[\text{N}_2]_{\text{eq}}[\text{H}_2\text{O}]_{\text{eq}}}{[\text{N}_2\text{O}]_{\text{eq}}[\text{H}_2]_{\text{eq}}} = \frac{k_3}{k_{-3}}.$$

We also know that adding reactions together leads to the multiplication of its equilibrium constants. Let's verify that this gives the correct equilibrium constant for the overall reaction:

$$K = K_1 K_2 K_3 = \frac{k_1 k_2 k_3}{k_{-1} k_{-2} k_{-3}} = \frac{\cancel{[\text{N}_2\text{O}_2]_{\text{eq}}} \cancel{[\text{N}_2\text{O}]_{\text{eq}}} [\text{H}_2\text{O}]_{\text{eq}} [\text{N}_2]_{\text{eq}} [\text{H}_2\text{O}]_{\text{eq}}}{[\text{NO}]_{\text{eq}}^2 \cancel{[\text{N}_2\text{O}_2]_{\text{eq}}} [\text{H}_2]_{\text{eq}} \cancel{[\text{N}_2\text{O}]_{\text{eq}}} [\text{H}_2]_{\text{eq}}}$$

$$= \frac{[\text{H}_2\text{O}]_{\text{eq}}^2 [\text{N}_2]_{\text{eq}}}{[\text{NO}]_{\text{eq}}^2 [\text{H}_2]_{\text{eq}}^2}$$

as it should.

This suggests that the rate of the forward net reaction is the product (or at least, proportional to the product) of forward rates of the elementary reactions,  $k_1 k_2 k_3$ , whereas the rate of the backward net reaction is the product  $k_{-1} k_{-2} k_{-3}$ .

**7.4.5. Elementary Reactions: Single Reactions.** When writing down rates of reactions for a chemical species, we first need to identify which reactions this species is involved in, and add a term describing the production or depletion of this species according to the rate constant. In other words, every arrow that points towards or away from the species will correspond a term in the rate equation. This is best explained by looking at many examples.

The rate of the reaction



which describes the unidirectional depletion of A is:

$$-\dot{\xi} = \frac{d[\text{A}]}{dt} = -k[\text{A}].$$

There is only one term because the reaction is unidirectional. There is only 1 arrow that points away from A and no arrows that point toward A. Thus, only 1 term is needed. This term,  $-k[\text{A}]$ , describes the depletion of A (conversion of A to B). It is proportional to the rate constant  $k$ , and to  $[\text{A}]$  (the concentration of A), because this elementary reaction describes a "1-body collision" (i.e. this could describe the decay of a molecule from an excited state to a ground state, or the folding of a protein). Hence, the negative sign.

If the reaction were two-sided,

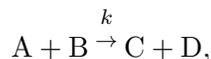


we would need 2 terms in the rate equation. One term describing the depletion of A, with a negative sign and rate constant  $k_1$ , and one term describing the production of A, with a positive sign and rate constant  $k_2$ :

$$-\dot{\xi} = \frac{d[A]}{dt} = -k_1[A] + k_2[B].$$

The first term is proportional to the concentration of A because this elementary reaction describes a “one-body collision” involving only 1 molecule of A. Also, if there were no amount of A, we wouldn’t be producing any B; similarly, the second term is proportional to B, as we need a nonzero concentration of B in order to produce A in the reverse reaction.

A unidirectional reaction

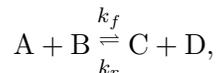


only describes the depletion of A. In order to deplete A, we need a “two-body collision” involving 1 molecule of A colliding with 1 molecule of B. Thus, the rate should be proportional to the product  $[A][B]$ , since the concentrations describe the probabilities of finding a molecule of A (or B) within a given volume element, and the product of  $[A]$  and  $[B]$  describes the joint probability of finding 1 molecule of A *and* 1 molecule of B in the same volume.

The rate contains only 1 term. This term has a negative sign, because it describes the depletion of A:

$$\frac{d[A]}{dt} = -k[A][B].$$

A bidirectional reaction



now describes both the depletion of A (in the forward reaction) and the production of A (in the reverse reaction). The first event proceeds at a rate  $k_f[A][B]$  while the second event happens at the rate  $k_r[C][D]$ . The rate law is:

$$\frac{d[A]}{dt} = -k_f[A][B] + k_r[C][D].$$

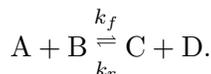
**7.4.6. Elementary Reactions: Simultaneous Reactions.** Suppose we have two simultaneous reactions:



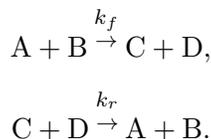
Both reactions describe the depletion of A. The rate of the reaction is:

$$-\dot{\xi} = \frac{d[A]}{dt} = -k_1[A] - k_2[A].$$

**7.4.7. Elementary Reactions: Reversible Reactions.** A reversible reaction



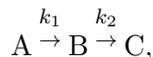
can be viewed as two simultaneous unidirectional forward reactions:



We can write down the rate for each reaction. The first reaction describes the depletion of A at a rate  $k_f[A][B]$  while the second reaction describes the production of A at a rate  $k_r[C][D]$ . Summing up these two rates gives:

$$\frac{d[A]}{dt} = -k_f[A][B] + k_r[C][D].$$

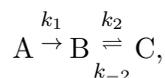
**7.4.7.1. Elementary Reactions: Consecutive Reactions.** Consider the consecutive elementary reactions:



A rate analysis yields:

$$\frac{d[A]}{dt} = -k_1[A], \quad \frac{d[B]}{dt} = k_1[A] - k_2[B] \quad \text{and} \quad \frac{d[C]}{dt} = k_2[B].$$

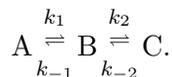
Consider the following variant:



The rate laws would be:

$$\frac{d[A]}{dt} = -k_1[A], \quad \frac{d[B]}{dt} = k_1[A] - k_2[B] + k_{-2}[C] \quad \text{and} \quad \frac{d[C]}{dt} = k_2[B] - k_{-2}[C].$$

Another variant of the above reaction could be:



The rate laws would be:

$$\begin{aligned}\frac{d[A]}{dt} &= -k_1[A] + k_{-1}[B], \\ \frac{d[B]}{dt} &= k_1[A] - k_2[B] - k_{-1}[B] + k_{-2}[C] \\ \frac{d[C]}{dt} &= k_2[B] - k_{-2}[C].\end{aligned}$$

**7.4.8. Series of Unidirectional Steps.** We have to be slightly careful when the same chemical species appears on both sides of the same reaction. Suppose we have the following reaction mechanism:<sup>2</sup>



The rate laws are:

$$\begin{aligned}\frac{d[A]}{dt} &= -k_1[A][X], \\ \frac{d[X]}{dt} &= k_1[A][X] - k_2[X][Y], \\ \frac{d[Y]}{dt} &= k_2[X][Y] - k_3[Y], \\ \frac{d[Z]}{dt} &= k_3[Y].\end{aligned}$$

In the rate equation for  $[X]$ , there are two terms. The first term follows from step 1 (forward direction) and describes the production<sup>3</sup> of  $X$  from the reactants of step 1. The production of  $X$  enters with a positive sign. The second term describes the depletion of  $X$  as a result of step 2 (forward direction). The depletion of  $X$  enters with a negative sign. Notice that there is no term of the form  $-k_{-1}[X]^2$  because step 1 is unidirectional.

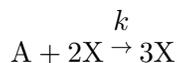
In the rate equation for  $[Y]$ , there are two terms,  $k_2[X][Y]$  and  $-k_3[Y]$ . These follow by inspection of steps 2 and 3: step 2 describes the production of  $Y$ ,

<sup>2</sup>This mechanism normally assumes that the concentration of reactant  $A$  is much larger than its equilibrium value. Another assumption is that the forward rates are much larger than the reverse rates. Thus, the reverse rates are negligible.

<sup>3</sup>It should be clear that step 1,  $A + X \rightarrow 2X$ , describes the production of  $X$ . This reaction describes the transformation of  $A$  into  $X$ , so  $X$  is indeed being produced. Another way to think about it is to manipulate the chemical reaction as an equation: subtracting  $2X$  on both sides gives,  $A - X \rightarrow 0$ , whose negative sign on the reactants side reminds us that  $A$  isn't being consumed in the forward direction, but produced instead.

which depends on the forward reaction. This leads to the term  $k_2[X][Y]$ . Note that there is no term of the form  $-k_{-2}[Y]^2$  because the reaction is in the forward direction only. The second term  $-k_3[Y]$  describes the depletion of Y as a result of its transformation into Y and follows from step 3. Notice that there is no term of the form  $+k_{-3}[Z]$  because step 3 is unidirectional (forward direction only).

The lesson here is to be careful when you see a species appear on both sides of a reaction. Make sure you get the sign right, depending on whether the species is depleted or produced. Another example is:

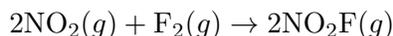


Again, this reaction describes the *production* of X in a 3-body collision. This sign can be seen by subtracting 3X on both sides (so that X shows up only on 1 side of the equation, but not on the other);<sup>4</sup> the X appears with a negative sign on the reactants side, implying that X is produced not depleted. The reactants side, A+2X, shows that this is a 3-body collision involving 1 molecules of A and 2 molecules of X; thus, its rate is proportional to  $+k[A][X]^2$ , not  $-k[A][X]^2$ .

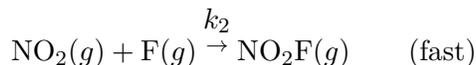
## 7.5. Tricks for Writing Down Rate Laws

Let's look at some techniques that help us write down rate laws when given a reaction mechanism. Examples are given below. This is far from a complete survey of all techniques. In general, we must look at the reaction mechanism (if it is available to us) and analyze it on a case-by-case basis.

**7.5.1. Rate-Determining Steps.** In many reactions, there is often one step that is significantly slower than all other steps. In this case, the rate of the reaction can be taken to be equal to the rate of the slowest step. Suppose that an overall reaction is:



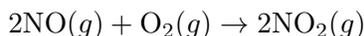
and suppose that the reaction mechanism is:



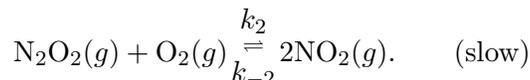
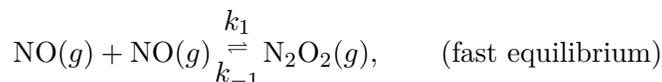
<sup>4</sup>The purpose of this is simply to see if X is produced or depleted. Alternatively, you can also subtract 2X on both sides to get  $A \rightarrow X$ , which shows that X is produced. This does not imply that the rate is  $k[A]$  instead of  $k[A][X]^2$ .

The first step is the slow step (suppose that we know this from experiments). It is called the *rate-limiting step*. The rate of the overall reaction is determined by this slow step,  $k_1[\text{NO}_2][\text{F}_2]$ . Note: the rate is *not* obtained from the net reaction as  $\propto [\text{NO}_2]^2[\text{F}_2]$  because the net reaction does not allow us to determine the rate or order.

**7.5.2. Fast Equilibrium.** In the above section, the elementary steps were unidirectional. Suppose we have bidirectional steps. If one of the reactions happens to be in “fast equilibrium”, we can use this information to solve for concentrations. For example, the overall reaction



proceeds according to the mechanism:



Since the slow step determines the overall rate we have:

$$\text{rate} = k_2[\text{N}_2\text{O}_2][\text{O}_2].$$

However,  $\text{N}_2\text{O}_2$  doesn't appear in the net reaction. We can express this intermediate's concentration in terms of  $\text{NO}$  concentration using the condition for fast equilibrium. The fast equilibrium condition is:

$$K_1 = \frac{k_1}{k_{-1}} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2}, \quad [\text{N}_2\text{O}_2] = K_1[\text{NO}]^2, \quad \text{rate} = k_2K_1[\text{NO}]^2[\text{O}_2].$$

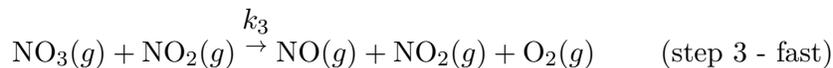
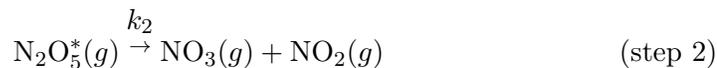
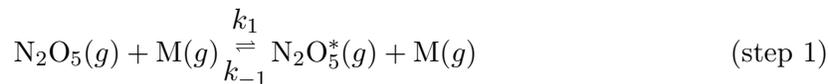
We note that the order here is the same as that of the net reaction. This is a coincidence and may not be the case in general.

**7.5.3. Steady-State Approximation.** If there is no step that is much slower than the others, another trick we can use is the *steady-state approximation*. This requires a reaction intermediate and we assume that this intermediate's concentration remains constant through the reaction. This assumption is reasonable because intermediates are rapidly produced and consumed. Therefore, they rapidly reach a steady-state concentration, which enables us to assume their concentration is constant.

Suppose that the net reaction



proceeds according to the mechanism:



A reaction intermediate is  $\text{N}_2\text{O}_5^*$ . Shortly after the start of the reaction, the concentration of the intermediate reaches a steady state. (Since they don't appear in the net reaction, intermediates can't be easily detected, mainly because they are short-lived, as they are rapidly consumed after being produced.) This means we can set its time derivative equal to zero:

$$\frac{d[\text{N}_2\text{O}_5^*]}{dt} = k_1[\text{N}_2\text{O}_5][\text{M}] - k_{-1}[\text{N}_2\text{O}_5^*][\text{M}] - k_2[\text{N}_2\text{O}_5^*] = 0.$$

This gives an algebraic equation which enables us to solve for the steady state concentration:

$$[\text{N}_2\text{O}_5^*] = \frac{k_1[\text{N}_2\text{O}_5][\text{M}]}{k_2 + k_{-1}[\text{M}]}$$

Using the rate law for step 2, we can write the rate of the overall reaction as:

$$\text{rate} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_2[\text{N}_2\text{O}_5^*] = \frac{k_1 k_2 [\text{N}_2\text{O}_5][\text{M}]}{k_2 + k_{-1}[\text{M}]}$$

We note that the factor of 1/2 here has been absorbed in the definition of  $k_2$  (this is how the textbook of Oxtoby [1] does it).

**7.5.4. Steady State, Elementary Reactions of the Type  $\text{A} \rightleftharpoons \text{B}$ .** Consider the simple reaction,



where  $k_f$  is the rate constant of the forward reaction and  $k_r$  is the rate constant of the backward reaction.

Suppose that we start with only species A present at time  $t = 0$ . Thus, there is a relationship between the concentrations of A and B at *all times*:

$$[\text{B}](t) + [\text{A}](t) = [\text{A}]_0.$$

If this is an elementary reaction, the rate of the reaction is the sum of two terms. The first term describes the rate of depletion of A while the second

term describes the rate of production of A:

$$-\dot{\xi} = \frac{d[A]}{dt} = -k_f[A] + k_r[B] = -k_f[A] + k_r \underbrace{([A]_0 - [A])}_{[B]}.$$

At equilibrium, the time derivative is zero, as the reaction has reached a steady state,

$$0 = k_f[A]_{\text{eq}} - k_r([A]_0 - [A]_{\text{eq}}).$$

This is the same as saying that at steady-state ( $d/dt=0$ ), the rates of the forward and backward reactions are equal:

$$k_f[A]_{\text{eq}} = k_r([A]_0 - [A]_{\text{eq}}).$$

We have a relationship between equilibrium concentration, initial concentration and the rate constants:

$$\boxed{[A]_{\text{eq}} = \frac{k_r[A]_0}{k_f + k_r}.$$

## 7.6. Reaction Rates From Kinetic Theory

Suppose we have an elementary reaction



whose rate is

$$rate = k[A][B],$$

so far we have not said anything about the value of  $k$  and how it depends on the parameters of the molecules involved in the reaction. Simple arguments from kinetic theory can be invoked to explain the behavior of  $k$ .

$k$  should depend on the frequency of molecular collisions, and therefore the mean speed of the molecules,  $\propto \sqrt{T/M}$ , where  $T$  is temperature and  $M$  is molar mass of the molecules. We also expect it to be proportional to the collision cross-section,  $\sigma$  and to the number densities of A and B (and therefore, their concentrations):

$$rate \propto \sigma \sqrt{\frac{T}{M}} [A][B].$$

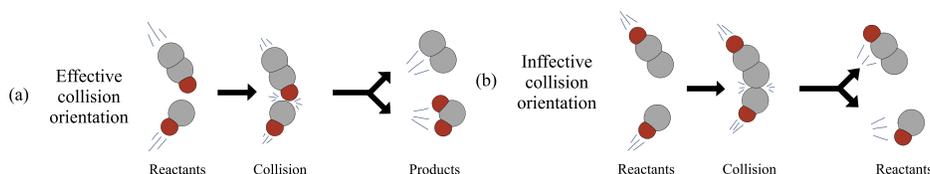
However, not all collisions will lead to reaction. Only those whose kinetic energy exceeds a minimum value  $E_a$  (activation energy) will succeed. Thus, the rate should be proportional to a Boltzmann factor of the form  $e^{-E_a/RT}$ :

$$rate \propto \sigma \sqrt{\frac{T}{M}} e^{-E_a/RT} [A][B]; \quad k \propto \sigma \sqrt{\frac{T}{M}} e^{-E_a/RT}.$$

Not every collision will lead to reaction even if the energy requirement is satisfied because the reactants may need to collide in certain relative orientations, as illustrated in Fig. 7.3. This “steric requirement” can be accounted for using another factor  $P$ ,

$$k \propto P\sigma\sqrt{\frac{T}{M}}e^{-E_a/RT}.$$

(Note:  $M$  is a type of effective or “reduced mass”, i.e.  $m_1m_2/(m_1 + m_2)$ , when molecular collisions between pairs of molecules are involved.)



**Figure 7.3.** Steric requirement for a reaction to proceed. (b) Not all collisions will lead to a reaction. (a) Only a fraction of them may: those with the correct orientation.

## 7.7. Arrhenius Law and Activation Energy Barriers

The activation energy,  $E_a$ , may be different if you go in the forward or reverse direction. Thus when stating  $k$  we must also state whether this refers to the forward or reverse direction.

The expression bears close resemblance to the Arrhenius law, which is usually expressed in the form:

$$k(T) = A(T)e^{-E_a/RT},$$

where  $A(T)$  is the pre-exponential factor and  $E_a$  is the activation energy. The activation energy is the height of the barrier required to reach the “transition state” (‡ symbol in Fig. 7.4). Of course, the value of  $E_a$  depends on whether we are referring to the forward or reverse (backward) reaction. We denote these two values as  $E_{a,f}$  and  $E_{a,r}$ . These two values can be very different, as seen in Fig. 7.4.

The standard Gibbs free energy change of a reaction is related to the equilibrium constant  $K$  through

$$K = e^{-\Delta G_{rxn}^0/RT}.$$

The rate of the forward reaction,  $k_f$ , is

$$k_f = A(T)e^{-E_{a,f}/RT},$$

where  $E_{a,fwd}$  is the difference between Gibbs free energy of the activated complex and that of the reactants (i.e. the barrier height of the forward

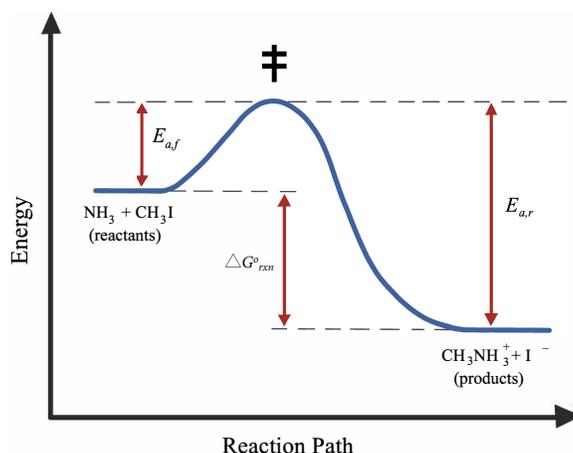


Figure 7.4. Activation energy barrier separates reactants from products.

reaction). Similarly for the reverse direction we write

$$k_r = A(T)e^{-E_{a,r}/RT},$$

from which we find:

$$K = \frac{k_f}{k_r} = e^{-(E_{a,f} - E_{a,r})/RT} = e^{-\Delta G_{rxn}^0/RT}, \quad \Delta G_{rxn}^0 = E_{a,f} - E_{a,r}.$$

In the above diagram, we see that  $\Delta G_{rxn}^0 < 0$ , so the reaction is spontaneous in the forward direction. Its speed in the forward direction, however, is determined by  $E_{a,f}$ , not  $\Delta G_{rxn}^0$ .

These expressions for  $k_f$  and  $k_r$  are called Arrhenius laws. They give the temperature dependence of the reaction rates. It also states that the rates depend on the activation energy. This activation energy is the energy required to reach the transition state (top of the energy barrier), either from the reactant side or the product side.

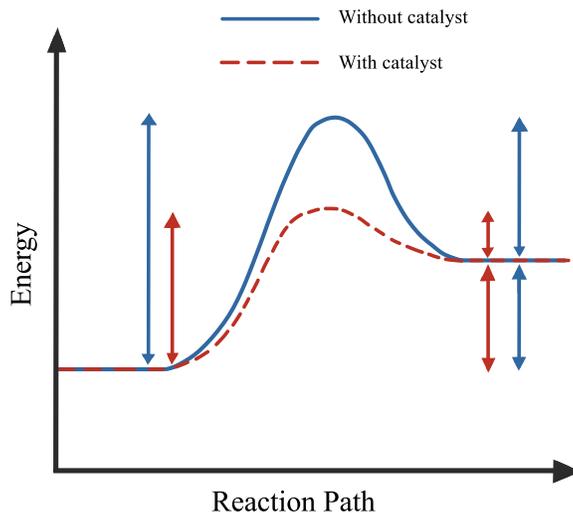
The standard *free energy change of the reaction* is the energy difference between reactants and products. Thus, we see how the free energy does not tell the whole story: it says nothing about the energy barrier, hence, it is not expected to predict the reaction rates. The reaction rates are predicted instead by the activation energy barrier.

## 7.8. Effect of Catalyst

In the previous section we have seen that the equilibrium constant of an uncatalyzed reaction is:

$$K = \frac{k_f}{k_r} = e^{-(E_{a,f} - E_{a,r})/RT}.$$

Suppose that we add a catalyst. The effect of a catalyst is to lower the “activation energy barrier” by some amount  $C$ , as illustrated in the Fig. 7.5.



**Figure 7.5.** A catalyst has the effect of lowering the activation energy barrier. This accelerates the rate of the reaction (which depends on  $E_{a,f}$  or  $E_{a,r}$ ), but does not affect the equilibrium (which depends on the different  $\Delta G_{rxn}^{\circ} = E_{a,f} - E_{a,r}$ ).

In this case, we have:

$$k'_f = A(T)e^{-(E_{a,f}-C)/RT}, \quad k'_r = A(T)e^{-(E_{a,r}-C)/RT},$$

and

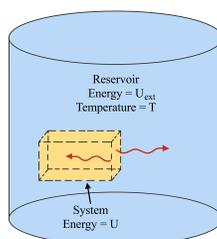
$$K' = \frac{k'_f}{k'_r} = e^{-(E_{a,f}-C-E_{a,r}+C)/RT} = e^{-(E_{a,f}-E_{a,r})/RT} = e^{-\Delta G_{rxn}^{\circ}/RT} = K,$$

which is the same equilibrium constant as the uncatalyzed reaction ( $K = K'$ ). The equilibrium constant depends only on the difference between the energies of the reactants and the products. Thus, *while the introduction of a catalyst speeds up both forward and reverse reactions by the same amount, it does not change the equilibrium.*

### 7.9. Origin of the Boltzmann Factor, $e^{-\epsilon/RT}$

The Boltzmann distribution gives the statistical distributions of the energy levels of atoms/molecules in a gas at thermal equilibrium at some temperature  $T$ . It is a purely “classical” distribution, and does not describe quantum (boson, fermion) statistics. Our derivation is based on the First Law of thermodynamics and the Boltzmann definition of entropy.

Suppose that a system and a reservoir, are together isolated from their surroundings, i.e. think of the system and reservoir together as the universe. The system is in contact with the reservoir as shown in Fig. 7.6.



**Figure 7.6.** System in contact with reservoir. Heat is allowed to exchange, but not particles. The system is taken to be a few molecules.

The system can be anything we want, but here we shall take the system to be a single atom or molecule from the gas. The energy of the reservoir is denoted  $U_{ext}$  and the energy of the system,  $U$ .

Consider two states (e.g. eigenstates) of our atom/molecule: state  $s_1$  and state  $s_2$ . They are assigned energies  $U(s_1)$  and  $U(s_2)$ , respectively. To these, correspond probabilities  $P(s_1)$  and  $P(s_2)$ .

For an isolated system (e.g., here, the system plus reservoir), all accessible microstates are equally probable. This assumption is reasonable because in thermodynamics we do not have any knowledge about the microscopic state of the system: any state that is degenerate is (from our point of view) no different than any other eigenstate of the same energy. The system can freely hop between eigenstates of the same energy, since there is no energy cost to doing so.

Their probabilities are then proportional to the degeneracy (multiplicity) of the reservoir:  $\Omega_{ext}(s_1)$  and  $\Omega_{ext}(s_2)$ .  $\Omega_{ext}(s_i)$  is the number of microstates of the reservoir that are consistent with the system being in state  $s_i$ , and the total energy (system + reservoir) fixed. We need not be concerned about the actual value of  $\Omega_{ext}$  because we will invoke the First Law to relate it to the macroscopic properties of the reservoir temperature ( $T$ ) and entropy ( $S_{ext}$ ).<sup>5</sup>

**7.9.1. Ratio of Probabilities.** In this section we will show that the ratio of probabilities  $P(s_2)/P(s_1)$  is a function of the energy *difference*  $\Delta = U(s_2) - U(s_1)$  and identify the precise functional form for this dependence on  $\Delta$ . We shall assume no particle exchange between the system and the

<sup>5</sup>This is the usefulness of the Boltzmann definition of entropy, which relates the microscopic world ( $\Omega$ ) to the macroscopic world ( $S$ ).

reservoir. We will also assume that the volume of the reservoir does not change significantly when the atom/molecule goes into an excited state.

Invoking the Boltzmann definition of entropy  $S = k_B \log \Omega$ ,

$$\frac{P(s_2)}{P(s_1)} = \frac{\Omega_{ext}(s_2)}{\Omega_{ext}(s_1)} = \frac{e^{S_{ext}(s_2)/k_B}}{e^{S_{ext}(s_1)/k_B}} = e^{[S_{ext}(s_2) - S_{ext}(s_1)]/k_B}$$

In the exponent, we have the change in entropy of the reservoir as the system goes from state 1 to state 2. This is an infinitesimal change from the reservoir's point of view. Thus we invoke the First Law and apply it to the reservoir (subscript *ext*):

$$S_{ext}(s_2) - S_{ext}(s_1) \approx \underbrace{dS_{ext} = \frac{1}{T}(dU_{ext} + P dV_{ext} - \mu dN_{ext})}_{\text{First Law}} \\ \approx \frac{1}{T}[U_{ext}(s_2) - U_{ext}(s_1)].$$

with  $dV_{ext} = 0$  (the  $P - V$  term is negligible compared to the  $dU$  term, when the atom goes into an excited state) and  $dN_{ext} = 0$  (no particle exchange). Then, since the energy lost by the reservoir is the energy gained by the system ( $\Delta U_{ext} = -\Delta U$ ):

$$S_{ext}(s_2) - S_{ext}(s_1) = \frac{1}{T}[U_{ext}(s_2) - U_{ext}(s_1)] = -\frac{1}{T}[U(s_2) - U(s_1)],$$

where  $U$  is the energy of the system (atom/molecule). Then,

$$\boxed{\frac{P(s_2)}{P(s_1)} = e^{-[U(s_2) - U(s_1)]/k_B T}.}$$

Thus, we have derived the famous result " $\frac{P(s_2)}{P(s_1)} = e^{-\Delta E/k_B T}$ ", where  $\Delta E$  is the energy separation between states 1 and 2.

**7.9.2. Canonical Distribution, No Particles Exchanged.** In this section we will derive an exact expression for  $P(s_2)$  [not the ratio  $P(s_2)/P(s_1)$ ] including the proper normalization factor.

Let us rewrite the previous equation as:

$$\boxed{\frac{P(s_2)}{P(s_1)} = e^{-[U(s_2) - U(s_1)]/k_B T} = \frac{e^{-U(s_2)/k_B T}}{e^{-U(s_1)/k_B T}}.}$$

This can be rearranged as follows:  $\frac{P(s_2)}{e^{-U(s_2)/k_B T}} = \frac{P(s_1)}{e^{-U(s_1)/k_B T}}$ , where the left hand side depends on  $s_2$  and the right hand side depends on  $s_1$ . The only way this can happen is if both sides are equal to a constant. With proper

normalization, we obtain the Boltzmann factor:

$$P(s) = \frac{1}{Z} e^{-U(s)/k_B T}$$

where  $Z = \sum_{s'} e^{-U(s')/k_B T}$  and  $\sum_{s'}$  is a sum over all states. This Boltzmann distribution is also called the canonical distribution.

**7.9.2.1. Sum Over Energies.** Because many states may correspond to the same energy, we can also express this in terms of a sum over energies, rather than a sum over states. Let  $g(\epsilon)$  denote the degeneracy of energy level  $\epsilon$  and  $P(\epsilon)$  (degeneracy = number of quantum states corresponding to the same energy  $\epsilon$ ) the probability of the system being found in energy  $\epsilon$ . Then,

$$P(\epsilon) = \frac{1}{Z} g(\epsilon) e^{-\epsilon/k_B T},$$

where  $Z = \sum_{\epsilon'} g(\epsilon') e^{-\epsilon'/k_B T}$  (summation over energy levels, not over quantum states).

**7.9.3. Degeneracy.** In case you forgot what quantum state degeneracy means, you can refresh your memory at:

[https://en.wikipedia.org/wiki/Degenerate\\_energy\\_levels](https://en.wikipedia.org/wiki/Degenerate_energy_levels)

You may have seen the case of the “particle in a box” or the “hydrogen atom” in Chem 20A. Both are famous examples illustrating quantum state degeneracy. For example, hydrogen atom energy levels only depend on  $n$ . The degeneracy of level  $n$  is determined by the quantum number  $l$  (angular momentum),  $m_l$  ( $z$ -projection of angular momentum) and  $m_s$  (spin).  $l$  is an integer ranging from 0 to  $n-1$  (so  $n$  different values of  $l$ ). Similarly, for given values of  $n$  and  $l$ ,  $m_l$  is an integer ranging from  $-l$  to  $+l$  (so  $2l+1$  different values of  $m_l$ ). Thus, the degeneracy of level  $n$  is  $\sum_{l=0}^{n-1} (2l+1) = n^2$ . If we add spin ( $m_s = -1/2, 1/2$ ), the degeneracy is multiplied by 2, i.e.  $g(n) = 2n^2$ .

**7.9.4. Particles Allowed to Exchange: the Grand Canonical distribution.** Now let's repeat the steps from the previous sections but allow for exchange of particles between the system and the reservoir. Suppose now that particles are allowed to be exchanged between the system and reservoir. Our starting point is the same as before:

$$\frac{P(s_2)}{P(s_1)} = \frac{\Omega_{ext}(s_2)}{\Omega_{ext}(s_1)} = \frac{e^{S_{ext}(s_2)/k_B}}{e^{S_{ext}(s_1)/k_B}} = e^{[S_{ext}(s_2) - S_{ext}(s_1)]/k_B}$$

In the exponent, we have the change in entropy of the reservoir as the system goes from state 1 to state 2. This is an infinitesimal change from the

reservoir's point of view. Thus, we invoke the identity

$$dS_{ext} = \frac{1}{T}(dU_{ext} + \cancel{PdV_{ext}} - \mu dN_{ext}).$$

We throw away the  $PdV$  term because it is so small, but keep the chemical term.<sup>6</sup>

$$\begin{aligned} S_{ext}(s_2) - S_{ext}(s_1) &= \frac{1}{T} \left[ \underbrace{U_{ext}(s_2) - U_{ext}(s_1)}_{\Delta U_{ext}} - \underbrace{\mu N_{ext}(s_2) + \mu N_{ext}(s_1)}_{-\mu \Delta N_{ext}} \right] \\ &= -\frac{1}{T} \left[ \underbrace{U(s_2) - U(s_1)}_{\Delta U} - \underbrace{\mu N(s_2) + \mu N(s_1)}_{-\mu \Delta N} \right] \end{aligned}$$

Here,  $U$  and  $N$  refer to the small system, hence the overall minus sign. The sign change is a consequence of conservation of energy,  $\Delta U_{ext} = -\Delta U$  (energy lost by reservoir is gained by the system) and conservation of mass  $\Delta N_{ext} = -\Delta N$  (# particles lost by reservoir is gained by the system). Then,

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-[U(s_2) - \mu N(s_2)]/k_B T}}{e^{-[U(s_1) - \mu N(s_1)]/k_B T}}.$$

The Gibbs factor is

$$P(s) = \frac{1}{\Xi} e^{-[U(s) - \mu N(s)]/k_B T}.$$

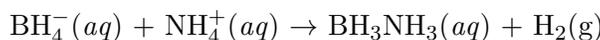
where the normalization factor,  $\Xi$ , viewed as a function of temperature  $T$ ,

$$\Xi(T) = \sum_{s'} e^{-[U(s') - \mu N(s')]/k_B T}$$

is the grand partition function or Gibbs sum.

## 7.10. Problems

**Problem 115.** The rate constant of the elementary reaction



is  $k = 1.94 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$  at  $30.0^\circ\text{C}$ , and the reaction has an activation energy of  $161 \text{ kJ mol}^{-1}$ .

(a) Compute the rate constant of the reaction at a temperature of  $40.0^\circ\text{C}$ .

(b) After equal concentrations of  $\text{BH}_4^-(aq)$  and  $\text{NH}_4^+(aq)$  are mixed at  $30.0^\circ\text{C}$ ,  $1.00 \times 10^4 \text{ s}$  is required for half of them to be consumed. How long will it take to consume half of the reactants if an identical experiment is performed at  $40.0^\circ\text{C}$ ?

<sup>6</sup>We do not bother to write  $\mu_{ext}$  because at equilibrium,  $\mu = \mu_{ext}$ ; just like temperature,  $T = T_{ext}$ .

**Solution.** (a) Recall the Arrhenius equation

$$k = A \exp(-E_a/RT)$$

Given  $k = 1.94 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$  at  $30.0^\circ\text{C}$  and  $E_a = 161 \text{ kJ mol}^{-1}$ ,

$$A = \frac{1.94 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}}{\exp(-161 \text{ kJ mol}^{-1}/(8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(303 \text{ K}))}$$

$$A = 1.106 \times 10^{24} \text{ L mol}^{-1} \text{ s}^{-1}$$

At  $40.0^\circ\text{C}$

$$\begin{aligned} k &= A \exp(-161 \text{ kJ mol}^{-1}/(8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(313 \text{ K})) \\ &= 1.49 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1} \end{aligned}$$

b) This reaction is second order, but the following reasoning applies to reactions of an order. The larger the rate constant, the more rapid is the reaction. Fast reactions require less time to reach any designated point in their progress. Increasing the temperature of this reaction from  $30.0^\circ\text{C}$  to  $40.0^\circ\text{C}$  increases  $k$  from  $1.94 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$  to  $1.49 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ , which is a factor of 7.68. The 50% conversion requires only  $1.30 \times 10^3 \text{ s}$  at  $40.0^\circ\text{C}$  instead of 10000 s it requires at  $30.0^\circ\text{C}$ . ■

**Problem 116.** The first-order reaction  $X \rightarrow Y$  has a half-life of 10 minutes. Determine the percentage of the reactant remaining after one hour has elapsed.

**Solution.**

$$k = \log(2)/t_{1/2} = \log(2)/(10 * 60 \text{ s}) = 0.0011552 \text{ s}^{-1}$$

$$\frac{[X]}{[X]_0} = \exp[-kt] = \exp[-(0.0011552 \text{ s}^{-1})(3600 \text{ s})] = 0.0156275$$

**Problem 117.** For a first-order reaction the time needed for the concentration of the reactant to be  $[X] = (1/e)[X]_0$  is called the relaxation time and is equal to the inverse of the rate constant. Show that this relaxation time is the average lifetime of the reactant population.

**Solution.** The concentration at time  $t$  is given by  $[X] = [X]_0 e^{-kt}$

The fraction of molecules present at a time between  $t$  and  $t + dt$  is  $E(t) =$

$$\frac{[X]}{\int_0^\infty [X] dt}$$

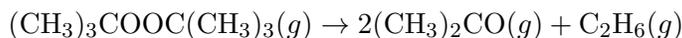
$$\int_0^\infty [X] dt = \int_0^\infty [X]_0 e^{-kt} dt = [X]_0/k$$

$E(t)$  can be used as a PDF, so:  $\bar{t} = \int_0^\infty tE(t)dt$

$$E(t) = ke^{-kt}$$

$$\bar{t} = \int_0^\infty tE(t)dt = k \int_0^\infty te^{-kt}dt = k/k^2 = 1/k. \quad \blacksquare$$

**Problem 118.** DTBP  $[(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3]$  decomposes into acetone and ethane by the following reaction:



Given the table of data below which begins with a sample of pure DTBP, what is the approximate order of the reaction with respect to DTBP?

Time (min)	$P_{tot}$ (atm)
0	0.2362
2	0.2466
6	0.2613
10	0.2770
14	0.2911
18	0.3051
20	0.3122
22	0.3188
26	0.3322
30	0.3449
34	0.3570
38	0.3687
40	0.3749
42	0.3801
46	0.3909

**Solution.**  $P_{\text{DTBP}}(t = 0) = P_{tot}(t = 0)$ ,  $P_{\text{Ethane}}(t = 0) = 0$ ,  $P_{\text{Acetone}}(t = 0) = 0$

$$P_{tot}(t) = P_{\text{DTBP}}(t) + P_{\text{Ethane}}(t) + P_{\text{Acetone}}(t)$$

Because of stoichiometric constraints:  $P_{tot}(t) = P_{\text{DTBP}}(0) - x + P_{\text{Ethane}}(0) + x + P_{\text{Acetone}}(0) + 2x$

$$P_{tot}(t) = P_{\text{DTBP}}(0) - x + x + 2x$$

$$x = (P_{tot}(t) - P_{\text{DTBP}}(0))/2$$

$$P_{\text{DTBP}}(t) = P_{\text{DTBP}}(0) - x = P_{tot}(0) - x = \frac{3}{2}P_{tot}(0) - \frac{1}{2}P_{tot}(t)$$

So finding the partial pressures of DTBP gives us the following table:

Time (min)	$P_{\text{DTBP}}$ (atm)
0	0.2362
2	0.2310
6	0.2237
10	0.2158

14	0.2088
18	0.2018
20	0.1982
22	0.1949
26	0.1882
30	0.1819
34	0.1758
38	0.1700
40	0.1669
42	0.1643
46	0.1589

Since the partial pressure changes the reaction can't be 0th order by DTBP. The following table tests first order with  $\log(P_{\text{DTBP}})$ :

Time (min)	$\log(P_{\text{DTBP}}) \log(\text{atm})$
0	-1.443
2	-1.465
6	-1.497
10	-1.533
14	-1.566
18	-1.600
20	-1.618
22	-1.635
26	-1.670
30	-1.704
34	-1.738
38	-1.772
40	-1.790
42	-1.806
46	-1.839

This yields a linear relation with a slope of about 0.089, so the reaction is first order relative to DTBP. ■

**Problem 119.** What activation energy would result in a doubling of the rate of a reaction when the temperature is increased by 10°C near room temperature? Compare your answer with typical bond energies.

**Solution.** From the Arrhenius equation  $k = Ae^{-E_a/RT}$  we obtain the van t' Hoff equation:

$$\log \frac{k_2}{k_1} = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Since the rate constant is independent of concentration we can say:

$$k_2 = 2k_1$$

when a reaction rate doubles (and we assume the concentration of reactants do not change). So,

$$\log \frac{2k_1}{k_1} = -\frac{E_a}{R} \left( \frac{\Delta T}{T_1 T_2} \right)$$

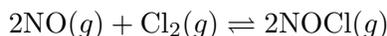
where  $\Delta T = T_2 - T_1$  (in this form of equation).

$$E_a = \frac{R \log(2)(T_1 T_2)}{\Delta T} = \frac{(8.315 \text{ J/mol/K})(0.693)(308 \text{ K})(298 \text{ K})}{10 \text{ K}} - 52,885 \text{ J/mol} = 52.9 \text{ kJ/mol}$$

Typical bond energies are 300-800 kJ/mol. So, this " $E_a$ " is small compared to typical bond energies. Remember that  $E_a$  is the energy required to get to the transition state of a reaction and bonds are generally not completely broken in this transition state. ■

**Problem 120.** The rate constant for the disappearance of chlorine in the third-order reaction of NO with  $\text{Cl}_2$  to form  $\text{NOCl}$  is  $4.5 \text{ M}^{-2}\text{s}^{-1}$  at  $0^\circ \text{C}$  and  $8.0 \text{ M}^{-2}\text{s}^{-1}$  at  $22^\circ \text{C}$ . What is the activation energy for this reaction?

**Solution.** Write the reaction



We are told the reaction is third order so we can infer the rate law:

$$-\frac{d[\text{Cl}_2(g)]}{dt} = k[\text{NO}(g)]^2[\text{Cl}_2(g)]$$

Use the equation:

$$\log \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{\Delta T}{T_1 T_2} \right)$$

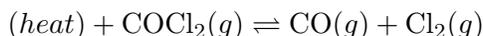
where  $\Delta T = T_2 - T_1$ .

$$\log \frac{8.0 \text{ M}^{-2}\text{s}^{-1}}{4.5 \text{ M}^{-2}\text{s}^{-1}} = \frac{E_a}{8.3145 \text{ J/mol/K}} \left( \frac{22 \text{ K}}{(273.15 \text{ K})(293.15 \text{ K})} \right)$$

solve for  $E_a$  to get  $E_a = 18 \text{ kJ/mol}$ . ■

**Problem 121.** Reaction (I) from Problem 61 is endothermic. Suppose that an equilibrium mixture of the three gases is heated. How will the degree of dissociation of  $\text{COCl}_2$  change?

**Solution.** We can rewrite the reaction as follows:



to denote an endothermic reaction. A simple way to view the question is to look at the revised chemical reaction and realize that "heat" is a reaction

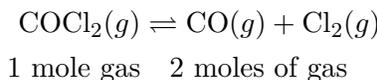
reactant (as opposed to a product). If we add heat, the reaction will be out of equilibrium and shift to the right toward more products. The best way to approach this question is to find the dependence of  $K$  on  $T$

$$K = \frac{A_f}{A_b} e^{-\Delta H^\circ/RT}$$

We assume  $A_f/A_b$  is temperature independent.  $\Delta H^\circ > 0$  (endothermic). Therefore, as  $T$  goes up,  $e^{-\Delta H^\circ/RT}$  goes up, and  $K$  goes up. (As  $T \uparrow$ ,  $K \uparrow$ ). The degree of dissociation of the reactant  $\text{COCl}_2(g)$  increases. ■

**Problem 122.** In relation to Problem 61, predict the effects on the amount of CO of a decrease in volume for reaction (I) and of a decrease in amount of FeO(s) in reaction (II).

**Solution.** Decrease in volume for reaction (I)



The decrease in volume will increase the total pressure and the system will relieve this stress by reducing the number of moles of gaseous species. Since there are 2 moles of gas on the product side for every 1 mole of gas on the reactant side, the reaction will shift to the left and the amount of  $\text{CO}(g)$  will decrease.

Decrease in amount of FeO(s) for reaction (II)

Since FeO(s) is a pure substance, it is not in the equilibrium equation and therefore any change in the amount of FeO(s) does not affect the equilibrium constant,  $K$  (or  $K_p$ ) and the amount of  $\text{CO}(g)$  would not change. ■

**Problem 123.** At high temperature, nitrogen dioxide decomposes into NO and  $\text{O}_2$ :  $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$  by the second order rate law  $d[\text{NO}_2]/dt = -k[\text{NO}_2]^2$ . At 592 K, the rate constant is  $5.0 \times 10^{-1}$  liter/mol/s and at 656 K it is 4.7 liter/mol/s. Calculate the activation energy for this process.

**Solution.**

$$\log \frac{K(T_2)}{K(T_1)} = -\frac{E_a}{R} \left( \frac{T_1 - T_2}{T_1 T_2} \right)$$

Therefore

$$\begin{aligned} E_a &= -\frac{RT_1 T_2}{\Delta T} \log \frac{K(T_2)}{K(T_1)} = -(8.314)(592)(656) \frac{1}{-64} \log \frac{4.7 \times 10}{5.0 \times 10^{-1}} \text{ kJ/mol} \\ &= 113 \text{ kJ/mol} \end{aligned}$$

■

**Problem 124.** Regarding Problem 123, what is the activation energy for the reverse reaction? Make a sketch of energy versus reaction coordinate

illustrating your answer. [Note that the rate equation and the equilibrium equation differ by a factor of 2.]

**Solution.** 1st calculate  $\Delta H^\circ$  for  $\text{NO}_2(g) \rightarrow \text{NO}(g) + (1/2)\text{O}_2(g)$

$$\log \frac{K(T_2)}{K(T_1)} = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\begin{aligned} \Delta H^\circ &= -\frac{RT_1T_2}{\Delta T} \log \frac{K(T_2)}{K(T_1)} \\ &= -\frac{(8.314 \text{ J/mol/K})(592 \text{ K})(700 \text{ K})}{-108 \text{ K}} \log \frac{0.358 \text{ atm}^{1/2}}{0.0604 \text{ atm}^{1/2}} = 56.7 \text{ kJ/mol} \end{aligned}$$

Now,  $\Delta H^\circ = 2(\Delta H^\circ) = 2(56.7 \text{ kJ/mol}) = 113 \text{ kJ/mol}$

$$E_{a,b} = E_{a,f} - \Delta E_a$$

and  $\Delta E_a \approx \Delta H^\circ$ . Therefore,

$$E_{a,b} \approx 113 \text{ kJ/mol} - 113 \text{ kJ/mol} = 0$$

■

**Problem 125.** Regarding Problem 123, the equilibrium constant for the reaction  $\text{NO} + (1/2)\text{O}_2 \rightleftharpoons \text{NO}_2$  is  $0.0604 \text{ atm}^{1/2}$  at 592 K and  $0.358 \text{ atm}^{1/2}$  at 700 K. What is the rate for the reverse reaction,  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$  at 592 K?

**Solution.** First reaction has  $K_p$ . Second reaction has  $K'_p = (K_p)^2$ . When you multiply a chemical reaction equation by  $n$  you must raise its equilibrium constant to the power of  $n$ . The rate law is given in terms of molarity so convert the  $K'_p$  to  $K'$  as follows:

$$\begin{aligned} K'_p &= K'(RT)^{\Delta n_g} & \Delta n_g &= 3 \text{ mol}(gas) - 2 \text{ mol}(gas) \\ K'_p &= K'(RT)' \\ K' &= \frac{K'_p}{RT} = \frac{(K_p)^2}{RT} = \frac{(0.0604 \text{ atm}^{1/2})^2}{(0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(592 \text{ K})} = 7.51 \times 10^{-5} \text{ M} \\ K' &= \frac{k_f}{k_b} \rightarrow k_b = \frac{k_f}{K'} \end{aligned}$$

$$k_b = \frac{5.0 \times 10^{-1} \text{ L/mol/s}}{7.51 \times 10^{-5} \text{ mol/L}} = 6.658 \times 10^3 \text{ L}^2/\text{mol}^2/\text{s} = 6.7 \times 10^3 \text{ L}^2/\text{mol}^2/\text{s}$$

■

**Problem 126.** The gas phase decomposition of ozone,  $\text{O}_3$  (i.e.  $2 \text{O}_3 \rightarrow 3 \text{O}_2$ ) is second order with respect to ozone:

$$-\frac{d[\text{O}_3]}{dt} = k[\text{O}_3]^2$$

This “constant”  $k$  can be a function of the concentration of other species, and in fact, at 100°C,  $k$  is found to depend on the partial pressure of molecular oxygen according to the following table:

$P_{\text{O}_3}/\text{torr}$	$P_{\text{O}_2}/\text{torr}$	$k/\text{M}^{-1}\text{s}^{-1}$
6.0	800	0.16
6.0	600	0.22
6.0	400	0.35

(Note that the data presented above involves a low percentage of  $\text{O}_3$  in  $\text{O}_2$ .)

- (a) What is the rate law for the  $\text{O}_2$  concentration under these conditions?
- (b) What is the value (with units) of the rate constant in the rate law that includes the dependence on  $[\text{O}_2]$ ?
- (c) If the table presented above was obtained by measuring  $[\text{O}_3]$  as a function of time, what graphs might you construct to obtain the  $k$  values?
- (d) Why does the  $\text{O}_2$  produced by the decomposition of  $\text{O}_3$  not seriously affect the accuracy of the graphs?
- (e) The half-life of a reaction is the time required for the concentration to fall to half its initial value. What would be the half-life of the ozone in each of the above experiments, i.e. for each of the initial conditions in the table presented above?

**Solution.** (a) In general,  $k = 2k'[\text{O}_2(g)]^\alpha$ , where  $k'$  is a constant. Now, from the experimental data, choose two experiments to compare.  $k_1 = 2k'[\text{O}_2(g)]_1^\alpha$  and  $k_2 = 2k'[\text{O}_2(g)]_2^\alpha$

$$\frac{k_1}{k_2} = \frac{2k'[\text{O}_2(g)]_1^\alpha}{2k'[\text{O}_2(g)]_2^\alpha} = \left( \frac{[\text{O}_2(g)]_1}{[\text{O}_2(g)]_2} \right)^\alpha$$

taking logs

$$\log(k_1/k_2) = \alpha \log([\text{O}_2(g)]_1/[\text{O}_2(g)]_2)$$

we can solve for  $\alpha$

$$\begin{aligned} \alpha &= \frac{\log(k_1/k_2)}{\log([\text{O}_2(g)]_1/[\text{O}_2(g)]_2)} = \frac{\log\left(\frac{0.16 \text{ M}^{-1}\text{s}^{-1}}{0.22 \text{ M}^{-1}\text{s}^{-1}}\right)}{\log\left(\frac{0.034 \text{ M}}{0.026 \text{ M}}\right)} \\ &= \frac{\log(0.727)}{\log(1.308)} = \frac{-0.319}{0.268} = -1.1 \end{aligned}$$

The rate law can be expressed as

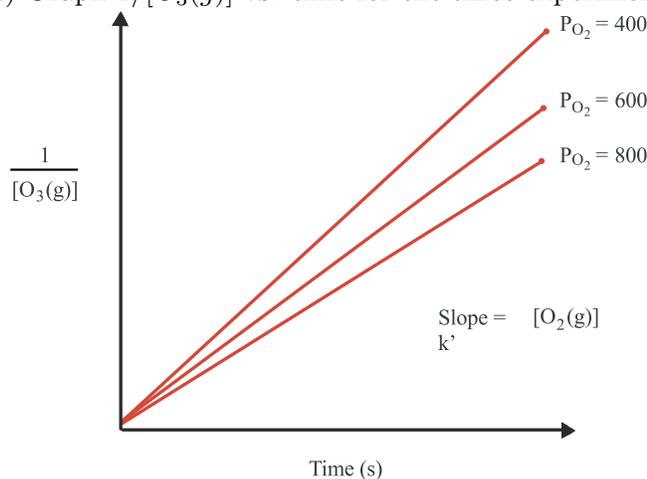
$$-\frac{d[\text{O}_3(g)]}{dt} = 2k'[\text{O}_3(g)]^2[\text{O}_2(g)]^{-1.1}.$$

(b) Since  $[\text{O}_2(g)] \gg [\text{O}_3(g)]$ , we can use  $\text{rate} = 2k'[\text{O}_2(g)]^{-1.1}$  only to calculate the rate constant  $k'$ .

$$0.16 \text{ M}^{-1} \text{ s}^{-1} = 2k'(0.034 \text{ M})^{-1.1}$$

$$k' = 1.9 \times 10^{-3} \text{ s}^{-1}$$

(c) Graph  $1/[\text{O}_3(g)]$  vs. time for the three experiments.



(d) The  $[\text{O}_2(g)]$  is so much larger than the  $[\text{O}_3(g)]$  that any  $\text{O}_2(g)$  produced from  $\text{O}_3(g)$  would not appear to change the overall  $[\text{O}_2(g)]$ . In other words, since  $[\text{O}_2(g)]$  is so large, we can treat it as a constant compared to  $[\text{O}_3(g)]$ .

(e) Using  $[A]/[A]_0 = e^{-kt_{1/2}}$  and appropriate initial concentration and rate, calculate the half-life for each experiment. Setting  $[A] = [A]_0/2$  per the definition of half-life we obtain  $\log(1/2) = -kt_{1/2}$ ,  $[A]_0$  goes away and  $t_{1/2} = 0.693/k$ . Plug in "k" and solve for  $t_{1/2}$ .

$$\text{Experiment 1 } t_{1/2} = 0.693/0.16 \text{ s}^{-1} = 4.3 \text{ s}$$

$$\text{Experiment 2 } t_{1/2} = 0.693/0.22 \text{ s}^{-1} = 3.2 \text{ s}$$

$$\text{Experiment 3 } t_{1/2} = 0.693/0.35 \text{ s}^{-1} = 2.0 \text{ s}$$

Why did we drop the  $\text{M}^{-1}$  part from the units of  $k$  designated in the table? ■

**Problem 127.** The following data have been obtained for the instantaneous rate of the following reaction occurring in solution:  $3\text{A} + 2\text{B} \rightarrow \text{A}_3\text{B}_2$ .

[A]/M	[B]/M	$-(d[A]/dt)/(M.s^{-1})$
0.10	0.10	$6.0 \times 10^{-4}$
0.30	0.30	$5.4 \times 10^{-3}$
0.50	0.10	$1.5 \times 10^{-2}$
0.50	0.50	$1.5 \times 10^{-2}$

(a) Calculate the order of the reaction with respect to A and with respect to B, and calculate the value of  $k$  (including its units).

(b) Suppose that you have 2.0 liters of a solution that is 0.50 M in A and 0.50 M in B. How many moles of  $A_3B_2$  are formed in the first second of reaction?

(c) How long will it take for the concentration of A to fall to 0.05 M from the initial conditions described in (b)?

(d) A reaction proceeds by the following mechanism:  $mA + nB + pC \rightarrow$  products, with  $m, n$  and  $p$  all positive integers. Doubling the concentration of A, B and C increases the overall rate of reaction by a factor of 16. Tripling the concentration of C has the same effect as tripling the concentration of A. An increase in the concentration of B has a larger effect than an increase in the concentration of A. What are  $m, n$  and  $p$ ? What is unrealistic about this mechanism?

**Solution.** (a) In general the rate is

$$k[A]^\alpha[B]^\beta$$

Increasing [A] by  $5 \times$  (0.10 M  $\rightarrow$  0.50 M) while holding the [B] constant at 0.10 M, the rate increases by  $25 \times$  ( $6.0 \times 10^{-4}$  M/s  $\rightarrow$   $1.5 \times 10^{-2}$  M/s)

$$\therefore \alpha = 2.$$

Increasing [B] by  $5 \times$  (0.10 M  $\rightarrow$  0.50 M) while holding the [A] constant at 0.50 M, the rate remains constant at  $1.5 \times 10^{-2}$  M/s.

$$\therefore \beta = 0.$$

Thus,

$$rate = k[A]^2.$$

Now, to calculate  $k$  we will use the rate law determined with one set of experimental data (your choice). However, for the calculation of  $k$  and for the number of moles of  $A_3B_2$  formed (part b) there are a number of possible approaches (two answers). It is unclear that the “rate” data refers to the “reaction rate” and includes the  $1/3$  factor for “A” or if the “rate” data

should be corrected by multiplication. i.e.,

$$\text{rate} = -\frac{1}{3} \frac{d[A]}{dt}$$

The table gives us  $d[A]/dt$ . So, the most correct way to view the data is that a reaction rate must be calculated from the change in concentration of A with time data. If you assumed the data included the  $1/3$  factor you will receive full credit. Thus,

$$k = \frac{(1/3)(6.0 \times 10^{-4} \text{ M/s})}{(0.10 \text{ M})^2} = 0.020 \text{ M}^{-1} \text{ s}^{-1}.$$

(b)  $[A] = [B] = 0.5 \text{ M}$ .  $\text{rate} = 1.5 \times 10^{-2} \text{ M/s}$  for  $-d[A]/dt$ . But  $-(1/3)d[A]/dt = +d[A_3B_2]/dt$  and

$$\frac{d[A_3B_2]}{dt} = \frac{1}{3}(1.5 \times 10^{-2} \text{ M/s}) = 5.0 \times 10^{-3} \text{ M/s}.$$

So,  $(5.0 \times 10^{-3} \text{ M/s})(1 \text{ s}) = 5.0 \times 10^{-3} \text{ mol/L}$  and  $(5.0 \times 10^{-3} \text{ mol/L})(2.0 \text{ L}) = 1.0 \times 10^{-2} \text{ mol } A_3B_2$  produced.

(c) From  $[A] = [A]_0 e^{-kt}$  we have  $\log([A]/[A]_0) = -kt$  and  $t = -(1/k) \log[A]/[A]_0$ . Plug in the values given

$$t = -\left(\frac{1}{0.020 \text{ M}^{-1} \text{ s}^{-1}}\right) \log\left(\frac{0.05 \text{ M}}{0.50 \text{ M}}\right) = 115 \text{ s} \approx 120 \text{ s}$$

(d) 1st step: setup the general rate law

$$k[A]^m[B]^n[C]^p$$

Why can we represent the rate law by using the reaction coefficients?

1nd ste: determine  $m, n, p$

Doubling all concentrations results in a 16x increase in the rate

$$(2)^x = 16, \quad x = 4$$

Thus, the overall order of this reaction is 4th order. Tripling [A] or [C] results in the same rate increase

$$m = p$$

Then,

$$\begin{aligned} m + n + p &= 4, & \text{with } m &= p \\ m = p &= 1, & n &= 2 \end{aligned}$$

Thus, we have that the rate is

$$k[A][B]^2[C]$$

Why is this mechanism unrealistic: Remember, this is a mechanism (elementary step) and the collision of four molecules is very unlikely. ■

# Entropy Production, Chemical Kinetics and Irreversibility

In the context of chemical reactions we have stated that the reaction rate,  $\dot{\xi}$ , can be written down by inspection of the reaction mechanism (elementary reactions) as a sum of terms describing various molecular collision events times a reaction rate. We also previously stated, in the context of the Second Law, that differences in the chemical potential,  $\Delta(\mu/T)$  give rise to a driving force for chemical transformations (or mass transport, if the properties are spatially inhomogeneous). The method of molecular collisions for determining  $\dot{\xi}$  agrees with experiments and molecular dynamics simulations. On the other hand,  $\dot{\xi}$  should also depend on  $\Delta(\mu/T)$ . But exactly how? An arbitrary function of  $\Delta(\mu/T)$  could be expressed as a power series in  $\Delta(\mu/T)$ . For small deviations from equilibrium, the affinity is very low and only the first power matters. Thus,  $\dot{\xi}$  should depend linearly on  $\Delta(\mu/T)$  in this near-equilibrium regime.

This chapter is a very short introduction to a vast subject. To learn more about non-equilibrium phenomena in the context of thermodynamics, see [5, 7, 6]. Our presentation follows Chapter 14 of McQuarrie [5]. We use both upper and lower case letters for the state variables, with the latter referring to “per unit volume” quantities, i.e.  $u \equiv U/V$  is the internal energy per unit volume.

About notation: we consider the case of two variables (time,  $t$ , and space,  $x$ ) and write  $d/dx$  for the spatial derivative, where it is understood that when differentiating we keep  $t$  constant (i.e. it means partial differentiation,  $\partial/\partial x$ ). In several spatial dimensions,  $\partial/\partial x$  is replaced by the gradient operator,  $\nabla$ . (And of course, an equation that involves  $d/dx$  and  $d/dt$  implies that both are partial derivatives:  $\partial/\partial x$  and  $\partial/\partial t$ , respectively.)

### 8.1. Entropy Production

The change in the entropy of a system,  $dS$ , can be decomposed into two terms,

$$dS = d_e S + d_i S,$$

where  $d_e S$  is the entropy *supplied to the system by its surroundings* ( $e$ , external), and  $d_i S$  is the entropy produced inside the system ( $i$ , internal).

The Second Law states that  $d_i S = 0$  for a reversible process and positive for irreversible transformations of the system, i.e.

$$d_i S \geq 0.$$

This statement is true regardless of the nature of the system. We are thus led to the following alternative statement of the Second Law:  $dS \geq d_e S$ . Because of the constraint  $d_i S \geq 0$ , the term  $d_i S$  is called *entropy production*, and describes the various irreversible phenomena which may occur inside the system.

It will be convenient to divide  $S$  by  $V$  to get the specific entropy  $s$ , i.e. the entropy per unit volume. We are also interested in its rate of change with respect to time. Division of  $ds$  by  $dt$  will be called the rate of entropy production:

$$\dot{s} = \frac{ds}{dt} = \frac{dS}{dt V}.$$

Furthermore, we shall assume that the fundamental equation of thermodynamics (also known as the Gibbs equation) holds at every point in space, and even away from equilibrium:

$$dU = TdS - PdV + \sum_i \mu_i dn_i.$$

This equation was previously assumed to hold for a reversible process. Here, *we assume that it holds for an irreversible process as well*. This assumption may be justified in a volume element that is sufficiently small. We will write it in terms of specific quantities,  $u = U/V$ ,  $s = S/V$ ,  $[X_i] = n_i/V$ . For constant volume ( $dV = 0$ ),

$$du = Tds + \sum_i \mu_i d[X_i].$$

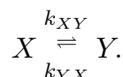
Dividing by  $dt$ , and solving for  $ds/dt$ , we get the rate of change in the entropy:

$$(8.1) \quad \dot{s} \equiv \frac{ds}{dt} = \frac{1}{T} \frac{du}{dt} - \sum_i \frac{\mu_i}{T} \frac{d[X_i]}{dt}.$$

The first term is the heat transfer (can be positive or negative). The second term, which is always non-negative<sup>1</sup> ( $\geq 0$ ), is entropy production, an irreversible process. Entropy production describes the thermodynamic lost work. It quantifies irreversibility, and is therefore a measure of inefficiency.  $\frac{d[X_i]}{dt}$  is discussed in the next section.

## 8.2. Chemical Reaction Away From Equilibrium

Suppose that we have a reversible first-order elementary chemical reaction



The reaction rate is:

$$(8.2) \quad \dot{\xi} = -\frac{d[X]}{dt} = \frac{d[Y]}{dt} = k_{XY}[X] - k_{YX}[Y].$$

Close to equilibrium,  $\dot{\xi}$  should be a linear function of  $\mathcal{A}$  (lowest order term in a power series in  $\mathcal{A}$ ). Indeed, according to Eq. (8.2),  $\dot{\xi}$  should be a function of  $\mathcal{A}$  because it depends on the differences in concentrations of  $X$  and  $Y$ . Close to equilibrium, where  $\mathcal{A}$  is small, we expect  $\dot{\xi}$  to depend linearly on  $\mathcal{A}$ :

$$(8.3) \quad \dot{\xi} = L \left( \frac{\mathcal{A}}{T} \right) = L \left( \frac{\mu_X - \mu_Y}{T} \right),$$

where  $L$  is a coefficient to be determined.

At equilibrium,  $\dot{\xi} = 0$ , and we have  $k_{XY}[X]_{\text{eq}} = k_{YX}[Y]_{\text{eq}}$ , or  $k_{XY} = k_{YX}[Y]_{\text{eq}}/[X]_{\text{eq}}$ . In the first term, let's substitute this relationship for  $k_{XY}$ ; in the second term, let's multiply it by  $1 = [Y]_{\text{eq}}/[Y]_{\text{eq}}$ :

$$\dot{\xi} = \underbrace{k_{YX} \cdot \frac{[Y]_{\text{eq}}}{[X]_{\text{eq}}}}_{k_{XY}} \cdot [X] - k_{YX} \cdot [Y] \cdot \underbrace{\frac{[Y]_{\text{eq}}}{[Y]_{\text{eq}}}}_1 = k_{YX} \cdot [Y]_{\text{eq}} \left( \frac{[X]}{[X]_{\text{eq}}} - \frac{[Y]}{[Y]_{\text{eq}}} \right).$$

On the other hand, consider the affinity,  $\mu_X - \mu_Y$ , in the case where we have ideal solutions. Choosing the reference conditions to be the chemical

<sup>1</sup>This term is also equal to  $\dot{\xi}(-\Delta G_{rxn}/T)$ . If a reaction proceeds from left to right,  $\Delta G_{rxn} < 0$ , and  $\dot{\xi} > 0$ . (And conversely, if the reaction proceeds from right to left,  $\Delta G_{rxn} > 0$ ,  $\dot{\xi} < 0$ .) At equilibrium, of course,  $\Delta G_{rxn} = 0$ . Thus, the term can never be negative.

equilibrium concentrations:

$$\mu_X = \mu_X^\circ + RT \log \frac{[X]}{[X]_{\text{eq}}}, \quad \mu_Y = \mu_Y^\circ + RT \log \frac{[Y]}{[Y]_{\text{eq}}}.$$

Then,

$$\frac{\mu_X - \mu_Y}{T} = R \left( \log \frac{[X]}{[X]_{\text{eq}}} - \log \frac{[Y]}{[Y]_{\text{eq}}} \right),$$

Adding and subtracting the same quantity is like adding zero; a given term does not change. Thus, we rewrite

$$\frac{[X]}{[X]_{\text{eq}}} = \frac{([X] - [X]_{\text{eq}}) + [X]_{\text{eq}}}{[X]_{\text{eq}}} = \frac{[X] - [X]_{\text{eq}}}{[X]_{\text{eq}}} + 1,$$

and similarly for  $Y$ . The term  $\frac{[X] - [X]_{\text{eq}}}{[X]_{\text{eq}}}$  now is a small parameter if we are close to equilibrium. Thus, the logs are now of the form  $\log(1 + x)$ , where  $x$  is small. Taylor expansion for small  $x$  gives  $\log(1 + x) \approx x$  and

$$\frac{\mu_X - \mu_Y}{T} \approx R \left( \frac{[X]}{[X]_{\text{eq}}} - \frac{[Y]}{[Y]_{\text{eq}}} \right).$$

Thus,

$$\dot{\xi} = k_{YX} \cdot [Y]_{\text{eq}} \left( \frac{[X]}{[X]_{\text{eq}}} - \frac{[Y]}{[Y]_{\text{eq}}} \right) = \underbrace{k_{YX} \cdot [Y]_{\text{eq}}}_{L} \cdot \underbrace{\left( \frac{\mu_X - \mu_Y}{T} \right)}_{\mathcal{A}/T} = L \left( \frac{\mathcal{A}}{T} \right).$$

This is an example of a flux-force term.  $L$  is the flux and  $\mathcal{A}/T$  is the force. Therefore, we have established the following equivalence close to equilibrium:

$$\dot{\xi} = -\frac{d[X]}{dt} = \frac{d[Y]}{dt} = k_{XY}[X] - k_{YX}[Y] \approx \underbrace{k_{YX} \cdot [Y]_{\text{eq}}}_{L} \cdot \underbrace{\left( \frac{\mu_X - \mu_Y}{T} \right)}_{\mathcal{A}/T}.$$

**8.2.1. Entropy Production.** For the previous reaction (consider the system to be isolated), at constant  $u$  the Gibbs equation is

$$\dot{s} = -\sum_i \frac{\mu_i}{T} \frac{d[X_i]}{dt} = -\frac{\mu_X}{T} \frac{d[X]}{dt} - \frac{\mu_Y}{T} \frac{d[Y]}{dt} = -\frac{d[X]}{dt} \left( \frac{\mu_X}{T} - \frac{\mu_Y}{T} \right) = \dot{\xi} \left( \frac{\mathcal{A}}{T} \right),$$

where  $\mathcal{A}$  is called the *affinity*. Recall that  $\mathcal{A} = -\Delta G_{rxn}$ , where  $\Delta G_{rxn} \equiv \left( \frac{\partial G}{\partial \xi} \right)_{T,P} = \sum_i \nu_i \mu_i$ , with the convention that  $\nu_i$  is negative for reactants and positive for products. Thus, differences in chemical potential drive entropy production. Since entropy production describes the evolution of the reaction toward equilibrium, affinity is a driving force of the chemical reaction.

**8.2.2. Example with Three Components.** Consider the reaction:



Let's check that the affinity is:

$$\frac{\mathcal{A}}{T} = \frac{\mu_X + \mu_Y - \mu_Z}{T}.$$

The flow of reaction from left to right is:

$$\dot{\xi} = -\frac{d[X]}{dt} = -\frac{d[Y]}{dt} = +\frac{d[Z]}{dt}$$

so the equation for  $\dot{s}$  is

$$\dot{s} = -\frac{\mu_X}{T} \frac{d[X]}{dt} - \frac{\mu_Y}{T} \frac{d[Y]}{dt} - \frac{\mu_Z}{T} \frac{d[Z]}{dt} = -\frac{d[X]}{dt} \left( \frac{\mu_X}{T} + \frac{\mu_Y}{T} - \frac{\mu_Z}{T} \right) = \dot{\xi} \left( \frac{\mathcal{A}}{T} \right),$$

where  $\mathcal{A}/T = \left( \frac{\mu_X}{T} + \frac{\mu_Y}{T} - \frac{\mu_Z}{T} \right)$ .

### 8.3. External vs Internal Variables

As mentioned previously, the change in the entropy of a system,  $dS$ , can be decomposed into two terms,

$$dS = d_e S + d_i S,$$

where  $d_e S$  is the entropy *supplied to the system by its surroundings* ( $e$ , external), and  $d_i S$  is the entropy produced inside the system ( $i$ , internal). The second law states that  $d_i S = 0$  for a reversible process and positive for irreversible transformations of the system, i.e.

$$d_i S \geq 0.$$

The entropy supplied,  $d_e S$ , however, may be positive, zero or negative, depending on the interaction of the system with its surroundings. Thus, for an adiabatically insulated system (i.e. a system which can exchange neither heat nor matter with its surroundings),  $d_e S$  is equal to zero, and it follows that

$$\boxed{dS \geq 0.} \quad (\text{for an adiabatically insulated system})$$

For a so-called **closed system**, which may only exchange heat with its surroundings, we have

$$d_e S = \frac{\delta Q}{T}, \quad (\text{Carnot's theorem})$$

where  $\delta Q$  is the heat supplied to the system by its surroundings and  $T$  is the absolute temperature at which heat is received by the system. It then follows that

$$dS = d_e S + d_i S = \frac{\delta Q}{T} + \underbrace{d_i S}_{d_i S \geq 0} \rightarrow \boxed{dS \geq \frac{\delta Q}{T}} \quad (\text{for a closed system})$$

For open systems (heat+matter exchange allowed w/surroundings),  $d_e S$  contains also a term connected with the transfer of matter. The theorem of Carnot-Clausius,  $d_e S = \delta Q/T$ , does not apply to such systems (we will see later how to correct it). However,  $dS = d_e S + d_i S$  and  $d_i S \geq 0$  remain valid.

**8.3.1. General Form of Entropy Production.** Previously, we used the first law (fundamental equation for  $dS$ ) to write down an equation for the time-derivative of the entropy:

$$\dot{s} \equiv \frac{ds}{dt} = \frac{1}{T} \frac{du}{dt} - \sum_i \frac{\mu_i}{T} \frac{d[X_i]}{dt}.$$

The first term,  $\frac{1}{T} \frac{du}{dt}$ , is associated with heat transfer (can be positive or negative). The last term can be rewritten as  $\dot{\xi}(\mathcal{A}/T)$  or  $\dot{\xi}(-\Delta G_{rxn}/T)$ , using  $\dot{\xi} = \frac{1}{\nu_i} \frac{d[X_i]}{dt}$ , since  $\mathcal{A} = -\sum_i \mu_i \nu_i$  and  $\mathcal{A} = -\Delta G_{rxn}$ . This term is also equal to  $\dot{\xi}(-\Delta G_{rxn}/T)$ . If a reaction proceeds from left to right,  $\Delta G_{rxn} < 0$ , and  $\dot{\xi} > 0$ . And conversely, if the reaction proceeds from right to left,  $\Delta G_{rxn} > 0$ ,  $\dot{\xi} < 0$ . At equilibrium,  $\Delta G_{rxn} = 0$ . Thus, the term can never be negative. This nonnegative ( $\geq 0$ ) term, is called entropy production, and describes an irreversible process. We obtain a restatement of the Clausius theorem,

$$\dot{s} \geq \frac{1}{T} \frac{du}{dt}.$$

We have seen in the specific case of a reaction  $X \rightleftharpoons Y$  that the reaction term is equal to<sup>2</sup>

$$\dot{\xi}(\mathcal{A}/T) = -\frac{d[X]}{dt} \left( \frac{\mu_X - \mu_Y}{T} \right).$$

We have also found that for that particular reaction ( $X \rightleftharpoons Y$ ),

$$\dot{\xi} = \frac{k_{YX}[Y]_{\text{eq}}}{R} \left( \frac{\mu_X - \mu_Y}{T} \right) = L \left( \frac{\mathcal{A}}{T} \right)$$

where  $L = k_{YX}[Y]_{\text{eq}}/R = k_{XY}[X]_{\text{eq}}/R$ . Thus,  $\dot{s}$  has the form

$$\dot{s} = L \left( \frac{\mathcal{A}}{T} \right) \left( \frac{\mathcal{A}}{T} \right) = L X X,$$

where  $X = \left( \frac{\mathcal{A}}{T} \right)$  is a *force*.  $LX$  is a *flux*. The flux, often denoted  $J = LX$ , is proportional to the force (no forces, no fluxes).

<sup>2</sup>The form  $\dot{\xi}(\mathcal{A}/T)$  of the chemical term is generally true for any reaction.  $\mathcal{A}/T$  is a *driving force* for the chemical reaction (i.e. differences in chemical potential lead to transformation, whereas equilibrium is reached when the chemical potentials are equal).  $\dot{\xi}$  is a *flux*.

This turns out to be a general principle. In the general case there may be several forces (and fluxes) acting on the system. Then,  $\dot{s}$  will be of the form:

$$\dot{s} = \sum_{i=1}^N \sum_{j=1}^N L_{ij} X_i X_j,$$

where the  $L_{ij}$  are called *Onsager coefficients* and the  $X_i$ 's are the thermodynamic forces. The quantities

$$J_j = L_{1j} X_1 + L_{2j} X_2 + L_{3j} X_3 + \cdots + L_{Nj} X_N$$

are called *fluxes*. We can think of the fluxes as the leading terms of a Taylor expansion of  $J_j$  as a power series in  $X_1, X_2, \dots, X_N$ . Close to equilibrium, only the first order term is needed. Also, there are no constant terms because the fluxes all vanish if all the forces vanish. The Onsager coefficients are reciprocal,  $L_{ij} = L_{ji}$ .

Some examples of commonly encountered fluxes and forces can be found in Table 8.1.

**Table 8.1.** Fluxes and forces.

	Flux, $J$	Force, $X$
Heat	$J_u$	$\frac{d(1/T)}{dx} = -\frac{1}{T^2} \frac{dT}{dx}$
Matter	$J_i$	$-T \frac{d(\mu_i/T)}{dx}$
Electric current density	$J_I = I/A$	$-\frac{1}{T} \frac{d\phi}{dx}$ (voltage/ $T$ )
Chemical reaction	$\dot{\xi}$	$\mathcal{A} = -\sum_i \nu_i \mu_i$

## 8.4. Particle Flux and Heat Flux

So far we have looked at chemical reactions localized in the same volume element. These chemical reactions are driven by differences in the chemical potential. Now let's look at spatially dependent processes. For simplicity, we consider at processes that vary along a single dimension ( $x$ ). The system is subdivided into slices of thickness  $\Delta x = x_2 - x_1$ , as shown in Fig. 8.1.

$\Delta x$  is small enough so that  $T, P, \mu$  are constant over the volume element and so that local thermodynamic equilibrium can be assumed.

Recall (see section 6.11.21) that in the case of two volume elements  $A$  and  $B$  adjacent to each other (setting  $dV = 0$ ), we found that

$$dS = (T_A^{-1} - T_B^{-1})dU_A - \left( \frac{\mu_A}{T_A} - \frac{\mu_B}{T_B} \right) dn_A,$$

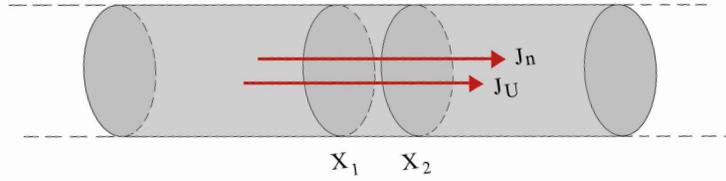


Figure 8.1. Flux of heat ( $J_U$ ) and particles ( $J_n$ ).

where  $\mu_{A/B}$  are in molar units. (This equation was obtained by applying the fundamental equation of thermodynamics in the entropy representation.)

Now take  $A$  and  $B$  to be thin slices centered around  $x_1$  and  $x_2$  in the above diagram. Dividing by  $dt$  gives the equation for entropy production:

$$\dot{S} = \frac{dU_1}{dt} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) + \frac{dn_1}{dt} \left( \frac{\mu_2}{T_2} - \frac{\mu_1}{T_1} \right) \geq 0.$$

which can be written in the form,

$$\dot{S} = J_U X_U + J_n X_n,$$

where

$$J_U = \frac{dU_1}{dt} = -\frac{dU_2}{dt}, \quad J_n = \frac{dn_1}{dt} = -\frac{dn_2}{dt}, \quad X_U = \frac{1}{T_1} - \frac{1}{T_2}, \quad X_n = \frac{\mu_2}{T_2} - \frac{\mu_1}{T_1}.$$

$X_U$  is the thermal force and  $X_n$  is the chemical force.

Writing  $\Delta(1/T) = 1/T_2 - 1/T_1$ ,  $\Delta(\mu/T) = \mu_2/T_2 - \mu_1/T_1$ , and dividing by the volume  $V = A\Delta x$  gives:

$$\dot{s} = -\frac{1}{A} \frac{dU_1}{dt} \frac{\Delta(1/T)}{\Delta x} + \frac{1}{A} \frac{dn_1}{dt} \frac{\Delta(\mu/T)}{\Delta x}.$$

Taking the limit of small  $\Delta x$  gives:

$$\dot{s} = -\frac{1}{A} \frac{dU_1}{dt} \frac{d(1/T)}{dx} - \frac{1}{A} \frac{dn_1}{dt} \frac{d(-\mu/T)}{dx},$$

which can be written as

$$(8.4) \quad \dot{s} = J_u \frac{d(1/T)}{dx} + J_n \frac{d(-\mu/T)}{dx},$$

where the derivatives are called gradients of  $1/T$  and  $-\mu/T$ , respectively, and

$$J_u = -\frac{1}{A} \frac{dU_1}{dt}, \quad J_n = -\frac{1}{A} \frac{dn_1}{dt}$$

are fluxes.

### 8.5. Conservation of Mass

In the case of diffusion and reaction taking place simultaneously, the flow of the reaction from reactant to product is:

$$\boxed{\underbrace{\frac{d_{tot}[X_j]}{dt}}_{\text{total rate}} = \underbrace{-\frac{dJ_j}{dx}}_{\text{mass transport}} + \underbrace{\nu_j \dot{\xi}}_{\xi = \frac{1}{\nu_j} \frac{d[X_j]}{dt}}, \quad j = 1, \dots, n}$$

where  $[X_j] = n_j/V$ ,  $J_j$  are the component fluxes ( $n$ : number of components), all directed along the  $x$  axis, i.e.  $\nu_j$  are the stoichiometric constants in a chemical reaction, and  $\dot{\xi}$  is its rate in the volume element. This is merely the addition of two terms: the component flux term  $-dJ_j/dx$  due to mass transport, plus the chemical reaction term which we know from chemical kinetics, by writing down the rate law,  $\dot{\xi} = (1/\nu_j)d[X_j]/dt$ , for the reaction. Our convention was to take  $\nu_j$  as negative for the reactants and positive for the products. Since  $\nu_j$  are dimensionless,  $\dot{\xi}$  has units of mol/m<sup>3</sup>/s.

This is the total rate of change, which is the sum of two terms. The second term ( $\dot{\xi}$ ) we have seen already. But where does the first term come from?

Consider a volume  $V = A \cdot dx$  of length  $dx$  and transport along the  $x$  direction. The volume has cross-sectional area  $A$  and length beginning at  $x$  and ending at  $x+dx$ . The change in the number of moles of a component,  $n_j$ , in a small volume  $V$ , is due to the difference between the flux of the components in and out of the volume. We have

$$\frac{dn_j}{dt} = -A [J_j(x+dx) - J_j(x)]$$

where  $A$  is the cross sectional area of the volume orthogonal to the flux direction. Positive fluxes  $J_j$  indicate particles flowing toward positive  $x$ . The flux  $-J_j(x+dx)$  denotes a *decrease* in  $n_j$ , as particles leave the volume  $dx$  at  $x+dx$ .  $+J_j(x)$  denotes particles entering  $dx$  at  $x$ .

The fluxes have units of moles per area per unit time. The area is equal to the volume divided by  $dx$ . In the limit of small  $dx$ , we therefore have

$$\frac{dn_j}{dt} = -V \frac{[J_j(x+dx) - J_j(x)]}{dx} = -V \frac{dJ_j(x)}{dx}.$$

By dividing this equation left and right by the (constant) volume, one obtains the desired result for  $\dot{\xi} = 0$

$$\boxed{\frac{d[X_j]}{dt} = -\frac{dJ_j(x)}{dx}}$$

where  $[X_j] = n_j/V$ . This equation describes the conservation of moles (mass) within the volume.

The total rate of change,  $d_{tot}[X_j]/dt$ , is then formed by adding this mass transport term,  $-\frac{dJ_j}{dx}$ , to the chemical reaction term,  $\nu_j\dot{\xi}$ .

The mass transport term,  $-\frac{dJ_j}{dx}$ , is called a *surface term* because it describes particle flux entering and leaving the volume element (by crossing its surface). The chemical reaction term,  $\nu_j\dot{\xi}$  is called a *volume term* because the chemical reaction takes place everywhere inside the volume (with zero influence from the surroundings).

### 8.6. Conservation of Energy

Similarly, we have a conservation law

$$\frac{du}{dt} = -\frac{d}{dx}J_u.$$

Here  $u = U/V$  is the internal energy density,  $J_u$  is the energy flux (e.g. heat flow). Here, there is no “volume term” because energy is not created within the volume unless a “heat source” is added. This equation expresses the fact that energy can only be transferred, never created.

On the other hand, if there is a “heat source” is placed within the volume, then a volumetric term is added:

$$\frac{du}{dt} = -\frac{d}{dx}J_u + \dot{q}_V,$$

where  $\dot{q}_V$  is a volumetric heat source (units:  $\text{W}/\text{m}^3$ ).

### 8.7. Entropy Balance

The entropy balance equation is

$$\frac{dS}{dt} = -A[J_s(x+dx) - J_s(x)] + V\sigma$$

where  $\sigma$  is the entropy production per unit volume. Since  $A = V/dx$ , we have, in the limit of small  $dx$

$$\frac{dS}{dt} = -V\frac{[J_s(x+dx) - J_s(x)]}{dx} + V\sigma = -V\frac{dJ_s(x)}{dx} + V\sigma.$$

Dividing by volume  $V$ :

$$(8.5) \quad \frac{ds}{dt} = -\frac{dJ_s(x)}{dx} + \sigma.$$

Let's see if we can find explicit forms for  $J_s$  and  $\sigma$ . Substituting  $\frac{d[X_j]}{dt} = -\frac{d}{dx}J_j + \nu_j\dot{\xi}$  and  $\frac{du}{dt} = -\frac{d}{dx}J_u$  into

$$\dot{s} \equiv \frac{ds}{dt} = \frac{1}{T} \frac{du}{dt} - \sum_i \frac{\mu_i}{T} \frac{d[X_i]}{dt},$$

and comparison with Eq. (8.5) enables us to identify  $J_s$  and  $\sigma$ :

$$\begin{aligned}
 \frac{ds}{dt} &= \frac{1}{T} \frac{du}{dt} - \frac{1}{T} \sum_j \mu_j \frac{d[X_j]}{dt} = \frac{1}{T} \left( -\frac{dJ_u}{dx} \right) - \frac{1}{T} \sum_j \mu_j \left( -\frac{d}{dx} J_j + \nu_j \dot{\xi} \right) \\
 &= -\frac{d}{dx} \left[ \frac{1}{T} \left( J_u - \sum_{j=1}^n \mu_j J_j \right) \right] \\
 &\quad \underbrace{\hspace{10em}}_{\text{entropy flux, } J_s} \\
 (8.6) \quad &+ \underbrace{J_u \frac{d}{dx} \left( \frac{1}{T} \right) + \sum_{j=1}^n J_j \frac{d}{dx} \left( -\frac{\mu_j}{T} \right) + \dot{\xi} \left( -\frac{\Delta G_{rxn}}{T} \right)}_{\text{entropy production rate, } \sigma}
 \end{aligned}$$

where  $\Delta G_{rxn} = \sum_i \nu_i \mu_i$ , with the convention that  $\nu_i$  is negative for reactants and positive for products. In the second line we have twice used the product rule for differentiation:  $d(fg)/dx = f \cdot dg/dx + g \cdot df/dx$ .

The surface term,  $-dJ_s/dx$ , is given in terms of the entropy flux,

$$J_s = \left[ \frac{1}{T} \left( J_u - \sum_{j=1}^n \mu_j J_j \right) \right].$$

It describes two phenomena: the measurable heat flux (“reduced” heat flow  $J_u/T$ ) and the enthalpy of matter transfer (heating due to flows of matter). The enthalpy flux is carried by the component fluxes,  $J_j$ . The entropy flux term is a “surface term” which describes changes in entropy of the system due to inputs from the surroundings.

The volume term, which is also called “entropy production”,

$$\sigma = \underbrace{J_u \frac{d}{dx} \left( \frac{1}{T} \right)}_{\text{heat conduction}} + \underbrace{\sum_{j=1}^n J_j \frac{d}{dx} \left( -\frac{\mu_j}{T} \right)}_{\text{mass diffusion}} + \underbrace{\dot{\xi} \left( -\frac{\Delta G_{rxn}}{T} \right)}_{\text{chemical reaction}}$$

has 3 contributions. The first term arises from heat conduction (temperature gradients), since  $d(1/T)/dx = (-1/T^2)dT/dx$ . The second term is connected to diffusion, which is driven by gradients in the chemical potential; here,  $(d/dx)(\mu_j/T)$ . The third term is due to chemical reactions.

The entropy flux term describes external contributions from the surroundings. It can be positive, negative or zero. This is the  $d_e S$  term. The entropy production term is non-negative,  $\sigma \geq 0$ . Entropy production is the  $d_i S$  term.

### 8.8. Entropy Production vs External Entropy Flow

We recall that  $dS \geq 0$  for an isolated system  $S$ . If the system is not isolated, we have the decomposition  $dS = d_e S + d_i S$ . Some books write  $dS_{exch}$  in lieu of  $d_e S$  and  $dS_{prod} = d_i S$ . Thus,  $dS$  consists of two parts. One part is the entropy created in the system by any spontaneous processes occurring within it, and the other part is the change in entropy resulting from the exchange of energy as heat between the system and its surroundings. We *always* have  $d_i S \geq 0$ .  $d_e S$  can be positive, zero or negative. This quantity is given by  $d_e S = \delta Q/T$ , where  $T$  is the *temperature of the surroundings*. If the exchange is carried out reversibly,  $\delta Q = \delta Q^{rev}$ ; if it is irreversible,  $\delta Q = \delta Q^{irr}$ . For any process (reversible or irreversible),

$$dS = d_i S + d_e S = d_i S + \frac{\delta Q}{T}.$$

For a reversible process,  $d_i S = 0$  and  $\delta Q = \delta Q^{rev}$ , so that we have  $dS = (\delta Q^{rev}/T)$ . For an irreversible process,  $d_i S > 0$  and  $\delta Q = \delta Q^{irr}$ , so that  $dS > (\delta Q^{irr}/T)$ . Combining these two relations together we obtain the Clausius statement of the second law,  $dS \geq (\delta Q/T)$ .

**8.8.1. Fluxes Depend Linearly on Forces.** Consider two systems, 1 and 2 in contact with each other. Particles and heat can be exchanged between them. The two combined systems are isolated from their surroundings, thus explaining the term  $d_e S = 0$ . We are left with the entropy production,  $d_i S$ , as the only contribution to the entropy:<sup>3</sup>

$$\frac{d_i S}{dt} = \frac{dU_1}{dt} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) + \frac{dn_1}{dt} \left( \frac{\mu_2}{T_2} - \frac{\mu_1}{T_1} \right) = J_U X_U + J_n X_n \geq 0.$$

where  $X_U = 1/T_1 - 1/T_2$ ,  $X_n = \mu_2/T_2 - \mu_1/T_1$ ,  $J_U = dU_1/dt = -dU_2/dt$  and  $J_n = dn_1/dt = -dn_2/dt$ . The fluxes and forces are related to each other. Experimentally, the relation is often linear. For example, Fourier's law of heat conduction says that the flux of energy as heat is directly proportional to the temperature difference,

$$J_U \propto T_2 - T_1.$$

But  $T_2 - T_1 \propto (T_2 - T_1)/T_1 T_2 = 1/T_1 - 1/T_2 = X_U$ , so we write  $J_U \propto 1/T_1 - 1/T_2 = X_U$ . Similarly, Fick's law of (isothermal) diffusion says that the flux of matter is directly proportional to the concentration difference,

$$J_n \propto c_2 - c_1$$

<sup>3</sup>The right hand side was explained previously. It is obtained from the fundamental equation in the entropy representation.

which can be expressed<sup>4</sup> in the form  $J_n \propto \mu_2 - \mu_1$  (constant  $T$ ). Finally, we have Ohm's law,  $V = RI$ , which states that the electrical current,  $I$ , is proportional to the potential difference,  $V = \phi_2 - \phi_1$ . Thus, in all cases,  $J \propto X_i$  (fluxes linearly depend on the forces).

**8.8.2. From Discrete to Continuous Case.** In the continuum case, it is gradients of thermodynamic quantities that determine the forces (not differences). We have seen that

$$\frac{d_i S}{dt} = \frac{dU_1}{dt} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) + \frac{dn_1}{dt} \left( \frac{\mu_2}{T_2} - \frac{\mu_1}{T_1} \right) \geq 0.$$

We take the continuum limit by dividing by  $V = A \cdot \Delta x$  and taking the limit  $\Delta x \rightarrow 0$ :

$$\sigma \equiv \frac{1}{V} \frac{d_i S}{dt} = \left( -\frac{1}{A} \frac{dU_1}{dt} \right) \frac{\Delta(1/T)}{\Delta x} + \frac{1}{A} \left( \frac{dn_1}{dt} \right) \frac{\Delta(\mu/T)}{\Delta x},$$

where  $\Delta(1/T) = 1/T_2 - 1/T_1$ ,  $\Delta(\mu/T) = \mu_2/T_2 - \mu_1/T_1$ . Thus,

$$\sigma = J_u \frac{d(1/T)}{dx} + J_n \frac{d(-\mu/T)}{dx} \geq 0,$$

where  $J_u = -\frac{1}{A} \frac{dU_1}{dt}$  and  $J_n = -\frac{1}{A} \frac{dn_1}{dt}$ .

**8.8.3. Application to Isothermal Diffusion.** As an example of the application to continuous systems, we will consider diffusion in an isothermal system (isothermal diffusion). Let  $T$  be constant, so it can be factored out of each term. The entropy production is:

$$\sigma = \frac{1}{T} \sum_{i=1}^n J_i \left( -\frac{d\mu_i}{dx} \right)_{P,T},$$

where  $n$  is the number of components in the system. The chemical potentials are not all independent of each other because of the Gibbs-Duhem equation ( $\sum_i n_i d\mu_i + SdT - VdP = 0$ ), which for constant  $T, P$  reads,  $\sum_{i=1}^n n_i d\mu_i = 0$ . Dividing by  $V$  and  $dx$  gives,  $\sum_{i=1}^n c_i \left( -\frac{d\mu_i}{dx} \right) = 0$ . Solving for  $d\mu_1/dx$ ,

$$\frac{d\mu_1}{dx} = -\frac{1}{c_1} \sum_{i=2}^n c_i \left( \frac{d\mu_i}{dx} \right)_{P,T}.$$

<sup>4</sup>The proof is similar to our previous discussion.  $c_1$  and  $c_2$  are different concentrations of the same substance. Write  $\mu_1 = \mu^\circ + RT \log(c_1/c^\circ)$  and  $\mu_2 = \mu^\circ + RT \log(c_2/c^\circ)$ , so that  $\mu_2 - \mu_1 = RT (\log c_2/c^\circ - \log c_1/c^\circ)$ . Write  $c_2/c^\circ = [(c_2 - c^\circ) + c^\circ]/c^\circ = (c_2 - c^\circ)/c^\circ + 1$  and similarly for  $c_1$ , and Taylor expand in the small parameter  $(c_2 - c^\circ)/c^\circ$ . Then,  $\mu_2 - \mu_1 \approx \frac{RT}{c^\circ} (c_2 - c_1)$ .

Then,

$$\begin{aligned} T\sigma &= J_1 \left( -\frac{d\mu_1}{dx} \right) + \sum_{i=2}^n J_i \left( -\frac{d\mu_i}{dx} \right) = \frac{J_1}{c_1} \sum_{i=2}^n c_i \left( \frac{d\mu_i}{dx} \right) + \sum_{i=2}^n J_i \left( -\frac{d\mu_i}{dx} \right) \\ &= \sum_{i=2}^n \underbrace{\left( J_i - \frac{c_i}{c_1} J_1 \right)}_{J_i^d} \left( -\frac{d\mu_i}{dx} \right), \end{aligned}$$

where  $J_i^d = \left( J_i - \frac{c_i}{c_1} J_1 \right) = c_i \left( \frac{J_i}{c_i} - \frac{J_1}{c_1} \right) = c(v_i - v_1)$ , since particle flux equals concentration times velocity ( $J_i = c_i v_i$ ). (If  $v_i = v_1$ , then entropy production is zero.) Thus,  $J_i^d$  is the flux of solute  $i$  relative to solvent (1).

**8.8.4. Example of Binary Solution.** Let's consider a binary solution, such as sucrose in water or sodium chloride in water. In such cases, there is only 1 independent flow:

$$T\sigma = J_2^d \left( -\frac{d\mu_2}{dx} \right)_{T,P}.$$

The force is  $X = \frac{d\mu_2}{dx}$ . There is just one flux force equation  $J = LX$ :

$$J_2^d = L_{22} \left( -\frac{d\mu_2}{dx} \right)_{T,P} = -L_{22} \left( -\frac{d\mu_2}{dx} \right).$$

Using  $\mu_2 = \mu_2^\circ(T, P) + RT \log c_2$  ( $c_2$  in units of mol/L). Then,

$$\frac{d\mu_2}{dx} = \frac{d\mu_2}{dc_2} \cdot \frac{dc_2}{dx} = \frac{RT}{c_2} \left( \frac{dc_2}{dx} \right). \quad (\text{chain rule})$$

So that

$$\boxed{J_2^d = -L_{22} \frac{RT}{c_2} \frac{dc_2}{dx}}.$$

We get Fick's law of diffusion, which gives the concentration flux as  $J_c = -D \frac{dc}{dx}$ , where  $D = L_{22} RT/c$ .

From the conservation of mass,

$$\frac{dc}{dt} = -\frac{d}{dx} J_c,$$

where  $J_c$  is the concentration flux (particle flux,  $J_n$ , divided by  $V$ ), substitution of  $J_c = -D \frac{dc}{dx}$  gives the diffusion equation

$$\boxed{\frac{dc}{dt} = D \frac{d^2 c}{dx^2}},$$

which we derived in Section 1.5.1 using Einstein's method.

## 8.9. Diffusion Leads to Entropy Production

Diffusion is an irreversible process. This is obvious from experiments: releasing a gas in the corner of the room leads to its spreading across the room until the concentration is uniform. The gas will never return to its original position. This can be seen also from the diffusion equation, which is not time-reversal invariant: the transformation  $t \rightarrow -t$  leads to a sign change. That diffusion leads to entropy production can be seen by computing the flow of entropy.

Recall from Section 1.5.1 that the solution to the diffusion equation for initial conditions,  $c(x, 0) = n\delta(x)$ , is:

$$c(x, t) = \frac{n}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}.$$

**8.9.1. Entropy Production and the Gibbs-Shannon Entropy.** It can be shown that Boltzmann entropy,  $S = k_B \log \Omega$  is a special case of the more general Gibbs-Shannon entropy: for a discrete probability distribution  $p$  on the countable set  $\{x_1, x_2, \dots\}$ , with  $p_i = p(x_i)$ , the Gibbs-Shannon entropy is defined as

$$S = -k_B \sum_{i \geq 1} p_i \log p_i.$$

Indeed, taking  $p_i = 1/\Omega$  (the uniform distribution,  $\sum_{i=1}^{\Omega} \frac{1}{\Omega} = 1$ ), we get:

$$S = k_B \sum_{i=1}^{\Omega} \frac{1}{\Omega} \log \Omega = k_B \log \Omega.$$

For a continuous probability density function  $p(x)$ , the Shannon entropy is

$$S = -k_B \int_{\mathbb{R}} p(x) \log p(x) dx.$$

The entropy of the Gaussian density is seen to be:

$$S = -k_B \int_{\mathbb{R}} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-x^2/2\sigma^2} \left( -\log(\sqrt{2\pi\sigma^2}) - \frac{x^2}{2\sigma^2} \right) dx = \frac{k_B}{2} (1 + \log(2\pi\sigma^2))$$

where  $\sigma^2 = 2Dt$  for the solution to the diffusion equation. Differentiation of  $S$  with respect to  $t$  gives:

$$\frac{dS}{dt} = \frac{d}{dt} \frac{k_B}{2} (1 + \log(4\pi Dt)) = \frac{k_B}{2} \frac{1}{4\pi Dt} \cdot 4\pi D = \frac{k_B}{2t} > 0,$$

which is positive for all times  $t > 0$ , meaning that diffusion leads to entropy production. Note that  $dS/dt$  decreases with time as the steady state is approached, eventually reaching 0 asymptotically.

Now, a slightly more general proof. We can still show that  $dS/dt > 0$  without assuming a Gaussian distribution, but instead only invoking the form of the diffusion equation (and not its solution). Take the time derivative

of  $S$ , then substitute the right hand side of the diffusion equation,  $\frac{d\rho}{dt} = D\frac{d^2\rho}{dx^2}$ , for each instance of  $d\rho/dt$ :

$$\begin{aligned}\frac{dS}{dt} &= -k_B \int \left[ \frac{d\rho}{dt} \log \rho(x) + \rho(x) \frac{1}{\rho(x)} \frac{d\rho}{dt} \right] dx \\ &= -k_B D \int \left[ \frac{d^2\rho}{dx^2} \log \rho(x) + \frac{d^2\rho}{dx^2} \right] dx.\end{aligned}$$

Integration by parts eliminates the second term. Integration by parts of the first term leads to:

$$\frac{dS}{dt} = -k_B D \int \frac{d\rho}{dx} (-1) \frac{1}{\rho} \frac{d\rho}{dx} dx,$$

which is a non-negative quantity:

$$\frac{dS}{dt} = k_B D \int \left( \frac{d\rho}{dx} \right)^2 \frac{1}{\rho} dx \geq 0,$$

because the integrand is the product of two positive quantities:  $(d\rho/dx)^2 \geq 0$  and  $\rho^{-1} > 0$ .

### 8.10. Heat Conduction Leads to Entropy Production

We have seen that the heat conduction term

$$\sigma = J_u \frac{d}{dx} \left( \frac{1}{T} \right) = -J_u \cdot \frac{1}{T^2} \frac{dT}{dx}$$

leads to entropy production. From this equation, we see that the force  $X = \frac{dT}{dx}$ . There is a flux-force relation,  $J = LX$ , of the form:

$$J_u = -L_{qq} \frac{dT}{dx}.$$

where  $L_{qq}$  is a “constant” (Onsager coefficient; the subscript  $qq$  refers to heat), which we will call  $\alpha$  in a moment. Starting from the equation for energy conservation (with no heat source term),

$$\frac{du}{dt} = -\frac{d}{dx} J_u.$$

Inserting the flux-force relation, invoking  $du = d(U/V) = \delta Q/V$  ( $dV = 0$ , so no work, change in internal energy is due to heat transfer) and  $(\delta Q/V) = \rho c_V dT$  ( $\rho$ : density,  $c_V$ : specific heat capacity,  $C/\rho V$ ), we obtain the famous Fourier’s heat conduction equation

$$(8.7) \quad \boxed{\frac{dT}{dt} = \alpha \frac{d^2 T}{dx^2}},$$

where  $\alpha = k/\rho c_V$  is the thermal diffusivity of the medium where heat flows and  $k$  is the thermal conductivity (units: W/m.K). Its functional form is

identical to that of the diffusion equation. Therefore, heat conduction also leads to entropy production.

### 8.11. Summary: Onsager's Formulation of the Second Law

The Second Law can be formulated in terms of the entropy production  $\sigma$ , namely,  $\sigma \geq 0$ . In Onsager's formulation, the entropy production is given by the product sum of so-called conjugate fluxes,  $J_i$ , and forces  $X_i$ , in the system. The second law becomes

$$(8.8) \quad \sigma = \sum_i J_i X_i \geq 0$$

where  $\sigma$  is larger than or equal to zero. Each flux is taken to be a linear combination of all forces,

$$(8.9) \quad J_i = \sum_j L_{ij} X_j$$

and the reciprocal relations

$$L_{ij} = L_{ji}$$

apply. They are called Onsager's reciprocal relations. In order to use the theory, one first has to identify a complete set of extensive independent variables,  $\alpha_i$ . The resulting conjugate fluxes and forces are

$$J_i = \frac{d\alpha_i}{dt}, \quad \text{and} \quad X_i = \left( \frac{\partial S}{\partial \alpha_i} \right)_{\alpha_{j \neq i}},$$

respectively. Here  $t$  is the time and  $S$  is the entropy of the system. The three equations above contain then all the information on the behavior of the system. Accurate expressions for the fluxes are required to model real systems. The simplest descriptions of heat, mass, charge, and volume transport are the equations of Fourier, Fick, Ohm, Darcy and Newton. Fourier's law expresses the measurable heat flux in terms of the temperature gradient by:

$$J'_q = -\lambda \frac{dT}{dx}$$

where  $\lambda$  is the thermal conductivity,  $T$  is the absolute temperature, and  $x$  is the direction of transport. Fick's law gives the mass flux of one of the components in terms of the gradient of its molar concentration  $c$ :

$$J = -D \frac{dc}{dx}$$

where  $D$  is the diffusion coefficient. Ohm's law gives the electric current in terms of the gradient of the electric potential:

$$J_I = -\kappa \frac{d\phi}{dx}$$

where  $\kappa$  is the electrical conductivity, and  $\phi$  is the electric potential. Darcy's law says that the volume flow  $J_v$  in a tube is proportional to the pressure gradient  $dP/dx$  via the coefficient  $L_p$ :

$$J_v = -L_p \frac{dP}{dx}.$$

The fluxes are all caused by a gradient, or driving force. Fick's law, for instance, says that there is no mass flux if there is no concentration gradient. We know from experiments that a temperature gradient and an electric potential gradient also can give rise to a mass flux. To neglect such effects can have severe consequences. In general situations, we must take all driving forces into account. Equations (8.8) and (8.9) form the second law of thermodynamics

$$(8.10) \quad \sigma \equiv \frac{dS}{dt} = \sum_i J_i X_i = \sum_i \sum_j L_{ij} X_j X_i \geq 0.$$

In a stationary state there is no accumulation of internal energy, mass or charge. This means that the heat, molar and electric fluxes are independent of position. The derivative of the above equations with respect to  $x$  are then zero. For the first equation, we have:

$$-\frac{d}{dx} J'_a = \frac{d}{dx} \lambda \frac{dT}{dx} = 0.$$

Equations like these can be used to calculate the temperature, concentration, electric potential and pressure as a function of the position, when their values on the boundaries of the system and  $\lambda$ ,  $D$ ,  $\kappa$ ,  $L_p$  and  $\eta$  are known.

## 8.12. Problems

**Problem 128.** Suppose that we have a metal rod whose two end points are held at different temperatures. This is a non-equilibrium situation because thermodynamic equilibrium would imply that the entire rod is at the same temperature. Instead, the temperature is a function of position along the length of the rod. It is a steady state situation because the temperature does not vary with time (i.e. each point along the rod is at a fixed temperature). Use the concepts of non-equilibrium thermodynamics (namely, the heat conduction equation) to calculate the temperature as a function of position between the two end points of the rod. The rod is 10 cm long. The walls are kept at constant temperature, 4 and 25° C, respectively. Assume that the thermal conductivity is constant.

**Solution.** The heat conduction equation is Eq. 8.7. In the steady state, we have  $d^2T/dx^2 = 0$ . Thus,  $T$  is of the form,  $T(x) = a + bx$ . The constants

$a$  and  $b$  follow from the boundary conditions. We have  $T(0)=278$  K and  $T(10)=298$  K. It follows that  $T(x) = (278 + 2x/\text{cm})$  K. ■

**Problem 129.** Indoor ice rinks employ a cooling system placed underneath a concrete slab (similar to radiant floor cooling systems, but lower temperatures). On top of the concrete slab is the ice. Suppose that we place a temperature sensor  $d = 8$  cm under the concrete slab. Calculate the entropy production per surface area due to the heat transport through the concrete slab. The temperature sensor reads 243 K. This is the temperature of the radiant cooling system. The concrete is in contact with ice (273 K). The thermal conductivity of the pavement is  $0.7$  W/K.m ( $\lambda$  parameter in the Fourier's law). Note: this is a 1D problem with depth as the relevant spatial variable.

**Solution.** Fourier's law for heat conduction is  $J_u = -\lambda(dT/dx)$ , where  $x$  is the depth coordinate. The entropy production per surface area is (let  $\Delta T = T_{top} - T_{below}$ ):

$$\begin{aligned} \left| \int_0^d \sigma dx \right| &= \left| \int_0^d J_u \frac{d}{dx} \left( \frac{1}{T} \right) dx \right| = \left| \lambda \frac{\Delta T}{d} \left( \frac{1}{T_{top}} - \frac{1}{T_{below}} \right) \right| \\ &= \left| 0.7 \frac{(30)}{0.08} \left( \frac{1}{273} - \frac{1}{243} \right) \right| = 0.12 \frac{\text{W}}{\text{K.m}^2}. \end{aligned}$$

**Problem 130.** For the previous problem, calculate the lost work per surface area near the top of the concrete slab (at the interface of ice and concrete). Lost work is the work lost due to entropy production (a type of  $T\Delta S$  term, where  $\Delta S$  is due to entropy production).

**Solution.** The lost work ( $A$ : area)

$$\Delta W_{lost} = T_{top} \cdot A \int_0^d \sigma dx$$

per surface area  $A$  is  $\Delta W_{lost}/A = 273 \text{ K} \cdot 0.12 \text{ W/K.m}^2 = 33 \text{ W/m}^2$ . It is typical for heat conduction around room temperature that the entropy production is large. ■

**Problem 131.** Suppose that a closed 1D system (ideal gas in a pipe) does not undergo any irreversible changes ( $\sigma = 0$ ) and its temperature is spatially uniform [ $d(1/T)/dx = 0$ ] and equal to 300 K everywhere, but that there is an enthalpy flux driven by particle flow. Moreover, the entropy of the system does not change  $ds/dt = 0$  (isentropic process). There is flow in the pipe which we measure to have an average local velocity of 10 m/s at  $x = 0$  and 12 m/s at  $x = 1$  m. (Such an acceleration is possible if the pipe diameter narrows slightly; you can assume that the velocity increases uniformly from

10 to 12 m/s over this distance.) The concentration of the substance in the pipe is  $1 \text{ mol/m}^3$  and uniform everywhere. Then, because of the nature of this enthalpy flux, we expect the heat flux to be spatially non-uniform. Calculate the gradient in the measurable heat flux,  $dJ_u/dx$ .

**Solution.** Since the particle flux  $J = cv$ , at  $x = 0$  we have

$$J(0) = (1 \text{ mol/m}^3)(10 \text{ m/s})$$

and

$$J(1) = (1 \text{ mol/m}^3)(12 \text{ m/s}).$$

This gives a gradient  $dJ/dx$  of  $(1 \text{ mol/m}^3)(2 \text{ m/s})/(1 \text{ m}) = 2 \text{ mol/m}^3/\text{s}$ . For ideal gas, the chemical potential is  $\mu = \frac{\partial U}{\partial n}$ , where  $U = \frac{3}{2}nRT$ . Thus,  $\mu = \frac{3}{2}RT$ , where  $T = 300 \text{ K}$ . Then invoke:

$$\frac{ds}{dt} = -\frac{d}{dx} \left[ \frac{1}{T} (J_u - \mu J_j) \right] = 0$$

Thus,  $\frac{d}{dx} J_u = \mu \frac{d}{dx} J_j$ , where  $\mu = \frac{3}{2}RT$ . Plug in the numbers. ■

**Problem 132.** If two systems  $A$  and  $B$  are in thermal contact, the assembly ( $A + B$ ) being isolated, exchange a heat quantity  $1 \text{ kJ}$  every second (i.e.,  $1 \text{ kW}$ ), calculate the entropy production if  $T_A = 200 \text{ K}$  and  $T_B = 300 \text{ K}$ . Is the entropy production positive or negative (explain)?

**Solution.** Heat flows from  $B$  to  $A$  (from hot body to the cold body), so  $\delta Q = \delta Q_B = -\delta Q_A = -1 \text{ kJ}$ .

$$\sigma = \frac{\delta Q}{dt} \left( \frac{1}{T_B} - \frac{1}{T_A} \right) > 0 = -(1 \text{ kW}) \left( \frac{1}{300 \text{ K}} - \frac{1}{200 \text{ K}} \right) = \frac{5}{3} \frac{\text{kW}}{\text{K}}.$$

Entropy production is always positive. ■

**Problem 133.** Explain what is the driving *force*,  $X$ , of a chemical reaction. What is the corresponding *flux*,  $J$ ? What are the units of the flux and force?

**Problem 134.** Does a chemical reaction produce entropy? Why (or why not)?

**Solution.** Yes, spontaneous irreversible reactions produce entropy, the entropy production is  $\dot{\xi}(-\Delta G_{rxn}/T)$ . ■

# Appendices

## A.1. Vector

For our purposes, it will be sufficient to define a vector  $\mathbf{x}$  as a  $n$ -tuple:

$$\vec{x} = (x_1, x_2, \dots, x_n),$$

where  $x_i \in \mathbb{R}$  are all real numbers. These numbers  $x_1, \dots, x_n$  are called the coordinates of the vector. The coordinates are normally taken to be Cartesian, although other coordinate systems are possible. The vector  $x$  lives in  $\mathbb{R}^n$ .

## A.2. Euclidean Length

A vector  $\mathbf{r}$  with components  $\mathbf{r} = (x, y, z)$  has Euclidean length:

$$|\mathbf{r}| \equiv r \equiv \sqrt{x^2 + y^2 + z^2}.$$

## A.3. Dot Product of Two Vectors

The notation  $\mathbf{x} \cdot \mathbf{y}$  denotes a dot product. In 3D ( $\mathbf{x}, \mathbf{y} \in \mathbb{R}^3$ ) the dot product of these vectors whose components are  $\mathbf{x} = (x_1, x_2, x_3)$  and  $\mathbf{y} = (y_1, y_2, y_3)$  can be expressed as:

$$\mathbf{x} \cdot \mathbf{y} = x_1y_1 + x_2y_2 + x_3y_3.$$

The geometric definition of the dot product is the projection of  $\mathbf{x}$  along the vector  $\mathbf{y}$ :

$$\mathbf{x} \cdot \mathbf{y} = |\mathbf{x}||\mathbf{y}| \cos \theta,$$

where  $\theta$  is the angle between  $\mathbf{x}$  and  $\mathbf{y}$ .  $|\mathbf{x}|$  and  $|\mathbf{y}|$  denote the Euclidean length of the vectors  $\mathbf{x}$  and  $\mathbf{y}$ , respectively. One often writes  $x$  and  $y$  for the length (omitting the norm symbol) for simplicity.

#### A.4. Derivative of a Function of One Variable

Let  $f(x)$  be a function from  $U$  to  $V$ , where  $U$  and  $V$  are subsets on the real line ( $U, V \subset \mathbb{R}$ ). Let  $x$  be a point in the interior of  $U$ .<sup>1</sup> If  $f$  is differentiable, then<sup>2</sup>

$$f(x+h) = f(x) + h \cdot Df(x) + o(|h|),$$

where  $o(|h|)$  is a function that tends to 0 as  $|h| \rightarrow 0$ .  $Df(x)$  is called the *derivative* of  $f$  at the point  $x$ . This definition is equivalent to the statement:

$$Df(x) = \lim_{|h| \rightarrow 0} \frac{f(x+h) - f(x)}{h}.$$

The derivative  $Df(x)$  is also denoted as  $df(x)/dx$  or  $f'(x)$ .

#### A.5. More Than One Variable: Partial Derivative

When  $f$  is a function of more than one variable, we must specify *which variable* we differentiate with respect to. Hence, the notion of *partial derivative*. Partial derivatives are required in thermodynamics because the thermodynamic potentials depend on several variables.

Suppose that  $f$  depends on two variables,  $f(x, y)$ . We have the option of differentiating with respect to  $x$  or  $y$ . (In fact, we *must* specify which variable we differentiate with respect to.) These derivatives are called partial derivatives and are defined by differentiating with respect to the variable of choice while holding the other constant:

$$\frac{\partial f}{\partial x} = \lim_{h \rightarrow 0} \frac{f(x+h, y) - f(x, y)}{h}, \quad \frac{\partial f}{\partial y} = \lim_{h \rightarrow 0} \frac{f(x, y+h) - f(x, y)}{h}.$$

As stated, these derivatives are evaluated at the point  $(x, y)$ . For example, partial differentiation of  $f(xy) = xy$  with respect to  $x$  yields  $\partial f/\partial x = y$ . (If you don't see why, take  $y$  to be constant, any constant, say,  $y = 4$ , i.e.  $f = 4x$ , whose derivative with respect to  $x$  is 4.) Likewise  $\partial f/\partial y = x$ . Another example is  $f(x, y) = y \sin(x)$ . Its derivative with respect to  $x$  is:

$$\frac{\partial f}{\partial x} = y \cos(x)$$

<sup>1</sup>It is easier to take interior points rather than points on the boundary because calculating the derivative of  $f$  at  $x$  requires looking at the neighborhood of  $x$ . At the boundary, there is one side with no neighborhood.

<sup>2</sup>You can think of  $h$  as a "small parameter".

because this is what we get if we treat  $y$  as if it were a constant. Similarly, the derivative with respect to  $y$  is:

$$\frac{\partial f}{\partial y} = \sin(x).$$

In thermodynamics, the practice is to explicitly state which variables are held constant. For example, the internal energy  $U(S, V, N)$  is a function of three variables ( $S$ : entropy,  $V$ : volume,  $N$ : number of particles) and its total derivative is denoted:

$$dU(S, V, N) = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN.$$

The notation  $\left(\frac{\partial U}{\partial S}\right)_{V,N}$  means “derivative of  $U$  with respect to  $S$  while holding  $V$  and  $N$  constant”. In general, however, it is not necessary to specify which variables are held constant because the definition of partial derivative makes it clear that all variables except the one of interest are to be held constant.

## A.6. Taylor's Theorem

Let  $f$  be a function that is  $n$  times differentiable at a point  $x_0$ . Then,

$$f(x_0 + \epsilon) = f(x_0) + \epsilon \cdot \frac{df}{dx}(x_0) + \frac{1}{2!} \epsilon^2 \cdot \frac{d^2 f}{dx^2}(x_0) + \cdots + \frac{1}{n!} \epsilon^n \cdot \frac{d^n f}{dx^n}(x_0) + o(|\epsilon|^n),$$

where  $o(|\epsilon|^n)$  is a quantity such that

$$\lim_{|\epsilon| \rightarrow 0} \frac{o(|\epsilon|^n)}{|\epsilon|^n} = 0.$$

In plain English, Taylor's theorem says that if  $\epsilon$  is small enough, and  $f$  is smooth enough (sufficiently differentiable), we can expand  $f$  around the neighborhood of  $x_0$  using  $n$  of its derivatives. These  $n$  derivatives are evaluated at  $x_0$  and thus are  $n$  numbers. Together with  $f(x_0)$ , we only need  $n+1$  numbers to approximate the function in this neighborhood.

When  $n \rightarrow \infty$ , this expansion is called Taylor's series. When  $x_0 = 0$  the Taylor series is called a Maclaurin series. To obtain the Taylor series from an analytical formula for  $f$ , we start by evaluating the derivatives of  $f$  at the point  $x = x_0$ .

**A.6.1. Examples.** The Taylor (Maclaurin) series for  $f(x) = e^x$  about  $x_0 = 0$  is

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}.$$

The Taylor series of  $f(x) = \cos(x)$  about  $x_0 = 0$  is

$$\cos(x) = \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n}}{(2n)!}.$$

The case of  $e^x$  is trivial since all derivatives of this function are  $e^x$  (which, when evaluated at  $x = 0$  give 1). For  $\cos(x)$ , the derivatives alternate between sin and cos together with some sign changes:

$$\begin{array}{ll} \frac{df}{dx}(x) = -\sin(x) & \frac{df}{dx}(0) = 0, \\ \frac{d^2f}{dx^2}(x) = -\cos(x) & \frac{d^2f}{dx^2}(0) = -1, \\ \frac{d^3f}{dx^3}(x) = \sin(x) & \frac{d^3f}{dx^3}(0) = 0, \\ \frac{d^4f}{dx^4}(x) = \cos(x) & \frac{d^4f}{dx^4}(0) = 1, \\ \vdots & \end{array}$$

which leads to

$$\cos(x) = 1 - \frac{1}{2!}x^2 + \frac{1}{4!}x^4 - \frac{1}{6!}x^6 + \dots = \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n}}{(2n)!}.$$

## A.7. Chain Rule

The chain rule is needed when we differentiate a function with respect to a variable that is found within the *argument* of the function. Example:

$$\frac{d}{dy}f(\lambda y) = \frac{df}{d\lambda y} \cdot \frac{d(\lambda y)}{dy} = \frac{df}{d\lambda y} \lambda.$$

A function  $f$  expressed in the form  $f(\cdot)$  is a function of some argument  $\cdot$ . The argument is the slot in which we insert a number or variable in order to evaluate the function's value at that point. Here, the argument of  $f$  is  $\lambda y$ . However, the variable we differentiate with respect to is  $y$ .  $y$  is found in the argument of  $f$ , i.e.  $\lambda y$  is a function of  $y$ . In the first equality, the term  $\frac{df}{d\lambda y}$  means "derivative of  $f$  with respect to its argument".

In two variables, the idea is the same except that we use partial derivatives to stress which argument of the function is targeted. For example, if we must differentiate  $f(x, \lambda y)$  with respect to  $y$ , the chain rule gives:

$$\frac{\partial}{\partial y}f(x, \lambda y) = \frac{\partial f}{\partial \lambda y} \cdot \frac{\partial(\lambda y)}{\partial y} = \frac{\partial f}{\partial \lambda y} \lambda.$$

Here,  $\frac{\partial f}{\partial y}$  means derivative of  $f$  with respect to its *second argument*. A better notation for  $\frac{\partial f}{\partial y}$  would be  $D_2 f$  to emphasize the second argument, rather than  $y$  (since  $y$  is different from  $\lambda y$ ).

### A.8. Total Differential

For a function of one variable,  $f(x)$ , the total differential is defined as:

$$df(x) = f'(x)dx = \frac{df}{dx} \cdot dx.$$

It is also defined as

$$df(x) = f(x + dx) - f(x).$$

Taylor expansion of  $f(x + dx) = f(x) + f'(x)dx + O(|dx|^2)$  leads to:

$$df(x) = \cancel{f(x)} + f'(x)dx + O(dx^2) - \cancel{f(x)} = f'(x)dx + O(|dx|^2),$$

where  $O(|dx|^2)$  represents higher-order terms ( $(dx)^2$  and higher). And for this to agree with  $df(x) = f'(x)dx = \frac{df}{dx} \cdot dx$ , then we must have that  $O(|dx|^2) = 0$ .

For a function of two variables,

$$\begin{aligned} df(x, y) = f(x + dx, y + dy) - f(x, y) &= \cancel{f(x, y)} + \frac{\partial f}{\partial x} \cdot dx \\ &+ \frac{\partial f}{\partial y} \cdot dy + O(|dx, dy|^2) - \cancel{f(x, y)}, \end{aligned}$$

where  $O(|dx, dy|^2)$  denotes higher order terms. For the rules of calculus to hold, we must have that  $O(|dx, dy|^2) = 0$ . Then,

$$df(x, y) = \frac{\partial f}{\partial x} \cdot dx + \frac{\partial f}{\partial y} \cdot dy.$$

This can be generalized to any number of variables. For example, a function of 3 variables,  $U \equiv U(S, V, N)$ , has:

$$dU(S, V, N) = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV + \frac{\partial U}{\partial N} dN.$$

And for the case  $U \equiv U(S, V, \{N_i\})$

$$dU(S, V, \{N_i\}) = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV + \sum_i \frac{\partial U}{\partial N_i} dN_i.$$

Comparing this to the fundamental equation of thermodynamics,  $dU = TdS - PdV + \sum_i \mu_i dN_i$ , we get thermodynamic definitions for  $T, P, \mu_i$ :

$$T \equiv \frac{\partial U}{\partial S}, \quad P \equiv -\frac{\partial U}{\partial V}, \quad \mu_i \equiv \frac{\partial U}{\partial N_i}.$$

### A.9. Exact Differentials

In the statement of the first law ( $dU$  is an exact differential), we invoked the concept of exact differentials or exact *forms*. Exact forms are those that are obtained as the differential of some function  $f(x, y)$ :

$$\omega(\text{exact}) \equiv df = f_x(x, y)dx + f_y(x, y)dy = \nabla f \cdot d\vec{r},$$

where here  $f_x$  denotes the partial of  $f$  with respect to  $x$  and  $d\vec{r} = (dx, dy)$ . The fundamental theorem of calculus says that integration of an exact 1-form  $df$  on a closed interval  $[a, b]$  is equal to the difference of  $f$  at the boundaries of the interval,  $\partial[a, b] = \{a, b\}$ :

$$\int_{[a,b]} \omega = \int_a^b \omega = \int_a^b df = f(b) - f(a).$$

Another equivalent statement is:

$$\int_a^b \nabla f \cdot d\vec{r} = f(b) - f(a),$$

where  $\nabla f = (\partial_x f, \partial_y f)$  and  $d\vec{r} = (dx, dy)$ . Thus, for exact differentials, their integrals only depend on the end points and not on the path taken to reach the end point.

On the other hand, more general expressions of the form

$$\omega = f_1(x, y)dx + f_2(x, y)dy$$

are called *differential forms* (1-forms). While all exact differentials are 1-forms, not all 1-forms happen to be exact.

It is helpful at this point to introduce Euler's test to help us determine whether an expression containing first-order differentials is exact. Take, for example, the following differential 1-form:

$$\omega = (xy)dx + (xy)dy.$$

If this were an exact differential we would write  $\omega = df$  for some  $f$ . If this were the case then  $df$ , according to the definition of differential, must also be equal to (subscript denotes which variable is held constant):

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

But since mixed partials should be equal:

$$\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y}\right).$$

This "Euler test" provides a *necessary condition* for exact differential. Let's check to see if this is the case:  $\partial_y(xy) = x$  whereas  $\partial_x(xy) = y$ , which are not equal for all  $x, y$ . So we cannot say that  $\omega$  is an exact differential.

On the other hand,

$$\omega = ydx + xdy$$

meets the necessary condition since  $\partial_y(y) = 1$  and  $\partial_x(x) = 1$  are equal. In fact, we see that  $\omega = d(xy)$ . Thus, it is an exact differential because it is the derivative  $d$  of some function  $f(x, y) = xy$ .

Any expression  $\omega$  which can be written in the form  $df$  for some  $f$  is an exact differential. In fact, this is the correct definition of **exact differential**. Euler's test provides a necessary condition. The sufficient condition is provided by identifying the function  $f$  for which  $\omega = df$  over some specified domain.<sup>3</sup> The latter task of finding  $f$  requires more work.

## A.10. Einstein Summation Convention

Whenever two indices are repeated in the same term, a summation is implied. For example, in the dot product of  $\mathbf{u} = (u_x, u_y, u_z)$  and  $\mathbf{v} = (v_x, v_y, v_z)$  we have:

$$\mathbf{u} \cdot \mathbf{v} = u_\alpha v_\alpha \equiv \sum_{i=1}^3 u_i v_i = u_x v_x + u_y v_y + u_z v_z.$$

It is simpler to write  $u_\alpha v_\alpha$  than the entire summation.

## A.11. Multivariate Taylor Expansion

In 1D the Taylor expansion of  $f(x+h)$  at  $x$  is:

$$f(x+h) = f(x) + f'(x)h + \frac{1}{2}f''(x)h^2 + \frac{1}{3!}f^{(3)}(x)h^3 + \dots$$

In  $n$ -D, a scalar-valued function  $f(\mathbf{x})$ , where  $\mathbf{x} \in \mathbb{R}^n$ , is expanded as:

$$\begin{aligned} f(\mathbf{x} + \mathbf{h}) = f(\mathbf{x}) &+ \sum_{i=1}^n \frac{\partial f(\mathbf{x})}{\partial x_i} h_i + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n \frac{\partial^2 f(\mathbf{x})}{\partial x_i \partial x_j} h_i h_j \\ &+ \frac{1}{3!} \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n \frac{\partial^3 f(\mathbf{x})}{\partial x_i \partial x_j \partial x_k} h_i h_j h_k + \dots \end{aligned}$$

**A.11.1. Abbreviation for Partial Derivatives.** We will often use the shorthand notation to abbreviate the notation for partial differentiation:

$$\partial_\alpha \equiv \frac{\partial}{\partial x_\alpha}$$

<sup>3</sup>The choice of domain is important because some forms may not be exact over all space, but may be exact over a restricted domain.

In this notation, and using the summation convention, the multivariate Taylor expansion looks particularly neat:

$$\boxed{f(\mathbf{x} + \mathbf{h}) = f(\mathbf{x}) + h_i \partial_i f(\mathbf{x}) + \frac{1}{2} h_i h_j \partial_i \partial_j f(\mathbf{x}) + \frac{1}{3!} h_i h_j h_k \partial_i \partial_j \partial_k f(\mathbf{x}) \dots}$$

(summation convention) The components of  $\mathbf{h}$  have been moved to the left-hand-side of all derivative operators to avoid any possible confusion about which quantity is differentiated.

### A.12. Example: Derivative of $1/r$

This example is often encountered when dealing with potentials (gravitational, electromagnetic). The first order partial derivative of

$$\frac{1}{r} \equiv \frac{1}{|\mathbf{r}|} = \frac{1}{\sqrt{x^2 + y^2 + z^2}}$$

with respect to  $x$  is:

$$\frac{\partial}{\partial x} \left( \frac{1}{r} \right) \equiv \partial_x \left( \frac{1}{r} \right) = -\frac{1}{2} \frac{(2x)}{(x^2 + y^2 + z^2)^{3/2}} = -\frac{x}{r^3}.$$

Similar expressions are found for differentiation with respect to  $y$  or  $z$ . Thus, for any component  $\alpha = x, y, z$  we have:

$$\boxed{\frac{\partial}{\partial r_\alpha} \left( \frac{1}{r} \right) \equiv \partial_\alpha \left( \frac{1}{r} \right) = -\frac{r_\alpha}{r^3}}$$

where  $r_\alpha$  can be any of  $x, y, z$  depending on the choice of index  $\alpha = x, y, z$ .

### A.13. Probability Concepts

Molecular velocities are an inherently probabilistic concept. This is because we are usually dealing with a large number of molecules and we do not have perfect knowledge of every single molecule's position and velocity. The best we can do is describe their behavior statistically. Their description requires us to introduce tools to manipulate random variables. Random variables can be continuous or discrete, depending on whether they take continuous or discrete values, respectively. An example of a continuous random variable is the length of an object. Another example of continuous random variable is the velocity component of a molecule chosen at random. The velocity component, for example  $v_x$ , takes values in the interval  $(-\infty, \infty)$ . The speed of a molecule,  $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$ , is another example of a continuous random variable, taking values in the interval  $[0, \infty)$ . Length is a random variable which can take positive real values, a continuous interval,  $[0, \infty)$ . An example of a discrete random variable is the number of counts within a time interval. Counts can only take discrete values  $(1, 2, 3, \dots)$ , in this

case, the positive integers. Similarly, the roll of a (normal) die is a discrete random variable, which can only take values in the set  $\{1, 2, 3, 4, 5, 6\}$ .

### A.14. Continuous Random Variables

A continuous random variable  $X$  cannot be a simple variable because it describes the value of a measurement made in a given experiment and all statistical properties of this measurement.<sup>4</sup> Instead it is better to think of  $X$  as a *function* that encodes the statistical properties of the measurement. To this end, let us associate with  $X$  a probability density function (PDF),  $p(x)$ .

### A.15. Probability Distribution Functions

A PDF,  $p(x)$ , describes the likelihood that a random variable will take a certain value. For example, the probability,  $\mathbb{P}$ , that a random variable  $X$  will take a value in the interval  $[a, b]$  is given by:

$$\mathbb{P}(a < X < b) = \int_a^b p(x)dx$$

where  $p(x)$  is the probability density function for the random variable  $X$ . The requirements are that  $p(x)$  should be non-negative ( $\geq 0$ ) and normalized to 1:

$$p(x) \geq 0, \forall x, \quad \int_{-\infty}^{\infty} p(x)dx = 1,$$

where the limits of integration (denoted here by  $[-\infty, \infty]$ ) range over the domain of definition of the random variable, i.e. if this domain is  $[0, 1]$  then the limits of integration are from 0 to 1. Its main purpose is to compute average values. For example, the average (mean) value of  $X$  is:

$$\mathbb{E}X \equiv \bar{X} \equiv \langle X \rangle = \int_{-\infty}^{\infty} xp(x)dx.$$

The average of a function of  $X$  is obtained by replacing the random variable  $X$  by a dummy integration variable  $x$ , multiplying by  $p(x)$  and integrating over  $x$ :

$$\mathbb{E}f(X) \equiv \overline{f(X)} \equiv \langle f(X) \rangle = \int_{-\infty}^{\infty} f(x)p(x)dx.$$

---

<sup>4</sup>This experiment could consist, for example, of choosing a molecule at random within an ensemble and recording its velocity (assuming this is even possible!). Every time a molecule is chosen, it will usually be a different molecule than in previous experiments, especially if the ensemble is very large. Even if the same molecule is chosen twice, this will be done at different times, and its velocity will be different. In each case, the result (velocity measurement) will be very different. Hence, we need a statistical description that will tell us what is the average velocity, what is the variance (spread of values), etc.

A famous example of a PDF is the normal (Gaussian) distribution, whose pdf is

$$p(x) = \frac{1}{\sqrt{2\pi}} e^{-x^2/2}.$$

**Meaning of the PDF:** The PDF  $p(x)$  has the following meaning. The quantity  $p(x)dx$  is the probability  $\mathbb{P}$  that the random variable  $X$  lies in the interval  $[x, x + dx]$ :

$$p(x)dx = \mathbb{P}(x \leq X \leq x + dx),$$

where  $dx$  is an infinitesimally small quantity and  $\mathbb{P}(\cdot)$  denotes the probability  $\mathbb{P}$  of the event  $\cdot$  occurring. The quantity  $p(x)dx$  in itself is rarely used. Instead, one integrates this expression<sup>a</sup> to find the probability that  $X$  will take some value in a finite interval  $[a, b]$ :

$$\mathbb{P}(a \leq X \leq b) = \int_a^b p(x)dx.$$

<sup>a</sup>Since  $\mathbb{P}(x \leq X \leq x + dx) = \mathbb{P}(X \leq x + dx) - \mathbb{P}(X \leq x) = d\mathbb{P}(X \leq x)$ , integrating  $\mathbb{P}(x \leq X \leq x + dx) = d\mathbb{P}(X \leq x)$  from  $a$  to  $b$  yields  $\int_a^b d\mathbb{P}(X \leq x) = \mathbb{P}(X \leq b) - \mathbb{P}(X \leq a) = \mathbb{P}(a \leq X \leq b)$  whereas integrating  $p(x)dx$  yields  $\int_a^b p(x)dx$ . Since the two are equal, we have that  $\mathbb{P}(a \leq X \leq b) = \int_a^b p(x)dx$ .

## A.16. Mean Value

The mean value of a random variable  $X$ , denoted  $\mathbb{E}X$ , is defined as:

$$\mathbb{E}X \equiv \int_{-\infty}^{\infty} xp(x)dx.$$

That is, to obtain the mean value of  $X$ , we replace the random variable  $X$  by a regular variable  $x$  that represents its value, then multiply by  $p(x)$  and integrate over all  $x$ .

We note that this expression differs from the *sample mean*,  $\frac{1}{n} \sum_{i=1}^n x_i$ . The sample mean is only an estimate of the mean.

## A.17. Variance

The *variance* of  $X$  is defined as the sum of square differences between  $X$  and its mean, weighted by the pdf:

$$\sigma^2 = \int_{-\infty}^{\infty} p(x)(x - \mathbb{E}X)^2 dx$$

The square can be expanded to give  $\int_{-\infty}^{\infty} p(x)(x^2 + (\mathbb{E}X)^2 - 2x\mathbb{E}X)dx$  and thus

$$\sigma^2 = \mathbb{E}(X^2) - (\mathbb{E}X)^2.$$

The square root of the variance is called the standard deviation and is denoted  $\sigma$ .

### A.18. Average of a Function of a Random Variable

The average (or mean, or expectation value) of a function  $f$  of a random variable  $X$  is defined as:

$$\mathbb{E}f(X) \equiv \int_{-\infty}^{\infty} f(x)p(x)dx.$$

As an example, take  $f(x) = x^n$ . This is called the  $n$ -th moment of  $X$ :

$$\mathbb{E}(X^n) \equiv \int_{-\infty}^{\infty} p(x)x^n dx.$$

The case  $n = 1$  (*first moment*) is called the “mean value of  $X$ ”:

$$\mathbb{E}X \equiv \int_{-\infty}^{\infty} p(x)x dx \quad \text{“mean value of } X \text{”}$$

The *variance* of  $X$  is defined as  $\sigma^2 = \int_{-\infty}^{\infty} p(x)(x - \mathbb{E}X)^2 dx$ , which also equals  $\sigma^2 = \mathbb{E}(X^2) - (\mathbb{E}X)^2$ . Thus, the variance is the second moment of  $X$  minus the square of the average of  $X$ .

**A.18.1. Example 1.** Suppose that the kinetic energy,  $K(v) = \frac{1}{2}mv^2$ , of an object of mass  $m$  is to be calculated using experimentally measured values of the velocity  $v$ . Thus,  $v$  is a random variable  $V$ . Since  $v$  is a random variable,  $K(v)$  is also a random variable. You determine from experiments that the velocities,  $v$ , are Gaussian-distributed around 100 m/s, with a standard deviation of 1 m/s, i.e.  $p(v) = \frac{1}{\sqrt{2\pi}}e^{-(v-100)^2/2}$ . What is the average kinetic energy,  $\mathbb{E}K(V)$ ? You expect that  $\mathbb{E}K(V)$  should be close to  $K(100) = \frac{1}{2}m(100)^2$ . However, the exact value of  $\mathbb{E}K(V)$  will depend on the distribution  $p(v)$ . We need to calculate:

$$\begin{aligned} \mathbb{E}K(V) &= \int_{-\infty}^{\infty} \frac{1}{2}mv^2 \frac{1}{\sqrt{2\pi}}e^{-(v-100)^2/2} dv \\ &= \frac{m}{2\sqrt{2\pi}} \int_{-\infty}^{\infty} v^2 e^{-(v-100)^2/2} dv \approx \frac{m}{2} 1.0001 \cdot 10^4. \end{aligned}$$

So fairly close to  $K(100)$  but slightly higher.

**A.18.2. Example 2.** Suppose that  $f(\theta) = \cos(\theta)$  and  $p(\theta) = 1$  for  $\theta \in [-\frac{1}{2}, \frac{1}{2}]$  and  $p = 0$  elsewhere (uniform distribution). Denote the random variable as  $\Theta$ . Using  $p(\theta)$  you can easily check that  $\mathbb{E}\Theta = \int_{-1/2}^{1/2} \theta d\theta = 0$ .

The average of  $\cos(\Theta)$  is:

$$\mathbb{E} \cos(\Theta) = \int_{-1/2}^{1/2} \cos(\theta) d\theta \approx 0.9589.$$

Note: it is not equal to 1 even though the average of  $\Theta$  is 0.

### A.19. More than One (Continuous) Random Variable

If we are to compute the average of an expression that is a function of more than one random variable, we need to use the *joint probability density*  $p_{XY}(x, y)$ , which is everywhere non-negative ( $p_{XY}(x, y) \geq 0$ ) and integrates to 1:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p_{XY}(x, y) dx dy = 1.$$

The average of a function  $g(X, Y)$  would be:

$$\mathbb{E}g(X, Y) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p_{XY}(x, y)g(x, y) dx dy.$$

Given a joint PDF,  $p_{XY}(x, y)$ , the *marginal density* function for  $X$  is obtained by integrating over  $y$ :

$$p_X(x) = \int_{-\infty}^{\infty} p_{XY}(x, y) dy.$$

Similarly, the marginal density for  $Y$  is obtained by integrating over all  $x$ :

$$p_Y(y) = \int_{-\infty}^{\infty} p_{XY}(x, y) dx.$$

Note: you can easily check that both marginals  $p_X(x)$  and  $p_Y(y)$  are bona fide densities, i.e. nonnegative and normalized to 1.

### A.20. Statistical Independence

The marginal density is a useful concept if you are asked to check whether or not two random variables are statistically independent. Two random variables  $X$  and  $Y$  are *statistically independent* if the joint probability density is written as the product of densities of each variable:

$$p_{XY}(x, y) = p_X(x)p_Y(y),$$

where  $p_X(x)$  and  $p_Y(y)$  are the marginal densities of  $X$  and  $Y$ , respectively. They can be computed from  $p_{XY}(x, y)$  by integrating.

There are at least two consequences of statistical independence that we can immediately point out. First, one concerns expectation values. Consider

the average of a function  $g(X, Y)$  of two r.v.  $X$  and  $Y$ :

$$\begin{aligned}\mathbb{E}g(X, Y) &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p_{XY}(x, y)g(x, y)dx dy \\ &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p_X(x)p_Y(y)g(x, y)dx dy.\end{aligned}$$

If  $g$  factors as a product of a function of  $X$  times a function of  $Y$ , for example  $g(X, Y) = XY$  then the expectation value of  $XY$  is equal to the product of expectation values of  $X$  and that of  $Y$ :

$$\begin{aligned}\mathbb{E}(XY) &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p_X(x)p_Y(y)xy dx dy = \int_{-\infty}^{\infty} p_X(x)x dx \cdot \int_{-\infty}^{\infty} p_Y(y)y dy \\ &= \mathbb{E}X \cdot \mathbb{E}Y.\end{aligned}$$

The second consequence pertains to the calculation of probabilities in general, which also factors as a product. For example, the joint probability:

$$\begin{aligned}\mathbb{P}(X \in A, Y \in B) &= \int_{\{(x,y)|x \in A, y \in B\}} p_{XY}(x, y) dx dy \\ &= \int_{\{(x,y)|x \in A, y \in B\}} p_X(x)p_Y(y) dx dy \\ &= \int_{\{x|x \in A\}} p_X(x) dx \cdot \int_{\{y|y \in B\}} p_Y(y) dy \\ &= \mathbb{P}(X \in A)\mathbb{P}(Y \in B).\end{aligned}$$

**A.20.1. Example: the Gaussian (normal) Distribution.** The normal distribution  $N(\mu, \sigma^2)$  with mean  $\mu$  and variance  $\sigma^2$  is defined by the PDF:

$$p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

The prefactor  $\frac{1}{\sqrt{2\pi\sigma^2}}$  is such that  $p(x)$  adds up to 1:

$$\int_{-\infty}^{\infty} p(x) dx = 1$$

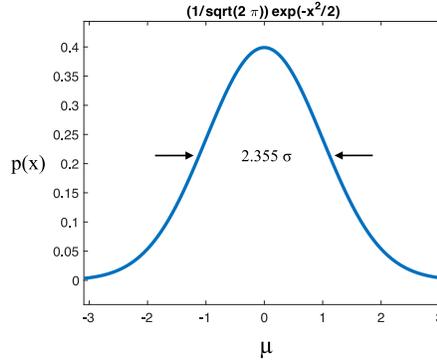
This can be verified using the well-known result for a Gaussian integral  $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\pi/a}$ , where  $a > 0$ .

This PDF is plotted in Fig. A.1. The width is proportional<sup>5</sup> to  $\sigma$  and mean value is  $\mathbb{E}X$ .

If a random variable  $X$  follows a Gaussian distribution with mean  $\mu = \mathbb{E}X$  and variance  $\sigma^2$  we write

$$X \sim N(\mu, \sigma^2).$$

<sup>5</sup>In fact, the full width at half maximum of the Gaussian is  $2\sqrt{2\log 2}\sigma \approx 2.355\sigma$ . You can check this by finding the values of  $x$  for which  $\frac{1}{2} \frac{1}{\sqrt{2\pi\sigma^2}} = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}}$  or  $\frac{1}{2} = e^{-\frac{x^2}{2\sigma^2}}$ , since the maximum of the function is  $\frac{1}{\sqrt{2\pi\sigma^2}}$  (set  $x = 0$ ). Taking logs of both sides gives  $x = \pm\sqrt{2\sigma^2 \log 2}$ .



**Figure A.1.** Gaussian density.

A.20.1.1. *The Gaussian Probability Density.* The Gaussian probability density (in 1D) with mean zero is:

$$p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}}.$$

Its integral is 1:

$$\int_{\mathbb{R}} p(x) dx = 1$$

This can be easily checked using the standard result from integration tables:

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

$\sigma$  is called the standard deviation.  $\sigma$  is related to the width of the bell curve.  $\sigma^2$  is called the variance. The function  $p(x)$  has a bell shape centered at 0 and a full-width at half-maximum of approximately  $\approx 2.355\sigma$ .

**A.20.2. Other Examples of Probability Distributions.** The Gibbs distribution for the probability of the system  $X$  being in state  $x$  (random variable  $X$  taking the value  $x$ ) is:

$$\mathbb{P}(X = x) = \frac{1}{Z(\beta)} \exp(-\beta E(x))$$

where  $Z(\beta)$  is a normalization factor called the *partition function*:

$$Z(\beta) = \int dx \exp(-\beta E(x)).$$

$\beta$  is a free parameter called the inverse temperature ( $\beta = 1/k_B T$ ). When integrated over  $x$ , this distribution is normalized:

$$\int \mathbb{P}(X = x) dx = \frac{1}{Z(\beta)} \int dx \exp(-\beta E(x)) = \frac{Z(\beta)}{Z(\beta)} = 1.$$

The Rayleigh distribution has density

$$p(x) = \frac{x}{\sigma^2} \exp\left(-\frac{x^2}{2\sigma^2}\right), \quad x \geq 0,$$

where  $\sigma$  is a parameter of the distribution.

The Gaussian distribution is

$$p(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{x^2}{2\sigma^2}\right),$$

where  $\sigma$  is a parameter of the distribution.

**A.20.3. Boltzmann Factor.** Another example of probability density is the Boltzmann distribution, or the Boltzmann factor. The latter gives the probability of a system to be in the state  $i$ , with energy  $E_i$ :

$$p(\text{state } i) \propto \exp\left(-\frac{E_i}{k_B T}\right)$$

A *state* is a set of quantum numbers. For example, if we specify the values of  $n, l, m_l, m_s$  for an electron in an atom, we have specified a state. Note: *state* is different from *energy level*. More than 1 state can correspond to the same energy. That is the case for the hydrogenic atom, where only the principal quantum number  $n$  determines the energy. For a given  $n$ , all values of  $l, m_l, m_s$  give the same energy.

The meaning of the Boltzmann factor is the probability of finding the system in a given state when the temperature is  $T$ , assuming classical particles (not fermions or bosons). In the limit  $T \rightarrow 0$  only the ground state is occupied (the reader should check this!). In the high-temperature limit ( $T \rightarrow \infty$ ) all levels are equally likely to be populated; the distribution behaves like a uniform distribution.

**A.20.4. Derivation of the Maxwellian Distribution.** We seek to determine the constants  $a$  and  $c$  in:

$$f(v_i) = c \exp(-av_i^2). \quad (i = x, y, z)$$

A.20.4.1. *Finding  $c$ .* In Section 1.3.3, the constant  $c$  was obtained from the normalization condition:

$$\int_{-\infty}^{\infty} dv_i f(v_i) = c \int_{-\infty}^{\infty} dv_i \exp(-av_i^2), \quad a > 0$$

which led to  $c = \sqrt{a/\pi}$ .

A.20.4.2. *Finding  $a$ .*  $a$  can be found by invoking the two previous results:

$$\langle \epsilon_{kin} \rangle = \frac{3}{2} k_B T, \quad \langle \epsilon_{kin} \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} m \langle v_z^2 \rangle.$$

But  $\langle v_z^2 \rangle$  is an average which can be computed using the probability density for  $\vec{v}$ :<sup>6</sup>

$$\begin{aligned} k_B T = m \langle v_z^2 \rangle &= m \int_{-\infty}^{\infty} dv_z v_z^2 f(v_z) = m \sqrt{\frac{a}{\pi}} \int_{-\infty}^{\infty} dv_z v_z^2 \exp(-av_z^2) \\ &= -m \sqrt{\frac{a}{\pi}} \frac{d}{da} \left( \int_{-\infty}^{\infty} e^{-av_z^2} dv_z \right) = -m \sqrt{\frac{a}{\pi}} \frac{d}{da} \left( \sqrt{\frac{\pi}{a}} \right) = m \sqrt{\frac{a}{\pi}} \frac{1}{2} \frac{\sqrt{\pi}}{a^{3/2}} = \frac{m}{2a}. \end{aligned}$$

Therefore,  $a = \frac{m}{2k_B T}$  and  $c = \sqrt{\frac{a}{\pi}} = \sqrt{\frac{m}{2\pi k_B T}}$ , so that:

$$f(v_i) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(-\frac{mv_i^2}{2k_B T}\right), \quad f(\vec{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right).$$

A.20.4.3. *Mean Square Displacement.* The mean square displacement,  $\langle x(t)^2 \rangle$ , or also denoted  $\langle X_t^2 \rangle$  where  $X_t$  is the random variable for position at time  $t$ , for the 1D diffusion equals  $2Dt$ . This is proved as follows. Apart from the factor  $n$ , Eq. (A.4) is merely the probability density for finding a particle at  $x$  at time  $t$ :

$$p_t(x) = \frac{c(x, t)}{n} = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}.$$

So using the definition of the average (let  $a = 1/4Dt$ ):

$$\begin{aligned} \langle X_t^2 \rangle &= \int_{-\infty}^{\infty} x^2 p_t(x) dx = \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} x^2 e^{-x^2/4Dt} dx = \sqrt{\frac{a}{\pi}} \int_{-\infty}^{\infty} x^2 e^{-ax^2} dx \\ &= -\sqrt{\frac{a}{\pi}} \frac{d}{da} \left( \int_{-\infty}^{\infty} e^{-ax^2} dx \right) = -\sqrt{\frac{a}{\pi}} \frac{d}{da} \left( \sqrt{\frac{\pi}{a}} \right) = \frac{1}{2} \sqrt{\frac{a}{\pi}} \left( \frac{\sqrt{\pi}}{a^{3/2}} \right) = \frac{1}{2a} \end{aligned}$$

which is equal to  $2Dt$ .

A.20.4.4. *Transition Probabilities.* Equation (A.4),  $\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$ , asks the question: what is the concentration at point  $x$  at time  $t + \tau$ . This concentration consists of a sum of contributions from all possible spatial positions located some distance  $\Delta$  away from  $x$  weighted by the probability of undergoing a jump of size  $\Delta$  to reach the point  $x$ . This weighting factor is  $\phi(\Delta)$ . This makes intuitive sense and can be taken as the definition of the function  $\phi(\Delta)$ .

<sup>6</sup>Alternatively, we could have started by using the 3D probability density for  $\vec{V}$  by writing,  $\langle v_z^2 \rangle = \int f(\vec{v}) v_z^2 d^3\vec{v}$ , because this is equal, by normalization of the two functions  $f(v_x)$  and  $f(v_y)$ , to

$$\underbrace{\int_{-\infty}^{\infty} dv_x f(v_x)}_{=1} \underbrace{\int_{-\infty}^{\infty} dv_y f(v_y)}_{=1} \int_{-\infty}^{\infty} dv_z v_z^2 f(v_z) = \int_{-\infty}^{\infty} dv_z v_z^2 f(v_z)$$

But this step can be skipped in favor of simply using  $f(v_z)$  the probability density for the  $V_z$  component.

Those familiar with probability theory may recognize Eq. (A.4) as the definition of transition probability density for a Markov process. The probability density  $p_t(x)$  of finding the particle at position  $x$ , time  $t$ , obeys the condition

$$p_s(x) = \int_{-\infty}^{\infty} p_t(y)p(x, s|y, t)dy, \quad s > t$$

where  $p(x, s|y, t)$  a conditional probability density describing the probability of the random process to be found at the point  $x$  at time  $s$  ( $s > t$ ) under the condition that it was at the point  $y$  at an earlier time  $t$ . It is known as the *transition probability density*. Taking  $p_s(x)$  to be proportional to the concentration  $c(x, s)$ , where  $s = t + \tau$  yields Eq. (A.4).

## A.21. Angular Averaging

A PDF can also depend on several variables. For example,  $p(r, \theta, \phi)$ . It is called a *joint probability density*. It is possible to integrate over some of these variables and obtain a *reduced* probability density, also known as *marginal probability density*. Suppose that  $p_{XY}(x, y)$  is a joint probability density for the random variables  $X$  and  $Y$ , i.e.

$$\int \int p_{XY}(x, y)dx dy = 1 \text{ (normalization), } p_{XY}(x, y) \geq 0.$$

Integrating with respect to  $y$  eliminates the random variable  $Y$  and yields a probability density for the random variable  $X$  only:

$$p_X(x) \equiv \int p_{XY}(x, y)dy$$

An example of marginal distribution is an *angle-averaged* distribution. Suppose that we have a (joint) probability density function,  $p(r, \theta, \phi)$ , for the three random variables  $r, \theta, \phi$  and that we want to average over  $\theta$  and  $\phi$ . This is done as follows:

$$p(r) \equiv \frac{\int_{-1}^1 \int_0^\pi p(r, \theta, \phi)d(\cos \theta)d\phi}{\int_{-1}^1 \int_0^\pi d(\cos \theta)d\phi} = \frac{1}{4\pi} \int_{-1}^1 \int_0^\pi p(r, \theta, \phi)d(\cos \theta)d\phi$$

where the denominator is added for normalization purposes. The specific case shown in the above equation is the example of *averaging over the unit sphere*.

The need for marginal distribution arises when physical quantities are being averaged away by some process, such as molecular tumbling motion. The end result,  $p(r)$ , contains no information about the angles except the effect of averaging over those angles.

In the next section, we will perform angle-averaging of the intermolecular interactions. This is done because molecular rotations (tumbling) causes the angles to be random functions of time. In experiments, we almost always

measure time-averaged quantities because the measurement times (milliseconds to seconds) are much longer than the molecular rotations (picoseconds or less).

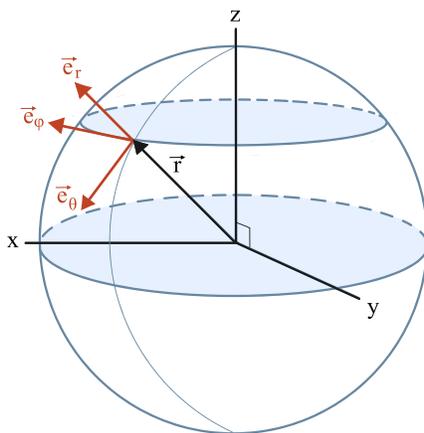
Note: it is the PDF that is averaged over the angles and not the interaction energy itself. In the high-temperature limit, those two operations are identical. At finite temperatures, there is a difference. In the last section below, we will show how the Keesom interaction can be derived by averaging the interaction energy over the angles, but weighted by the Boltzmann factor. Nearly identical results are obtained.

## A.22. Spherical Coordinates

The spherical coordinates are defined by

$$x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta$$

and the unit vectors are shown in Fig. A.2.



**Figure A.2.** Orthogonal frame in spherical coordinates.

The inverse transformation is

$$r = \sqrt{x^2 + y^2 + z^2}, \quad \theta = \cos^{-1} \left( \frac{z}{\sqrt{x^2 + y^2 + z^2}} \right), \quad \phi = \tan^{-1} \left( \frac{y}{x} \right)$$

## A.23. Dirac Delta Function

The Dirac delta can be loosely thought of as a function on the real line which is zero everywhere except at the origin, where it is infinite,

$$\delta(x) = \begin{cases} +\infty, & x = 0 \\ 0, & x \neq 0 \end{cases}$$

and which is also constrained to satisfy the identity

$$\int_{-\infty}^{\infty} \delta(x) dx = 1.$$

This is not a rigorous mathematical definition, but it will be enough for our purpose later in Section A.24.2, where it will be used to express the initial condition to the diffusion equation whereby at time  $t = 0$  *all* molecules are at  $x = 0$  and nowhere else.

The Dirac delta function has another purpose, namely, to extract the value of a function at some point  $a$  under the integral sign:

$$\int_{-\infty}^{\infty} f(x)\delta(x - a) dx = f(a).$$

This is called the “sifting property” of the Dirac delta function.

You can also think of it as a sharply peaked Gaussian density:

$$\delta(x) = \lim_{\sigma \rightarrow 0} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}}.$$

There are many other representations of the Dirac delta function.

In 3D the Dirac delta function has the meaning  $\delta(\mathbf{x}) = \delta(x)\delta(y)\delta(z)$ .

## A.24. Integration Over a Sphere

Suppose that you are asked to average a function over the unit sphere. We simply integrate over the solid angle  $d\Omega = \sin\theta d\theta d\phi$ . This is equivalent to setting  $r = 1$  in the volume integral in spherical coordinates and omitting the  $dr$  integration (which is equivalent to adding a Dirac delta function  $\delta(r - 1)$  in the integrand). The area element in spherical coordinates is shown in Fig. A.3.

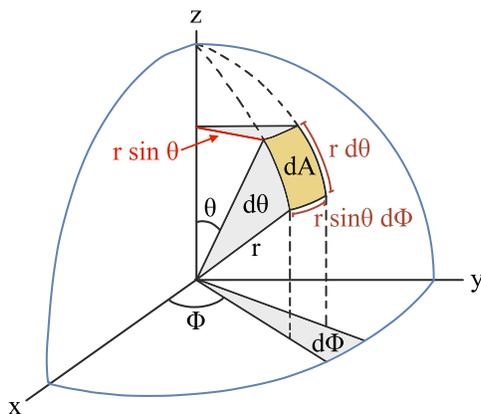


Figure A.3. Area element in spherical coordinates.

**A.24.1. Change of Variables Formula.** Suppose that  $x$ ,  $y$  and  $z$  are expressed in terms of new coordinates  $u, v, w$ . The volume integral

$$\int_R f(x, y, z) dx dy dz$$

of the function  $f$  over the region  $R$  is also equal to

$$\int_R f(x(u, v, w), y(u, v, w), z(u, v, w)) \left| \frac{\partial(x, y, z)}{\partial(u, v, w)} \right| du dv dw$$

where  $u, v, w$  is a parametrization of the region  $R$ . The integral is still computed over the region  $R$ , except that the limits of integration are specified in the  $u, v, z$  coordinates.  $\left| \frac{\partial(x, y, z)}{\partial(u, v, w)} \right|$  is the Jacobian of the transformation, which is computed from the determinant:

$$\left| \frac{\partial(x, y, z)}{\partial(u, v, w)} \right| = \begin{vmatrix} x_u & x_v & x_w \\ y_u & y_v & y_w \\ z_u & z_v & z_w \end{vmatrix}$$

where  $x_u$  denotes the partial of  $x$  with respect to  $u$ , i.e.  $x_u = \frac{\partial x}{\partial u}$ , etc.

You can check that in spherical coordinates the Jacobian is  $r^2 \sin \theta$ . Thus, the volume element

$$dV = dx dy dz = r^2 \sin \theta dr d\theta d\phi.$$

i.e. compute the determinant:

$$\begin{vmatrix} x_r & x_\theta & x_\phi \\ y_r & y_\theta & y_\phi \\ z_r & z_\theta & z_\phi \end{vmatrix} = \begin{vmatrix} \sin \theta \cos \phi & -r \sin \theta \sin \phi & r \cos \theta \cos \phi \\ \sin \theta \sin \phi & r \sin \theta \cos \phi & r \cos \theta \sin \phi \\ \cos \theta & 0 & -r \sin \theta \end{vmatrix}$$

**A.24.2. Exercise: the 3D case.** Using Taylor expansions in multiple variables, we can extend the analysis from the previous section and show that the diffusion equation in 3D is of the form:

$$\frac{\partial c}{\partial t} = D \nabla^2 c(\mathbf{x}, t),$$

where  $c = c(\mathbf{x}, t)$ ,  $\mathbf{x} = (x, y, z)$  is a vector and  $\nabla^2$  is the Laplacian, i.e.  $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ . Find the solution to this diffusion equation in 3D for similar initial conditions, i.e.  $c(\mathbf{x}, 0) = n\delta(\mathbf{x})$ . Show that the mean-square displacement in 3D is  $6Dt$  (c.f.  $2Dt$  in 1D).

**A.24.3. Exercise: Mean-Square Displacement.** The mean-square displacement is defined as  $\mathbb{E}(X^2)$ . Using the definition of average this means solve  $\mathbb{E}(X^2) = \int_{\mathbb{R}} x^2 p(x, t) dx$ . Calculate this average using the probability density we found when solving the diffusion equation:

$$p(x, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}$$

where  $\int_{\mathbb{R}} p(x, t) dx = 1$ . Show that  $\mathbb{E}(x^2) = 2Dt$ . Note: the reason we don't use  $\mathbb{E}X = 0$  is that it's equal to zero and therefore trivial.

**A.24.4. Exercise: Solution for Arbitrary Initial Conditions.** When solving the diffusion equation we assumed that the concentration at time zero, was proportional to  $\delta(x)$ . This led to the following result:

$$p(x, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}.$$

Suppose instead that we have the initial condition  $c(x, 0) = g(x)$ . Show that the solution would be a convolution:

$$c(x, t) = \int_{\mathbb{R}} p(x - y, t) g(y) dy.$$

In 3D this would be of the form:

$$c(\mathbf{x}, t) = \int_{\mathbb{R}^3} p(\mathbf{x} - \mathbf{y}, t) g(\mathbf{y}) d^3\mathbf{y},$$

where  $d^3\mathbf{y} = dy_1 dy_2 dy_3$  is a volume element.

## A.25. Gradient

The gradient of a function of three variable  $f(x, y, z)$  is defined in Cartesian coordinates as the vector

$$\nabla f = \frac{\partial f}{\partial x} \hat{\mathbf{x}} + \frac{\partial f}{\partial y} \hat{\mathbf{y}} + \frac{\partial f}{\partial z} \hat{\mathbf{z}}.$$

In spherical coordinates (using the “physics convention” for the angles  $\theta, \varphi$  shown in Fig. A.4), the gradient is

$$\nabla f = \frac{\partial f}{\partial r} \hat{\mathbf{r}} + \frac{1}{r} \frac{\partial f}{\partial \theta} \hat{\boldsymbol{\theta}} + \frac{1}{r \sin \theta} \frac{\partial f}{\partial \varphi} \hat{\boldsymbol{\varphi}}.$$

For a function, such as  $V(r)$ , that depends only on  $r$ , then only the first term matters:

$$\nabla V(r) = \frac{\partial V}{\partial r} \hat{\mathbf{r}}.$$

## A.26. Legendre Transformation

The Legendre transformation is central to the structure of thermodynamics and classical mechanics. In classical mechanics it establishes the correspondence between Lagrangian and Hamiltonian mechanics. Here we follow the presentation of Arnold's outstanding book [28]. In thermodynamics it is used for two purposes. The first is to change the “natural variables” to a more convenient set of variables. The natural variables are the independent variables that can be controlled in the laboratory. The precise set of natural variables one should use is a choice that depends on the application.

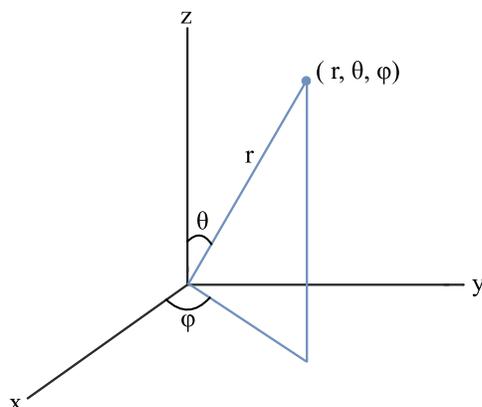


Figure A.4. Spherical coordinates.

The second purpose is the statement of thermodynamic equilibrium. The second law says entropy should be maximized. However, this can also be shown to mean that energy is minimized, as we will explain below. Legendre transforms can be used to transform nonlinear partial differential equations (PDEs) into linear ones, for which known methods can be used to solve them.

The Legendre transformation of  $f(x)$  is the function  $f^*(p)$  defined by

$$f^*(p) = \max_x \{px - f(x)\}.$$

In the case of multiple variables,  $\vec{x}$  and  $\vec{p}$  are vectors and the definition is:

$$f^*(\vec{p}) = \max_x \{\vec{p} \cdot \vec{x} - f(\vec{x})\}.$$

**A.26.1. How to Obtain the Legendre Transform. (Definition)** Let  $y = f(x)$  be a convex function,  $f''(x) > 0$ . The Legendre transformation of the function  $f$  is a new function  $g$  of a new variable  $p$ , which is constructed in the following way (Fig. A.5).

- We draw the graph of  $f$  in the  $x, y$  plane.
- Let  $p$  be a given number.
- Consider the straight line  $y = px$ .
- We take the point  $x = x(p)$  at which the curve is farthest from the straight line in the vertical direction: for each  $p$  the function  $px - f(x) = F(p, x)$  has a maximum with respect to  $x$  at the point  $x(p)$ .
- Now we define the function  $g(p) = F(p, x(p))$  and call it the *Legendre transformation of  $f$* , which is basically  $F$  but in which we have substituted  $x = x(p)$  ( $x$  as a function of  $p$ ).

- The point  $x(p)$  is obtained by solving for  $x$  in the expression obtained from the extremal condition  $\partial F/\partial x = 0$ , i.e.  $f'(x) = p$ . Since  $f$  is convex, the point  $x(p)$  is unique (if it exists).

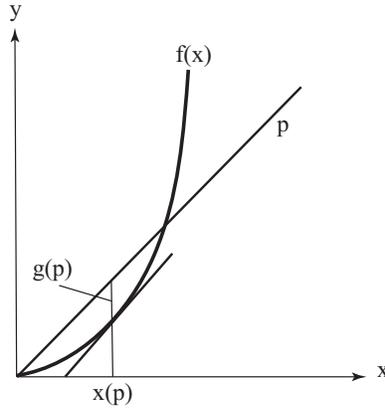


Figure A.5. Legendre transformation.

Example. Let  $f(x) = x^2$ . Then  $F(p, x) = px - x^2$ ,  $x(p) = (1/2)p$ ,  $g(p) = (1/4)p^2$ .

Example. Let  $f(\dot{x}) = m\dot{x}^2/2$ . Then  $g(p) = p^2/2m$ . This can be seen as follows:

$$F(p, \dot{x}) = \dot{x}p - f(\dot{x})$$

$$F_{\dot{x}} = 0 = p - f'(\dot{x}) \implies p = f'(\dot{x}) = m\dot{x} \implies \dot{x}(p) = \frac{p}{m}$$

$$g(p) = F(p, \dot{x}(p)) = \frac{p^2}{m} - \frac{p^2}{2m} \implies g(p) = \frac{p^2}{2m}.$$

Example. Let  $f(x) = x^\alpha/\alpha$ . Then  $g(p) = p^\beta/\beta$ , where  $(1/\alpha) + (1/\beta) = 1$  ( $\alpha > 1, \beta > 1$ ).

This can be seen as follows:

$$F(x, p) = xp - \frac{x^\alpha}{\alpha}$$

$$F_x = 0 \implies p = \frac{\alpha x^{\alpha-1}}{\alpha} = x^{\alpha-1} \implies x(p) = p^{\frac{1}{\alpha-1}}$$

$$g(p) = p \cdot p^{\frac{1}{\alpha-1}} - \frac{p^{\frac{\alpha}{\alpha-1}}}{\alpha} = p^{\frac{\alpha}{\alpha-1}} \left( \frac{\alpha-1}{\alpha} \right) = p^\beta \beta$$

where  $\beta = \frac{\alpha}{\alpha-1}$  or  $(1/\beta) + (1/\alpha) = 1$ .

Example. Let  $f(x)$  be a convex polygon. Then  $g(p)$  is also a convex polygon, in which the vertices of  $f(x)$  correspond to the edges of  $g(p)$ , and the edges of  $f(x)$  to the vertices of  $g(p)$ . For example, the corner depicted in Fig. A.6 is transformed to a line segment under the Legendre transformation.

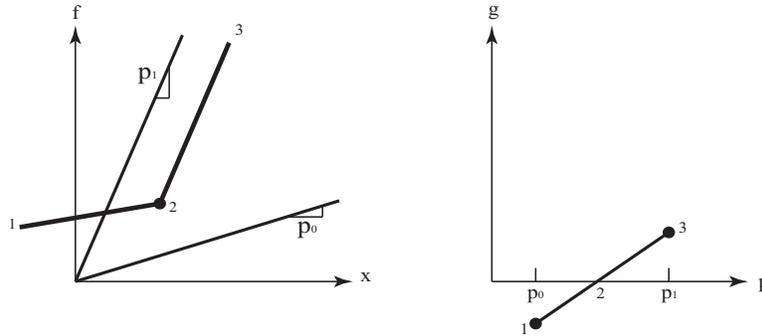


Figure A.6. Legendre transformation taking an angle to a line segment.

**A.26.2. Cyclic Property of Partial Derivatives.** In order to establish the energy minimization principle (see Section A.27) we also need to introduce the cyclic property of partial derivatives. Suppose that we have a constraint<sup>7</sup> of the form  $F(x, y, z) = 0$  then  $x$ ,  $y$  and  $z$  depend on each other. Then we can write:

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

Substitution of the first equation into the second one gives:

$$\begin{aligned} dz &= \left(\frac{\partial z}{\partial x}\right)_y \left[ \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \right] + \left(\frac{\partial z}{\partial y}\right)_x dy \\ &= \left[ \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x \right] dy + \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y dz. \end{aligned}$$

Rearranging gives:

$$\left[ 1 - \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y \right] dz = \left[ \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x \right] dy.$$

Because  $dz$  and  $dy$  are arbitrary variations, their coefficients must vanish for this equation to hold in the general case. Setting the first term equal to zero gives the reciprocal relation of partial derivatives:

$$\boxed{\left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{\left(\frac{\partial x}{\partial z}\right)_y}}.$$

<sup>7</sup>For example, the constraint  $x^2 + y^2 + z^2 - 1 = 0$  defines a sphere.

Setting the second term equal to zero, and applying the reciprocal relation in order to replace  $\left(\frac{\partial x}{\partial y}\right)_z$  by  $\left(\frac{\partial y}{\partial x}\right)_z$ , gives

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

### A.27. Maximizing Entropy vs Minimizing Energy

The second law says that for isolated systems the entropy is a nondecreasing function that reaches a maximum value at equilibrium. The total energy of the system is  $U(S, X)$ , where  $X$  denotes any set of extensive variables (e.g.  $V, N_i$ , etc.). Using the inverse function theorem of calculus, we can solve for  $S$  in terms of  $U$  and get  $S(U, X)$ . “Maximum” entropy ( $dS \geq 0$ ) means that:

$$\left(\frac{\partial S}{\partial X}\right)_U = 0 \quad \text{and} \quad \left(\frac{\partial^2 S}{\partial X^2}\right)_U < 0 \quad \text{at equilibrium}$$

From calculus we have that

$$\left(\frac{\partial U}{\partial X}\right)_S = -\frac{\left(\frac{\partial S}{\partial X}\right)_U}{\left(\frac{\partial S}{\partial U}\right)_X} = -T \left(\frac{\partial S}{\partial X}\right)_U = 0.$$

Thus, the energy is at an extremum at equilibrium. We can also show that  $\left(\frac{\partial^2 U}{\partial X^2}\right)_S = -T \left(\frac{\partial^2 S}{\partial X^2}\right)_U$ .

In terms of the Helmholtz potential,  $A(T, V, N_i) = U - TS$ , we start from  $U$  and replace  $S$  by  $T$ . The transformation is:

$$\boxed{\tilde{A}(T, V, N_i) = \max_S \{U(S, V, N_i) - TS\},}$$

where max is the maximum over all possible  $S$ . We write  $\tilde{A}$  to indicate that  $A$  was obtained by maximization. This maximum will be reached whenever  $T$  is equal to the temperature  $\partial_S U$ , i.e.,  $T = \left(\frac{\partial U}{\partial S}\right)_{V, N_i}$ . The particular choice of  $S$  that fulfills the condition  $T = \left(\frac{\partial U}{\partial S}\right)_{V, N_i}$  is denoted  $S(T)$ . The transform is written as:

$$\tilde{A}(T, V, N_i) = U - TS$$

where  $S$  is understood to stand for  $S(T)$  obtained from the condition  $T = \left(\frac{\partial U}{\partial S}\right)_{V, N_i}$ . We will furthermore denote  $S$  by  $\tilde{S}$ , to indicate that  $S$  is the value of the entropy at equilibrium. If we combine this with the fact that

at equilibrium, the internal energy is minimized

$$\boxed{\tilde{U}(\tilde{S}) = \min_X(U(\tilde{S}, X))},$$

we may write the Helmholtz potential as:

$$\tilde{A} = \max_S \left\{ \min_X(U(S, X)) - TS \right\} = \min_X \left\{ \max_S(U(S, X) - TS) \right\},$$

where in the second equality we have interchanged the order of the min and max. But the bracketed term is simply  $\tilde{A}(T, X)$ . Thus, we conclude that

$$\boxed{\tilde{A} = \min_X(\tilde{A}(T, X))}$$

and the Helmholtz free energy is minimized at equilibrium.

Likewise, for the enthalpy

$$H(S, P) = U + PV$$

we have

$$\tilde{H} = \max_V \left\{ \min_X(U(V, X)) + PV \right\} = \min_X \left\{ \max_V(U(V, X) + PV) \right\},$$

so that

$$\boxed{\tilde{H} = \min_X(\tilde{H}(P, X))}.$$

For the Gibbs free energy we have a double transformation, or equivalently a transformation in two variables where  $V$  is replaced by  $P$  and  $S$  is replaced by  $T$ :

$$G(P, T) = U + PV - TS.$$

Using the formula transformation in two variables:

$$\begin{aligned} \tilde{G} &= \max_{S,V} \left\{ \min_X(U(S, V, X)) + PV - TS \right\} \\ &= \min_X \left\{ \max_{S,V}(U(S, V, X) + PV - TS) \right\}, \end{aligned}$$

we find

$$\boxed{\tilde{G} = \min_X(\tilde{G}(P, T, X))}.$$

Thus, at thermal equilibrium the Gibbs free energy is minimized, the Helmholtz free energy is minimized and the enthalpy is also minimized.

**A.27.1. Legendre Transformation in Classical Mechanics.** In classical mechanics, we begin with the Lagrangian,  $L$ , which is a function of particle position and velocities,  $L \equiv L(q, \dot{q}, t)$ , where  $q$  denotes particle generalized positions and  $\dot{q}$  denotes the generalized velocities:

$$q = (q_x^1, q_y^1, q_z^1, \dots, q_x^N, q_y^N, q_z^N).$$

where  $N$  is the number of particles. Similarly for  $\dot{q}$ , we have a  $3N$ -dimensional vector of generalized velocities. The Lagrange equations of motion are the Euler-Lagrange equations<sup>8</sup>:

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_j} \right) = \frac{\partial L}{\partial q_j}.$$

In general,  $L$  is the difference between kinetic ( $T$ ) and potential ( $V$ ) energies:  $L = T - V$ . For example, a particle with kinetic energy  $T = \frac{1}{2}m\dot{z}^2$  and gravitational potential energy  $V = -mgz$  has Lagrangian  $L = T - V = \frac{1}{2}m\dot{z}^2 + mgz$ . The Euler-Lagrange equations of motion become

$$0 = \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_j} \right) - \frac{\partial L}{\partial q_j} = \frac{d}{dt}(m\dot{z}) - mg = m\ddot{z} - mg,$$

which yields Newton's law ( $F = ma$ ), or more succinctly,  $\ddot{z} = g$ . This equation is second-order in time. Sometimes, equations that are first-order in time may offer certain advantages. This is possible if we define the Hamiltonian as the Legendre transform of the Lagrangian:

$$(A.1) \quad H(p, q, t) = p \cdot \dot{q}(p) - L(q, \dot{q}(p), t),$$

where  $p \cdot \dot{q}$  denotes the dot product of

$$p = (p_x^1, p_y^1, p_z^1, \dots, p_x^N, p_y^N, p_z^N)$$

with

$$\dot{q} = (\dot{q}_x^1, \dot{q}_y^1, \dot{q}_z^1, \dots, \dot{q}_x^N, \dot{q}_y^N, \dot{q}_z^N),$$

<sup>8</sup>These equations are obtained from the principle of least action,  $\delta S = 0$ , where  $S[q(t)] = \int_{t_1}^{t_2} L(q(t), \dot{q}(t), t) dt$ .  $\delta S$  is obtained by perturbing its argument  $q$ :  $\delta S[q(t)] = S[q(t) + \delta q(t)] - S[q(t)]$  and Taylor-expanding the first term. The exact nature of the variation  $\delta q(t)$  is important: here, we consider variations in the path  $\delta q(t)$  where the initial and final points are unchanged:  $\delta q(t_1) = \delta q(t_2) = 0$ . Taylor expanding the functional to first order and integrating by parts,

$$\begin{aligned} \delta S &= \int_{t_1}^{t_2} \delta L(q(t), \dot{q}(t), t) dt = \int_{t_1}^{t_2} \{L((q + \delta q)(t), (\dot{q} + \delta \dot{q})(t), t)\} dt - \int_{t_1}^{t_2} L(q(t), \dot{q}(t), t) dt \\ &= \int_{t_1}^{t_2} \left\{ \overbrace{L(q(t), \dot{q}(t), t)} + \delta q \frac{\partial L}{\partial q} + \delta \dot{q} \frac{\partial L}{\partial \dot{q}} + \dots \right\} dt - \int_{t_1}^{t_2} \overbrace{L(q(t), \dot{q}(t), t)} dt \\ &= \int_{t_1}^{t_2} \left\{ \frac{\partial L}{\partial q} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}} \right\} \delta q(t) dt = 0 \end{aligned}$$

(The surface term from integration by parts vanished due to the boundary condition  $\delta q(t_1) = \delta q(t_2) = 0$ .) Since  $\delta S = 0$  should hold for arbitrary  $\delta q(t)$ , the integrand must vanish, yielding the Euler-Lagrange equation  $\frac{\partial L}{\partial q} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}} = 0$ .

and  $\dot{q}(p)$  denotes the velocity expressed in terms of the momentum. The quantity  $\dot{q}(p)$  is obtained from the equation<sup>9</sup>

$$p = \frac{\partial L}{\partial \dot{q}},$$

which, for the case of a kinetic energy term  $\frac{1}{2}m\dot{z}^2$  yields  $p = m\dot{z}$ , or  $\dot{z}(p) = p/m$ , the usual concept of linear momentum. The equations of motion are obtained by taking the total differential of (A.1):

$$\begin{aligned} \text{(A.2)} \quad dH &= \sum_i \left[ \left( \frac{\partial H}{\partial q_i} \right) dq_i + \left( \frac{\partial H}{\partial p_i} \right) dp_i \right] + \left( \frac{\partial H}{\partial t} \right) dt \\ &= \sum_i \left[ \left( -\frac{\partial L}{\partial q_i} \right) dq_i + \left( \dot{q}_i + p_i \frac{\partial \dot{q}_i}{\partial p_i} - \frac{\partial L}{\partial \dot{q}_i} \frac{\partial \dot{q}_i}{\partial p_i} \right) dp_i \right] - \left( \frac{\partial L}{\partial t} \right) dt \\ &= \sum_i \left[ -\frac{\partial L}{\partial q_i} dq_i + \dot{q}_i dp_i + p_i d\dot{q}_i - \frac{\partial L}{\partial \dot{q}_i} d\dot{q}_i \right] - \left( \frac{\partial L}{\partial t} \right) dt. \end{aligned}$$

Substituting the definition of conjugate momenta,  $p_i = \frac{\partial L}{\partial \dot{q}_i}$ ,

$$\text{(A.3)} \quad dH = \sum_i \left[ \underbrace{-\frac{\partial L}{\partial q_i} dq_i + \dot{q}_i dp_i + p_i d\dot{q}_i - p_i d\dot{q}_i}_{\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_i} \right) = \frac{\partial L}{\partial q_i}} \right] - \left( \frac{\partial L}{\partial t} \right) dt$$

and equating the coefficients of like differentials between (A.3) and (A.2), we get the Hamilton equations of motion which are first-order in time<sup>10</sup>:

$$\boxed{\dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad \dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}.}$$

You can check, for example, that the Lagrangian

$$L(q, \dot{q}) = \sum_i \frac{1}{2} m_i \dot{q}_i^2 - U(q)$$

transforms to the Hamiltonian:

$$H(q, p) = \sum_i \frac{p_i^2}{2m_i} + U(q).$$

The Hamiltonian is a convex function of the momenta, just like the Lagrangian is a convex function of the velocities.

<sup>9</sup>With this definition of the conjugate momenta,  $p_j = \frac{\partial L}{\partial \dot{q}_j}$ , the Euler-Lagrange equation,

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_j} \right) = \frac{\partial L}{\partial q_j}, \text{ reads } \dot{p}_j = \frac{\partial L}{\partial q_j}.$$

<sup>10</sup>These Hamilton equations,  $\dot{p}_i = -\frac{\partial H}{\partial q_i}$ ,  $\dot{q}_i = \frac{\partial H}{\partial p_i}$ ,  $\frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}$ , are to be contrasted with the Lagrangian equations,  $p_j = \frac{\partial L}{\partial \dot{q}_j}$  and  $\dot{p}_j = \frac{\partial L}{\partial q_j}$ .

**A.27.2. Legendre Transformation in Thermodynamics.** We have seen how the Legendre transform preserves convexity and therefore plays a role in energy minimization of thermodynamic potentials at equilibrium. Chemists also use the Legendre transform because it enables us to change the independent variables to a set of variables that is more convenient. Those are called the “natural variables”.

The differential of the internal energy  $U(S, V, N)$  is

$$dU \equiv \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN = TdS - PdV + \mu dN,$$

where

$$T \equiv \left(\frac{\partial U}{\partial S}\right)_{V,N}, \quad P \equiv -\left(\frac{\partial U}{\partial V}\right)_{S,N}, \quad \mu \equiv \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

to the Helmholtz free energy<sup>11</sup>  $A(T, V, N) = U - TS$ ,

$$dA = dU - SdT - TdS = -SdT - PdV + \mu dN.$$

Thus, we have changed the independent variables from  $(S, V, N)$  to  $(T, V, N)$ . This is the case because the expression for  $dA$  contains the differentials  $dT$ ,  $dV$  and  $dN$  whereas  $dU$  contained the differentials  $dS$ ,  $dV$  and  $dN$ . Please note that since we have swapped the variables  $S$  and  $T$  by way of the Legendre transform, the new variable  $T$  is required to be equal to the energy  $\partial_S U$ :

$$T \equiv \left(\frac{\partial U}{\partial S}\right)_{V,N}.$$

(This was the condition for finding the function  $x(p)$  in the formal definition of the Legendre transformation, see pages 1 and 2 of these lecture notes.) Finally, the convexity of the function has been preserved, i.e. the new thermodynamic potential is convex.

There is also the enthalpy  $H(S, P, N) = U + PV$ , whose differential becomes

$$dH = TdS + VdP + \mu dN$$

or to the free enthalpy (Gibbs' potential)  $G(T, P, N) = U - TS + PV$ , whose differential is

$$dG = dU - TdS - SdT + PdV + VdP = -SdT + VdP + \mu dN.$$

A thermodynamic potential is chosen according to which variables are the most convenient to use from an experimental standpoint. For example, if pressure is held constant in an experiment, then  $G$  is the potential of choice. If volume is held constant, then  $A$  is convenient to use.

<sup>11</sup>We note that  $A = U - TS$  differs from the above-defined Legendre transformation by a minus sign. The origins of this sign difference is historical. In spite of this sign difference, the technique is the same.

**A.27.3. Involutivity of the Legendre transformation.** The Legendre transform to be involutive, meaning that applying twice recovers the original function without loss of information. Consider a function  $f$  which is differentiable as many times as necessary, with  $f''(x) > 0$ . It is easy to verify that a Legendre transformation takes convex functions to convex functions. Therefore, we can apply it twice.

**Theorem.** The Legendre transformation is involutive, i.e., its square is the identity: if under the Legendre transformation  $f$  is taken to  $g$ , then the Legendre transform of  $g$  will again be  $f$ .

**Proof.** In order to apply the Legendre transform to  $g$ , with variable  $p$ , we must by definition look at a new independent variable (which we call  $x$ ), construct the function

$$G(x, p) = xp - g(p),$$

and find the point  $p(x)$  at which  $G$  attains its maximum:  $\partial G/\partial p = 0$ , i.e.,  $g'(p) = x$ . Then the Legendre transform of  $g(p)$  will be the function of  $x$  equal to  $G(x, p(x))$ .

We will show that  $G(x, p(x)) = f(x)$ . To this end we notice that  $G(x, p) = xp - g(p)$  has a simple geometric interpretation: it is the ordinate of the point with abscissa  $x$  on the line tangent to the graph of  $f(x)$  with slope  $p$  (Fig. A.7). For fixed  $p$ , the function  $G(x, p)$  is a linear function of  $x$ , with  $\partial G/\partial x = p$ , and for  $x = x(p)$  we have  $G(x, p) = xp - g(p) = f(x)$  by the definition of  $g(p)$ .

Let us now fix  $x = x_0$  and vary  $p$ . Then the values of  $G(x, p)$  will be the ordinates of the points of intersection of the line  $x = x_0$  with the line tangent to the graph of  $f(x)$  with various slopes  $p$ . By the convexity of the graph it follows that all these tangents lie below the curve, and therefore the maximum of  $G(x, p)$  for a fixed  $x(p_0)$  is equal to  $f(x)$  (and is achieved for  $p = p(x_0) = f'(x_0)$ ).

**A.27.4. Inequalities.** By definition of the Legendre transform,  $F(x, p) = px - f(x)$  is less than or equal to  $g(p)$  for any  $x$  and  $p$ . From this we have Young's inequality:

$$px \leq f(x) + g(p).$$

**Example.** If  $f(x) = \frac{1}{2}x^2$ , then  $g(p) = \frac{1}{2}p^2$  and we obtain the well-known inequality  $px \leq \frac{1}{2}x^2 + \frac{1}{2}p^2$  for all  $x$  and  $p$ .

**Example.** If  $f(x) = x^\alpha/\alpha$ ,  $g(p) = p^\beta/\beta$ , where  $(1/\alpha) + (1/\beta) = 1$ , and we obtain Young's inequality  $px \leq (x^\alpha/\alpha) + (p^\beta/\beta)$  for all  $x > 0$ ,  $p > 0$ ,  $\alpha > 1$ ,

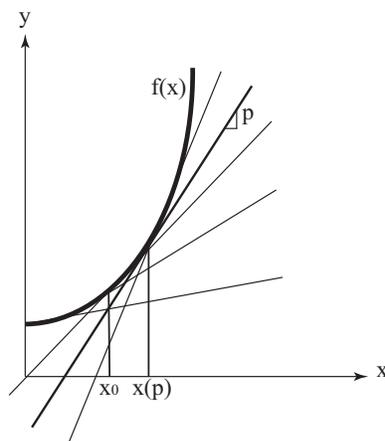


Figure A.7. Involutivity of the Legendre transformation

$\beta > 1$  and  $(1/\alpha) + (1/\beta) = 1$ .

**Example.** Let  $f$  be a quadratic form  $f(x) = \sum f_{ij}x_i x_j$ . The reader can show that its Legendre transform is again a quadratic form  $g(p) = \sum g_{ij}p_i p_j$ , and that the values of both forms at corresponding points coincide:

$$f(x(p)) = g(p) \text{ and } g(p(x)) = f(x).$$

## A.28. Problems

**Problem 135.** You are a member of a club. (a) The club consists of only 50 members. In how many ways can a president, vice president, secretary, and treasurer be chosen (amongst the 50 members)? (b) In how many ways can a committee of 4 members be chosen? (Hint: in the first case, order matters; in the second case, order does not matter.)

**Solution.** (A)  $\frac{50!}{(50-4)!}$ , (B)  $\frac{50!}{46!4!}$  ■

**Problem 136.** Two students are working separately on the same homework problem. If the first student has probability  $\frac{1}{2}$  of solving it and the second student has probability  $\frac{3}{4}$  of solving it (due to higher IQ), what is the probability that at least one of them solves it given that the probability of both of them solving it simultaneously is  $3/8$ ?

**Solution.** For overlapping events,

$$\mathbb{P}(A \text{ or } B) = \mathbb{P}(A) + \mathbb{P}(B) - \mathbb{P}(A \text{ and } B).$$

$$\mathbb{P}(A \text{ or } B) = \frac{1}{2} + \frac{3}{4} - \frac{3}{8}$$

■

**Problem 137.** Find the Taylor series for  $f(x) = \frac{1}{1-x}$  about  $x = 0$ , where  $|x| < 1$ . Explicitly compute all the terms needed to arrive at a general expression for the Taylor series of  $f$  at  $x$ .

**Solution.**

$$\text{First term} \rightarrow f(x=0) = \frac{1}{1-0} = 1$$

$$\text{Second term} \rightarrow \left( \frac{df}{dx} \Big|_{x=0} \right) x = (-1)(1-0)^{-2}(-1)x = x$$

$$\text{Third term} \rightarrow \left( \frac{1}{2!} \right) \left( \frac{d^2f}{dx^2} \Big|_{x=0} \right) x^2 = \left( \frac{1}{2} \right) 2(1-0)^{-3} x^2 = x^2$$

$$\frac{1}{1-x} = 1 + x + x^2 + x^4 + \dots = \sum_{n=0}^{\infty} x^n$$

■

**Problem 138.** The osmotic pressure  $\Pi$  can be described by the function:

$$\Pi(x_2) = -RT \log(1 - x_2)$$

where  $0 < x_2 < 1$  is the mole fraction of the solute,  $R > 0$  is the universal gas constant and  $T > 0$  is the thermodynamic temperature also held at a constant value.

- (a) Write down the Taylor expansion of the function that defines  $\Pi$  at  $x_2 = a$ .  
 (b) Use Taylor series

$$\log(1+x) = x - \frac{x^2}{2} + \frac{x^3}{4} - \frac{x^4}{4} + \frac{x^5}{5} - \dots$$

to prove that when  $x_2 \ll 1$ ,  $\Pi$  is proportional to  $x_2$  at a certain temperature.

**Solution.** (a) Taylor expansion of the function is

$$\begin{aligned} \Pi(x_2) &= -RT \log(1 - x_2) \\ &= RT \left[ \log(1 - a) - \frac{x - a}{1 - a} - \frac{1}{2} \frac{(x - a)^2}{(1 - a)^2} - \frac{1}{3} \frac{(x - a)^3}{(1 - a)^3} - \frac{1}{4} \frac{(x - a)^4}{(1 - a)^4} - \dots \right] \\ &= RT \left[ \log(1 - a) - \sum_{n=1}^{\infty} \frac{1}{n} \left( \frac{x - a}{1 - a} \right)^n \right] \end{aligned}$$

(b) With  $-1 < x \leq 1$ , when  $x_2 \ll 1$ , we can neglect the higher-order terms in the Taylor expansion and using

$$\log(1+x) \approx x$$

we obtain

$$\log(1 - x_2) \approx -x_2$$

and

$$\Pi(x_2) \approx x_2 RT$$

**Problem 139.** In the ground state of the hydrogen atom, the PDF describing the likelihood of finding the electron at  $r$  is:

$$p(r) = \frac{1}{\pi a_0^3} e^{-2r/a_0}$$

where  $a_0$  is Bohr radius. Compute the average potential energy

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

Express the result finally in the units of eV. ( $\epsilon_0 = 8.8542 \times 10^{-12}$  F/m,  $a_0 = 5.2918 \times 10^{-11}$  m,  $e = 1.6022 \times 10^{-19}$  C)

**Solution.**

$$\begin{aligned} \mathbb{E}V &= -\frac{e^2}{4\pi^2\epsilon_0 a_0^3} \int_{r=0}^{\infty} e^{-2r/a_0} \frac{1}{r} 4\pi r^2 dr = -\frac{e^2}{\pi\epsilon_0 a_0^3} \int_{r=0}^{\infty} e^{-2r/a_0} r dr \\ &= -\frac{e^2}{\pi\epsilon_0 a_0^3} \times \frac{a_0^2}{4} = -\frac{e^2}{4\pi\epsilon_0 a_0} = -27.2 \text{ eV} \end{aligned}$$

**Problem 140.** The mean value of a random variable  $X$  taking values in discrete space can be calculated from the weighted sum:

$$\mathbb{E}X = \sum_{i=1}^N \mathbb{P}(X = x_i) x_i$$

where  $x_i$  ranges over all the allowed values of  $X$ , e.g. 1, 2, ..., N, whereas  $\mathbb{P}(X = x)$  is the probability of that  $X$  takes the value  $x$ . Calculate the average of an eight-sided die roll.

**Solution.**  $\mathbb{E}X = \sum_{i=1}^8 (1/8)x_i = (1/8) \times \sum_{i=1}^8 x_i = 36/8 = 4.5$

**Problem 141.** Let  $X$  be a random variable with PDF  $f(x)$ . The mean value of  $X$ , when  $X$  takes continuous (not discrete) values in the range  $(-\infty, \infty)$ , can be calculated by an integral:

$$\mathbb{E}X = \int_{-\infty}^{\infty} f(x)x dx$$

where  $x$  is the value of the random variable  $X$ . Calculate the average position  $X$  of a particle with the following PDF (if it is not normalized, normalize it):

$$f(x) = \begin{cases} x^2 + 4 & -4 < x < 0 \\ x + 4 & 0 < x < 4 \end{cases}$$

**Solution.** First, normalize the probability distribution function (normalization factor of  $A$ ):

$$\begin{aligned}
 1 &= A\left(\int_{-4}^0 x^2 + 4dx + \int_0^4 x + 4dx\right) \\
 1 &= A\left(\frac{x^3}{3} + 4x\Big|_{-4}^0 + \frac{x^2}{2} + 4x\Big|_0^4\right) \\
 1 &= A(64/3 + 16 + 16/2 + 16), \quad 1 = \frac{184A}{3}, \quad A = \frac{3}{184}
 \end{aligned}$$

Now, the average:

$$\begin{aligned}
 \mathbb{E}X &= \frac{3}{184}\left(\int_{-4}^0 x(x^2 + 4)dx + \int_0^4 x(x + 4)dx\right) \\
 \mathbb{E}X &= \frac{3}{184}\left(\int_{-4}^0 x^3 + 4xdx + \int_0^4 x^2 + 4xdx\right) \\
 \mathbb{E}X &= \frac{3}{184}\left(\frac{x^4}{4} + 2x^2\Big|_{-4}^0 + \frac{x^3}{3} + 2x^2\Big|_0^4\right) \\
 \mathbb{E}X &= \frac{3}{184}(-64 - 32 + 64/3 + 32) \\
 \mathbb{E}X &= \frac{3}{184}(-64 - 32 + 64/3 + 32) \\
 \mathbb{E}X &= \frac{-16}{23}
 \end{aligned}$$

■

**Problem 142.** Taylor-expand to low order (just a few terms needed) the Coulomb interaction energy about the point  $R = r_0$ , where  $r_0$  is the molecular radius. In the Coulomb interaction, the fall-off with distance is described by the  $1/R$  dependence (which gets smaller as  $R$  increases). In the Taylor expansion, however, only positive powers of  $R$  occur. Show how the Taylor series describes the fall-off of the interaction energy with distance.

**Solution.** From  $V(R) = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{R}$ , we get, from Taylor expansion about  $r_0$  using the “small parameter”  $R - r_0$ :

$$V(R) = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r_0} - \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r_0^2} (R - r_0) + \frac{2}{4\pi\epsilon_0} \frac{q_1 q_2}{r_0^3} (R - r_0)^2 + \dots$$

The zeroth order term,  $\frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r_0}$  is constant (doesn't change with  $R$ ). As  $R$  increases beyond  $r_0$ ,  $R - r_0$  is positive, but the first order term has an overall negative sign, and this reflects the decrease in interaction energy as the intermolecular distance increases. The second-order term is positive, but its magnitude is smaller than the first-order term. ■

The problems below are related to probability. CDF stands for cumulative distribution function,  $\mathbb{P}(X < x)$ , where  $X$  is a random variable. The CDF related to the PDF,  $p(x)$ , according to  $\mathbb{P}(X < x) = \int_{-\infty}^x p(x)dx$ . (The lower limit may be different from  $-\infty$ ; it is the lowest value that  $X$  is allowed to

take.) The CDF can be used to compute probabilities between two limits, e.g.,  $\mathbb{P}(a < X < b) = \mathbb{P}(X < b) - \mathbb{P}(X < a)$ .

**Problem 143.** Let  $X$  be a continuous random variable with PDF

$$p(x) = \begin{cases} kx^2 & 0 < x < 1 \\ 0 & \text{otherwise} \end{cases}$$

- (i) Determine the value of  $k$  and sketch  $p(x)$
- (ii) Derive a formula for the corresponding CDF. (You can assume that the lower limit of integration for the CDF is 0.) Sketch the CDF.
- (iii) Find  $\mathbb{P}(\frac{1}{4} < X \leq 2)$ .
- (iv) Compute the mean and variance of the random variable  $X$  associated with this PDF.

**Solution.** (i) We must have  $k > 0$ . The normalization condition yields:

$$\int_0^1 kx^2 dx = k \frac{x^3}{3} \Big|_0^1 = \frac{k}{3} = 1$$

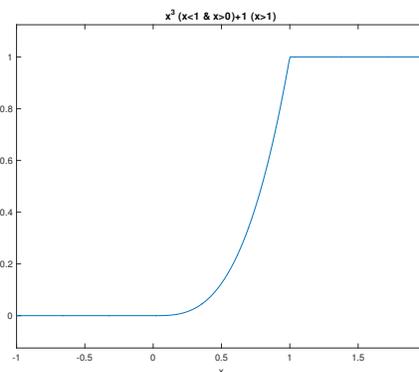
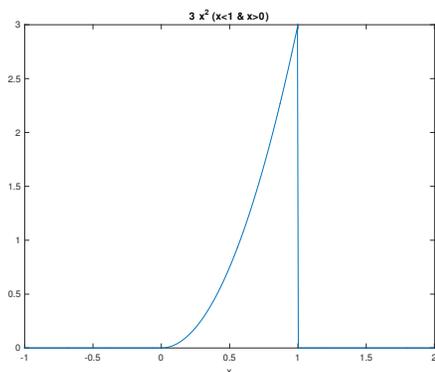
which gives  $k = 3$ . Thus,

$$p(x) = \begin{cases} 3x^2 & 0 < x < 1 \\ 0 & \text{otherwise} \end{cases}$$

(ii) The CDF is

$$\mathbb{P}(X < x) = \begin{cases} 0 & x < 0 \\ \int_0^x 3\xi^2 d\xi = x^3 & 0 \leq x < 1 \\ \int_0^1 3\xi^2 d\xi = 1 & 1 \leq x \end{cases}$$

These functions are sketched below:



(iii)  $\mathbb{P}(\frac{1}{4} < X \leq 2) = \mathbb{P}(X < 2) - \mathbb{P}(X < \frac{1}{4}) = 1 - (\frac{1}{4})^3 = \frac{63}{64}$ . (Note:  $\mathbb{P}(X < 2) = \mathbb{P}(X \leq 2)$  because the distribution function is continuous; so we need not worry about the equal sign.)

(iv) We need to compute:

$$\begin{aligned}\mathbb{E}X &= \int xp(x)dx = \int_0^1 x(3x^2)dx = \frac{3x^4}{4} \Big|_0^1 = 3/4. \\ \mathbb{E}(X^2) &= \int x^2p(x)dx = \int_0^1 x^2(3x^2)dx = \frac{3x^5}{5} \Big|_0^1 = 3/5.\end{aligned}$$

Variance is

$$\mathbb{E}(X^2) - (\mathbb{E}X)^2 = 3/5 - (3/4)^2 = 3/80 = 0.0375$$

■

**Problem 144.** The Stefan-Boltzman law says that the power irradiated by a black body is proportional to the fourth power of its temperature:

$$p = cT^4$$

where  $c$  is a constant. This law has been used to measure the temperature of stars in the galaxy. By measuring the light output (power), we can infer the value of  $T$ . Suppose that  $p$  is Gaussian-distributed with mean  $\mu$  and variance  $\sigma^2$ , find the distribution of  $T$ . Obtain both the CDF and PDF. In particular, show that you can obtain the PDF from the CDF and vice-versa.

**Solution.** We need to find an expression for:

$$\mathbb{P}(T < t) = \mathbb{P}((p/c)^{1/4} < t) = \mathbb{P}(p < ct^4)$$

and since  $p$  follows a normal law  $N(\mu, \sigma)$ ,

$$\mathbb{P}(T < t) = \mathbb{P}(p < ct^4) = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{ct^4} e^{-(\zeta-\mu)^2/2\sigma^2} d\zeta = \text{Erf}(ct^4)_{\mu,\sigma}.$$

This is the CDF. The PDF is obtained by differentiating with respect to  $t$ :

$$p_T(t) = \frac{d\mathbb{P}(T < t)}{dt} = \frac{4ct^3}{\sqrt{2\pi\sigma^2}} e^{-(ct^4-\mu)^2/2\sigma^2}$$

We can check that integrating the PDF from  $-\infty$  to  $t$  gives the CDF

$$\begin{aligned}\int_{-\infty}^t p_T(\tau) d\tau &= \int_{-\infty}^t \frac{4c\tau^3}{\sqrt{2\pi\sigma^2}} e^{-(c\tau^4-\mu)^2/2\sigma^2} d\tau \\ &= \int_{-\infty}^{ct^4} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(\xi-\mu)^2/2\sigma^2} d\xi = \mathbb{P}(p < ct^4) = \mathbb{P}(T < t).\end{aligned}$$

In the second equality we made a change of variables  $\xi = c\tau^4$ ,  $d\xi = 4c\tau^3 d\tau$ .

■

**Problem 145.** Suppose that we have

$$F(t) = A \cos(\omega t)$$

where  $\omega$  is a normal random variable with mean  $\omega_0$  and variance  $\Delta\omega^2$ . Find the properties of the random variable  $F$ , i.e. derive the PDF, CDF, its mean and standard deviation (or variance).

**Solution.** We note that  $\omega = t^{-1} \cos^{-1}(F/A)$ . Then,

$$\begin{aligned} \mathbb{P}(F < f) &= \mathbb{P}(\omega < t^{-1} \cos^{-1}(f/A)) \\ &= \int_{-\infty}^{t^{-1} \cos^{-1}(f/A)} \frac{1}{\sqrt{2\pi\Delta\omega^2}} e^{-(w-\omega_0)^2/2\Delta\omega^2} dw. \end{aligned}$$

The PDF is obtained by differentiating the CDF with respect to  $f$ :

$$\begin{aligned} p_F(f) &= \frac{d\mathbb{P}(F < f)}{df} = \frac{1}{\sqrt{2\pi\Delta\omega^2}} e^{-(t^{-1} \cos^{-1}(f/A) - \omega_0)^2/2\Delta\omega^2} \cdot \frac{d}{df} t^{-1} \cos^{-1}(f/A) \\ &= -\frac{t^{-1}}{\sqrt{2\pi\Delta\omega^2}} e^{-(t^{-1} \cos^{-1}(f/A) - \omega_0)^2/2\Delta\omega^2} \cdot \frac{1}{\sqrt{1 - f^2/A^2}} \cdot \frac{1}{A}. \end{aligned}$$

■

**Problem 146.** Let the PDF of a continuous r.v.  $X$  be given by:

$$p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\mu)^2/(2\sigma^2)}$$

Prove, via direct calculation of the integrals, that the mean and variance of  $X$  are:  $\mathbb{E}X = \mu$  and  $\text{var}(X) = \sigma^2$ .

**Solution.** The mean is

$$\mathbb{E}X = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} x e^{-(x-\mu)^2/(2\sigma^2)} dx$$

Writing  $x$  as  $(x - \mu) + \mu$ , we have

$$\mathbb{E}X = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} (x - \mu) e^{-(x-\mu)^2/(2\sigma^2)} dx + \mu \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} e^{-(x-\mu)^2/(2\sigma^2)} dx$$

Letting  $y = x - \mu$  in the first integral we obtain

$$\mathbb{E}X = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} y e^{-y^2/(2\sigma^2)} dy + \mu \int_{-\infty}^{\infty} p(x) dx$$

The first integral is zero since the integrand is an odd function. In the second integral, we used the normalization condition ( $\int p(x) dx = 1$ ). Thus,

$$\mathbb{E}X = \mu$$

Now for the variance:

$$\text{var}(X) = \mathbb{E}(X - \mu)^2 = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} (x - \mu)^2 e^{-(x-\mu)^2/(2\sigma^2)} dx$$

We note that

$$\int_{-\infty}^{\infty} e^{-(x-\mu)^2/(2\sigma^2)} dx = \sigma\sqrt{2\pi}.$$

Differentiating with respect to  $\sigma$ , we obtain:

$$\int_{-\infty}^{\infty} \frac{(x-\mu)^2}{\sigma^3} e^{-(x-\mu)^2/(2\sigma^2)} dx = \sqrt{2\pi}.$$

Multiplying both sides by  $\sigma^2/\sqrt{2\pi}$ , we have

$$\frac{1}{\sqrt{2\pi}\sigma^2} \int_{-\infty}^{\infty} (x-\mu)^2 e^{-(x-\mu)^2/(2\sigma^2)} dx = \sigma^2$$

Thus,

$$\text{var}(X) = \sigma^2$$

■

**Problem 147.** Let  $Y = Ae^X + B$ . (a) Find the distribution of  $Y$  when  $X$  is a uniform r.v. over the interval  $(0,1)$ , i.e. its density takes the value 1 over the interval and 0 elsewhere.

(b) Find the distribution of  $Y$  when  $X$  follows a normal law with mean  $\mu$  and variance  $\sigma^2$ .

**Solution.** The PDF of  $X$ , as stated in the problem, is:

$$p_X(x) = \begin{cases} 1 & 0 < x < 1 \\ 0 & \text{otherwise} \end{cases}$$

From the definition of a CDF,  $\mathbb{P}(Y < y) = \int_{-\infty}^y p(y)dy$ , and differentiating it with respect to  $y$ , we get that  $p(y) = (d/dy)\mathbb{P}(Y < y)$ . Next, we need to know  $\mathbb{P}(Y < y)$ . The CDF of  $Y$  is (for  $A + B < y < Ae + B$ )

$$\begin{aligned} \mathbb{P}(Y < y) &= \mathbb{P}(Ae^X + B < y) = \mathbb{P}(X < \log A^{-1}(y-B)) = \int_{-\infty}^{\log A^{-1}(y-B)} p_X(x)dx \\ &= \int_0^{\log A^{-1}(y-B)} dx = \log A^{-1}(y-B) \end{aligned}$$

To get the PDF of  $Y$  we differentiate the CDF with respect to  $y$ :

$$p_Y(y) = \frac{d\mathbb{P}(Y < y)}{dy} = \frac{d}{dy} \log A^{-1}(y-B) = \frac{A^{-1}}{A^{-1}(y-B)} = \frac{1}{y-B}$$

for  $A + B < y < Ae + B$  and 0 otherwise.

From the definition of a CDF,  $\mathbb{P}(Y < y) = \int_{-\infty}^y p(y)dy$ , and differentiating it with respect to  $y$ , we get that  $p(y) = (d/dy)\mathbb{P}(Y < y)$ . Next, we need to know  $\mathbb{P}(Y < y)$ . Since  $Y = Ae^X + B$ , the probability

$$\begin{aligned} \mathbb{P}(Y < y) &= \mathbb{P}(Ae^X + B < y) = \mathbb{P}(Ae^X < y - B) = \mathbb{P}(e^X < (y - B)/A) \\ &= \mathbb{P}(X < \log[(y - B)/A]) \end{aligned}$$

And because  $X$  follows a normal law with mean  $\mu$  and variance  $\sigma^2$ ,

$$\mathbb{P}(Y < y) = \int_{-\infty}^{\log[(y-B)/A]} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\mu)^2/2\sigma^2} dx$$

From this, we have:

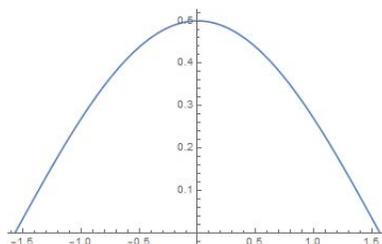
$$\begin{aligned} \frac{d\mathbb{P}(Y < y)}{dy} &= \frac{d}{dy} \int_{-\infty}^{\log[(y-B)/A]} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\mu)^2/2\sigma^2} dx \\ &= \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(\log[(y-B)/A]-\mu)^2/2\sigma^2} \cdot \frac{1}{(y-B)} \end{aligned}$$

where we made use of the formula for differentiation of an integral (only term 2 applies, the other two are zero):

$$\frac{d}{dy} \left( \int_{a(y)}^{b(y)} f(x, y) dx \right) = \underbrace{\int_{a(y)}^{b(y)} \frac{\partial}{\partial y} f(x, y) dx}_1 + \underbrace{f(b(y), y) \cdot b'(y)}_2 - \underbrace{f(a(y), y) \cdot a'(y)}_3$$

■

**Problem 148.** Normalize the probability function given by  $f(x) = \cos(x)$  so that it becomes a probability *density* function  $p(x)$  (shown below) over the interval  $[-\pi/2, \pi/2]$ . What is the normalization constant? Calculate the mean (expectation value) and standard deviation  $\sigma$  of a random variable  $X$  defined in the interval  $[-\pi/2, \pi/2]$ , i.e. calculate  $\mathbb{E}X = \int_{-\pi/2}^{\pi/2} xp(x)dx$  and the square root of the variance,  $\sigma^2 = \text{var}(X) = \int_{-\pi/2}^{\pi/2} (x - \mathbb{E}X)^2 p(x)dx$ . (Note: I write  $X$  for the random variable, and  $x$  for its numerical value.)



**Solution.** A PDF is said to be normalized if it can be described by the following relationship

$$\int f(x)dx = 1.$$

The integral is calculated over all space where  $X$  takes its values. For example,  $X$  could be defined over the interval  $[-\infty, \infty]$ , or  $[-\pi/2, \pi/2]$ . Solving for the normalization constant,  $C$

$$\int_{-\pi/2}^{\pi/2} C \cos(x)dx = 1, \quad C = 1/2.$$

The mean value,  $\mathbb{E}X$  is

$$\mathbb{E}X = \int_{\mathbb{R}} xp(x)dx$$

If  $p(x) = (1/2)\cos(x)$  then  $\mathbb{E}X$  is zero, since  $x$  is odd and  $\cos(x)$  is even:

$$\mathbb{E}X = \int_{-\pi/2}^{\pi/2} x(1/2)\cos(x)dx = \cos(x) + x\sin(x) \Big|_{-\pi/2}^{\pi/2} (1/2) = 0$$

The standard deviation  $\sigma$  is the square root of the variance  $\sigma^2$

$$\begin{aligned} \sigma^2 &= \int_{\mathbb{V}} p(x)(x - \mathbb{E}X)^2 dx = \int_{-\pi/2}^{\pi/2} \frac{1}{2} \cos(x)x^2 dx \\ &= \frac{1}{2} (2x \cos(x) + (-2 + x^2) \sin(x)) \Big|_{-\pi/2}^{\pi/2} = 0.4674 \\ \sigma &= \sqrt{0.4674} = 0.6837 \end{aligned}$$

■

**Problem 149.** This problem may be helpful to those who need practice doing Taylor expansions. Consider a function,  $f(x)$ , that is infinitely differentiable at a point  $x_0$  (i.e. a “nice” function). The Taylor expansion of this function for points  $x$  centered around the point  $x_0$  is given by

$$\sum_{n=0}^{\infty} f^{(n)}(x_0) \frac{(x - x_0)^n}{n!}$$

where  $f^{(n)}(x_0)$  is the  $n^{\text{th}}$  derivative of  $f(x)$  at  $x = x_0$ . Consider the function  $f(x) = \exp(x)$ . The Taylor expansion,  $T(x)$ , of  $\exp(x)$  for  $x$  near  $x_0 = 2$  is

$$\begin{aligned} T(x) &= f(x_0) + f^{(1)}(x_0)(x - x_0) + f^{(2)}(x_0) \frac{(x - x_0)^2}{2!} + \dots \\ &= \exp(2) + \exp(2)(x - 2) + \exp(2) \frac{(x - 2)^2}{2!} + \dots \end{aligned}$$

Let  $T_n(x)$  denote the Taylor expansion truncated at the  $n$ -th term:

$$T_n(x) = f(x_0) + f^{(1)}(x_0)(x - x_0) + \dots + f^{(n)}(x_0) \frac{(x - x_0)^n}{n!}.$$

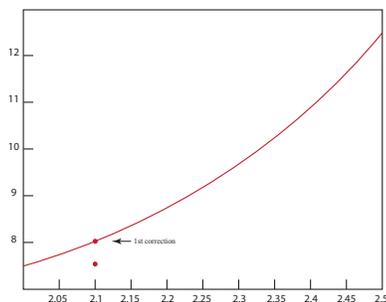
Notice that when  $x = x_0$ , all terms after the first go to zero because  $x - x_0 = 0$  which then gives  $T(x) = f(x_0)$ . When  $x \neq x_0$  and near  $x_0$ , the second term  $f^{(1)}(x_0)(x - x_0)$  acts as a linear approximation. Subsequent terms act as correction terms that bring  $T_n(x)$  progressively close to  $f(x)$  as  $n$  increases.

(a) Check graphically that the second term in  $T(x)$  acts as a linear approximation of  $f(x)$  for  $x \neq x_0$  and near to  $x_0$ . Plot  $f(x) = \exp(x)$  for  $x = [2, 2.5]$  then plot  $T(x = 2)$  and the first two terms of  $T(x = 2.1)$  for  $x_0 = 2$ .

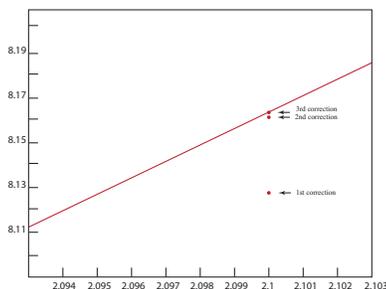
(b) Let's add more terms to  $T_n(x = 2.1)$  and look at its limiting behavior. Plot  $T_n(x = 2.1)$  keeping the first three terms (i.e.  $n = 2$ ), then repeat for the first four terms ( $n = 3$ ). You should see that adding more terms brings  $T_n(x = 2.1)$  closer to  $f(x = 2.1) = \exp(2.1)$ .

For any  $\epsilon > 0$  and  $x$  we can show that  $|T_n(x) - f(x)| < \epsilon$  for large enough  $n$  (this is called point-wise convergence, i.e. convergence at any  $x$ ). One can also show that the Taylor expansion is unique.

**Solution.** (a) The arrow for “1<sup>st</sup> correction” is  $T_1(x = 2.1)$



(b) Here the graph is zoomed in such that  $T_2(2.1)$  and  $T_3(2.1)$  do not overlap



**Problem 150.** Taylor expansions are often used as approximations to  $f(x)$  when  $x$  is near the point of expansion  $x_0$ . The farther  $x$  is from  $x_0$  the more terms we need for a good approximation. Here is some practice for you; these functions are found in chemistry:

- Taylor expand  $f(T) = \log(T/\tau)$  as  $T \rightarrow \tau$  where  $\tau$  is a reference temperature to make  $T/\tau$  dimensionless.
- Taylor expand  $f(x) = (1 - x^2)^{-1}$  as  $x \rightarrow 0$ .
- Taylor expand  $f(T) = \exp(-T^{-1})$  as  $T \rightarrow \infty$ .
- Taylor expand  $f(x) = \sqrt{1 - x}$  as  $x \rightarrow 0$ .

**Solution.** (a) Let's do a change of variables where  $c = \frac{T}{\tau} - 1$ . As  $T \rightarrow \tau$ ,  $c \rightarrow 0$ . Then

$$f(T) = f(c) = \log(c + 1)$$

$$f(0) = \log(1) = 0$$

$$f^{(1)}(0) = 1$$

By taking successive derivatives, we arrive at

$$f(c) = c - \frac{c^2}{2} + \frac{c^3}{3} + \dots$$

$$f(T) = \left(\frac{T}{\tau} - 1\right) - \frac{\left(\frac{T}{\tau} - 1\right)^2}{2} + \frac{\left(\frac{T}{\tau} - 1\right)^3}{3} + \dots$$

(b) Recall the sum of a geometric series for  $|r| < 1$

$$\sum_n^{\infty} r^n = \frac{1}{1-r}$$

We can fit the given function,  $f(x) = (1 - x^2)^{-1}$  into the above equation by change of variables where  $c = x^2$ . For  $|c| < 1$ , the geometric series  $\frac{1}{1-c} = \sum_{n=0}^{\infty} c^n$

$$\frac{1}{1-c} = 1 + c + c^2 + \dots$$

with  $c = x^2$  leads to:

$$f(x) = 1 + x^2 + x^4 + \dots$$

A Taylor expansion is a polynomial expansion and is unique for a given function. Therefore,  $f(x) = 1 + x^2 + x^4 + \dots$  is the Taylor expansion of  $\frac{1}{1-x^2}$ .

(c) Let  $-T^{-1} = c$

$$f(T) = f(c) = \exp(c)$$

$$\exp(c) = 1 + c + \frac{c^2}{2!} + \frac{c^3}{3!} + \dots$$

$$f(T) = 1 - \frac{1}{T} + \frac{1}{2!T^2} - \frac{1}{3!T^3} + \dots$$

(d) Let's take the first few derivatives

$$f^{(1)}(x) = -\frac{1}{2}(1-x)^{-1/2}$$

$$f^{(2)}(x) = -\left(\frac{1}{2}\right)^2 (1-x)^{-3/2}$$

$$f^{(3)}(x) = -3\left(\frac{1}{2}\right)^3 (1-x)^{-5/2}$$

$$f^{(4)}(x) = -5 \times 3\left(\frac{1}{2}\right)^4 (1-x)^{-7/2}$$

$$f^{(n)}(x) = -|2n-3|!! \left(\frac{1}{2}\right)^n (1-x)^{-(2n-3)/2}$$

where  $m!! = m \times (m - 2) \times (m - 4) \times \cdots \times 1$  for  $m$  odd.

$$f(x) = 1 - \frac{x}{2} - \frac{x^2}{8} - \frac{x^3}{16} - \cdots$$

■

**Problem 151.** The triple product rule, also known as the cyclic relation, is a formula commonly found in thermodynamics. If a function of three variables can be expressed as  $f(x, y, z) = 0$ , then each variable can be expressed as a function of the remaining two variables. Show that,

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

where  $\left(\frac{\partial x}{\partial y}\right)_z$  denotes the derivative of the function  $x(y, z)$  with respect to  $y$  (holding  $z$  constant), etc. Does the triple product rule hold true for the ideal gas law? Show your work.

**Solution.** Since we have  $f(x, y, z) = 0$  we may solve for  $x$  as a function of  $y$  and  $z$ , and write the total differential of  $x(y, z)$ :

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

Likewise, we may solve for  $y$  as a function of  $x$  and  $z$ . The total differential of  $y(x, z)$  is:

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

Substitute  $dy$  into  $dx$

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

Because  $dx$  and  $dz$  are arbitrary displacements, their coefficients must vanish. Setting the coefficient of  $dx$  to zero gives the reciprocal relationship:

$$(A.4) \quad \left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

Thus, the inverse of a partial derivative is the same as inverting a fraction. Setting the coefficient of  $dz$  to zero:

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

Using a reciprocal relation such as Eq. (A.4) for  $\left(\frac{\partial x}{\partial z}\right)_y$  gives:

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

Take the ideal gas law to be  $p v = k T$  where we take  $v$  used here to be the molar volume and  $k$  is Boltzmann's constant.

$$\left(\frac{\partial p}{\partial v}\right)_T : p + v \frac{\partial p}{\partial v} = 0 \rightarrow \frac{\partial p}{\partial v} = -\frac{p}{v}$$

$$\left(\frac{\partial v}{\partial T}\right)_p : p \frac{\partial v}{\partial T} = k \rightarrow \frac{\partial v}{\partial T} = \frac{k}{p}$$

$$\left(\frac{\partial T}{\partial p}\right)_v : v = k \frac{\partial T}{\partial p} \rightarrow \frac{\partial T}{\partial p} = \frac{v}{k}$$

Now multiply the expressions together to confirm they equal -1

$$\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_v = -\frac{p}{v} \frac{k}{p} \frac{v}{k} = -1$$

■

**Problem 152.** Partial derivatives of a multivariable function are those which are taken for each individual variable while treating the remaining variables as constants. This is more rigorously achieved by taking limits. The definitions of the derivatives of a function  $f$  of three variables  $(x, y, z)$  with respect to each argument are:

$$f_x(x, y, z) = \frac{\partial f(x, y, z)}{\partial x} = \lim_{h \rightarrow 0} \frac{f(x+h, y, z) - f(x, y, z)}{h}$$

$$f_y(x, y, z) = \frac{\partial f(x, y, z)}{\partial y} = \lim_{h \rightarrow 0} \frac{f(x, y+h, z) - f(x, y, z)}{h}$$

$$f_z(x, y, z) = \frac{\partial f(x, y, z)}{\partial z} = \lim_{h \rightarrow 0} \frac{f(x, y, z+h) - f(x, y, z)}{h}$$

Find the partial derivatives  $f_x(x, y, z)$ ,  $f_y(x, y, z)$ , and  $f_z(x, y, z)$  by computing directly these limits in the case of  $f(x, y, z) = xy^2z$ .

**Solution.** Each of the three limits given above are applied to the function  $f(x, y, z) = xy^2z$ .

$$f_x(x, y, z) = \frac{\partial(xy^2z)}{\partial x} = \lim_{h \rightarrow 0} \frac{(x+h)y^2z - xy^2z}{h} = \lim_{h \rightarrow 0} y^2z = y^2z$$

$$f_y(x, y, z) = \frac{\partial(xy^2z)}{\partial y} = \lim_{h \rightarrow 0} \frac{x(y+h)^2z - xy^2z}{h} = \lim_{h \rightarrow 0} \frac{xz(2yh + h^2)}{h} = \lim_{h \rightarrow 0} xz(2y+h)$$

As  $h$  approaches zero, it is much smaller than  $2y$ . Thus, only the first term is nonzero:  $2xyz$ .

$$f_z(x, y, z) = \frac{\partial(xy^2z)}{\partial z} = \lim_{h \rightarrow 0} \frac{xy^2(z+h) - xy^2z}{h} = xy^2$$

■

**Problem 153.** Use your knowledge of partial derivatives and the ideal gas law to show that

$$V \frac{\partial P}{\partial V} = -P \quad \text{and} \quad V \frac{\partial P}{\partial V} + T \frac{\partial P}{\partial T} = 0$$

**Solution.**

$$\begin{aligned} V \frac{\partial P}{\partial V} &= V \left( -\frac{k_B T}{V^2} \right) = -k_B \frac{T}{V} = -P \\ V \frac{\partial P}{\partial V} + T \frac{\partial P}{\partial T} &= -k_B \frac{T}{V} + T \left( \frac{k_B}{V} \right) = 0 \end{aligned}$$

■

**Problem 154.** Show that the second-order quasilinear partial PDE with independent variables  $(x, t)$

$$a(u_x, u_t)u_{xx} + 2b(u_x, u_t)u_{xt} + c(u_x, u_t)u_{tt} = 0,$$

can be transformed into the linear PDE

$$a(u_x, u_t) \frac{\partial^2 w}{\partial u_x^2} - 2b(u_x, u_t) \frac{\partial^2 w}{\partial u_x \partial u_t} + c(u_x, u_t) \frac{\partial^2 w}{\partial u_t^2} = 0$$

by way of a Legendre transformation.

**Solution.** We transform the old variables  $u(x, t)$  to new ones  $w(\xi, \eta)$ . Setting,

$$\xi = u_x, \quad \eta = u_t, \quad w_\xi = x, \quad w_\eta = t,$$

so that the Legendre transform is:

$$w(\xi, \eta) = x\xi + t\eta - u(x, t)$$

The Jacobian of the transformation is

$$J = \begin{vmatrix} u_{xx} & u_{xt} \\ u_{xt} & u_{tt} \end{vmatrix} = u_{xx}u_{tt} \neq 0.$$

Using the same approach as Problem 155 solution, we obtain the following transformations:

$$u_{xx} = Jw_{\eta\eta}, \quad u_{xt} = -Jw_{\xi\eta}, \quad \text{and} \quad u_{tt} = Jw_{\xi\xi}.$$

Substitution into the original PDE gives:

$$a(u_x, u_t)Jw_{\eta\eta} - 2b(u_x, u_t)(-Jw_{\xi\eta}) + c(u_x, u_t)Jw_{\xi\xi} = 0.$$

Dividing through by  $J$  and then using  $\xi = u_x$  and  $\eta = u_t$  gives the desired result. ■

**Problem 155.** Consider the minimal surface equation:

$$\nabla \cdot \left( \frac{\nabla u}{(1 + |\nabla u|^2)^{1/2}} \right) = 0,$$

(a) Explain what is the minimal surface equation.

(b) Show that for  $n = 2$ , the minimal surface equation may be rewritten as

$$(1 + u_{x_2}^2)u_{x_1x_2} - 2u_{x_1}u_{x_2}u_{x_1x_2} + (1 + u_{x_1}^2)u_{x_2x_2} = 0.$$

(c) Show that this nonlinear equation can be transformed, by means of a Legendre transformation (whose new variables are denoted  $p_1, p_2$ ), to a linear equation

$$(1 + p_2^2)v_{p_2p_2} + 2p_1p_2v_{p_1p_2} + (1 + p_1^2)v_{p_1p_1} = 0.$$

**Solution.** (b) For  $n = 2$ , we have that (using  $x_1 = x$  and  $x_2 = y$ ):

$$\nabla u = \left( \frac{\partial u}{\partial x}, \frac{\partial u}{\partial y} \right) = (u_x, u_y)$$

and

$$|\nabla u|^2 = (\nabla u) \cdot (\nabla u) = u_x^2 + u_y^2.$$

Thus,

$$\begin{aligned} \nabla \cdot \left( \frac{\nabla u}{(1 + |\nabla u|^2)^{1/2}} \right) &= (u_x, u_y) \cdot \left( \frac{u_x}{(1 + u_x^2 + u_y^2)^{1/2}}, \frac{u_y}{(1 + u_x^2 + u_y^2)^{1/2}} \right) \\ &= \frac{\partial}{\partial x} \left( \frac{u_x}{(1 + u_x^2 + u_y^2)^{1/2}} \right) + \frac{\partial}{\partial y} \left( \frac{u_y}{(1 + u_x^2 + u_y^2)^{1/2}} \right) \\ &= \frac{u_{xx} + u_{xx}u_y^2 - u_xu_yu_{xy}}{(1 + u_x^2 + u_y^2)^{3/2}} + \frac{u_{yy} + u_{yy}u_x^2 - u_xu_yu_{xy}}{(1 + u_x^2 + u_y^2)^{3/2}} \\ &= \frac{(1 + u_y^2)u_{xx} - 2u_xu_yu_{xy} + (1 + u_x^2)u_{yy}}{(1 + u_x^2 + u_y^2)^{3/2}} = 0. \end{aligned}$$

For the equation to hold, we must have the numerator equal to zero. That is,

$$(1 + u_y^2)u_{xx} - 2u_xu_yu_{xy} + (1 + u_x^2)u_{yy} = 0.$$

(c) The idea is to transform from  $u(x_1, x_2)$  to  $v(p_1, p_2)$ . The Legendre transform is:

$$v(p_1, p_2) = \vec{p} \cdot \vec{x} - u(x_1, x_2) = p_1x_1 + p_2x_2 - u(x_1(p_1, p_2), x_2(p_1, p_2))$$

where  $p_1 = u_{x_1}$  and  $p_2 = u_{x_2}$ . We assume the mapping from  $(x_1, x_2)$  to  $(p_1, p_2)$  is one-to-one and invertible so the condition (here we view  $u_{x_1}$  and  $u_{x_2}$  as independent variables)

$$J = \begin{vmatrix} u_{x_1x_1} & u_{x_1x_2} \\ u_{x_2x_1} & u_{x_2x_2} \end{vmatrix} = u_{x_1x_1}u_{x_2x_2} - u_{x_1x_2}^2 \neq 0$$

holds. Now we find a PDE for  $v$  with independent variables  $p_1, p_2$ . The inverse transformation has the following Jacobian:

$$J' = \begin{vmatrix} v_{p_1p_1} & v_{p_1p_2} \\ v_{p_2p_1} & v_{p_2p_2} \end{vmatrix} = v_{p_1p_1}v_{p_2p_2} - v_{p_1p_2}^2 \neq 0.$$

By the involutivity of the Legendre transformation, we just have  $JJ' = \mathbf{1}$ , or in matrix form,

$$\begin{bmatrix} u_{x_1x_1} & u_{x_1x_2} \\ u_{x_2x_1} & u_{x_2x_2} \end{bmatrix} \begin{bmatrix} v_{p_1p_1} & v_{p_1p_2} \\ v_{p_2p_1} & v_{p_2p_2} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}.$$

From this, we obtain the following set of equations:

$$\begin{aligned} u_{x_1x_2}v_{p_1p_1} + u_{x_1x_2}v_{p_2p_1} &= 1 \\ u_{x_1x_1}v_{p_1p_2} + u_{x_1x_2}v_{p_2p_2} &= 0 \\ u_{x_2x_1}v_{p_1p_1} + u_{x_2x_2}v_{p_2p_1} &= 0 \\ u_{x_2x_1}v_{p_1p_2} + u_{x_2x_2}v_{p_2p_2} &= 1. \end{aligned}$$

Note that  $u_{x_1x_2} = u_{x_2x_1}$  and  $v_{p_1p_2} = v_{p_2p_1}$ , and observe that:

$$\begin{aligned} u_{x_1x_1} &= u_{x_1x_1} - u_{x_1x_2} \times 0 \\ &= u_{x_1x_1} - u_{x_1x_2}(u_{x_1x_1}v_{p_1p_2} + u_{x_1x_2}v_{p_2p_2}) \\ &= u_{x_1x_1} - u_{x_1x_2}u_{x_1x_1}v_{p_1p_2} - u_{x_1x_2}^2v_{p_2p_2} \\ &= u_{x_1x_1}(1 - u_{x_1x_2}v_{p_1p_2}) - u_{x_1x_2}^2v_{p_2p_2} \\ &= u_{x_1x_1}(u_{x_2x_2}v_{p_2p_2}) - u_{x_1x_2}^2v_{p_2p_2} \\ &= (u_{x_1x_1}u_{x_2x_2} - u_{x_1x_2}^2)v_{p_2p_2} \\ &= Jv_{p_2p_2}. \end{aligned}$$

Similarly, we find that  $u_{x_1x_2} = -Jv_{p_1p_2}$  and  $u_{x_2x_2} = Jv_{p_1p_1}$ . Substituting these transformed variables into the original differential equation gives:

$$(1 + p_2^2)Jv_{p_2p_2} + 2Jp_1p_2v_{p_1p_2} + (1 + p_1^2)Jv_{p_1p_1} = 0.$$

Dividing through by  $J$  gives the desired result. ■



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