# CHEM 370: PHYSICAL CHEMISTRY 1 - THERMODYNAMICS

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# P-Chem 1

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## Part 1: Thermodynamics

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## Detailed Licensing

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# CHAPTER OVERVIEW

## 1: Thermodynamics

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# 1.1: Thermodynamic Variables and Equations of State

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Classical thermodynamics provides a conceptual framework from which we can understand the behavior of molecular systems at a quantitative level. This chapter introduces some of the concepts relating to properties of a system and its surroundings that we will need to study classical thermodynamics. In this chapter, we will focus on how the macroscopic properties of a system are related to and depend on the properties of the constituent atoms and molecules. As an example we will discuss the ideal-gas equation, its range of validity, and how it can be extended to real gases or fluids of interacting molecules.

**Learning Objectives**

- Build a precise vocabulary of thermodynamic definitions before applying them to biochemical systems.
- Understand state variables and how they are mathematically related in an equation of state.
- Be able to manipulate the ideal gas equation of state.
- Understand how real gases deviate from ideality and how real gases and can be modeled by the virial equation of state, which is an expression for the pressure of a gas as a polynomial in the density.

## 1.1.1: Basic Definitions

We begin our discussion of thermodynamics with some definitions that will allow us to make general statements about how energy is exchanged and converted into various forms.

A **system** is any part of the universe that is of interest to us. This might be the Sun-Earth-Moon system, a human lung, fruit fly, a single bacteria cell, or a container on a bench top. Some example systems are shown in figure 1.1.1.

Figure 1.1.1: Some systems of varying complexity include the sun-earth-moon system, a human lung, a fruit fly, a single bacteria cell, or a Erlenmeyer flask.

Everything else in the universe that is not part of the system is called the **surroundings.** The system + the surroundings constitutes the **universe.**

We can classify systems into 3 types: open systems, closed systems, or isolated systems. An **open system** is able to exchange both matter and heat with the surroundings. A **closed system** cannot exchange matter with the surroundings but *can* exchange heat with the surroundings. An **isolated system** cannot exchange any heat or any matter with surroundings. These three types of systems are depicted in figure 1.1.2:

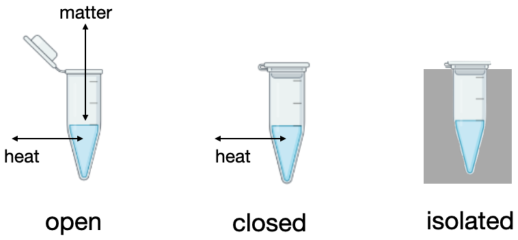

Figure figure 1.1.2: An open system can exchange both matter and heat with the surroundings. A closed system cannot exchange matter with the surroundings but can exchange heat. An isolated system cannot exchange heat or matter with the surroundings.

The branch of science called **thermodynamics** is interested in the relationships between properties of a system and how properties change as the system changes state. A **property** is any mathematically quantifiable parameter of the system. Some properties could include the pressure, the temperature, the density, the index of refraction, etc ….

We can distinguish between two types of properties: intensive and extensive. **Intensive** properties are *independent* of the quantity (amount of matter) being measured. Some intensive properties include the density, pressure, and temperature. On the other hand,

**Extensive** properties *depend* on the quantity (amount) being measured. Some extensive properties are the mass, the volume, and the number of moles.

Intensive properties can be constructed as the ratio between two extensive properties. For example the **density** is

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{1.1.1}$$

Notice that both **mass** and **volume** are extensive (depend on the amount), but the density (the ratio of the mass over volume) is intensive.

Similarly, the **pressure** is defined as

$$\text{pressure} = \frac{\text{force}}{\text{area}} \tag{1.1.2}$$

The SI units of pressure is the Pascal (Pa) and 1 Pa = 1 N$\cdot$ m$^{-2}$ = 1 kg$\cdot$m$^{-1}\cdot$ s$^{-2}$ = 1 J$\cdot$ m$^{-3}$. Table 1.1.1 relates some common units of pressure.

**Table 1.1.1:** Some common units of pressure

| |
|---|
| 1 Pa = 1 N m$^{-2}$ |
| 1 bar = 100 kPa (10$^5$ Pa) |
| 1 atm = 101.32 kPa |
| 1 torr (mm Hg) = 1/760 atm |

Note: **Energy** by itself (measured in Joules or calories) is an *extensive* property. Often, we report energies as a molar ratio in units of J/mol or cal/mol which is an *intensive* property.

A common way to define an intensive property is to define the **molar** quantity by dividing some extensive variable by the number of moles. For example, the **molar volume** is defined as:

$$\bar{V} = \frac{V}{n} \tag{1.1.3}$$

Here **n** is the number of moles and $\bar{\mathbf{V}}$ is called the molar volume and is an intensive quantity.

Temperature is another important thermodynamic parameter that will be defined in serval ways throughout this text. For now, we will define the **temperature** as the measure of the motion of the atoms within the system. This definition of temperature implies that the "thermodynamic" temperature is measured in Kelvin, because the Kelvin scale is the absolute temperature scale. In the limit that T=0 K (absolute zero), the motion of the atoms approaches zero. We can convert between temperature in Kelvin and Celsius scales using the relation:

$$T(\text{in Kelvins}) = T(\text{in }^\circ C) + 273.15 \tag{1.1.4}$$

**Caution**

Note: Absolute temperatures (in K) must be used in thermodynamic calculations.

See Practice Problems 1.1.1 and 1.1.2.

## 1.1.2: Thermodynamic Equations of State

An **equation of state** is a mathematical expression that fully describes the thermodynamic state of the system in terms of a set of physical properties. The most familiar example is the ideal gas law:

$$PV = nRT \tag{1.1.5}$$

or, introducing the molar volume (Equation 1.1.3):

$$P\bar{V} = RT \tag{1.1.6}$$

where $\mathbf{P}$ is the pressure, $\mathbf{V}$ is the volume, $\mathbf{n}$ is the number of moles, $\mathbf{T}$ is the temperature. $\mathbf{R}$ is the gas constant given in table 1.1.2:. Equation 1.1.5 is known as the **ideal gas equation of state**. The ideal gas equation of state (PV=nRT) allows us to see how the properties of an ideal gas are related.

**Table 1.1.2:** Common units for the ideal gas constant R.

| | |
|---|---|
| R = 8.314462618 J $K^{-1}$ $mol^{-1}$ = 0.08206 L atm $K^{-1}$ $mol^{-1}$ | L atm = 101.325 J |

The ideal gas equation of state will be a useful model for us to work with as we derive thermodynamic relationships because it is intuitive and algebraically easy to manipulate. At this point, it is worthwhile to make some comments concerning the ideal gas equation of state:

1. The ideal gas equation of state can be derived from first principles (kinetic theory of gases).
2. At sufficiently *high* temperature and *low* pressure, all gases fit the ideal gas law.
3. Assumptions made in the ideal gas law:
   - The gas molecules themselves occupy no volume.
   - There are no attractive or repulsive forces between gas molecules.
   - All collisions are perfectly elastic.

See Practice Problems 1.1.3 and 1.1.4.

Because of these assumptions, we expect all **real gases** to deviate from ideal behavior. To quantify this we define the **compressibility factor, Z,** as

$$Z=\frac{P\bar{V}}{RT} \tag{1.1.7}$$

Notice from Equation 1.1.5 that for an ideal gas, $Z=1$. All real gases will deviate from this ideal behavior. Figure 1.1.3 shows the compressibility factor $Z$ as a function of pressure for $N_2$ gas at different temperatures. A perfect ideal gas would have $Z=1$ for all pressures and temperatures. For $N_2$ gas we see that at sufficiently low pressure $Z\rightarrow 1$ and that at higher temperature (purple curve), the gas behalves more like an ideal gas (dotted line).

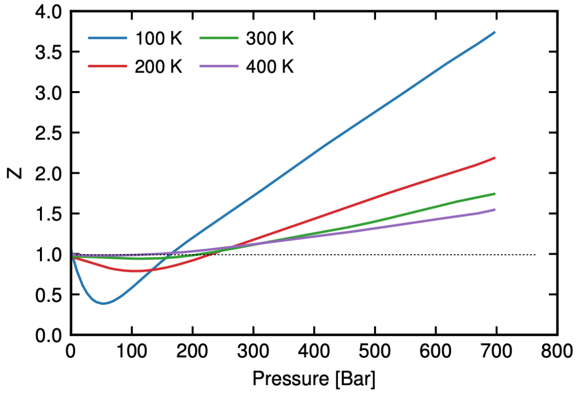

Figure 1.1.3: Compressibility factor of nitrogen gas as a function of pressure for different temperatures. The ideal gas limit is shown by the dotted line at Z=1.

In order to derive an equation of state for a non-ideal gas, we can consider a series expansion of the compressibility factor, $\mathbf{Z}$, in powers of the inverse molar volume, $\mathbf{1/\bar{V}}$:

$$Z=1+\frac{B_2}{\bar{V}}+\frac{B_3}{\bar{V}^2}+\frac{B_4}{\bar{V}^3}+\ldots \tag{1.1.8}$$

Equation 1.1.8 is called the **virial equation of state**, and $\mathbf{B_2}$ is called the **second virial coefficient**, $\mathbf{B_3}$ is called the third virial coefficient, etc…. The virial coefficients ($B_2$, $B_3$, …) are typically fit to experimental data and are temperature dependent. Notice that for a perfect ideal gas, the second and higher virial coefficients are all zero. The virial equation of state works well to describe any gas, but has the drawback of needing the virial coefficients from fitting to experimental data.

For gases that exhibit small deviations from ideal gas behavior, we can truncate Equation 1.1.8 to include just the second virial coefficient:

$$Z \approx 1 + \frac{B_2}{\bar{V}} \tag{1.1.9}$$

The second virial coefficient, $\mathbf{B_2}$ is related to the interactions between atoms described by a potential energy function $U(r)$, where $r$ is the distance between atom pairs. For a dilute system of non-polar molecules, the relationship between the second virial coefficient and the potential energy is

$$B_2 = N_A \frac{1}{2} \int_0^\infty \left[1 - e^{-U(r)/k_B T}\right] 4\pi r^2 dr \tag{1.1.10}$$

where $\mathbf{N_A}$ is Avogadro's number, $\mathbf{k_B}$ is Boltzmann's constant, and $\mathbf{T}$ is the temperature. In most cases, we cannot analytically solve the integral in Equation 1.1.10. Note that in the absence of interactions, $U(r) = 0$, then from Equation 1.1.10, $B_2 = 0$ and the gas behaves like an ideal gas as we would expect for non-interacting gas molecules.

See Practice Problems 1.1.5 — 1.1.7.

## 1.1.3: Examples

### ✓ Example 1.1.1

Classify each of the following systems as either open, closed, or isolated. (a) A red blood cell, (b) a gas in a piston without valves, (c) boiling water in a kettle on the stove, (d) A closed Thermos flask of hot coffee (approximately).

**Solution**

(a) open; (b) closed; (c) open; (d) isolated

### ✓ Example 1.1.2

Classify each of the following properties as intensive or extensive: (a) molar mass, (b) pressure, (c) temperature, (d) mass

**Solution**

(a) intensive; (b) intensive; (c) intensive; (d) extensive

### ✓ Example 1.1.3

A Bellingham homebrewer collects the amount of gas evolved during the fermentation process. Later, the brewer measures the volume of gas to be 0.64 L at a cold temperature of 12.3 °C and 1 atm. Assuming ideal gas behavior, what was the volume of the gas at the fermentation temperature of 37.0 °C and 1 atm.

**Solution**

We use the ideal gas equation: PV=nRT to set up a ratio between the low temperature and high temperature system:

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} \tag{1.1.11}$$

$$\frac{0.64 \text{ L}}{V_2} = \frac{285.45 \text{ K}}{310.15 \text{ K}} \tag{1.1.12}$$

$$V_2 = 0.695 \text{ L} \tag{1.1.13}$$

## 1.1.4: Practice problems

**Problem 1.1.1.** Classify each of the following systems as either open, closed, or isolated. (a) perfectly insulated water heater, (b) a glass thermometer (c) the universe (d) soup cooking on a stove (e) the earth (f) automobile (g) a sealed reaction flask

**Problem 1.1.2.** Classify each of the following properties as intensive or extensive: (a) density, (b) force, (c) molar volume, (d) heat.

**Problem 1.1.3.** Under which of the following sets of conditions would you expect a real gas to be adequately described by the ideal gas model (a) low pressure and low temperature; (b) low pressure and high temperature, (c) high pressure and high temperature, and (d) high pressure and low temperature.

**Problem 1.1.4.** An ideal gas in a piston is originally at a pressure of 118.0 atm and 85 °C. When the piston expands, its final volume, pressure, and temperature were 3.5 L, 1.0 atm, and 45 °C, respectively. What was the initial volume of the gas?

**Problem 1.1.5.** At 300 K, the second virial coefficient ($B_2$) of $CO_2$ gas is -120.5 $cm^3$ $mol^{-1}$ , for methane gas, $CH_4$, the second virial coefficient is -41.9 $cm^3$ $mol^{-1}$ , and for $N_2$ gas the second virial coefficient is -4.2 $cm^3$ $mol^{-1}$ . Rank these gases from most ideal gas to least idea gas at this temperature? Explain your reasoning.

**Problem 1.1.6.** Calculate the pressure of methane at 398.15 K if the molar volume is 0.2 L $mol^{-1}$, given that the second virial coefficient ($B_2$) of methane is -0.0163 L $mol^{-1}$. Compare your results with that obtained using the ideal gas equation. Is methane more or less compressible than an ideal gas at this temperature? (Assume that all other higher order virial coefficients can be neglected).

**Problem 1.1.7.** The **Boyle temperature** is the temperature at which the coefficient $B_2$ is zero. Therefore, a real gas behaves like an ideal gas at this temperature. **(a)** give a physical interpretation of this behavior. **(b)** Calculate the Boyle temperature for a gas whose second virial coefficient has the following form: $B_2 = a - \frac{b}{T}$ with the experimentally determined second virial coefficient measured at the following temperatures:

| Second virial coefficient ($B_2$) (L $mol^{-1}$) | Temperature (K) |
|---|---|
| -0.0237 | 292.95 |
| -0.0231 | 296.15 |
| -0.0228 | 298.15 |
| -0.0218 | 303.15 |
| -0.0201 | 313.15 |
| -0.0185 | 323.15 |
| -0.0117 | 373.15 |
| -0.0065 | 423.15 |

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# 1.2: The First Law of Thermodynamics

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Systems can undergo a change of state from some initial state to a final state accompanied by a change in the system’s energy. In this chapter, we analyze two types of energy: heat and work. This leads to a presentation of the first law of thermodynamics that deals with the conservation of energy, stating that any changes in the total internal energy of the system must be due to exchanges of either heat or work with the surroundings. Emphasis is placed on ideal gases because their equation of state is known. We also introduce an important property of a material, the heat capacity, that allows us to calculate the change in temperature as a function of heat. Finally, the concept of enthalpy is introduced that plays an important role in chemical reactions.

**Learning Objectives**

- Be able to explain and give some examples of state properties.
- Be able to define heat and work and understand heat and work are types of energy.
- Understand that heat and work are path-dependent (not state properties).
- Understand that energy is conserved: changes in the total internal energy must be due to either heat flow into/out of the system in relation to the surroundings or work being done on/ being performed by the system in relation to the surroundings.
- Be able to calculate the change in energy, enthalpy, work and heat exchange for the compression/expansion of an ideal gas and generalize these observations to other systems.

## 1.2.1: State properties and the internal Energy (U)

Previously, we introduced the concept of an equation of state that relates **state** properties (also called **state** variables or **state** functions). **State properties** describe the thermodynamic state of the system in terms of quantifiable observables such as temperature, pressure, volume, and number of moles for an ideal gas.

An important feature of state properties is that they are independent of the system’s history. In other words, if the system is changed from some *initial* state to a *final* state, the corresponding change in any state function does not depend on the path taken from the *initial* to *final* state or on any intermediate states. An example of a state property is the **total internal energy** of the system, which we will give the symbol **U**. The total internal energy includes the translational, rotational, vibrational, electronic, and nuclear energies of all the particles, as well as the energy due to intermolecular interactions.

Figure $1.2.1$ shows a schematic energy diagram of changing the system from some initial state $A$ into some final state $B$.

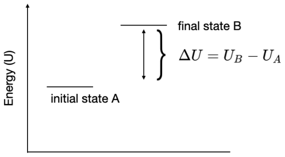

Figure $1.2.1$: The change in internal energy (U) in going from some initial state A to some final state B does not depend on the process of going from A to B but only on the difference in energy between A and B.

Notice that the overall change in energy, $\Delta U$ does not depend on how the system was change from $A \rightarrow B$. For state variables we write the change if energy

$$\Delta U = U_f - U_i \tag{1.2.1}$$

As an example, consider a piston containing an ideal gas as shown in figure $1.2.2$:

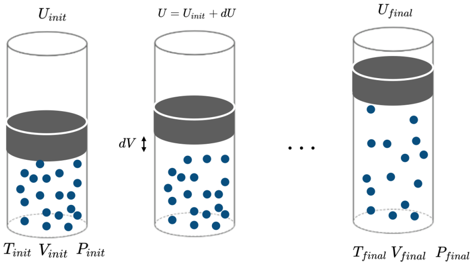

Figure 1.2.2: A gas at an initial temperature, pressure, and volume has an initial energy given by $U_{init}$. Expanding the piston an infinitesimal amount dV, the infinitesimal change in energy is dU. After expansion of the gas the system is in a new state with a different temperature, volume, pressure. The final energy is $U_{final}$.

Since the molecules do not interact, the total internal energy depends only on the kinetic energy of all the gas molecules, which is related to the temperature. We now expand the piston through a series of infinitesimal steps such that the temperature of the gas changes as the volume increases. At each infinitesimal step, the infinitesimal change in the internal energy is $dU$. Summing over all the infinitesimal steps gives the total change in internal energy as

$$\int_{U_i}^{U_f} dU = U_f - U_i = \Delta U \tag{1.2.2}$$

Mathematically, **U** is an *exact differential* (see Appendix), meaning that integration from an initial state to a final state is independent of the path. For any state property $dz$, the differential is exact, and we can write:

$$\int_{z_i}^{z_f} dz = \Delta z \tag{1.2.3}$$

Equation 1.2.3 will serve as a definition of a state property since all state properties are exact differentials because they are independent of the path.

## 1.2.2: Work

We have seen how the total internal energy is a state property of a system. At this point, we might ask ourselves what would be an example of a quantity that is *not* a state property? One such example would be the work done by the system in going from an initial to a final state. **Work** is the physical activity directed towards the production of accomplishing something. Work can be *performed on* the system by the surroundings, or work can be *done by* the system on the surroundings; however, work is not an intrinsic property of the system itself and is not a state property. The amount of work performed will depend on the path taken to change the state from some initial state to some final state. As an example, we can consider a hiker walking in the Sehome Arboretum. Figure 1.2.3 shows the situation of a hiker starting at some initial position *A* and reaching the final position B by two different paths. Because these paths are different, the hikers will have performed a different amount of work in traveling from point A to point B, depending on the path taken.

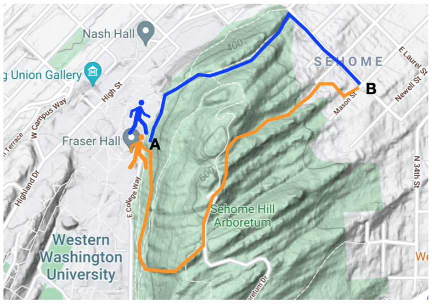

Figure 1.2.3: Two hikers in the Sehome Arboretum travel from the same initial point **A** to the same final point **B**, but they travel by different paths. Because the paths differ, the hikers will have performed a different amount of work in traversing from A to B.

In classical mechanics the work is defined as the force times the distance. For an infinitesimal displacement $\mathbf{dx}$ the work is

$$\delta w = F \cdot dx \tag{1.2.4}$$

where F is the applied force.

Note

Note: The quantity $\delta w$ denotes an infinitesimal increment of work. It should be noted that work is not a state function, meaning that the differential is inexact and Equation 1.2.3 cannot be applied. Instead, we write the total work over a path taken from some initial state to some final state as:

$$w = \int_{path} \delta w \tag{1.2.5}$$

Because the differential $\delta w$ is *inexact*, the integral over different paths with the same end points will be different.

In thermodynamics we generalize this concept of work to consider different types of work summarized in Table 1.2.1.

Table 1.2.1: Various types of work and their mathematical expressions

| Types of work | $\delta w$ | Generic force, displacement |
|---|---|---|
| mechanical work | F · dx | F is the force, dx is the distance |
| Surface work | γ · dA | γ is the surface tension, dA is the change in area |
| Electrical work | Q · dφ | Q is the electric charge, dφ is the electric potential change |
| Gravitational work | mg · dh | mg is the gravitational acceleration, dh is the change in height |
| Stretching work | τ · dL | τ is the tension, dL is the change in length |
| Expansion (compression) | P · dV | P is the pressure, dV is the change in volume |

We will mainly focus our attention on the expansion (compression) type work of work (sometimes called PV-work) of a gas in a cylinder. Figure 1.2.4 shows the situation of a gas in a cylinder with a piston with some opposing, external pressure, $\mathbf{P_{ex}}$, acting on the gas.

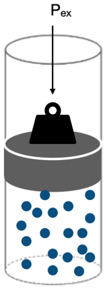

Figure 1.2.4: A gas in a cylinder with a piston. An external pressure pushing down on the piston acts to oppose the expansion of the gas.

Because the external pressure is pushing against the gas (the direction of the force is pointing down on the piston), we define the work of expansion as:

$$\delta w \equiv -P_{ex} \cdot dV \tag{1.2.6}$$

where $\boldsymbol{\delta}\mathbf{w}$ is some infinitesimal amount of work and $\mathbf{dV}$ is an infinitesimal change in the volume due to expansion or compression of the piston. Equation 1.2.6 is the definition of the work of expansion/compression of a gas. Let's look at some examples for how to calculate the work for a gas in a cylinder.

### 1.2.2.1: Example 1: Expansion of a gas against a constant pressure

As our first example, we consider the expansion of a gas against a constant pressure. The situation is shown in figure 1.2.5. Initially, two masses oppose the piston. Removal of one of the masses, causes the gas in the cylinder to expand against the constant pressure due to the remaining mass from an initial volume $\mathbf{V_i}$ to a final volume $\mathbf{V_f}$.

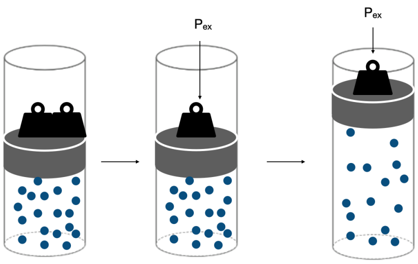

Figure 1.2.5: **Expansion of a gas against a constant pressure.** A gas is held at an initial volume $\mathbf{V_i}$ by two masses on a piston. Upon removal of one of the masses, the gas expands to a new volume $\mathbf{V_f}$ against a constant pressure $\mathbf{P_{ext}}$.

The total work performed by the gas can be calculated by integrating Equation 1.2.6

$$w = -\int_{V_i}^{V_f} P_{ext} \cdot dV \tag{1.2.7}$$

Because the external applied pressure in this case is constant, it can be taken out of the integral to give:

$$\begin{aligned} w &= -P_{ext} \int_{V_i}^{V_f} dV \\ &= -P_{ext} \Delta V \end{aligned} \tag{1.2.8}$$

where $\Delta V = (V_f - V_i)$. Notice that in the last line we have used the fact that the volume is a state variable so that $\Delta V = \int dV$.

> Key Result: The work performed during the expansion of a gas against a constant external pressure is $w = -P_{ext} \cdot \Delta V$

See Practice Problem 1.2.1.

### 1.2.2.2: Example 2: Free expansion of a gas against a vacuum.

We now consider a slightly different situation when a gas is allowed to freely expand into a vacuum. The situation is illustrated in figure 1.2.6. A gas is compressed to a volume $\mathbf{V_i}$ by a piston that is held in placed by a mass, and a vacuum is created by removal of air from the space above the piston. When the mass is removed, the gas will freely expand against the vacuum to fill the cylinder to a final volume of $\mathbf{V_f}$.

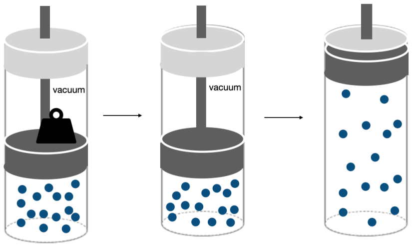

Figure 1.2.6: **Expansion of a gas into a vacuum.** In the cylinder on the left, an applied pressure is used to compress a gas, and a vacuum is created in the space above the piston. When the weight is removed (middle cylinder), the compressed gas will expand from an initial volume $\mathbf{V_i}$ against the vacuum until it occupies the available space (right cylinder) with final volume $\mathbf{V_f}$.

We can again use Equation 1.2.6 to obtain:

$$w = -P_{ext} \cdot \Delta V \tag{1.2.9}$$

However, here we note that the external pressure $P_{ext} = 0$ because the gas is expanding into a vacuum. Thus, the work performed by the expansion is $w = 0$.

> Key Result: There is no work performed in the free expansion of a gas against a vacuum. $w = 0$.

See Practice Problems 1.2.2 and 1.2.3.

### 1.2.2.3: Work is not a state property

Notice that in the first example the work performed in expanding the gas was $w = -P_{ext} \cdot \Delta V$, but in the second example, expanding the gas to the same final volume against a vacuum resulted in no work being performed. Thus, we see that the amount of work being performed *depends on the path taken* and hence work is not a state property.

Note: In this book we adopt the convention that work being performed **on the system** by the surroundings is positive. This means that work being performed **by the system** on the surroundings will be negative by convention. Work being done on the system by the surrounding is shown on the right of figure 1.2.6 with an arrow showing the direction of work pointing from the surroundings to the system. The left of figure 1.2.6 shows the situation of work being performed by the system with an arrow pointing form the system to the surroundings. For the situation on the right, the work will have a negative sign.

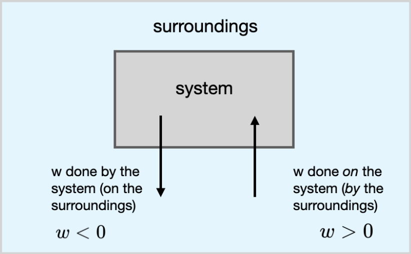

Figure 1.2.6 : Sign convention for work. Work performed by the system on the surrounding is depicted by an arrow pointing form the system to the surroundings and has a negative sign by convention. Work performed on the system (by the surroundings) is depicted by an arrow pointing from the surroundings into the system and is positive by convention.

## 1.2.3: Heat

Heat is another type of energy that can flow across the system boundary causing the system to change its state. As an example we can consider the situation shown in figure 1.2.7 of two liquids: one at 25 °C and one at 75 °C. If the two containers are brought into thermal contact, heat will flow out of the hotter (75 °C) liquid into the cooler (25 °C) liquid until thermal equilibrium is reached and both liquids reach the same final temperature.

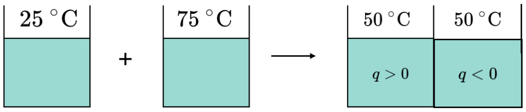

Figure 1.2.7: When two systems at different temperature are brought into thermal contact, heat will flow from the hotter system into the colder system until the two systems are at thermal equilibrium.

### 1.2.3.1: Heat is not a state property

Just like work, heat is not a state property, and the amount of heat flow into or out of the system depends on the path taken from the initial state to the final state. We will use the symbol $q$ to represent heat.

Note: In this book we adopt the same sign convention that we used for work. Heat being **absorbed by the system** from the surroundings will be defined as positive and represented with an arrow pointing from the surroundings to the system to indicate the direction of heat flow. On the other hand, heat **given off by the system** into the surroundings will have a negative sign and will be depicted with an arrow pointing from the system into the surroundings as shown in figure 1.2.8.

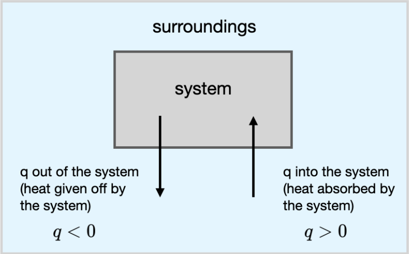

Figure 1.2.8: **Sign convention for heat.** Heat flowing out of the system into the surroundings (exothermic) is depicted by an arrow pointing form the system to the surroundings and has a negative sign by convention. Heat flowing into the system from the surroundings (endothermic) is depicted by an arrow pointing from the surroundings into the system and is positive by convention.

### 1.2.3.2: The Zeroth Law of Thermodynamics

The concept that heat flows from hot to cold establishes what is known as the **zeroth law of thermodynamics**. The zeroth law states that if system A is in thermal equilibrium with system B, and system B is in thermal equilibrium with system C, then system A must also be in thermal equilibrium with systems C. Figure 1.2.9 summarizes the zeroth law of thermodynamics.

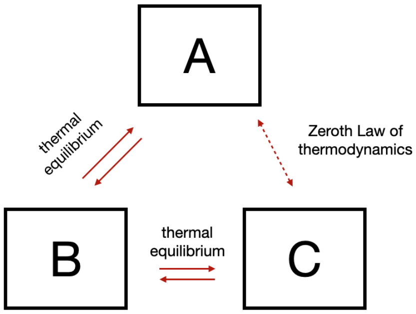

Figure 1.2.9: The Zeroth Law of Thermodynamics establishes that if two systems (A and B) are in thermal equilibrium with each other and another system (C) is brought into thermal equilibrium with one of the systems (B), then C is also in thermal equilibrium with system A.

Although conceptually simple, the zeroth law is important because it formally establishes temperature as a well-defined quantity.

## 1.2.4: First Law of Thermodynamics

Having defined **heat** and **work** as types of energy, we are now in a position to state the **first law of thermodynamics**. The first law states that the change in energy ($\Delta U$) of a system is equal to the sum of the work done on the system ($w$) and heat ($q$) put into the system. Mathematically, we can express the first law as:

$$\Delta U = q + w \tag{1.2.10}$$

We see from Equation 1.2.10 that the first law of thermodynamics is a statement about the **conservation of energy**. In order for the energy of the system to change, energy must be transferred to/from the surroundings in the form of either heat or work.

For dealing with infinitesimal changes of energy ($dU$) the first law can be written in differential form:

$$dU = \delta q + \delta w \tag{1.2.11}$$

### 1.2.4.1: Reversible vs. Irreversible Processes

Both **Example 1** and **Example 2** above are examples of an *irreversible* process, meaning that the expansion against a constant pressure or against a vacuum occurs spontaneously in one direction, but the reverse process does not occur spontaneously. This directionality of spontaneous change results from the fact that the system is not maintained at equilibrium during the expansion. When the gas is expanding, the pressure inside is not equal to the external applied pressure causing a net force to push the gas molecules into the larger volume.

Imagine the equilibrium situation shown in figure 1.2.10 where the internal pressure of the gas is equal to the external pressure applied by the piston.

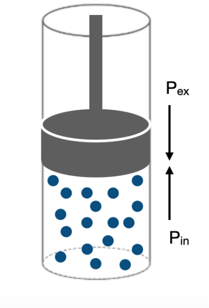

Figure 1.2.10: A gas in a cylinder at equilibrium with the surroundings. At equilibrium the pressure exerted by the gas on the piston ($\mathbf{P_{in}}$) is equal and opposite to the pressure exerted by the surroundings on the piston ($\mathbf{P_{ex}}$).

We could now consider expanding the gas through a series of infinitesimal steps where equilibrium is maintained throughout the expansion by adjusting the external pressure so that it is always equal to the internal pressure of the gas. Note that in this case the external applied pressure will not be constant since it is adjusted to maintain equilibrium at each step. The situation is illustrated in figure 1.2.11. At each infinitesimal step, there is no net force pushing the gas to change volume in any one direction so the process is said to be **reversible**.

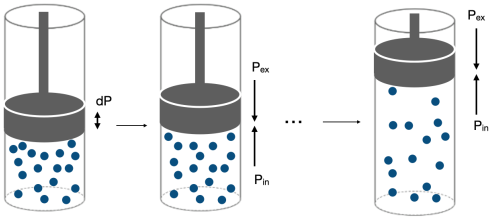

Figure 1.2.11: Reversible expansion of a gas. A gas in a cylinder initially at volume $\mathbf{V_i}$ is slowly expanded to a final volume $\mathbf{V_f}$ such that the internal pressure $\mathbf{P_{in}}$ remains equal and opposite to the external pressure $\mathbf{P_{ex}}$ at each infinitesimal step. During a reversible process, quasi-equilibrium is maintained throughout.

A **reversible process** is a process which is at equilibrium at each infinitesimal step. Because work depends on the path (not a state property), the amount of work performed (and thus also the amount of heat flow) will depend on if the process occurs reversibly or irreversibly. As an example we will consider the *reversible* expansion of a gas.

### 1.2.4.1.1: Example 3: Isothermal Reversible Expansion of a Gas

Consider the isothermal reversible expansion of a gas. The situation is similar to the situation illustrated in figure 1.2.11. The gas is initially at a volume $\mathbf{V_i}$ and is expanded reversibly to a final volume of $\mathbf{V_f}$ while maintaining a constant temperature. Because the processes is reversible, the external pressure ($\mathbf{P_{ext}}$) is always equal to the internal pressure of the gas ($\mathbf{P_{in}}$) which can both be replaced by the variable $P = P_{in} = P_{ext}$ . The work is again calculated by integrating Equation 1.2.6:

$$w = -\int_{V_i}^{V_f} P \cdot dV \tag{1.2.12}$$

Note that in this case, we cannot take the variable $\mathbf{P}$ outside of the integral because the pressure is not constant but depends on the volume during the expansion. In order to proceed, we need to know how the pressure $\mathbf{P}$ depends on the volume $\mathbf{V}$. For an ideal gas, we know the relation from the ideal gas equation of state:

$$P = \frac{nRT}{V} \tag{1.2.13}$$

Substituting this into Equation 1.2.12 gives:

$$w = -\int_{V_i}^{V_f} \frac{nRT}{V} \cdot dV \tag{1.2.14}$$

We can now use the fact that $\mathbf{n}$ (constant number of moles), $\mathbf{R}$, and $\mathbf{T}$ (isothermal = constant temperature) are constants and can be pulled out of the integral so that the integrand only depends on the volume:

$$\begin{aligned} w &= -nRT \int_{V_i}^{V_f} \frac{dV}{V} \\ &= -nRT \ln\left(\frac{V_f}{V_i}\right) \end{aligned} \tag{1.2.15}$$

**Note**

We have used the integral: $\int \frac{1}{x} dx = \ln x + C$

Key Result: For the *reversible* isothermal expansion of a gas, the work performed is $w = -nRT \ln\left(\frac{V_f}{V_i}\right)$

See Practice Problems 4 and 5

### Theorem 1.2.1: Maximum Work Theorem

A comparison of Equation 1.2.15 with the result above from Equation 1.2.8 shows that the amount of work performed is different if the process is performed reversibly than if the process is performed irreversibly. Figure 1.2.12 shows a plot of the Pressure vs. the Volume for the two different expansions. A plot of P vs. V is called a PV-diagram and the work performed is the area under the curve. Notice that the work performed (area under the curve) is *greater* for the reversible expansion than the work performed for the irreversible expansion. It turns out that for any reversible process, the amount of work performed is maximized as compared to the equivalent irreversible processes. This principle is called the **maximum work theorem.**

> Key result: The **maximum work theorem** states that for all processes leading from a specified initial state to some specified final state, the work performed is a maximum for a reversible process.

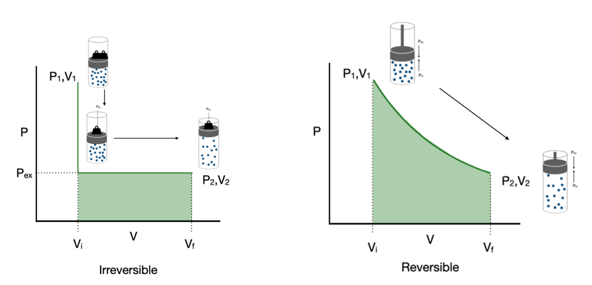

Figure 1.2.12: **Left**: The situation described in Example 1 of the irreversible expansion of a gas against a constant pressure. **Right**: The situation described in Example 3 of the reversible expansion of a gas. The area under the curve between the initial state and final state is the magnitude of the work performed by the piston. Note that that area under the curve is always greater in the reversible process.

## 1.2.5: The Heat Capacity

A useful property of a system is the **heat capacity**. The **heat capacity** is the amount of energy (heat) required to raise the temperature of a material by some infinitesimal amount $dT$.

$$\delta q = C \cdot dT \tag{1.2.16}$$

Equation 1.2.16 says that the amount of heat transferred to the systems ($\delta q$) is proportional to the change in temperature ($dT$) and the proportionality factor is the **heat capacity** of the material. How much the temperature rises in a material as it is heated depends on:

- the amount of heat delivered (q)
- the amount of substance present
- the chemical nature and physical state of the material

- the conditions under which the energy is added

Integrating both sides of Equation 1.2.16 from an initial temperature $\mathbf{T_i}$ to a final temperature $\mathbf{T_f}$ gives:

$$q=\int_{T_i}^{T_f} C\cdot dT \tag{1.2.17}$$

In general, the heat capacities $\mathbf{C}$ also depend on the temperature. However, for an ideal gas, the heat capacity is independent of temperature and can be taken out of the integral to give:

$$\begin{aligned} q &= C\int_{T_i}^{T_f} dT \\ q &= C\Delta T \end{aligned} \tag{1.2.18}$$

where $\Delta T=T_f-T_i$ and we have used the fact that temperature is a state property.

For a gas, the heat capacity depends on whether the gas undergoes a change of state at constant volume conditions (isochoric) or at constant pressure conditions (isobaric).

We denote the heat capacity at constant volume as $C_v$ and the heat capacity at constant pressure as $C_p$. At constant volume we have:

$$\delta q_v=C_v\cdot dT \tag{1.2.19}$$

and at constant pressure we have:

$$\delta q_p=C_p\cdot dT \tag{1.2.20}$$

where the subscript indicates whether we are under conditions of constant volume or pressure. Rearranging Equation 1.2.19 and Equation 1.2.20 we see that the heat capacity is given by:

$$C_v=\left(\frac{\partial q}{\partial T}\right)_V \tag{1.2.21}$$

and at constant pressure we have:

$$C_p=\left(\frac{\partial q}{\partial T}\right)_P \tag{1.2.22}$$

The heat capacities $C_p$ and $C_v$ are the slope of the curve of heat vs. temperature.

## 1.2.6: Enthalpy

We saw above that work and heat depend on the path taken from an initial state to a final state. Let's consider in more detail the *reversible* expansion/compression of a gas in a cylinder under the conditions of constant pressure (isobaric). From the first law of the thermodynamics we can write the change of energy as:

$$\begin{aligned} dU &= \delta q_p+\delta w \\ dU &= \delta q_p-P\cdot dV \end{aligned} \tag{1.2.23}$$

where the subscript on $\delta q_p$ indicates we are under conditions of constant pressure (isobaric) and we have used the fact that the reversible work is $\delta w=-P\cdot dV$ . Rearranging Equation 1.2.23 for $\delta q_p$ we have:

$$\begin{aligned} \delta q_p &= dU+PdV \\ \delta q_p &= d(U+PV) \end{aligned} \tag{1.2.24}$$

where the second line is true because the pressure $\mathbf{P}$ is constant. We now introduce a new quantity called the **enthalpy** that gets the symbol $\mathbf{H}$ that is defined as the energy + PV:

$$H=U+PV \tag{1.2.25}$$

Equation 1.2.25 is the definition of the enthalpy. Substituting Equation 1.2.25 into Equation 1.2.24 gives:

$$\delta q_p = dH \tag{1.2.26}$$

or, upon integrating both sides:

$$q_p = \Delta H \tag{1.2.27}$$

From Equation 1.2.26 and Equation 1.2.27, we see that the change in enthalpy of the system is equal to the amount of heat gained by the system under the conditions of constant pressure.

> Key result: Enthalpy is defined as: $H = U + PV$

> Key result: The change in enthalpy of the system is equal to the heat gained by the system **at constant pressure**: $q_p = \Delta H$

> Note
>
> Note: Although heat is not a state property and thus depends on the path, the enthalpy $H$ *is* a state property and so the change of enthalpy $\Delta H$ will be *independent* of the path taken.

## 1.2.7: Heat Capacity Revisited

Constant Pressure

Recall that the heat capacity for a gas depends on if the conditions are isobaric (constant P) or isochoric (constant V). At constant pressure, we copy the expression from Equation 1.2.20 above:

$$\delta q_p = C_p \cdot dT$$

We have also shown that the heat gained at constant pressure is equivalent to the change in enthalpy $\mathbf{dH}$ (Equation 1.2.26). Substituting Equation 1.2.26 into Equation 1.2.20 gives:

$$dH = C_p \cdot dT \tag{1.2.28}$$

or, rearranging in terms of $C_p$:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \tag{1.2.29}$$

Equation 1.2.29 shows that the slope of the enthalpy $\mathbf{H}$ with respect to the temperature $\mathbf{T}$ at constant pressure is the heat capacity $\mathbf{C_p}$.

Constant Volume

At constant volume, we copy the expression from Equation 1.2.19 above:

$$\delta q_v = C_v \cdot dT \tag{1.2.30}$$

From the first law of thermodynamics we have the change in energy $\mathbf{dU}$ is given by: $dU = \delta q_v - PdV$ where the subscript $\delta \mathbf{q_v}$ indicates we are at constant volume conditions. Since the volume is constant, there is *no work being performed* since $\mathbf{dV = 0}$. *At constant volume conditions* we can write:

$$dU = \delta q_v \tag{1.2.31}$$

since all the change in energy at constant volume is due to heat flow (no work). Substituting Equation 1.2.31 into Equation 1.2.30 gives:

$$dU = C_v \cdot dT \tag{1.2.32}$$

or, rearranging in terms of $\mathbf{C_v}$:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V \tag{1.2.33}$$

Equation 1.2.33 shows that the slope of the energy $\mathbf{U}$ with respect to the temperature $\mathbf{T}$ at constant volume is the heat capacity $\mathbf{C_v}$.

Relation between $C_v$ and $C_p$ for an ideal gas

To relate $\mathbf{C_v}$ and $\mathbf{C_p}$ for an ideal gas, we begin with the definition of the enthalpy: $H = U + PV$. Recall that for an ideal gas, $PV = nRT$. Substituting the ideal gas law into the definition of the enthalpy gives:

$$H = U + nRT \tag{1.2.34}$$

Note that because we have use the ideal gas law, Equation 1.2.34 only applies to an ideal gas. Taking $\mathbf{n}$ and $\mathbf{R}$ to be constants, we can write the differential form of Equation 1.2.34 as:

$$dH = dU + nRdT \tag{1.2.35}$$

Substituting Equation 1.2.32 and Equation 1.2.28 into Equation 1.2.35 and dividing out the $dT$ gives:

$$C_p = C_v + nR \tag{1.2.36}$$

Equation 1.2.36 relates the heat capacity at constant pressure $\mathbf{C_p}$ and the heat capacity at constant volume $\mathbf{C_v}$ for an ideal gas.

> Key result: For an ideal gas the heat capacity at constant pressure $C_p$ and the heat capacity at constant volume $C_v$ are related by $C_p = C_v + nR$

See Practice Problem 1.2.6.

## 1.2.8: Examples

### Example 1.2.1

One mole of an ideal gas in a cylinder is initially held at 12 atm of pressure and 298 K. Calculate the work done by a piston if the gas is expanded against a constant external pressure of 1.0 atm while the temperature is kept constant at 298 K.

**Solution**

For the expansion of an ideal gas at constant external pressure the work is given by Equation 1.2.8

$$w = -P_{ext} \cdot \Delta V$$

First, we use PV=nRT to find the initial and final volumes of the gas:

$$V_i = \frac{1 \text{ mole} \times \ 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{12 \text{ atm}}$$

$$V_i = 2.038 \text{ L}$$

Note that the final pressure inside the cylinder is equal to the external pressure of 1.0 atm:

$$V_f = \frac{1 \text{ mole} \times \ 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{1 \text{ atm}}$$

$$V_f = 24.45 \text{ L}$$

This gives the total work as:

$$w = -1.0 \text{ atm}(24.45 \text{ L} - 2.038 \text{ L})$$

$$w = -22.4 \text{ L atm}$$

$$w = -22.4 \text{ L atm} \times \frac{101.325 \text{ J}}{1 \text{ L atm}} = -2270 \text{ Joules}$$

Notice in the final step we convert L atm to Joules, which is the more conventional energy units. Also notice that the sign of the work is *negative* by our convention because the system is doing work on the surroundings (expansion).

✓ Example 1.2.2

During the reversible isothermal compression of 3.0 moles of an ideal gas at T=291 K, the pressure changes from 3.0 atm to 5.0 atm. Calculate the work done.

**Solution**

We use the fact that for the *reversible* isothermal expansion of a gas, the work performed is $w = -nRT\ln\left(\frac{V_f}{V_i}\right)$ (See Equation 1.2.15).

For an ideal gas at constant number of moles and constant temperature:

$$\frac{V_f}{V_i} = \frac{P_i}{P_f}$$

So the work (for an isothermal process) can be expressed in terms of the pressure as:

$$w = -nRT\ln\left(\frac{P_i}{P_f}\right)$$

$$w = -3.0 \text{ moles } \times \ 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \ \times \ 291 \text{ K } \ln\left(\frac{3.0}{5.0}\right)$$

$$w = 3707.6 \text{ Joules}$$

Note that the work is *positive* by our convention since the surroundings is doing work on the system (compression).

✓ Example 1.2.3

The molar heat capacity at constant volume of a monatomic idea gas is 3/2 R. How much heat must be added to raise the temperature of 2.0 moles of an ideal gas by 10 °C?

**Solution**

We use the fact that the heat at constant volume is given by Equation 1.2.19:

$$\delta q_v = C_v \cdot dT$$

Integrating both sides gives:

$$q_v = C_v \Delta T$$

Inserting the definition of the molar heat capacity $\bar{C}_v = C_v/n$ into our expression for the heat gives:

$$q_v = n\bar{C}_v\Delta T$$

where n is the number of moles. Now we solve for the heat:

$$q_v = 2.0 \text{ moles } \times \ \frac{3}{2} \ \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \ \times \ 10 \text{ K}$$

$$q_v = 249.42 \text{ Joules}$$

## 1.2.9: Practice Problems

**Problem 1.2.1.** Consider an experiment where a gas is compressed isothermally (constant temperature) from an initial pressure of 1.0 atm and a volume of 3.0 L to a final pressure of 4.0 atm and a volume of 1.0 L. The temperature remains constant at 20.0 °C. Calculate the work done if the compression is performed in a single step against a constant external pressure of 4.0 atm. (Report your answer in Joules).

**Problem 1.2.2.** You are traveling in a space ship whose cabin volume is 10.0 $\text{m}^3$. The air inside the cabin is maintained at 1 atm and 298 K, suitable for human space travel. Suddenly, the cabin springs a leak, allowing 1.8 moles of gas to escape into the vacuum before you are able to repair the damage. Calculate **a)** q, **b)** w, and **c)** $\Delta U$ for this process, assuming that the walls of the cabin are perfect insulators (adiabatic).

**Problem 1.2.3.** Calculate the work done when 50.0 g of iron reacts with hydrochloric acid:

$Fe$ (s) + 2 $HCl$ (aq) → $FeCl_2$ (aq) + $H_2$ (g) assuming the reaction takes place in **a)** a **closed** vessel of fixed volume, and **b)** an **open** beaker at 25 °C. (The atomic mass of iron is 55.85 g/mol)

**Problem 1.2.4.** In *Example 3* of the main text an expression was derived for the reversible isothermal expansion of an ideal gas. Now consider the reversible expansion of a gas under **isobaric** (constant P) conditions. Show that for the reversible isobaric expansion of an ideal gas the work is

$$w = -nR\Delta T \tag{1.2.37}$$

(Hint: start with the definition of the work of expansion as $dw = -P_{ex} \cdot dV$ .)

**Problem 1.2.5.** Derive an expression for $\Delta H$, $\Delta U$, $w$, and $q$ for the reversible expansion of an ideal gas under the following conditions: **a)** isobaric (Hint: see Problem 4), **b)** isochoric (constant V), **c)** isothermal (Hint: see Example 3), **d)** adiabatic (no heat flow, Hint: q=0).

**Problem 1.2.6.** The molar heat capacity for **liquid** methanol is $\bar{C}_v = 68.624$ J K$^{-1}$ mol$^{-1}$. The density of methanol is 0.792 g/mL. How much heat is released when 50 mL of liquid methanol is cooled from 60 °C to 10 °C? If the process is performed in an open container, what is the change in enthalpy $\Delta H$? (Hint: $\bar{C}_v \approx \bar{C}_p$ for a liquid).

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# SECTION OVERVIEW

## 1.3: Extended Explanations- The First Law of Thermodynamics

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# 1.3.1: Overview of Classical Thermodynamics

Understanding chemistry requires understanding the impact on matter of transformations of energy (e.g. chemical to thermal) and transfers of energy. The energy of interaction between particles dictates the structure of matter. Energy flow is important in chemical reactions and impacts how chemical reactions are used by living organisms and our technology to generate useful materials and do useful work. Classical thermodynamics provides the framework for understanding the macroscopic and microscopic implications energy in chemistry.

One of the pioneers in the field of modern thermodynamics was James P. Joule (1818 - 1889). Among the experiments Joule carried out, was an attempt to measure the effect on the temperature of a sample of water that was caused by doing work on the water. Using a clever apparatus to perform work on water by using a falling weight to turn paddles within an insulated canister filled with water, Joule was able to measure a temperature increase in the water.

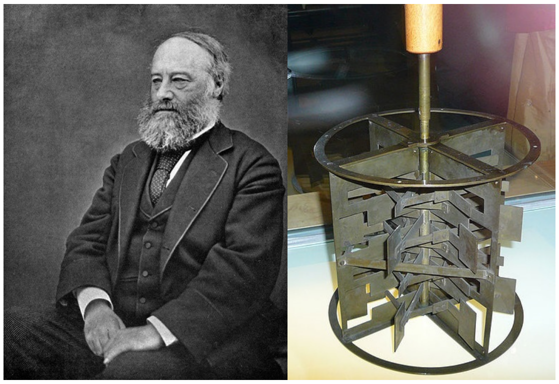


Figure 1.3.1.1: (left) James Prescott Joule (1818 - 1889) (right) Joule's apparatus for measuring the work equivalent of heat. (CC BY-SA 3.0; Dr. Mirko Junge)

Thus, Joule was able to show that work and heat can have the same effect on matter – a change in temperature! It would then be reasonable to conclude that heating, as well as doing work on a system will increase its energy content, and thus it's ability to perform work in the surroundings. This leads to one version of the **First Law of Thermodynamics**:

> *The capacity of a system to do work is increased by heating the system or doing work on it.*

The **internal energy** (U) of a system is a measure of its capacity to supply energy that can do work within the surroundings, making U the ideal variable to keep track of the flow of heat and work energy into and out of a system. Changes in the internal energy of a system ($\Delta U$) can be calculated by

$$\Delta U = U_f - U_i \tag{1.3.1.1}$$

where the subscripts $i$ and $f$ indicate initial and final states of the system. $U$ as it turns out, is a state variable. In other words, the amount of energy available in a system to be supplied to the surroundings is independent on how that energy came to be available. That's important because the manner in which energy is transferred is path dependent.

There are two main methods energy can be transferred to or from a system. These are suggested in the previous statement of the first law of thermodynamics. Mathematically, we can restate the first law as

$$\Delta U = q + w$$

or

$$dU = dq + dw$$

where q is defined as the amount of energy that flows into a system in the form of **heat** and w is the amount of energy gained by system from **work** done on the system. Note that in the field of physics the opposite sign convention is used for work, where work is done by the system on the surroundings, leading to dU = dq - dw.

## 1.3.1.1: Heat

Heat is the kind of energy that in the absence of other changes would have the effect of changing the temperature of the system. A process in which heat flows into a system is **endothermic** from the standpoint of the system ($q_{system} > 0$, $q_{surroundings} < 0$). Likewise, a process in which heat flows out of the system (into the surroundings) is called **exothermic** ($q_{system} < 0$, $q_{surroundings} > 0$). In the absence of any energy flow in the form or work, the flow of heat into or out of a system can be measured by a change in temperature. In cases where it is difficult to measure temperature changes of the system directly, the amount of heat energy transferred in a process can be measured using a change in temperature of the soundings. (This concept will be used later in the discussion of calorimetry).

An infinitesimal amount of heat flow into or out of a system can be related to a change in temperature by

$$dq = C\,dT$$

where C is the **heat capacity** and has the definition

$$C = \frac{dq}{\partial T}$$

Heat capacities generally have units of (J mol$^{-1}$ K$^{-1}$) and magnitudes equal to the number of J needed to raise the temperature of 1 mol of substance by 1 K. Similar to a heat capacity is a **specific heat** which is defined per unit mass rather than per mol. The specific heat of water, for example, has a value of 4.184 J g$^{-1}$ K$^{-1}$ (at constant pressure – a pathway distinction that will be discussed later.)

### ✓ Example 1.3.1.1: Heat required to Raise Temperature

How much energy is needed to raise the temperature of 5.0 g of water from 21.0 °C to 25.0 °C?

**Solution**

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

### Explanation of partial derivatives and example of a state variable.

A partial derivative, like a total derivative, is a slope. It gives a magnitude as to how quickly a function changes value when one of the dependent variables changes. Mathematically, a partial derivative is defined for a function $f(x_1, x_2, \ldots x_n)$ by

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

Because it measures how much a function changes for a change in a given dependent variable, infinitesimal changes in the in the function can be described by

$$df = \sum_i \left(\frac{\partial f}{\partial x_i}\right)_{x_j \neq i} dx_i$$

So that each contribution to the total change in the function $f$ can be considered separately.

For simplicity, consider an ideal gas. The pressure can be calculated for the gas using the ideal gas law. In this expression, pressure is a function of temperature and molar volume.

$$p(V,T) = \frac{RT}{V}$$

The partial derivatives of p can be expressed in terms of $T$ and $V$ as well.

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2} \tag{1.3.1.2}$$

and

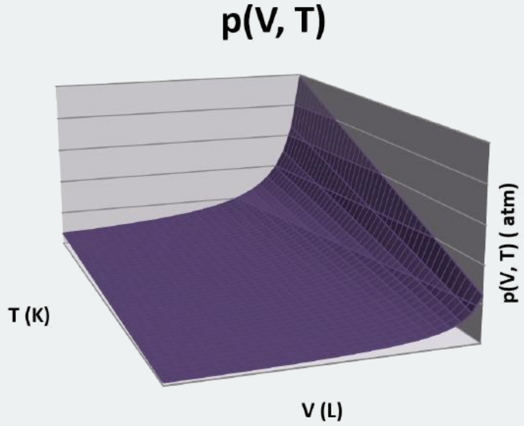
$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} \tag{1.3.1.3}$$

So that the change in pressure can be expressed

$$dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT \tag{1.3.1.4}$$

or by substituting Equations 1.3.1.2and 1.3.1.3

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



Macroscopic changes can be expressed by integrating the individual pieces of Equation 1.3.1.4over appropriate intervals.

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

This can be thought of as two consecutive changes. The first is an **isothermal** (constant temperature) expansion from $V_1$ to $V_2$ at $T_1$ and the second is an **isochoric** (constant volume) temperature change from $T_1$ to $T_2$ at $V_2$. For example, suppose one needs to calculate the change in pressure for an ideal gas expanding from 1.0 L/mol at 200 K to 3.0 L/mol at 400 K. The set up might look as follows.

$$\Delta p = \underbrace{\int_{V_1}^{V_2} \left(-\frac{RT}{V^2}\right) dV}_{\text{isothermal expansion}} + \underbrace{\int_{T_1}^{T_2} \left(\frac{R}{V}\right) dT}_{\text{isochoric heating}}$$

or

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

Alternatively, one could calculate the change as an isochoric temperature change from $T_1$ to $T_2$ at $V_1$ followed by an isothermal expansion from $V_1$ to $V_2$ at $T_2$:

$$\Delta p = \int_{T_1}^{T_2} \left(\frac{R}{V}\right) dT + \int_{V_1}^{V_2} \left(-\frac{RT}{V^2}\right) dV$$

or

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

This results demonstrates an important property of pressure in that pressure is a state variable, and so the calculation of changes in pressure do not depend on the pathway!

## 1.3.1.2: Work

Work can take several forms, such as expansion against a resisting pressure, extending length against a resisting tension (like stretching a rubber band), stretching a surface against a surface tension (like stretching a balloon as it inflates) or pushing electrons through a circuit against a resistance. The key to defining the work that flows in a process is to start with an infinitesimal amount of work defined by what is changing in the system.

Table 1.3.1.1: Changes to the System

| Type of work | Displacement | Resistance | dw |
|---|---|---|---|
| **Expansion** | dV (volume) | -$p_{ext}$ (pressure) | -$p_{ext}$dV |
| **Electrical** | dQ (charge) | Ω (resistence) | $-\Omega dQ$ |
| **Extension** | dL (length) | -t (tension) | t dL |
| **Stretching** | dA | -s (surf. tens.) | sdA |

The pattern followed is always an infinitesimal displacement multiplied by a resisting force. The total work can then be determined by integrating along the pathway the change follows.

### ✓ Example 1.3.1.2: Work from a Gas Expansion

What is the work done on 1.00 mol an ideal gas expanding from a volume of 22.4 L to a volume of 44.8 L against a constant external pressure of 0.500 atm?

**Solution**

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

since the pressure is constant, we can integrate easily to get total work

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

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

---

# 1.3.2: Pressure-Volume Work

Work in general is defined as a product of a force $\mathbf{F}$ and a path element $\mathbf{ds}$. Both are vectors and work is computed by integrating over their inner product:

$$w = \int \mathbf{F} \cdot \mathbf{ds}$$

Moving an object against the force of friction as done in the above dissipation experiment is but one example of work:

$$w_{friction} = \int \mathbf{F}_{\text{friction}} \cdot \mathbf{ds}$$

We could also think of *electrical* work. In that case we would be moving a charge *e* (e.g. the negative charge of an electron) against an electrical (vector) field $\mathbf{E}$. The work would be:

$$w_{electical} = \int e\mathbf{E} \cdot \mathbf{ds}$$

Other examples are the stretching of a rubber band against the elastic force or moving a magnet in a magnetic field etc, etc.

## Pressure-volume ($PV$) work

In the case of a cylinder with a piston, the pressure of gas molecules on the inside of the cylinder, $P$, and the gas molecules external to the piston, $P_{\text{ext}}$ both exert a force against each other. Pressure, $P$, is the force, $F$, being exerted by the particles per area, $A$:

$$P = \frac{F}{A}$$

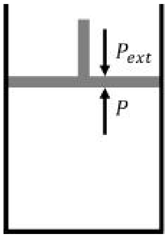


Figure 1.3.2.1 : A piston with internal pressure $P$ and external pressure $P_{\text{ext}}$.

We can assume that all the forces generated by the pressure of the particles operate parallel to the direction of motion of the piston. That is, the force moves the piston up or down as the movement of the piston is constrained to one direction. The piston moves as the molecules of the gas rapidly equilibrate to the applied pressure such that the internal and external pressures are the same. The result of this motion is work:

$$w_{volume} = \int \left(\frac{F}{A}\right)(A\, ds) = \int P\, dV \tag{1.3.2.1}$$

This particular form of work is called **pressure-volume ($PV$) work** and will play an important role in the development of our theory. Notice however that volume work is only ***one form*** of work.

### Sign Conventions

It is important to create a sign convention at this point: positive heat, positive work is always energy you put in into the system. If the system decides to remove energy by giving off heat or work, that gets a minus sign.

In other words: ***you pay the bill***.

To comply with this convention we need to rewrite volume work (Equation 1.3.2.1) as

$$w_{PV} = -\int \left(\frac{F}{A}\right)(A\, ds) = -\int P\, dV$$

> Hence, to decrease the volume of the gas ($\Delta V$ is negative), we must put in (positive) work.

Thermodynamics would not have come very far without cylinders to hold gases, in particular steam. The following figure shows when the external pressure, $P_{\text{ext}}$, is greater than and less than the internal pressure, $P$, of the piston.

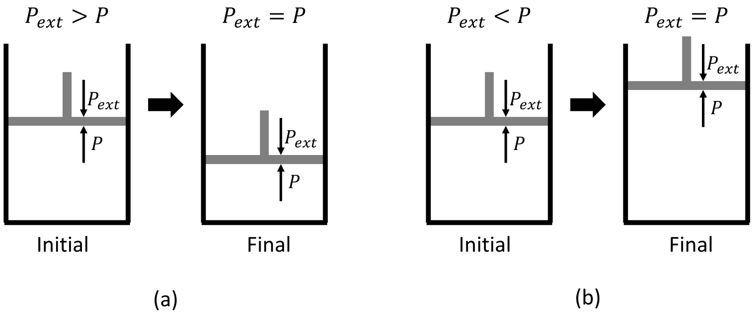


Figure 1.3.2.2 : Pistons showing a compression (left) and an expansion (right).

If the pressure, $P_{\text{ext}}$, being exerted on the system is constant, then the integral becomes:

$$w = -P_{\text{ext}} \int_{V_{initial}}^{V_{final}} dV = -P_{\text{ext}} \Delta V \tag{1.3.2.2}$$

Since the system pressure (inside the piston) is not the same as the pressure exerted on the system, the system is not in a state of equilibrium and cannot be shown directly on and $PV$ diagram. This type of process is called an irreversible process. For a system that undergoes irreversible work at constant external pressure, we can show the amount of work being done on a $PV$ diagram despite not being able to show the process itself.

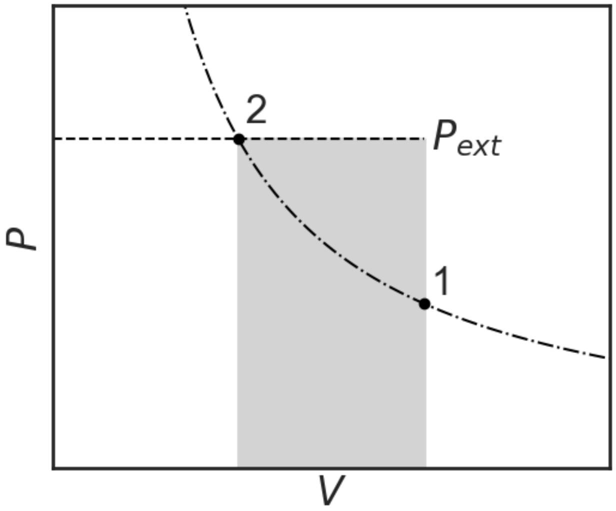


Figure 1.3.2.3 : A system is compressed under constant external pressure, $P_{\text{ext}}$, from state 1 to state 2. The shaded area shows the amount of work being done for the compression. The dash-dot line is an isotherm, a path of constant temperature, showing that the initial and final temperature of the irreversible compression are the same.

Note that the external pressure, $P_{\text{ext}}$, exerted on the system is constant. If the external pressure changes during the compression, we must *integrate* over the whole range:

$$w = -\int_{V_{initial}}^{V_{final}} P_{\text{ext}}(V)\, dV$$

---

# 1.3.3: Work and Heat are not State Functions

## 1.3.3.1: Heat and work are path functions

Heat ($q$) and work ($w$) are path functions, not state functions:

1. They are path dependent.
2. They are energy transfer → they are not intrinsic to the system.

**Path Functons**

Functions that depend on the path taken, such as work ($w$) and heat ($q$), are referred to as **path functions**.

## 1.3.3.2: Reversible versus irreversible

Let's consider a piston that is being compressed at constant temperature (isothermal) to half of its initial volume:

1. Start with cylinder 1 liter, both external and internal pressure 1 bar.
2. ***Peg*** the piston in a fixed position.
3. Put cylinder in a pressure chamber with $P_{ext} = 2$ bar.
4. Suddenly pull the peg.

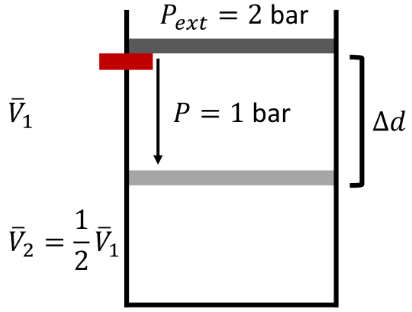


Figure 1.3.3.1 : A piston is being irreversibly and isothermally compressed under constant external pressure from state 1 to state 2.

The piston will shoot down till the internal and external pressures balance out again and the volume is 1/2 L. Notice that the external pressure was ***maintained*** constant at 2 bar during the peg-pulling and that the internal and external pressures were ***not*** balanced at all time. In a $P-V$ diagram of an ideal gas, $P$ is a hyperbolic function of $V$ under constant temperature (isothermal), but this refers to the *internal* pressure of the gas. It is the external one that counts when computing work and they are not necessarily the same. As long as $P_{external}$ is constant, work is represented by a rectangle.

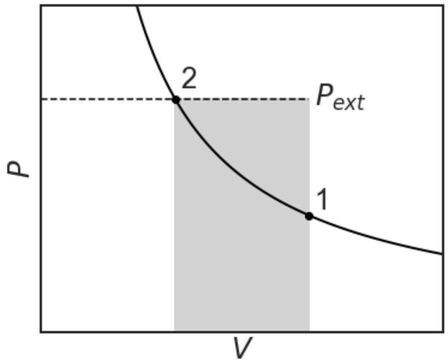


Figure 1.3.3.1 : The system is being irreversibly and isothermally compressed from state 1 to 2. The amount of work being done on the system is shown by the shaded area.

The amount of work being done is equal to the shaded region and in equation:

$$w = -\int_{V_1}^{V_2} P dV = -P_{ext}(V_2 - V_1) = -P\Delta V$$

This represents the maximum amount of work that can be done for an isothermal compression. Work is being done on the system, so the overall work being done is positive. Let's repeat the experiment, but this time the piston will compress reversibly over infinitesimally small steps where the $P_{ext} = P_{system}$ :

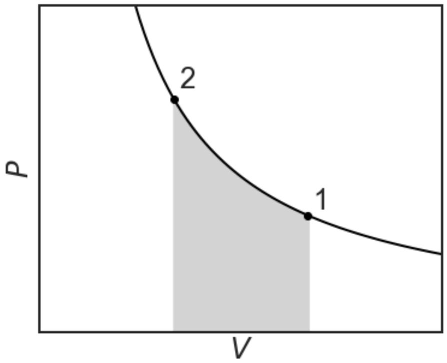


Figure 1.3.3.1 : The system is being reversibly and isothermally compressed from state 1 to 2. The amount of work being done on the system is shown by the shaded area. Note that for a compression, a reversible process does less work than an irreversible process.

For an ideal gas, the amount of work being done along the reversible compression is:

$$w = -\int_{V_1}^{V_2} P dV = -nRT \int_{V_1}^{V_2} \frac{1}{V} = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

The amount of work being done to the two systems are not the same in the two diagrams (see the gray areas). Work is not a state, but a path function, as it depends on the path taken. You may say, what's the big difference. In both cases, the system is compressed from state 1 to state 2. The key is the word ***suddenly***. By pegging the position in place for the first compression, we have created a situation where the external pressure is higher than the internal pressure ($P_{ext} > P$). Because work is done suddenly by pulling the peg out, the internal pressure is struggling to catch up with the external one. During the second compression, we have $P_{ext} = P$ at all times. It's a bit like falling off a cliff versus gently sliding down a hill. Path one is called an irreversible path, the second a reversible path.

**Reversible vs. Irreversible Processes**

A reversible path is a path that follows a series of states at rest (i.e., the forces are allowed to balance at all times). In an irreversible one the forces only balance at the very end of the process.

Notice that less work is being done on the reversible isothermal compression than the one-step irreversible isothermal compression. In fact, the minimum amount of work that can be done during a compression always occurs along the reversible path.

### 1.3.3.2.1: Isothermal Expansion

Let's consider a piston that is being expanded at constant temperature (isothermal) to twice of its initial volume:

1. Start with cylinder 1 liter in a pressure chamber with both an external and internal pressure of 2 bar.
2. ***Peg*** the piston in a fixed position.
3. Take the cylinder out of the pressure chamber with $P_{ext}$= 1 bar.
4. Suddenly pull the peg.

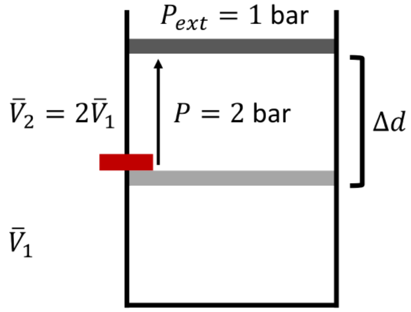


Figure 1.3.3.1 : A piston is being irreversibly and isothermally expanded under constant external pressure from state 1 to state 2.

The piston will shoot up till the internal and external pressures balance out again and the volume is 2 L. Notice that the external pressure was ***maintained*** constant at 1 bar during the peg-pulling and that the internal and external pressures were ***not*** balanced at all time.

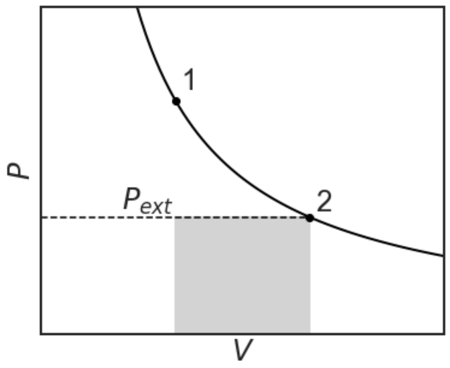


Figure 1.3.3.1 : The system is being irreversibly and isothermally expanded from state 1 to 2. The amount of work being done by the system is shown by the shaded area.

The amount of irreversible work being done is again equal to the shaded region and the equation:

$$w = -P\Delta V = -P_{ext}(V_2 - V_1) = -P\Delta V$$

This represents the minimum amount of work that can be done for an isothermal expansion. Work is being done on the system, so the overall work being done is negative. Let's repeat the experiment, but this time the piston will compress reversibly over infinitesimally small steps where the $P_{ext} = P_{system}$ :

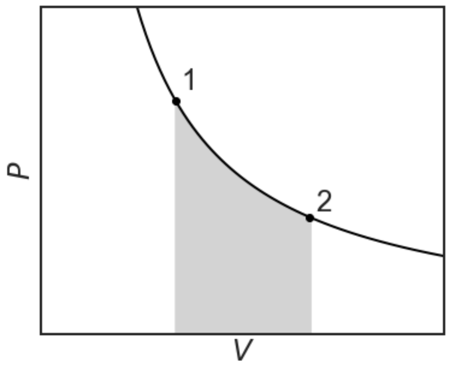


Figure 1.3.3.1 : The system is being reversibly and isothermally expanded from state 1 to 2. The amount of work being done by the system is shown by the shaded area. Note that for an expansion, a reversible process does more work than an irreversible process.

Notice that not only is more work is being done than the one-step irreversible isothermal expansion, but it is the same amount of work being done as the reversible isothermal compression. This is the maximum amount of work that can be done during an expansion.

# 1.3.4: Energy is a State Function

## 1.3.4.1: Work and heat are not state functions

> **A Better Definition of the First law of thermodynamics**
>
> The change in internal energy of a system is the sum of $w$ and $q$, which is a state function.

The realization that work and heat are both forms of energy transfer undergoes quite an extension by saying that internal energy is a state function. It means that although heat and work can be produced and destroyed (and transformed into each other), energy is conserved. This allows us to do some serious bookkeeping! We can write the law as:

$$\Delta U = w + q$$

But the (important!) bit about the state function is better represented if we talk about small changes of the energy:

$$dU = \delta w + \delta q$$

We write a straight Latin $d$ for $U$ to indicate when the change in a state function, where as the changes in work and heat are path-dependent. This is indicated by the 'crooked' $\delta$. We can represent changes as integrals, but only for $U$ can we say that regardless of path we get $\Delta U = U_2 - U_1$ if we go from state one to state two. (I.e. it only depends on the end points, not the path).

> Notice that when we write $dU$ or $\delta q$, we always mean infinitesimally small changes, i.e. we are implicitly taking a limit for the change approaching zero. To arrive at a macroscopic difference like $\Delta U$ or a macroscopic (finite) amount of heat $q$ or work $w$ **we need to integrate**.

We will now invoke the **first law of thermodynamics**:

- $dU = \delta q + \delta w$
- $\oint dU = 0$
- Internal energy is conserved

These are all ways of saying that internal energy is a state function.

---

# 1.3.5: An Adiabatic Process is a Process in which No Energy as Heat is Transferred

## 1.3.5.1: Isothermal expansion of an ideal gas

For a monatomic ideal gas we have seen that energy $\langle E \rangle$ observed as $U = 3/2nRT$. This means that energy is only dependent on temperature and if a gas is compressed **isothermally**, then the internal energy does not change:

$$\Delta U_{isothermal-idealgas} = 0$$

This means that the reversible work must ***cancel*** the reversible heat:

$$\Delta U_{rev} = w_{rev} + q_{rev} = 0$$

Therefore

$$w_{rev} = -q_{rev}$$

so from the expression of the reversible work for expansion in the last section

$$q_{rev} = nRT \ln \frac{V_2}{V_1}$$

If $V_2 > V_1$ (expansion), then you (or the environment) **must** put heat into the system because this is a positive number.

## 1.3.5.2: Adiabatic expansion of an ideal gas

Now suppose you make sure that no heat can enter the cylinder. (Put it in styrofoam or so). Then the path can still be reversible (slow pulling) but the process is then adiabatic.

> *This bat- part comes from a Greek verb βαινω (baino) that means walking, compare acro**bat**, someone who goes high places (acro-). The δια (dia) part means 'through' (cf. diagram, diorama, diagonal etc.) and the prefix α- (a-) denies it all (compare atypical versus typical).*

So the styrofoam prevents the heat from walking through the wall. When expanding the gas from $V_1$ to $V_2$ it still does reversible work but where does that come from? It can only come from the internal energy itself. So in this case any energy change should consist of work (adiabatic means: $\delta q = 0$).

$$dU = \delta w_{rev}$$

This implies that the temperature must drop, because if $U$ changes, then $T$ must change.

The change of energy with temperature at constant volume is known as the heat capacity (at constant volume) $C_v$

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

For an ideal gas $U$ only changes with temperature, so that

Image:CH431_Image61.gif

or:

Image:CH431_Image62.gif

We can now compare two paths to go from state $P_1, V_1, T_1$ to state $P_2, V_2, T_1$:

1. Reversible isothermal expansion A
2. Reversible adiabatic expansion B followed by reversible isochoric heating C

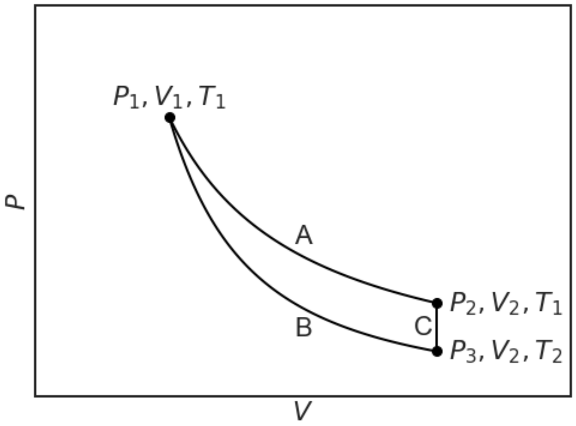


Figure __:

Notice that the temperature remains $T_1$ for path A (isotherm!), but that it drops to $T_2$ on the adiabat B, so that the cylinder has to be isochorically warmed up, C, to regain the same temperature.

$\Delta U_{tot}$ should be the same for both path A and the combined path B+C, because the end points are the same ($U$ is a state function!). As the and points are at the same temperature and $U$ only depends on $T$:

$$\Delta U_{tot} = 0$$

Along adiabat B:

$$q_{rev} = 0$$

Along isochoric heating C, there is no volume work because the volume is kept constant, so that:

Image:CH431_Image63.gif

This is the only reversible heat involved in path B+C. However, we know that $\Delta U_{tot}$ for path A is zero (isothermal!). This means that the volume work along B must cancel the heat along C:

The book keeping looks as follows, all paths are reversible:

$$\Delta U_{B+C} = \Delta U_A = 0 = q_B + w_B + q_C + w_C$$

We know that $q_B = 0$ since it is an adiabat and $w_C = 0$ since it is an isochore:

$$\Delta U_{B+C} = \Delta U_A = 0 = 0 + w_B + q_C + 0$$

Therefore:

$$w_B = -q_C$$

We had already seen before that along the isotherm A:

$$w_A = -q_A = -nRT \ln \frac{V_1}{V_2}$$

As you can see \w_A\) and $w_B$ are ***not*** the same. Work is a path function, even if reversible. As we are working with an ideal gas we can be more precise about $w_B$ and $q_c$ as well. The term $w_B$ along the adiabat is reversible volume work. Since there is no heat along B we can write a straight $d$ instead of $\delta$ for the work contributions (It is the only contribution and must be identical to the state function $dU$):

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# 1.3.6: The Temperature of a Gas Decreases in a Reversible Adiabatic Expansion

We can make the same argument for the heat along C. If we do the three processes A and B+C only to a tiny extent we can write:

Image:CH431_Image65.gif

And now we can integrate from $V_1$ to $V_2$ over the reversible adiabatic work along B and from $T_1$ to $T_2$ for the reversible isochoric heat along C. To separate the variables we do need to bring the temperature to the right side of the equation.:

Image:CH431_Image66.gif

The latter expression is valid for a reversible adiabatic expansion of a monatomic ideal gas (say Argon) because we used the $C_v$ expression for such a system. We can use the gas law $PV = nRT$ to translate this expression in one that relates pressure and volume see Eq 19.23

We can mathematically show that the temperature of a gas decreases during an adiabatic expansion. Assuming an ideal gas, the internal energy along an adiabatic path is:

$$\begin{aligned} d\bar{U} &= \delta q + \delta w \\ &= 0 - P d\bar{V} \\ &= -P d\bar{V} \end{aligned}$$

The constant volume heat capacity is defined as:

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

We can rewrite this for internal energy:

$$d\bar{U} = \bar{C}_V dT$$

Combining these two expressions for internal energy, we obtain:

$$\bar{C}_V dT = -P d\bar{V}$$

Using the ideal gas law for pressure of an ideal gas:

$$\bar{C}_V dT = -\frac{RT}{\bar{V}} d\bar{V}$$

Separating variables:

$$\frac{\bar{C}_V}{T} dT = -\frac{R}{\bar{V}} d\bar{V}$$

This is an expression for an ideal path along a reversible, adiabatic path that relates temperature to volume. To find our path along a PV surface for an ideal gas, we can start in TV surface and convert to a PV surface. Let's go from $(T_1, V_1)$ to $(T_2, V_2)$.

$$\int_{T1}^{T_2} \frac{\bar{C}_V}{T} dT = -\int_{\bar{V}_1}^{\bar{V}_2} \frac{R}{\bar{V}} d\bar{V}$$

$$\bar{C}_V \ln\left(\frac{T_2}{T_1}\right) = -R \ln\left(\frac{\bar{V}_2}{\bar{V}_1}\right) = R \ln\left(\frac{\bar{V}_1}{\bar{V}_2}\right)$$

$$\ln\left(\frac{T_2}{T_1}\right) = \frac{R}{\bar{C}_V} \ln\left(\frac{\bar{V}_1}{\bar{V}_2}\right)$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{\frac{R}{\bar{C}_V}}$$

We know that:

$$R = \bar{C}_P - \bar{C}_V$$

$$\frac{R}{\bar{C}_V} = \frac{\bar{C}_P - \bar{C}_V}{\bar{C}_V} = \frac{\bar{C}_P}{\bar{C}_V} - 1$$

$$\frac{R}{\bar{C}_V} = \gamma - 1$$

Therefore:

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{\gamma-1}$$

This expression shows that volume and temperature are inversely related. That is, as the volume increase from $V_1$ to $V_2$, the temperature must decrease from $T_1$ to $T_2$.

---

# 1.3.7: Work and Heat Have a Simple Molecular Interpretation

## 1.3.7.1: Statistical interpretation

We can use what we know about the statistical side of thermodynamics to give a simple interpretation to a change $dU$:

we see that because $\delta w_{rev} = -PdV$

Image:CH431_Image67.gif

Image:CH431_Image68.gif

See also section 17-5 :In this section it is shown that we can manipulate the partition function to find the pressure of a system by calculating the above moment of the distribution. Again we take the derivative of the logarithm of the partition function $Q$, this time versus V and show that the result resembles the last equation pretty closely (apart from a factor ▯). Thus we get:

Image:CH431_Image69.gif

Image:CH431_Image70.gif

***Once again we can find an important quantity of our system by manipulating the partition function $Q$.***

---

# 1.3.8: Pressure-Volume Work

## 1.3.8.1: Enthalpy

An important point is that pressure-volume work $-PdV$ is only one kind of work. It is the important one for gases but for most other systems we are interested in other kinds of work (e.g. electrical work in a battery).

A good way to measure $\Delta U$'s is to make sure there are no work terms at all. If so:

$$\Delta U_{nowork} = q + w = q + 0 = q$$

However, this means that the $-PdV$ volume work term should also be zero and this implies we must keep volumes the same. That can actually be hard. Therefore we define at new state function ENTHALPY

$$H \equiv U + PV$$

( The $\equiv$ symbol is used to show that this equality is actually a definition.)

If we differentiate we get:

$$dH = dU + d(PV) = dU + PdV + VdP$$

We know that under reversible conditions we have

$$dU = \delta w + \delta q = -PdV + \delta q$$

(+ other work terms that we assume zero)

Thus,

$$dH = -PdV + \delta q + PdV + VdP$$

$$dH = \delta q + VdP$$

That means that as long as there is no other work and we keep the pressure constant:

$$\Delta H = q_P$$

instead of

$$\Delta U = q_V$$

Working at constant $P$ is a lot easier to do than at constant $V$. This means that the enthalpy is a much easier state function to deal with than the energy U.

For example when we melt ice volumes change whether we like or not, but at long as the weather does not change too much pressure is constant. So if we measure how much heat we need to add to melt a mole of ice we get the molar heat of fusion:

Image:CH431 Image71.gif

Such enthalpies are measured and tabulated.

In this case the volume change is actually quite small, as it usually is for condensed matter. Only if we are dealing with gases is the difference between enthalpy and energy really important

So, $U\ H$ for condensed matter, but $U$ and $H$ differ for gases.

A good example of this is the difference between the heat capacity at constant V and at constant P. For most materials there is not much of a difference, but for an ideal gas we have

$$C_p = C - V + nR$$

Needless to say that the heat capacity is a path function: it depends on what you keep constant.

# 1.3.9: Heat Capacity is a Path Function

## 1.3.9.1: Determining enthalpies from heat capacities.

The functions $H$ and $C_p$ are related by differentiation:

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

This means that we can:

1. measure $C_p$ as a function of temperature
2. integrate this function and find $H(T)$

However, there are problems with this approach:

1. Reference point: we have to deal with the lower limit of integration.

   Ideally we start at zero Kelvin (but we cannot get there), but how do we compare one compound to the other?

2. At temperatures where there is a phase transition there is a sudden jump in enthalpy. E.g. when ice melts we have to first add the heat of fusion until all ice is gone before the temperature can go up again (assuming all is done under reversible well-equilibrated conditions).
3. At the jumps in H, the $C_p$ is infinite.

> *It should be stressed that there **are no absolute enthalpies**.*

---

# 1.3.10: Relative Enthalpies Can Be Determined from Heat Capacity Data and Heats of Transition

It should be stressed that there **are no absolute enthalpies**. All that is properly defined are differences in enthalpy ΔH and these are only defined for ***processes***

When dealing with enthalpies

**Define the Process**

For example for the process of:

Process 1: ***heating ice from -20°C to -0°C***

We could write $\Delta H_1 = \int C_{P,ice}.$ dT from T=253K to T=273K = H(273) -H(253). But before moving beyond the melting point first a different process needs to take place, that of

Process 2: ***melting***

This gives us $\Delta_{fus}H = H_{liquid} - H_{solid}$ (both at 273K!). When we heat the liquid water further to say +20°C we would have to integrate over the heat capacity of the liquid.

Process 3: ***heating water from 0°C to +20°C***

We could write

$$\Delta H_3 = \int C_{P,water} dT$$

from T=273K to T=293K = H(293)-H(273).

The total change in enthalpy between -20 and +20 would be the sum of the three enthalpy changes.

$$\Delta H_{totalprocess} = \Delta H_1 + \Delta_{fus} H + \Delta H_3$$

Of course we could consider doing the same calculation for any temperature between -20 and +20 and summarize all our results in a graph. The three processes can thus schematically be shown in Figure 19.10.1 .

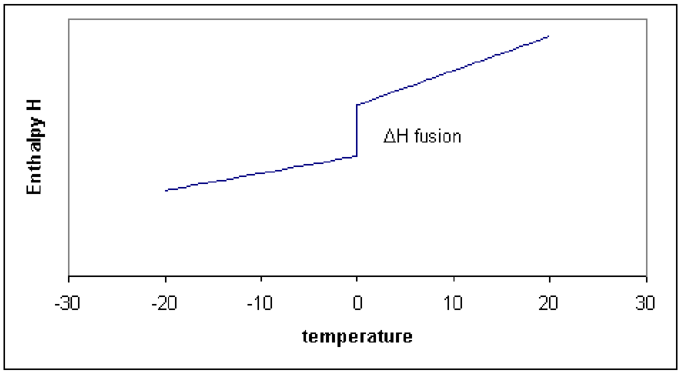


***Figure 19.10.1*** *: Schematic enthalpy function showing the jump at the melting point*

Notice that the slopes (i.e. the heat capacities!) before and after the melting point differ. The slope for the liquid is a little steeper because the liquid has more degrees of freedom and therefore the heat capacity of the liquid tends to be higher than of the solid. In the figure the enthlapy curves are shown as straight lines. This would be the case if the heat capacities are *constant* over the temperature interval. Although $C_p$ is typically a 'slow' or 'weak' function of temperature it usually does change a bit, which means that the straight lines for H become curves.

> *Although $C_p$ is typically a 'slow' or 'weak' function of temperature and is well approximated as a constant.*

Notice that for process two, the temperature is constant, that means that $\Delta T$ or $dT$ is zero, but ΔH is finite, consequently ΔH/ΔT is infinitly large. Taking the limit for ΔT going to zero, we get a derivative:

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

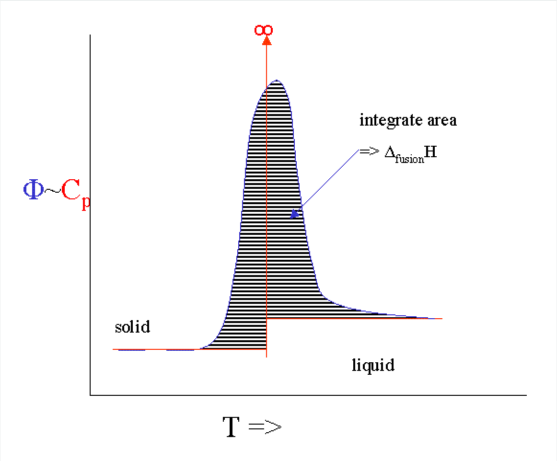
This derivative, the heat capacity must undergo a singularity: the slope is infinitely large (i.e, the $H$ curve goes straight up). When there are more phase transitions, more discontinuities in $H$ and singularities in $C_p$ result (Figure 19.10.1 ). Note that $H(T) - H(0)$, not $H(T)$ is plotted to avoid the question what the absolute enthalpy is.

### Scanningcalorimetry

There is technique that allows us to measure the heat capacity as a function of temperature fairly directly. It is called Differential Scanning Calorimetry (DSC). You put a sample in a little pan and put the pan plus an empty reference pan in the calorimeter. The instrument heats up both pans with a constant heating rate. Both pans get hotter by ***conduction***, but the heat capacity of the filled pan is obviously bigger. This means that the heat flow into the sample pan must be a bit bigger than into the empty one. This differential heat flow induces a tiny temperature difference ΔT between the two pans that can be measured. This temperature difference is proportional to the heat flow difference which is proportional to the heat capacity difference.

$$\Delta T \; \Delta \Phi \; \Delta_{betweenpans} C_p = C_p^{sample} \; (ifthepanscancel)$$

However, there are number of serious broadening issues with the technique. If you melt something you will never get to see the infinite singularity of the heat capacity. Instead it broadens out into a peak. If you integrate the peak you get the $\Delta_{\text{fusion}}$H and the onset is calibrated to give you the melting point.



The ideal heat capacity signal and its broadened DSC signal

It is even possible to heat the sample with a rate that fluctuates with a little sine wave. This "Modulated DSC" version can even give you the (small) difference in $C_p$ before and after the melting event.

---

# 1.3.11: Enthalpy Changes for Chemical Equations are Additive

## 1.3.11.1: Hess's law

As enthalpy and energy are state functions we should expect ***additivity*** of U and H when we study chemical reactions. This additivity is expressed in **Hess's Law**. The additivity has important consequences and the law finds wide spread application in the prediction of heats of reaction.

1. The reverse reaction has the negative enthalpy of the forward one.
2. If we can do a reaction in two steps we can calculate the enthalpy of the combined reaction by adding up:

| Reaction | Enthalpy |
|---|---|
| $C_{(s)}$ + ½ $O_{2(g)}$ -> $CO_{(g)}$ | $\Delta_rH$ = -110.5 kJ |
| $CO_{(g)}$ + ½ $O_{2(g)}$ -> $CO_{2(g)}$ | $\Delta_rH$ = -283.0 kJ |
| This means that | ----------------------+ |
| $C_{(s)}$ + O2(g) -> CO2(g) | $\Delta_rH$ = -393.5 kJ |

By this mechanism it is often possible to calculate the heat of a reaction even if this reaction is hard to carry out. E.g. we could burn both graphite and diamond and measure the heats of combustion for both. The difference would give us the heat of the transformation reaction from graphite to diamond.

### 1.3.11.1.1: Reaction-as-written convention (caution!)

The enthalpy is for the ***reaction-as-written***. That means that if we write:

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

with $\Delta_rH$ = -221 kJ (***not***: -110.5 kJ)

### 1.3.11.1.2: Reverse reactions

Because H is a state function the reverse reaction has the same enthalpy but with opposite sign

$$2CO(g) \rightarrow 2C(s) + O_2(g)$$

with $\Delta_rH$ = +221 kJ

### 1.3.11.1.3: Combining values

It is quite possible that you cannot really do a certain reaction in practice. For many reactions we can arrive at enthalpy values by doing some bookkeeping. For example, we can calculate the enthalpy for the reaction of $PCl_3$ with chlorine if we know the two reactions that the elements phosphorous and chlorine can undergo.

> *You do have to make sure you balance your equations properly!*

---

# 1.3.12: Heats of Reactions Can Be Calculated from Tabulated Heats of Formation

Reaction enthalpies are important, but difficult to tabulate. However, because enthalpy is a state function, it is possible to use **Hess' Law** to simplify the tabulation of reaction enthalpies. Hess' Law is based on the addition of reactions. By knowing the reaction enthalpy for constituent reactions, the enthalpy of a reaction that can be expressed as the sum of the constituent reactions can be calculated. The key lies in the canceling of reactants and products that °Ccur in the "data" reactions but not in the "target reaction.

**Example 1.3.12.1:**

Find $\Delta H_{rxn}$ for the reaction

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

Given

$$C(gr) + ½O_2(g) \rightarrow CO(g)$$

with $\Delta H_1 = -110.53\,kJ$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_2 = -393.51\,kJ$

**Solution**

The target reaction can be generated from the data reactions.

$$2\times[CO(g) \rightarrow C(gr) + O_2(g)]$$

plus

$$2\times[C(gr) + 2O_2(g) \rightarrow 2CO_2(g)]$$

equals

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

so

$$2\times\Delta H_1 = -787.02\,kJ$$

$$2\times\Delta H_2 = 221.06\,kJ$$

$$2\times\Delta H_1 + 2\times\Delta H_2 = -565.96\,kJ$$

## 1.3.12.1: Standard Enthalpy of Formation

One of the difficulties with many thermodynamic state variables (such as enthalpy) is that while it is possible to measure changes, it is impossible to measure an absolute value of the variable itself. In these cases, it is necessary to define a zero to the scale defining the variable. For enthalpy, the definition of a zero is that the standard enthalpy of formation of a pure element in its standard state is zero. All other enthalpy changes are defined relative to this standard. Thus it is essential to very carefully define a standard state.

**Definition: the Standard State**

The standard state of a substance is the most stable form of that substance at 1 atmosphere pressure and the specified temperature.

Using this definition, a convenient reaction for which enthalpies can be measured and tabulated is the **standard formation reaction**. This is a reaction which forms one mole of the substance of interest in its standard state from elements in their standard states. The enthalpy of a standard formation reaction is the **standard enthalpy of formation** ($\Delta H_{f^o}$). Some examples are

- $NaCl(s)$:

  $$Na(s) + ½Cl_2(g) \rightarrow NaCl(s)$$

  with $\Delta H_f^o = -411.2\,kJ/mol$
- $C_3H_8(g)$:

  $$3C(gr) + 4H_2(g) \rightarrow C_3H_8(g)$$

  with $\Delta H_f^o = -103.8\,kJ/mol$

It is important to note that the standard state of a substance is **temperature dependent**. For example, the standard state of water at -10 °C is solid, whereas the standard state at room temperature is liquid. Once these values are tabulated, calculating reaction enthalpies becomes a snap. Consider the heat combustion ($\Delta H_c$) of methane (at 25 °C) as an example.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

The reaction can expressed as a sum of a combination of the following standard formation reactions.

$$C(gr) + 2H_2(g) \rightarrow CH_4(g)$$

with $\Delta H_f^o = -74.6\,kJ/mol$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_f^o = -393.5\,kJ/mol$

$$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$$

with $\Delta H_f^o = -285.8\,kJ/mol$

The target reaction can be generated from the following combination of reactions

$$-1\times [C(gr) + 2H_2(g) \rightarrow CH_4(g)]$$

$$CH_4(g) \rightarrow C(gr) + 2H_2(g)$$

with $\Delta H_f^o = -1\times[-74.6\,kJ/mol] = 74.6\,kJ/mol$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_f^o = -393.5\,kJ/mol$

$$2\times [H_2(g) + ½O_2(g) \rightarrow H_2O(l)]$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

with $\Delta H_f^o = 2\times[-285.8\,kJ/mol] = -571.6\,kJ/mol.$

$$CH_4(g) + 2O_2(g) \rightarrow CO2_(g) + 2H_2O(l)$$

with $\Delta H_c^o = -890.5\,kJ/mol$

Alternately, the reaction enthalpy could be calculated from the following relationship

$$\Delta H_{rxn} = \sum_{products} \nu\cdot\Delta H_f^o - \sum_{reactants} \nu\cdot\Delta H_f^o$$

where $\nu$ is the stoichiometric coefficient of a species in the balanced chemical reaction. For the combustion of methane, this calculation is

$$\begin{aligned}
\Delta_{rxn} &= (1\,mol)\left(\Delta H_f^o(CO_2)\right) + (2\,mol)\left(\Delta H_f^o(H_2O)\right) - (1\,mol)\left(\Delta H_f^o(CH_4)\right) && (1.3.12.1)\\
&= (1\,mol)(-393.5\,kJ/mol) + (2\,mol)\,(-285.8\,kJ/mol) - (1\,mol)\,(-74.6\,kJ/mol) && (1.3.12.2)\\
&= -890.5\,kJ/mol && (1.3.12.3)
\end{aligned}$$

A note about units is in order. Note that reaction enthalpies have units of kJ, whereas enthalpies of formation have units of kJ/mol. The reason for the difference is that enthalpies of formation (or for that matter enthalpies of combustion, sublimation, vaporization, fusion, etc.) refer to specific substances and/or specific processes involving those substances. As such, the total enthalpy change is scaled by the amount of substance used. General reactions, on the other hand, have to be interpreted in a very specific way. When examining a reaction like the combustion of methane

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

with $\Delta H_{rxn} = -890.5\, kJ$. The correct interpretation is that the reaction of one mole of $CH_4$(g) with two moles of $O_2$(g) to form one mole of $CO_2$(g) and two moles of $H_2O$(l) releases 890.5 kJ at 25 °C.

## 1.3.12.2: Ionization Reactions

Ionized species appear throughout chemistry. The energy changes involved in the formation of ions can be measured and tabulated for several substances. In the case of the formation of positive ions, the enthalpy change to remove a single electron at 0 K is defined as the **ionization potential**.

$$M(g) \rightarrow M^+(g) + e^-$$

with $\Delta H(0K) \equiv 1^{st}\text{ ionization potential (IP)}$

The removal of subsequent electrons requires energies called the 2nd Ionization potential, 3rd ionization potential, and so on.

$$M^+(g) \rightarrow M^{2+}(g) + e^-$$

with $\Delta H(0K) \equiv 2^{nd} IP$

$$M^{2+}(g) \rightarrow M^{3+}(g) + e^-$$

with $\Delta H(0K) \equiv 3^{rd} IP$

An atom can have as many ionization potentials as it has electrons, although since very highly charged ions are rare, only the first few are important for most atoms.

Similarly, the **electron affinity** can be defined for the formation of negative ions. In this case, the first electron affinity is defined by

$$X(g) + e^- \rightarrow X^-(g)$$

with $-\Delta H(0K) \equiv 1^{st}\text{ electron affinity (EA)}$

The minus sign is included in the definition in order to make electron affinities mostly positive. Some atoms (such as noble gases) will have negative electron affinities since the formation of a negative ion is very unfavorable for these species. Just as in the case of ionization potentials, an atom can have several electron affinities.

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

with $-\Delta H(0K) \equiv 2^{nd} EA$.

$$X^{2-}(g) + e^- \rightarrow X^{3-}(g)$$

with $-\Delta H(0K) \equiv 3^{rd} EA$.

## 1.3.12.3: Average Bond Enthalpies

In the absence of standard formation enthalpies, reaction enthalpies can be estimated using average bond enthalpies. This method is not perfect, but it can be used to get ball-park estimates when more detailed data is not available. A **bond dissociation energy** $D$ is defined by

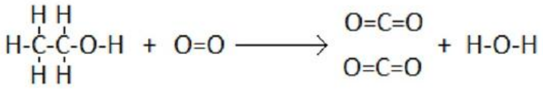
$$XY(g) \rightarrow X(g) + Y(g)$$

with $\Delta H \equiv D(X-Y)$

In this process, one adds energy to the reaction to break bonds, and extracts energy for the bonds that are formed.

$$\Delta H_{rxn} = \sum(\text{bonds broken}) - \sum(\text{bonds formed})$$

As an example, consider the combustion of ethanol:



In this reaction, five C-H bonds, one C-C bond, and one C-O bond, and one O=O bond must be broken. Also, four C=O bonds, and one O-H bond are formed.

| Bond | Average Bond Energy (kJ/mol) |
|---|---|
| **C-H** | 413 |
| **C-C** | 348 |
| **C-O** | 358 |
| **O=O** | 495 |
| **C=O** | 799 |
| **O-H** | 463 |

The reaction enthalpy is then given by

$$\begin{aligned}\Delta H_c &= 5(413\,kJ/mol)+1(348\,kJ/mol)+1(358\,kJ/mol)\\ &\quad +1(495\,kJ/mol)-4(799\,kJ/mol)-2(463\,kJ/mol)\\ &= -856\,kJ/mol\end{aligned} \tag{1.3.12.4}$$

Because the bond energies are defined for gas-phase reactants and products, this method does not account for the enthalpy change of condensation to form liquids or solids, and so the result may be off systematically due to these differences. Also, since the bond enthalpies are averaged over a large number of molecules containing the particular type of bond, the results may deviate due to the variance in the actual bond enthalpy in the specific molecule under consideration. Typically, reaction enthalpies derived by this method are only reliable to within ± 5-10%.

---

# 1.3.13: The Temperature Dependence of ΔH

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

At constant pressure

$$dH = C_p \, dT$$

And so for a temperature change from $T_1$ to $T_2$

$$\Delta H = \int_{T_2}^{T_2} C_p \, dT \tag{1.3.13.1}$$

Equation 1.3.13.1 is often referred to as *Kirchhoff's Law*. If $C_p$ is independent of temperature, then

$$\Delta H = C_p \, \Delta T \tag{1.3.13.2}$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral in Equation 1.3.13.1. A common *empirical* model used to fit heat capacities over broad temperature ranges is

$$C_p(T) = a + bT + \frac{c}{T^2} \tag{1.3.13.3}$$

After combining Equations 1.3.13.3 and 1.3.13.1, the enthalpy change for the temperature change can be found obtained by a simple integration

$$\Delta H = \int_{T_1}^{T_2} \left( a + bT + \frac{c}{T^2} \right) dT \tag{1.3.13.4}$$

Solving the definite integral yields

$$\Delta H = \left[ aT + \frac{b}{2}T^2 - \frac{c}{T} \right]_{T_1}^{T_2} \tag{1.3.13.5}$$

$$= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left( \frac{1}{T_2} - \frac{1}{T_1} \right) \tag{1.3.13.6}$$

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

Table 1.3.13.1: *Empirical Parameters for the temperature dependence of $C_p$*

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

### ✓ Example 1.3.13.1: Heating Lead

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

**Solution**

The enthalpy change is given by Equation 1.3.13.1 with a temperature dependence $C_p$ given by Equation 1.3.13.1 using the parameters in Table 1.3.13.1. This results in the integral form (Equation 1.3.13.6):

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

when substituted with the relevant parameters of Pb(s) from Table 1.3.13.1

$$\begin{aligned}\Delta H = &(22.14\,\frac{J}{mol\;K}(353\;K - 273\;K)\\&+\frac{1.172\times10^{-2}\,\frac{J}{mol\;K^2}}{2}((353\;K)^2-(273\;K)^2)\\&-9.6\times10^4\,\frac{J\,K}{mol}\left(\frac{1}{(353\;K)}-\frac{1}{(273\;K)}\right)\\ \Delta H = &\;1770.4\,\frac{J}{mol}+295.5\,\frac{J}{mol}+470.5\,\frac{J}{mol}\\&=2534.4\,\frac{J}{mol}\end{aligned}$$

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

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

### ✓ Example 1.3.13.2: Enthalpy of Formation

The enthalpy of formation of $NH_3(g)$ is -46.11 kJ/mol at 25 $^oC$. Calculate the enthalpy of formation at 100 $^oC$.

**Solution**

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

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

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

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

---

# 1.3.14: Enthalpy is a State Function

Our expression for internal energy at constant pressure:

$$\Delta U = q_P + w = q_P - P\Delta V$$

Rearrange:

$$q_P = \Delta U + P\Delta V = U_2 - U_1 + P(V_2 - V_1)$$

$$q_P = (U_2 + PV_2) - (U_1 + PV_1)$$

We can define this term as enthalpy:

$$H \equiv U + PV$$

This is a new state function.

---

# 1.3.E: The First Law of Thermodynamics (Exercises)

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region $\Delta x$; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position $\Delta x$ and the uncertainty in momentum $\Delta p$.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{1.3.E.1}$$

You can see from Equation 1.3.E.1 that as $\Delta p$ approaches 0, $\Delta x$ must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

### ? Exercise $1.3.E.1$

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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# 1.4: Thermochemistry

In this chapter we apply the first law of thermodynamics and the concept of enthalpy to chemical reactions. At standard state conditions we can use tabulated heats of formation to calculate the change in enthalpy for any reaction. At temperatures other than standard conditions we use the temperature dependence of the enthalpy to derive an expression for the change in enthalpy of a reaction at any temperature in relation to a reference temperature.

**Learning Objectives**

- Understand how the first law of thermodynamics describes energy changes in chemical reactions.
- Be able to calculate the change in enthalpy for a reaction using the standard enthalpy of formation.
- Be able to calculate the change in enthalpy for a reaction at non-standard temperature from a reference value and reference temperature.

## 1.4.1: Thermochemistry: Heat of reaction

Chemical reactions almost always involve heat transfer. In an **exothermic reaction**, heat is given off during the reaction, meaning that heat is transferred from the system to the surroundings. In an **endothermic reaction**, heat is absorbed during the reaction, meaning that heat is transferred from the surroundings into the system. Recall that under the conditions of constant pressure, the amount of heat, $\mathbf{q_p}$, is equal to the change in enthalpy. Most laboratory and biochemical reactions occur under conditions of constant pressure and so we can equate the change in enthalpy of a reaction $\mathbf{\Delta_r H}$ with the **heat of the reaction**. The subscript in $\mathbf{\Delta_r H}$ indicates that we are here concerned with a chemical reaction and the change of enthalpy associated with that reaction.

Since enthalpy is a state function (does not depend on the path) we can write:

$$\Delta_r H = H_{\text{products}} - H_{\text{reactants}} \tag{1.4.1}$$

Equation 1.4.1 says that the change in enthalpy of a reaction is the difference in enthalpies of the products and reactants. Consider the following reaction of the dimerization of nitrogen dioxide to form dinitrogen tetroxide:

$$2\,\mathrm{NO_2(g)} \rightarrow \mathrm{N_2O_4(g)} \tag{Reaction I}$$

For this reaction, 2 moles of $NO_2$*(g)* react to form 1 mole of $N_2O_4$*(g)*. The molar change in enthalpy will be:

$$\Delta_r H = H(\mathrm{N_2O_4}) - 2H(\mathrm{NO_2}) \tag{1.4.2}$$

Notice that because we have two moles of reactant $NO_2$*(g)* for every one mole of product $N_2O_4$*(g)* we multiply the molar enthalpy of $NO_2$*(g)* by the stoichiometric coefficient 2. The absolute molar enthalpies of the individual reactants and products are not easily measured. Fortunately, because enthalpy is a state function, the change in enthalpy for the reaction will be the same no matter what path is taken from reactant to product. To calculate $\mathbf{\Delta_r H}$ for the reaction, we break the reaction into two intermediate steps, shown schematically in figure 1.4.1. We first break the reactants into their constituent elements at standard state and then form the products from their constituent elements in the standard state. The reason for breaking the reaction into these intermediate steps is that we can look-up tabulated values for the standard heats of formation for these reactions. We can then sum together the change in enthalpy for the individual steps to obtain the overall change in enthalpy.

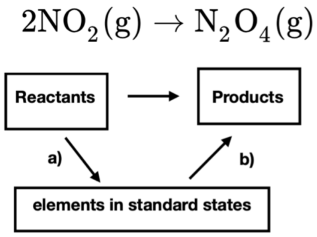


Figure 1.4.1: Schematic description of Hess's law. The total reaction is broken into two elementary steps. In step a) the reactants are broken into their constituent elements, and in step b) the products are formed from the constituent elements.

In our example, we first write the reaction for breaking reactant $NO_2$*(g)* into its elements at standard state:

$$2\,\mathrm{NO_2(g)} \rightarrow \mathrm{N_2(g)} + 2\,\mathrm{O_2(g)} \tag{Reaction I.a}$$

We can look up the change in molar enthalpy of formation, $\Delta_f \bar{H}^{\circ}$, for NO$_2$ *(g)*. Notice that the superscript $^{\circ}$ indicates standard state conditions. The change in enthalpy of formation, $\Delta_f H^o$ for NO$_2$*(g)* is for the formation of one mole of NO$_2$ *(g)* from its constituent elements as shown in this reaction:

$$\tfrac{1}{2}\mathrm{N_2(g)} + \mathrm{O_2(g)} \rightarrow \mathrm{NO_2(g)}$$

Notice that the $\Delta_r H^o$ for *Reaction I.a* above is -2 $\Delta_f H^o$ for NO$_2$ *(g)*.

Similarly, for the products we write the reaction for the formation of products from their constituent elements:

$$\mathrm{N_2(g)} + 2\,\mathrm{O_2(g)} \rightarrow \mathrm{N_2O_4(g)} \tag{Reaction I.b}$$

We can look up in a table the value of $\Delta_f H^o$ for N$_2$O$_4$ *(g)*. Notice that the $\Delta_r H^o$ for Reaction I.b is equal to $\Delta_f H^o$ for N$_2$O$_4$ (g) as shown in this reaction:

$$\mathrm{N_2(g)} + 2\,\mathrm{O_2(g)} \rightarrow \mathrm{N_2O_4(g)}$$

Summing *Reaction I.a* and *Reaction I.b* gives the overall reaction:

$$\begin{array}{lcc}
\text{a)} & 2\mathrm{NO_2}(g) \rightarrow \cancel{\mathrm{N_2}}(g) + \cancel{2\mathrm{O_2}} & -2\Delta_f H(\mathrm{NO_2}) \\
\text{b)} & \cancel{\mathrm{N_2}}(g) + \cancel{2\mathrm{O_2}}(g) \rightarrow \mathrm{N_2O_4}(g) & \Delta_f H(\mathrm{N_2O_4}) \\
\hline
\textit{Reaction I} & 2\mathrm{NO_2}(g) \rightarrow \mathrm{N_2O_4}(g) & \Delta_r H^{\circ}
\end{array}$$

and we can write the $\Delta_r H^o$ for the overall reaction as the sum of the two intermediate steps:

$$\Delta_r H^o = \Delta_f H^o(\mathrm{N_2O_4}) - 2\Delta_f H^o(\mathrm{NO_2}) \tag{1.4.3}$$

In general, we can write the change of enthalpy of a reaction at standard conditions as

$$\Delta_r H^o = \sum \nu \Delta_f H^o(\text{products}) - \sum \nu \Delta_f H^o(\text{reactants}) \tag{1.4.4}$$

where $\Delta_f H^o$ are the standard molar heats of formation, $\nu$ are the stoichiometric coefficients, and the sum is over the products minus the sum over the reactants. Equation 1.4.4 is a specific application of **Hess's law** which states that in a chemical reaction $\Delta_r H^o$ does not depend on the intermediate steps.

See Practice Problems 1.4.1 and 1.4.2.

## 1.4.2: Temperature dependence of heat of reaction

Hess's Law and Equation 1.4.4 allows us to calculate $\mathbf{\Delta_r H}^{\circ}$ at standard conditions using tabulated data for standard heats of formation. In order to calculate $\Delta_r H$ at non-standard state conditions, we need to know how $\Delta_r H$ varies with temperature. Recall that the slope of the enthalpy vs. temperature at constant pressure gives the heat capacity:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \tag{1.4.5}$$

or, rearranging we get:

$$dH = C_p \cdot dT \tag{1.4.6}$$

For considering changes in $\Delta_r H$ with temperature, we replace $\mathbf{H}$ in Equation 1.4.6 with $\mathbf{\Delta_r H}$ to get:

$$d\Delta_r H = \Delta_r C_p \cdot dT \tag{1.4.7}$$

where $\mathbf{\Delta_r C_p}$ is the difference in heat capacities of products and reactants and is given by a Hess's Law-type analog:

$$\Delta_r C_p = \sum \nu C_p^{(\text{products})} - \sum \nu C_p^{(\text{reactants})} \tag{1.4.8}$$

where the sum is over the individual heat capacities of the products minus the reactants weighted by their stoichiometric coefficients. We integrate both sides of Equation 1.4.7 from an initial reference state to a final state:

$$\int_{T^\circ}^{T_2} d\Delta_r H = \int_{T^\circ}^{T_2} \Delta_r C_p \cdot dT$$

$$\Delta_r H_{T_2} - \Delta_r H_{T^\circ} = \int_{T^\circ}^{T_2} \Delta_r C_p \cdot dT$$

$$\Delta_r H_{T_2} = \Delta_r H_{T^\circ} + \int_{T^\circ}^{T_2} \Delta_r C_p \cdot dT \tag{1.4.9}$$

Equation 1.4.9 allows us to compute the $\mathbf{\Delta H}$ of a reaction at any non-standard temperature if we know how $\mathbf{\Delta_r C_p}$ depends on temperature. Usually this is determined experimentally and $\mathbf{\Delta_r C_p}$ is fit to a polynomial function that interpolates the data. However, if the heat capacity is independent of temperature (as it is for an ideal gas), we can take $\mathbf{\Delta_r C_p}$ out of the integral to obtain:

$$\Delta_r H_{T_2} = \Delta_r H_{T^\circ} + \Delta_r C_p \int_{T^\circ}^{T_2} dT$$

$$\Delta_r H_{T_2} = \Delta_r H_{T^\circ} + \Delta_r C_p (T_2 - T^\circ) \tag{1.4.10}$$

Equation 1.4.10 is known as **Kirchhoff's law** and is valid if $\mathbf{\Delta_r C_p}$ is independent of temperature. We can see schematically that Kirchhoff's law results from taking the reaction at $T_2$ and breaking it into three steps:

1. Heat/cool the reactant from $T_2$ to $T^\circ$ using $\Delta H = C_p^{reactants} \Delta T$.
2. Find $\Delta_r H$ of the reaction at $T^\circ$ using the tabulated heats of formation and Hess's law.
3. Cool/heat the products from $T^\circ$ back to $T_2$ using $\Delta H = C_p^{products} \Delta T$

Summing these three steps results in Kirchhoff's law Equation 1.4.10 where $\mathbf{\Delta_r C_p}$ is the difference in heat capacities between the products and reactants. figure $PageIndex2$ shows a schematic of this process.

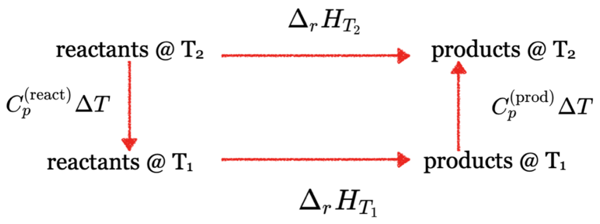


Figure $PageIndex2$: Schematic depiction of Kirchhoff's law: The $\Delta_r H$ at some non-standard temperature $T_2$ is calculated in a three-step process where in step 1) the reactants are heated/cooled from $T_2$ to $T_1$. In step 2) the reactants are converted into products at a reference temperature for which $\Delta_r H$ is known. In step 3) the products are cooled/heated from the reference temperature $T_1$ back to the temperature of interest $T_2$.

See Practice Problem 1.4.3.

## 1.4.3: Examples

### ✓ Example 1.4.1

Methane gas is burned in a Bunsen burner. Use Hess's law to calculate $\Delta_r H^\circ$ of the combustion of methane at 298 K and 1 bar. The standard molar enthalpies of formation at 298 K and 1 bar are:

| | |
|---|---|
| $CH_4$ (g) | $\Delta_f \bar{H}^\circ$ = -74.85 kJ/mol |
| $CO_2$ (g) | $\Delta_f \bar{H}^\circ$ = -393.5 kJ/mol |
| $H_2O$ (g) | $\Delta_f \bar{H}^\circ$ = -241.8 kJ/mol |

**Solution**

For the combustion of methane, the balanced chemical reaction is:

$CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2(g) + 2\,H_2O\,(g)$

From Equation 1.4.4:

$\Delta_r H^\circ$ = [ $\Delta_f H^\circ$ ($CO_2$)+ 2 $\Delta_f H^\circ$ ($H_2O$) ] - [$\Delta_f H^\circ$ ($CH_4$) + 2 $\Delta_f H^\circ$ ($O_2$)]

By convention, we assigne a value of zero to $\Delta_f \bar{H}^\circ$ for elements in their most stable allotropic state, so $\Delta_f \bar{H}^\circ$ (O2) = 0 at 298 K. Using the tabulated values of $\Delta_f H^\circ$:

$\Delta_r H^\circ = [-393.5\text{ kJ/mol} + 2(-241.8\text{ kJ/mol})] - (-74.85\text{ kJ/mol})$

$\Delta_r H^\circ = -802.3\text{ kJ/mol}$

**Example 1.4.2**

Calculate the value of $\Delta_r \bar{H}$ for the dimerization of nitrogen dioxide to form dinitrogen tetroxide at 600 K.

$$2\,NO_2(g) \rightarrow N_2O_4(g) \tag{1.4.11}$$

The standard molar enthalpies of formation and molar heat capacities are:

| | | |
|---|---|---|
| $NO_2(g)$ | $\Delta_f \bar{H}^\circ$ = 33.9 kJ/mol | $\bar{C}_p$ = 37.9 J K$^{-1}$ mol$^{-1}$ |
| $N_2O_4(g)$ | $\Delta_f \bar{H}^\circ$ = 9.7 kJ/mol | $\bar{C}_p$ = 79.1 J K$^{-1}$ mol$^{-1}$ |

### Solution

First, we use Hess's law to find $\Delta_r \bar{H}^\circ$ of the reaction at standard conditions. From Equation 1.4.3 we have:

$\Delta_r H^\circ = \Delta_f \bar{H}^\circ(N_2O_4) - 2\Delta_f \bar{H}^\circ(NO_2)$

$\Delta_r H^\circ = 9.7\text{ kJ/mol} - 2(33.9\text{ kJ/mol}$

$\Delta_r H^\circ = -58.1\text{ kJ/mol}$

To find $\Delta_r \bar{H}$ at 600 K we use Equation 1.4.10. Assuming the molar heat capacity is independent of temperature we use:

$\Delta_r \bar{H} = \Delta_r H_{T^\circ} + \Delta_r C_p (T_2 - T^\circ)$

We find $\Delta_r C_p$ from Equation 1.4.8:

$\Delta_r \bar{C}_p = \bar{C}_p(N_2O_4) - 2\bar{C}_p(NO_2)$

$\Delta_r \bar{C}_p = 79.1\text{ J K}^{-1}\text{ mol}^{-1} - 2(37.9\text{ J K}^{-1}\text{ mol}^{-1})$

$\Delta_r \bar{C}_p = 3.3\text{J K}^{-1}\text{ mol}^{-1}$

$\Delta_r \bar{C}_p = 0.0033\text{kJ K}^{-1}\text{ mol}^{-1}$

Finally, we compute $\Delta_r \bar{H}$ at 600 K:

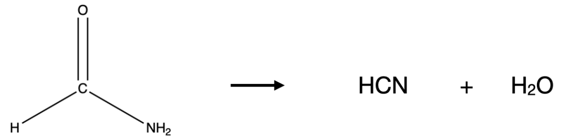
$\Delta_r \bar{H} = -58.1\text{ kJ/mol} + 0.0033\text{kJ K}^{-1}\text{ mol}^{-1}(600 - 298)$

$\Delta_r \bar{H} = -57.1\text{ kJ/mol}$

Notice that $\Delta_r \bar{H}$ at 600 K is not very different from $\Delta_r H^\circ$ at 298 K. For gas-phase reactions, the change in enthalpy due to the molar heat capacities tends to cancel between the reactants and products.

## 1.4.4: Practice Problems

**Problem 1.4.1.** Formamide ($HCONH_2$) is used in the industrial production of hydrogen cyanide. Calculate the change in enthalpy for the dehydration of formamide to form water and hydrogen cyanide.



using the tabulated heat of formation data:

| | |
|---|---|
| Water (g) | $\Delta_f \bar{H}^\circ$ = -241.8 kJ/mol |
| Formamide | $\Delta_f \bar{H}^\circ$ = -188.79 kJ/mol |
| Hydrogen cyanide | $\Delta_f \bar{H}^\circ$ = 129.286 kJ/mol |

**Problem 1.4.2.** Alcohol fermentation is the process in which carbohydrates are broken down into ethanol and carbon dioxide. The overall reaction is

$C_6H_{12}O_6$ (s) → 2 $C_2H_5OH$ (l) + 2 $CO_2$ (g)

Given that $\Delta_f \bar{H}^\circ$ for $C_2H_5OH$ (l) is -277.0 kJ/mol, $\Delta_f \bar{H}^\circ$ for $CO_2$ (g) is -393.5 kJ/mol, and $\Delta_f \bar{H}^\circ$ for $C_6H_{12}O_6$ (s) is -1274 kJ/mol, calculate $\Delta_r H^\circ$ for the fermentation reaction shown.

**Problem 1.4.3.** The thermal denaturation of a globular protein with $T_m = 40$ °C has $\Delta \bar{H} = 300$ kJ/mol for unfolding at the melting temperature ($T_m$). The difference in the constant-pressure molar heat capacity between the denatured state (unfolded) and the folded state (N) is 9.0 kJ mol$^{-1}$ K$^{-1}$. Find the molar enthalpy of denaturation at $T = 25$ °C. (Assume the heat capacity does not depend on temperature).

---

# 1.5: The Second Law of Thermodynamics

The first law of thermodynamics describes the conservation of energy but does not tell us anything about the direction or spontaneity of a reaction. In this chapter we introduce the concept of entropy as derived by Rudolf Clausius and formulate the second law of thermodynamics. The second law of thermodynamics is of central importance in science and tells us the direction of spontaneous change for any process. We then calculate the change of entropy for a number of example cases.

**Learning Objectives**

- Be able to provide a thermodynamic definition of entropy as the reversible heat divided by the temperature.
- Be able to articulate the second law of thermodynamics and understand its meaning and significance: the entropy of the universe increases for all spontaneous processes and the entropy of the universe remains unchanged for an equilibrium (reversible) process.
- Be able to calculate the change in entropy for the compression/expansion of an ideal gas.
- Be able to calculate the change in entropy for the various processes: heating/cooling, phase transition, ideal mixing.

## 1.5.1: Relevance of the first law of thermodynamics

So far we have been concerning ourselves with the interconversion of heat and work as two form of energy. The first law sets a limit on the *magnitude* of energy transfer by stating that energy cannot be created or destroyed, thus any change in energy ($\Delta U$) must be due to work ($w$) or heat ($q$) transferred to/from the system with the surroundings.

The mathematical statement of the first law, $\Delta U = q + w$ is a consequence of the fact that energy is neither created or destroyed but flows from one part of the universe (the system) to another (the surroundings) or is converted from one form to another. Although the first law limits the magnitude of energy change, it says nothing about the *directionality* of energy transfer or whether or not a process will be *spontaneous.*

Consider an example sketched in figure $1.5.1$. A rubber ball is held some height $h$ above a table. The ball has some potential energy due to gravity. When the ball is released, its potential energy is converted to kinetic energy, and the ball bounces off the table. Each time the ball bounces, it does not reach the same height as the previous bounce because some of the kinetic energy is being dissipated to the molecules in the table. Eventually, the ball comes to rest, and all its kinetic energy has been transferred to the molecules in the table. This increase in kinetic energy results in the temperature of the table rising, and we can say that the kinetic energy of the ball was converted into heat. This process occurs spontaneously once the ball is dropped and is indicated by the forward arrow labeled **a)** in figure $1.5.1$.

Let's now consider the reverse process in which the ball at rest on the table absorbs the kinetic energy of the molecules in the table and converts this energy into work by spontaneously levitating against the force of gravity. During this process, the molecules in the table lose some kinetic energy, causing the temperature of the table to decrease. Thus, heat has been converted to work needed to raise the ball to some height $h$. This process is indicated by the reverse arrow labeled **b)** in figure $1.5.1$.

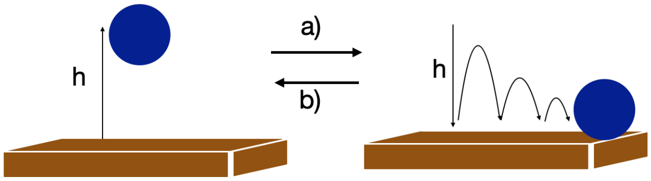


Figure $1.5.1$: **a)** A ball suspended at a height h will spontaneous bounce off the table, converting its potential energy into kinetic energy and heat. **b)** In the reverse process, the ball absorbs heat from the table, converts this heat to kinetic energy to elevate a distance h above the table.

In both cases, the total energy is conserved in compliance with the first law of thermodynamics, but the first process occurs spontaneously, while the second process does not occur spontaneously. For the second process to occur, all the molecules in the table would need to spontaneously synchronize their random motion and transfer their kinetic energy to the ball. If there are sufficiently many molecules in the table, the probability for these molecules to synchronize their random motion is extremely unlikely. The second law of thermodynamics will set a limit on the *direction* of energy transfer, such that case 1 (potential energy → kinetic energy → heat) is spontaneous, but that the reverse process, case 2 (heat → kinetic energy → potential energy), will not happen.

## 1.5.2: Thermodynamic Definition of Entropy

In this chapter we consider the **thermodynamic definition of entropy** as formulated by Rudolf Clausius (1822-1888). Let's consider again the *reversible* heat transfer of a system going from some initial state ($P_1$, $T_1$, $V_1$) to some final state ($P_2$, $T_2$, $V_2$). From the first law of thermodynamics we have $dU = \delta w + \delta q_{rev}$ where the subscript on $\delta q_{rev}$ indicates that the heat transfer we are considering is for a reversible process. Recall that both work and heat are not state properties and thus depend on the path taken. For reversible work we know that $\delta w = -P \cdot dV$ . Also, we know that $dU = C_v \cdot dT$ . Inserting these into the equation for the first law and solving for the unknown $\delta q_{rev}$, we have:

$$\delta q_{rev} = C_v \cdot dT + P \cdot dV \tag{1.5.1}$$

Equation 1.5.1 is an expression for the reversible heat. Integrating both sides of Equation 1.5.1 from an initial state $i$ to a final state $f$:

$$q_{rev} = C_v \Delta T + \int_i^f P \cdot dV \tag{1.5.2}$$

We see that the reversible heat depends on the path due to the work term $P \cdot dV$ . This is not surprising because the heat is not a state property.

Following Clausius, let's now consider a slightly different quality $\frac{\delta q_{rev}}{T}$. From Equation 1.5.1, dividing both side by $T$, we have:

$$\frac{\delta q_{rev}}{T} = C_v \cdot \frac{dT}{T} + \frac{P}{T} \cdot dV \tag{1.5.3}$$

Using the fact that $\frac{P}{T} = \frac{nR}{V}$ for an ideal gas, we can integrate both sides of Equation 1.5.3 *independently of the path!*

$$\begin{aligned} \int_i^f \frac{\delta q_{rev}}{T} &= C_v \int_i^f \frac{dT}{T} + nR \int_i^f \frac{dV}{V} \\ &= C_v \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right) \end{aligned} \tag{1.5.4}$$

Therefore, we conclude that the quantity $\frac{\delta q_{rev}}{T}$ is a state property! We define this new state property $\mathbf{S}$, so that:

$$dS = \frac{\delta q_{rev}}{T} \tag{1.5.5}$$

and, integrating both sides from an initial state $i$ to a final state $f$:

$$\int_i^f dS = \int_i^f \frac{\delta q_{rev}}{T} = \Delta S \tag{1.5.6}$$

where $\Delta S = S_f - S_i$ . The state property $\mathbf{S}$ is called the **entropy**.

> Key Result: The infinitesimal change in entropy is defined as $dS = \frac{\delta q_{rev}}{T}$ . Notice the entropy is defined in terms of the *reversible* heat.

From equation 1.5.4 and equation 1.5.6 we have that for the expansion of an ideal gas, the change in entropy is:

$$\Delta S = C_v \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right) \tag{1.5.7}$$

Notice that Equation 1.5.7 is valid for any expansion/compression of an ideal gas regardless of whether the process was carried our reversibly or irreversibly because entropy is a state property.

> Key Result: The change in entropy for the reversible or irreversible expansion/compression of an ideal gas is: $\Delta S = C_v \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$

Note

Note: Clausius was able to find a new state property by dividing the reversible heat $\delta \mathbf{q_{rev}}$ (not a state property) by the temperature. The temperature in this case is called an *integrating factor* that makes the integral $\int \frac{\delta q_{rev}}{T}$ exact.

### 1.5.3: Entropy for an irreversible vs. reversible process

So far, we have defined $\mathbf{dS}$ from Equation 1.5.5 in terms of the *reversible* heat $\delta \mathbf{q_{rev}}$. Note that the subscript *rev* indicates the process is reversible. While the entropy is a state property (independent of the path), the heat is not and will depend on the path. Therefore, the equivalence in Equation 1.5.5 is valid only for a reversible path. Even though the entropy is the same, the magnitude of the heat transfer is greater for the *reversible* process, so we have:

$$\delta q_{rev} > \delta q_{irrev} \tag{1.5.8}$$

Dividing both sides of Equation 1.5.8 by $\mathbf{T}$ and inserting the definition of entropy from equation 1.5.5 gives:

$$dS > \frac{\delta q_{irrev}}{T} \tag{1.5.9}$$

While the entropy change would be the same for an irreversible or reversible process, $\Delta S = \Delta S_{rev} = \Delta S_{irrev}$ , the heat flow is not the same, so for any irreversible process $\Delta S > q_{irrev}/T$.

Key Result: For any process the change in entropy is $dS \geq \frac{\delta q}{T}$. The equality holds only for a *reversible* process, whereas the inequality holds if the process is *irreversible*.

### 1.5.4: Entropy of the Surroundings

So far we have only focused on the entropy of the system. In this section we will consider the change in entropy of the *surroundings*. First, we notice that any heat gained (or lost) by the system must have come from (or gone to) the surroundings:

$$\delta q_{sys} =- \delta q_{surr} \tag{1.5.10}$$

We consider the surroundings as an infinitely large reservoir. *Any* amount of heat transferred to the surroundings ($\delta q_{surr}$) will only lead to an infinitesimally small change in the reservoir, given that the reservoir is sufficiently large. Infinitesimally small changes are characteristic of a *reversible* process, so any heat transfer from the perspective of the surroundings can be treated as reversible, since it will have the same effect on the surroundings as a reversible process. Thus, from equation 1.5.5, we can always write for the surroundings:

$$dS_{surr} = \frac{\delta q_{surr}}{T} \tag{1.5.11}$$

or

$$\Delta S_{surr} = \frac{q_{surr}}{T} \tag{1.5.12}$$

### 1.5.5: The Second Law of Thermodynamics

The Second Law of Thermodynamics deals with the change in entropy of the universe. The change of entropy of the universe is:

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} \tag{1.5.13}$$

Substituting Equation 1.5.12 into Equation 1.5.13 gives:

$$\Delta S_{universe} = \Delta S_{sys} + \frac{q_{surr}}{T} \tag{1.5.14}$$

*For a reversible process* we can substitute the equality of Equation 1.5.5 to give:

$$\begin{aligned} \Delta S_{universe} &= \frac{q_{rev}}{T} + \frac{q_{surr}}{T} \\ \Delta S_{universe} &= 0 \end{aligned} \tag{1.5.15}$$

where the last line follows from the fact that the heat gained by the surroundings is equal and opposite to the heat lost by the system ($q_{sys} = -q_{surr}$ ). We see that for a *reversible process* the change of entropy of the universe is zero.

Now, if the processes is *irreversible* we have to use the inequality of Equation 1.5.9. Substituting this into equation 1.5.14 gives for an *irreversible processes:*

$$\begin{aligned}\Delta S_{universe} &> \frac{q_{rev}}{T} + \frac{q_{surr}}{T} \\ \Delta S_{universe} &> 0\end{aligned} \tag{1.5.16}$$

where again the last line follows from the fact that the heat gained by the surroundings is equal and opposite to the heat lost by the system ($q_{sys} = -q_{surr}$ ). Thus, for an *irreversible* process, the change in entropy of the universe must be greater than zero.

This result is known as the **Second Law of Thermodynamics** which can be expressed in mathematical form as:

$$\Delta S_{universe} \geq 0 \tag{1.5.17}$$

Where the equality holds if the process is reversible, and the inequality applies if the process is irreversible.

> Key Result: The entropy of an *isolated* system always increases in an irreversible process and remains unchanged in a reversible process. It can never decrease. This statement is known as the **second law of thermodynamics** and is expressed mathematically as: $\Delta S_{universe} \geq 0$

See Practice Problem 1.5.1

## 1.5.6: Some applications of calculating the entropy

Having defined the second law of thermodynamics, we will now consider some specific examples of calculating $\Delta S$.

### 1.5.6.1: Example 1: Cyclic process

A cyclic process is any series of steps that returns the system to its original state. Because entropy is a state property:

$$\Delta S = \sum_i \Delta S_i = 0 \tag{1.5.18}$$

where $\Delta S_i$ is the entropy change for the $ith$ step and the change in entropy for the cycle is zero because S is a state property.

### 1.5.6.2: Example 2: Reversible adiabatic process

An **adiabatic process** is a process in which no heat is exchanged between the system and surroundings. For a reversible adiabatic processes, $\delta q_{rev} = 0$ since no heat is exchanged. Integrating Equation 1.5.5 gives:

$$\begin{aligned}\Delta S &= \int \frac{\delta q_{rev}}{T} \\ \Delta S &= 0\end{aligned} \tag{1.5.19}$$

where the second line follows for an adiabatic process ($\delta q_{rev} = 0$).

### 1.5.6.3: Example 3: Reversible phase change at constant T and P

At the phase transition temperature, both the forward and reverse reactions are in equilibrium. Therefore, at precisely the phase transition temperature, the phase transition is reversible. For example, the freezing of liquid water is reversible (at equilibrium) at the phase transition temperature of 0 °C.

$H_2O$ (l) ↔ $H_2O$ (s) T = 0 °C

From Equation 1.5.5 at constant **T** we can write:

$$\Delta S = \frac{q_{rev}}{T} \tag{1.5.20}$$

Recalling, that under constant pressure conditions, $q_p = \Delta H$, we can write, for a reversible phase transition:

$$\Delta S=\frac{\Delta H}{T} \tag{1.5.21}$$

where $\Delta H$ is the change in enthalpy of the associated phase transition.

### 1.5.6.4: Example 4: Constant pressure (reversible) heating (no phase change)

Consider heating a substance from some initial temperature $\mathbf{T_i}$ to some final temperature $\mathbf{T_f}$ reversibly. We assume that there are no phase transitions between $\mathbf{T_i}$ and $\mathbf{T_f}$. At constant pressure, we begin with the definition of the heat capacity:

$$\delta q=C_p\cdot dT \tag{1.5.22}$$

Substituting Equation 1.5.22 into the definition of the entropy, Equation 1.5.5 gives:

$$\begin{aligned}\Delta S&=\int_{T_i}^{T_f}C_p\frac{dT}{T}\\ \Delta S&=C_p\int_{T_i}^{T_f}\frac{dT}{T}\\ \Delta S&=C_p\ln\left(\frac{T_f}{T_i}\right)\end{aligned} \tag{1.5.23}$$

where we have assumed the heat capacity $\mathbf{C_p}$ is independent of temperature.

See Practice Problem 1.5.2

### 1.5.6.5: Example 5: Ideal mixing of two inert gases at constant T and P

In this example, we consider the mixing of two ideal gases. Consider the situation shown in figure 1.5.2. Two gases of different chemical identities A and B are contained in two flasks of volume $V_A$ and $V_B$. Let $n_A$ be the number of moles of gas A, and $n_B$ be the number of moles of gas B. When the stopcock separating the two flasks is open, the gases will spontaneously mix so that both gases fill the final volume of $V=V_A+V_B$ . Similarly, the total number of moles of the combined system is $n=n_A+n_B$ .

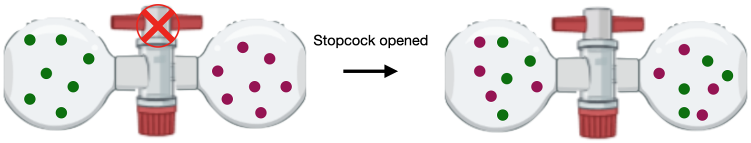


Figure 1.5.2. Ideal mixing of two inert gases. When the stopcock is opened, gas A initially contained in a volume $V_A$ with $n_A$ number of moles spontaneously mixes with $n_B$ moles of gas B initially contained in volume $V_B$. The final volume is $V=V_A + V_B$ and the total number of moles of gas is $n = n_A + n_B$.

The overall change in entropy for the mixing of two gases is the sum of the change in entropy for each gas:

$$\Delta S=\Delta S_A+\Delta S_B \tag{1.5.24}$$

At constant $\mathbf{T}$, the entropy change for gas A is given by the second term in Equation 1.5.7:

$$\Delta S_A=n_AR\ln\left(\frac{V}{V_A}\right) \tag{1.5.25}$$

and similarly for gas B:

$$\Delta S_B=n_BR\ln\left(\frac{V}{V_B}\right) \tag{1.5.26}$$

Substituting Equation 1.5.25 and Equation 1.5.26 into equation 1.5.24 gives:

$$\Delta S=n_AR\ln\left(\frac{V}{V_A}\right)+n_BR\ln\left(\frac{V}{V_B}\right) \tag{1.5.27}$$

Using the fact that the total volume is $V=nRT/P$ for an ideal gas, Equation 1.5.27 becomes:

$$\Delta S = -n_A R \ln\left(\frac{n_A}{n}\right) - n_B R \ln\left(\frac{n_B}{n}\right)$$
$$\Delta S = -n_A R \ln(x_A) - n_B R \ln(x_B) \tag{1.5.28}$$

where $x_A$ is the mole fraction of gas A defined as $x_A = n_A/n$ and $x_B$ is the mole fraction of gas B. Notice that because the mole fraction is less than one, $\Delta S$ for mixing of two ideal gases is be greater than zero.

See Practice Problem $1.5.3$

## 1.5.7: Examples

### ✓ Example 1.5.1

What is the change in entropy when one mole of liquid water is heated from its freezing point to its boiling point in an open container. The molar heat capacity of liquid water is 75.38 J mol$^{-1}$ K$^{-1}$.

**Solution**

Since the water is being heated at constant pressure, we use Equation 1.5.23:

$\Delta S = C_p \ln\left(\frac{T_f}{T_i}\right)$

or, after introducing the definition of the molar heat capacity:

$\Delta S = n\bar{C}_p \ln\left(\frac{T_f}{T_i}\right)$

Substituting in the values of the initial and final temperatures gives:

$\Delta S = 1 \text{ mole } \times 75.38 \text{ J mol}^{-1} \text{ K}^{-1} \ln\left(\frac{373.15 \text{ K}}{273.15 \text{ K}}\right)$

$\Delta S = 23.52 \text{ J K}^{-1}$

Notice that the entropy increases upon heating.

### ✓ Example 1.5.2

Show that for a *reversible* adiabatic expansion of an ideal gas $\Delta S = 0$, but for an *irreversible* adiabatic expansion of an (isolated) ideal gas $\Delta S > 0$

**Solution**

For a *reversible* process, (see Example 2), we have from the definition of the entropy:

$\Delta S = \int \frac{\delta q_{rev}}{T}$

Since the process is adiabatic, there is no heat exchange with the surroundings, meaning that $q_{rev} = 0$ and

$\Delta S = 0$

For an *irreversible* process, we have from Equation 1.5.9:

$\Delta S > \int \frac{\delta q_{irrev}}{T}$

Again, the process is adiabatic so there is no heat exchange with the surroundings, meaning that $q_{irrev} = 0$, giving:

$\Delta S > 0$

Note that this result applies only to an isolated system. It is possible to reduce the entropy of the system with the aid of the external surroundings. The entropy change of both system + surroundings taken together, however, cannot decrease.

## 1.5.8: Practice Problems

**Problem 1.5.1.** One mole of an ideal gas is isothermally expanded from 5.0 L to 10 L at 300 K. Compare the entropy changes for the system, surroundings, and the universe if the process is carried out **a)** reversibly, and **b)** irreversibly against a constant external pressure of 2.0 atm.

**Problem $1.5.2$.** The molar enthalpy of vaporization of water is $\Delta H_{vap} = 40.6$ kJ/mol at the boiling temperature of 100 °C. **a)** What is the value of $\Delta S$ when one mole of liquid water is converted to a gas at 100 °C. **b)** What is $\Delta S$ for the conversion of one mole of liquid water to a gas at a temperature of 120 °C. The molar heat capacity of liquid water is 75.38 J mol$^{-1}$ K$^{-1}$ and the molar heat capacity of water vapor is 36.57 J mol$^{-1}$ K$^{-1}$.

Hint consider $\Delta S$ of heating/cooling from *Example 4 (see Example 1.4.1)* in addition to $\Delta S$ for a phase transition in *Example 3*.

**Problem $1.5.3$.** Suppose you have a compartment that contains 1 mole of NO and a second compartment that contains 0.3 moles of $O_2$. Calculate the change in entropy $\Delta S$ of mixing the two gasses together. Assume the gasses do not react and are ideal gasses.

---

# 1.6: The Boltzmann Distribution and the Statistical Definition of Entropy

In this chapter we introduce the statistical definition of entropy as formulated by Boltzmann. This allows us to consider entropy from the perspective of the probabilities of different configurations of the constituent interacting particles in an ensemble. This conception of entropy led to the development of modern statistical thermodynamics. For systems that can exchange thermal energy with the surroundings, the equilibrium probability distribution will be the Boltzmann distribution. Knowing this equilibrium probability distribution allows us to calculate various thermodynamics observables.

**Learning Objectives**

- Understand the statistical definition of entropy and be able to use the number of available microstates of the system to calculate the entropy.
- Understand how all thermodynamic properties ultimately can be traced back to the number of occupied microstates and their probability.
- Be able to use the Boltzmann distribution to calculate the ratio of occupied energy states at a given temperature and the probability of a particle being in any particular energy level.

## 1.6.1: Microstates and Boltzmann Entropy

In our discussion of thermodynamics, thus far we have neglected the molecular nature of reality: that molecular systems are composed of many interacting atoms and molecules. In this chapter we will explore how the large number of particles in a system gives rise to thermodynamic observables. We have seen that the thermodynamic state of the system can be designated by a set of state properties (P, V, n, T, U, H, S). The macroscopic state of the system is called a **macrostate.** In contrast, a **microstate** is a specific configuration of all the constituent parts that make up the system.

As an illustrative example of a microstate is to consider the number of ways any given state may be constructed. Consider the question of how many unique ways there are to arrange four particles as shown in figure $|PageIndex1$ into two bins.

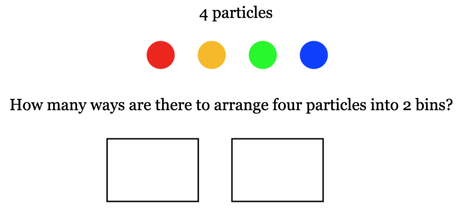


Figure $|PageIndex1$ Consider the number of possible ways to arrange four particles into two bins. The are a total of 16 unique configurations as shown in figure $|PageIndex1$.

It turns out that there are 16 different ways we could arrange four particles into two bins as shown in figure $|PageIndex2$.

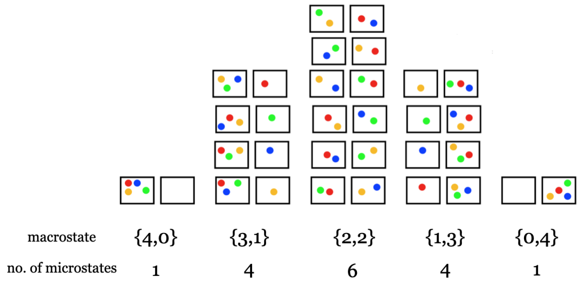


Figure $|PageIndex2$ The total number of ways to arrange four particles into two bins. There are five possible macrostates defined by the number of particles in each bin ({4,0}, {3,1}, {2,2}, {1,3},{0,4}). Whereas the macrostate {4,0} can only be achieved in one way, the macrostate {2,2} can be achieved in six different ways.

If we define each unique arrangement of the four particles as a microstate, then there are 16 possible microstates. The overall number of particles in each bin defines the macrostate, so from figure $|PageIndex2$ we see that there are four macrostates, and that the number of microstates making up the different macrostates is not equal. The macrostate that corresponds to a configuration with two particles in each bin ({2,2}) has the highest number of microstates (6), while the macrostates that correspond to configurations with all the particles in one of the bins ({4,0} and {0,4}) have the fewest number of microstates (1).

In general, we can calculate the number of microstates in a given distribution according to the formula:

$$W = \frac{N!}{n_1!n_2!,\ldots} \tag{1.6.1}$$

where W is the number of ways of distributing $N$ total particles into bins, and $n_1$, $n_2$, ... is the number of particles in each bin.

**Example 1.6.1**

*Example 1:* Use Equation 1.6.1 to calculate the number of ways to arrange four particles into two bins such that there are two particles in each bin ({2,2}).

**Solution**

We have four total particles, so $N = 4$. To calculate the number of ways to arrange four particles into a configuration with $n_1 = 2$ and $n_2 = 2$ we have:

$$\begin{aligned} W &= \frac{4!}{2!2!} \\ W &= \frac{4\times3\times2\times1}{2\times1\times2\times1} \\ W &= 6 \end{aligned} \tag{1.6.2}$$

We calculate that there are six different microstates corresponding to the macrostate with two particles in each bin ({2,2}), which agrees with the drawing in figure $|PageIndex2$.

See Practice Problems 1.6.1 and 1.6.2.

The **Boltzmann definition of entropy** relates the entropy as the natural logarithm of the number of microstates, **W**:

$$S = k_B \ln W \tag{1.6.3}$$

where $\mathbf{k_B}$ is a constant of proportionality known as Boltzmann's constant:

$$k_B = 1.380658 \times 10^{-23} \text{ J K}^{-1} \tag{1.6.4}$$

Since W is unitless, the units on $\mathbf{k_B}$ give entropy the correct thermodynamic units, and the value of Boltzmann's constant ensures that the statistical definition of entropy from Equation 1.6.3 is in agreement with the thermodynamic definition of entropy.

## 1.6.2: The Boltzmann Distribution

Equation 1.6.3 allows us to compute the entropy **S** for any given configuration of particles. Looking again at figure 1.6.2, we see that the configuration with two particles in each bin ({2,2}) has more accessible microstates (W=6) than a configuration with all four particles in one bin ({4,0} with W=1). Therefore, the macrostate with configuration {2,2} has a greater entropy than the macrostate with configuration {4,0}.

As a second example consider a system of four particles with two discrete energy levels as shown in figure 1.6.3.

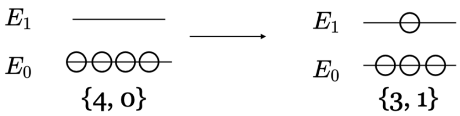


Figure 1.6.3: Two level system. Consider a system of four particles each with two accessible energy levels: a ground state energy with energy $E_0$ and a single excited state with energy $E_1$. If all particles are in the ground state, the total energy is $E = 4E_0$ as shown on the left. There is only one way to have all the particles in the ground state so W=1. If one of the particles is in the excited state, the total energy is $E = 3E_0 + E_1$ and W=4 since there are four possible ways to have a configuration with one particle in the excited state.

The particles can either be at the ground state energy $E_0$ or the excited state energy $E_1$. For example, the left side of figure 1.6.3 shows the microstate with all four particles in the ground state. In this state, the total energy is $E = 4E_0$, and there is only one possible microstate (W=1). The configuration on the left corresponds to the macrostate with the lowest entropy. The right side of figure 1.6.3 shows three particles in the ground state and one particle in the excited state. In the configuration on the right, the total energy is $E = 3E_0 + E_1$ and there are four possible microstates since any one our of the four particles could be in the excited state (W=4). The entropy of each of these configurations can be calculated from Equation 1.6.3 using equation \(\ref{EQ:statweight}).

We now ask ourselves, is there a dominant configuration of particles? The dominant configuration will be the configuration that maximizes $\mathbf{W}$, or equivalently the configuration that maximizes the entropy $\mathbf{S}$. Since W is a function of all the $n_i$, the dominant configuration (that maximizes S) will be given by:

$$\left(\frac{\partial \ln W}{\partial n_i}\right) = 0 \tag{1.6.5}$$

where $\mathbf{n_i}$ is the number of particles in energy level $i$.

In solving for the maximum entropy condition of Equation 1.6.5, we must also enforce the constraint that the total energy of the system is:

$$E_{total} = \sum_i n_i E_i \tag{1.6.6}$$

and that the total number of particles $\mathbf{N}$ is:

$$N = \sum_i n_i \tag{1.6.7}$$

Maximizing a function subject to constraints can be done using a mathematical technique called *Lagrange's method of undetermined multipliers*. The result is that at a given temperature $\mathbf{T}$, the fraction of particles with energy $E_i$ is given by:

$$\frac{n_i}{N} = \frac{e^{-E_i/k_BT}}{q}. \tag{1.6.8}$$

Equation 1.6.8 is known as the **Boltzmann distribution** and gives the probability of a particle occupying a given energy level $\mathbf{E_i}$ at temperature $\mathbf{T}$. The term in the denominator **q** is called the **partition function** and is given by:

$$q = \sum_i e^{-E_i/k_BT} = e^{-E_0/k_BT} + e^{-E_1/k_BT} + \ldots \tag{1.6.9}$$

The ratio of the number of particles (populations) between any two energy levels $\mathbf{n_1}$ and $\mathbf{n_2}$ is given by:

$$\frac{n_2}{n_1} = e^{-\Delta E/k_BT} \tag{1.6.10}$$

where $\mathbf{\Delta E}$ is the difference in energy between the two energy levels $\Delta E = E_2 - E_1$

Key Result: The Boltzmann distribution gives the distribution of particles that corresponds to the most probable populations and is given by the formula:

$$\frac{n_i}{N} = \frac{e^{-E_i/k_BT}}{\sum_i e^{-E_i/k_BT}}.$$

The ratio of the number of particles between any two energy levels is

$$\frac{n_2}{n_1} = e^{-\Delta E/k_BT}.$$

See Practice Problem 1.6.3.

## 1.6.3: Degenerate Energy Levels

Equation 1.6.8 and Equation 1.6.10 were derived without considering the case of **degeneracy**. In practice, there may be two or more distinct states with the same energy. Two distinct states with the same energy are called **degenerate** energy levels. We specify the degeneracy of a particular energy level $i$ with the symbol $\mathbf{g_i}$. Figure 1.6.4 shows a situation where the ground state is not degenerate ($\mathbf{g_0 = 1}$), and the excited state has a degeneracy of $\mathbf{g_1 = 2}$ because there are two possible states with the same energy $E_1$.

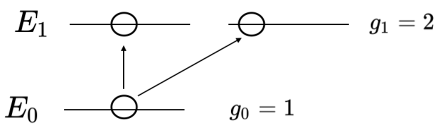


Figure 1.6.4: Degenerate energy levels. In this example there is only one ground state level with energy $E_0$, but there are two possible excited state energy levels with the same energy $E_1$. A particle in the ground state can be excited into either of the two excited states. Because these two states have the same energy they are called **degenerate** energy levels. In this example, the excited state $E_1$ has a degeneracy $g_1 = 2$ while the ground state has a degeneracy $g_0 = 1$.

For the case where there are degenerate energy levels, we generalize the probabilities given by Equation 1.6.8 and equation I.5. 1.6.10. The general Boltzmann distribution will be:

$$\frac{n_i}{N} = \frac{g_i e^{-E_i/k_BT}}{q}. \tag{1.6.11}$$

with $g_i$ the degeneracy of state $i$ and the partition function:

$$q = \sum_i g_i e^{-E_i/k_BT} = g_0 e^{-E_0/k_BT} + g_1 e^{-E_1/k_BT} + \dots \tag{1.6.12}$$

The ratio of the number of particles (populations) between any two energy levels $\mathbf{n_1}$ and $\mathbf{n_2}$ is given by:

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} e^{-\Delta E/k_BT} \tag{1.6.13}$$

## 1.6.4: Examples

### ✓ Example 1.6.2

Calculate the number of microstates for 8 particles to be arranged into 4 bins such that the configuration of particles is {6,0,0,2}

**Solution**

The number of microstates is given by Equation 1.6.1:

$$W = \frac{N!}{n_1!n_2!,\dots}$$

$$W = \frac{8!}{6!0!0!2!}$$

$$W = 28$$

### ✓ Example 1.6.2

**a)** Write an expression for the partition function for the two-level system shown in Figure I.5.D with energy in the ground state $E_0$ and degeneracy $g_0 = 1$ and energy in the excited state $E_1$ and degeneracy $g_1 = 2$. **b)** Let the energy of the ground state be $E_0 = 0$ and the energy in the excited state be $E_1 = 2.41 \text{ kJ mol}^{-1}$. Evaluate the value of the partition function at T=298 K. **c)** What is the probability to find the system in the ground state at T=298 K?

**Solution**

**a)** Using Equation 1.6.12, for a two-level system we have:

$$q = g_0 e^{-E_0/k_BT} + g_1 e^{-E_1/k_BT}$$

and substituting the values of the degeneracy gives:

$$q = e^{-E_0/k_BT} + 2e^{-E_1/k_BT}$$

**b)** When energies are given in molar units (kJ mol$^{-1}$), it is useful to use the gas constant $R = 8.314$ J mol$^{-1}$ K$^{-1}$ $= N_A k_B$ . The the partition function becomes:

$$q = 1 + 2e^{-2410/(8.314 \cdot 298)}$$

$$q = 1.756$$

**c)** The probability for the system to be in the ground state is given by Equation 1.6.11:

$$p_0 = \frac{g_0 e^{-E_0/k_BT}}{q}$$

$$p_0 = \frac{1}{q}$$

Inserting the value of q from part b):

$$p_0 = 0.569$$

## 1.6.5: Practice Problems

**Problem 1.6.1.** Calculate the total number of ways to arrange 16 particles into four bins such that there are four particles in each bin ({4,4,4,4}). What can you say about the entropy of this macrostate as compared to any other macrostate? Explain your answer.

**Problem 1.6.1.** Suppose we have 8 particles that are arranged into 4 bins. Calculate the number of microstates (W) for each of the following distributions of particles: **a)** {5,1,1,1}, **b)** {4,2,2,0}, **c)** {2,6,0,0}

**Problem 1.6.1.** Suppose a protein can exist in two conformations that have an energy difference of 2.0 kJ/mol. What is the estimated ratio of the two conformations at 300 K?

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# 1.7: The Gibbs and Helmholtz Energy

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In this chapter we introduce two additional state properties: the Gibbs energy and the Helmholtz energy. These additional variables are useful for allowing us to determine the direction of spontaneous change without having to directly calculate the change in entropy of the universe from the second law. The Gibbs energy has particular importance in biochemistry.

**Learning Objectives**

- Know the thermodynamic definitions of the Gibbs energy and Helmholtz energy and why these two properties are important.
- Understand that the change in Gibbs energy has both an enthalpic and entropic contribution.
- Know that at constant pressure and temperature the Gibbs energy decreases for a spontaneous process, and at constant volume and temperature the Helmholtz energy decreases for a spontaneous process.
- Be able to identify the fundamental differentials for dU, dH, dG, and dA and how these can be used to arrive at thermodynamic relationships.

## 1.7.1: The Gibbs and Helmholtz energy

The first law of thermodynamics (Chapter I.2) accounts for the conservation of energy and the second law of thermodynamics (Chapter I.4) determines the spontaneity. Together, these laws should allow us to deal with any biophysical problem, but their direct application is not always convenient. In addition to our current set of state properties it is useful to define two additional state properties: the **Gibbs energy** and the **Helmholtz energy**.

Recall that we have already define the **total internal energy** U and the **enthalpy** H=U+PV. Similarly, we now define the **Gibbs energy:**

$$G = H - TS \tag{1.7.1}$$

The Gibbs energy (G) is the enthalpy minus the product of the temperature and the entropy.

We also define the **Helmholtz energy:**

$$A = U - TS \tag{1.7.2}$$

The Helmholtz energy (A) is the total internal energy minus the product of the temperature and the entropy.

If we are interested in infinitesimal changes in the Gibbs or Helmholtz energies we can consider the differential form of equations 1.7.1 and 1.7.2

$$dG = dH - TdS - SdT \tag{1.7.3}$$

$$dA = dU - Tds - SdT \tag{1.7.4}$$

**Note**

Note: In the differential form of Equation 2 we have made use of the product rule for derivatives: d(AB)=BdA+AdB

## 1.7.2: The Significance of the Gibbs and Helmholtz energy

In order to understand why the Gibbs and Helmholtz energies are important, we need to recall the second law of thermodynamics which states

$$dS_{sys} + dS_{surr} \geq 0 \tag{1.7.5}$$

Recalling that for the surroundings:

$$dS_{surr} = \frac{\partial q_{surr}}{T} = -\frac{\partial q_{sys}}{T} \tag{1.7.6}$$

We can substitute equation 1.7.6 into Equation 1.7.5 to obtain an alternative expression for the second law in terms of only the system variables:

$$dS_{sys} - \frac{\delta q_{sys}}{T} \geq 0 \implies TdS_{sys} - \delta q_{sys} \geq 0 \tag{1.7.7}$$

Equation 1.7.7 follows from the second law of thermodynamics. We will now consider two particular cases. Since all the quantities refer to the system we will drop the subscript "sys" in the remaining discussion.

## 1.7.3: Case 1: Constant T and P Conditions

At constant P, the heat transfer is equivalent to the enthalpy:

$$\delta q_p = dH \tag{1.7.8}$$

Substitution of equation 1.7.8 into equation 1.7.7 gives:

$$TdS – dH \geq 0 \tag{1.7.9}$$

Substituting the differential form of the Gibbs energy (equation 1.7.3) into equation 1.7.9 gives:

$$dG + SdT \leq 0 \tag{1.7.10}$$

At constant T, the second term SdT=0 because T is not changing, giving the final result:

$$dG \leq 0 \tag{1.7.11}$$

or upon integrating both sides from an initial to final state:

$$\Delta G \leq 0 \tag{1.7.12}$$

The equality holds for a reversible (equilibrium) process, and the inequality holds for any spontaneous process at constant T and P.

> Key Result: At constant T and P conditions $\Delta G \leq 0$ for a spontaneous process and ΔG=0 for a reversible process.

Since we are at constant T, the differential form of dG from equation 1.7.3 simplifies to:

$$dG = dH - TdS \tag{1.7.13}$$

Integrating both sides at constant T and P from an initial state to a final state gives:

$$\Delta G = \Delta H - T\Delta S \tag{1.7.14}$$

from which we see that the Gibbs energy has an enthalpic term and an entropic term.

> Key Result: $\Delta G = \Delta H – T\Delta S$. This expression is valid at constant T and P.

## 1.7.4: Case 2: Constant T and V Conditions

For the case of constant volume, the heat transfer is equivalent to the total internal energy:

$$\delta q_v = dU \tag{1.7.15}$$

Substitution of Equation 1.7.15 into equation 1.7.7 gives:

$$TdS – dU \geq 0 \tag{1.7.16}$$

Substituting the differential form of the Helmholtz energy (equation 1.7.4) into Equation 1.7.16 gives:

$$dA + SdT \leq 0 \tag{1.7.17}$$

Again at constant T, the second term SdT=0 because T is not changing, giving the final result:

$$dA \leq 0 \tag{1.7.18}$$

or upon integrating both sides from an initial to final state:

$$\Delta A \leq 0 \tag{1.7.19}$$

The equality holds for a reversible (equilibrium) process, and the inequality holds for any spontaneous process at constant T and V.

> Key Result: At constant T and V conditions $\Delta A \leq 0$ for a spontaneous process and ΔA=0 for a reversible process.

Since we are at constant T, the differential form of dA from Equation 2 simplifies to:

$$dA = dU - TdS \tag{1.7.20}$$

Integrating both sides at constant T and V from an initial state to a final state gives:

$$\Delta A = \Delta U - T\Delta S \tag{1.7.21}$$

> Key Result: $\Delta A = \Delta U – T\Delta S$ . This expression is valid at constant T and V.

## 1.7.5: Four Fundamental differentials of thermodynamics

The first law of thermodynamics in differential form is:

$$dU = \delta q + \delta w \tag{1.7.22}$$

For a reversible process we have defined the entropy as $dS = \delta q_{rev}/T$ and the reversible work as $\delta w = -P \cdot dV$ . Substituting these identities into equation 1.7.22 gives the following differential form of the first law:

$$dU = TdS - PdV \tag{1.7.23}$$

Note that Equation 1.7.23 is valid for a reversible process in which the only work is due to compression/expansion.

The enthalpy is defined as:

$$H = U + PV \tag{1.7.24}$$

From Equation 1.7.24 we can write a differential form of the enthalpy as:

$$dH = dU + PdV + VdPn \tag{1.7.25}$$

where we have again used the product rule from calculus on the PV term. Substituting equation 1.7.23 into equation 1.7.25 for the dU term gives another differential relation for dH:

$$dH = TdS - \cancel{PdV} + \cancel{PdV} + VdP = TdS + VdP \tag{1.7.26}$$

Similarly, substitution of equation 1.7.23 into the dU term in the differential form for dA in equation 1.7.4 gives another differential for dA:

$$dA = \cancel{TdS} - PdV - \cancel{TdS} - SdT = -PdV - SdT \tag{1.7.27}$$

Finally, substitution of equation 1.7.26 into the dH term differential form for dG in equation 1.7.3 gives another differential for dG:

dGdGamp;=amp;=amp;TdS+VdP−TdS−SdTamp;VdP−SdT(24)

$$dG = \cancel{TdS} + VdP - \cancel{TdS} - SdT = VdP - SdT \tag{1.7.28}$$

These results are summarized in table 1.7.1.

Table 1.7.1: the four fundamental differential relations for dU, dH, dG, and dA.

| Differential Relation | Equation |
|---|---|
| dU=TdS−PdV | 1.7.23 |
| dH = TdS – VdP | 1.7.26 |
| dA=−PdV−SdT | 1.7.27 |

| Differential Relation | Equation |
|---|---|
| dG=VdP−SdT | 1.7.28 |

## 1.7.6: Pressure dependence of ΔG

The fundamental differentials from table 1.7.1 are useful for deriving various thermodynamic relationships. As an example, we can use equation 1.7.28 to derive the pressure dependence of ΔG. Starting from equation 1.7.28, at **constant T** the second term SdT=0, giving:

$$dG = VdP \tag{1.7.29}$$

or

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{1.7.30}$$

Integrating both sides of equation 1.7.29 from an initial pressure $P_i$ to a final pressure $P_f$ gives:

$$\Delta G = \int_{P_i}^{P_f} VdP \tag{1.7.31}$$

Solids and liquids are nearly incompressible, so the volume does not change significantly with changes in the pressure. Therefore, for **solids and liquids** the volume can be treated as constant in equation 1.7.31, and upon integration gives:

$$\Delta G = V\Delta P \tag{1.7.32}$$

Note that equation 1.7.32 is valid for solids and liquids. For an ideal gas we can substitute V=nRT/P for the volume in equation 1.7.31:

$$\begin{aligned} \Delta G &= \int_{P_i}^{P_f} \frac{nRT}{P} dP \\ \Delta G &= nRT \int_{P_i}^{P_f} \frac{dP}{P} \\ \Delta G &= nRT \ln\left(\frac{P_f}{P_i}\right) \end{aligned} \tag{1.7.33}$$

If we set the initial pressure to 1 bar (standard pressure), and replace the initial Gibbs energy $G_i$ with the symbol for G at the standard state $G^o$, then equation 1.7.33 becomes:

$$G = G^\circ + nRT \ln\left(\frac{P}{1 \text{ bar}}\right) \tag{1.7.34}$$

See Practice Problem 1.7.2.

## 1.7.7: Examples

### Example 1.7.1

Show that at constant pressure, the entropy is given by:

$$S = -\left(\frac{\partial G}{\partial T}\right)_P$$

**Solution**

Starting with equation 1.7.28:

dG=VdP−SdT

At constant pressure (dP=0), we have:

dG=−SdT

> or, solving for S:
>
> $S = -\left(\frac{\partial G}{\partial T}\right)_P$

## 1.7.8: Practice Problems

**Problem $1.7.1$:** Starting with equation 1.7.23, show that temperature has the thermodynamic definitions $T = \left(\frac{\partial U}{\partial S}\right)_V$.

**Problem $1.7.2$:** Assume we have 2.00 moles of ideal gas at 20.0 mbar and 37.0 $^oC$ and compress it to 100. mbar while keeping the temperature constant. What is the change in the free energy of this sample?

---

## SECTION OVERVIEW

# 1.8: Extended Explanations - Helmholtz and Gibbs Energies

# 1.8.1: Helmholtz Energy

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

$$dU = TdS - PdV$$

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

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

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

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

$$A \equiv U - TS$$

$$dA = dU - TdS - SdT \tag{1.8.1.1}$$

If we also set $T$ constant, we see that Equation 1.8.1.1becomes

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

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

✓ Example 22.1.1 : What A stands for

A good example is the case of the mixing of two gases. Let's assume isothermal conditions and keep the total volume constant. For this process, $\Delta U$ is zero (isothermal, ideal) but the

$$\Delta S_{molar} = -y_1 R \ln y_1 - y_2 R \ln y_2$$

This means that

$$\Delta A_{molar} = RT(y_1 \ln y_1 + y_2 \ln y_2).$$

This is a negative quantity because the mole ratios are smaller than unity. So yes this spontaneous process has a negative $\Delta A$. If we look at $\Delta A = \Delta U - T\Delta S$ we should see that the latter term is the same thing as $-q_{rev}$ So we have :

$$\Delta A = \Delta U - q_{rev} = w_{rev}$$

This is however the *maximal work that a system is able to produce* and so the Helmholtz energy is a direct measure of how much work one can get out of a system. $A$ is therefore often called the Helmholtz ***free*** energy. Interestingly this work **cannot** be volume work as volume is constant. so it stands for the maximal ***other*** work (e.g. electrical work) that can be obtained under the unlikely condition that volume is constant.

## 1.8.1.1: Natural variables of A

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

$$dA = dU - TdS - SdT$$

$$dA = TdS - PdV - TdS - SdT = -PdV - SdT$$

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

---

# 1.8.2: Gibbs Energy Determines the Direction of Spontaneity at Constant Pressure and Temperature

The Helmholtz energy $A$ is developed for isochoric changes and as we have often said before it is much easier to deal with isobaric ones where $P =$ constant. We can therefore repeat the above treatment for the enthalpy and introduce another state function the Gibbs energy

$$\begin{aligned} G &\equiv H - TS \\ &= U + PV - TS \\ &= A + PV \end{aligned}$$

If we take both $T$ and $P$ constant we get

$$dU - TdS + PdV \leq 0$$

$$dG \leq 0$$

$G$ either decreases (spontaneously) or is constant (at equilibrium). Calculating the state function between two end points we get:

$$\Delta G = \Delta H - T\Delta S \leq 0 (T, P \text{ constant})$$

This quantity is key to the question of spontaneity under the conditions we usually work under. If for a process $\Delta G$ is positive it does not occur spontaneous and can only be made to occur if it is 'pumped', i.e. coupled with a process that has a negative $\Delta G$. The latter is spontaneous.

> If $\Delta G = 0$ then the system is as ***equilibrium***.

## 1.8.2.1: Direction of the spontaneous change

Because the $\Delta S$ term contains the temperature $T$ as coefficient the spontaneous direction of a process, e.g. a chemical reaction can **change** with temperature depending on the values of the enthalpy and the entropy change $\Delta H$ and $\Delta S$. This is true for the melting process, e.g. for water below $0^oC$ we get water=>ice, above this temperature ice melts to water, but it also goes for chemical reactions.

**✓ Example**

Consider

$$\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightleftharpoons \text{NH}_4\text{Cl}(\text{s})$$

$\Delta_r H$ at 298K / 1 bar is -176.2 kJ. The change in entropy is -0.285 kJ/K so that at 298K $\Delta G$ is -91.21 kJ. Clearly this is a reaction that will proceed to the depletion of whatever is the limiting reagent on the left.

However at 618 K this is a different story. Above this temperature $\Delta G$ is positive! (assuming enthalpy and entropy have remained the same, which is almost but not completely true) The reaction will not proceed. Instead the *reverse* reaction would proceed spontaneously. The salt on the right would decompose in the two gases -base and acid- on the left.

## 1.8.2.2: Meaning of the $\Delta G$ term

As we have seen, $\Delta A$ can be related to the maximal amount of work that a system can perform at constant $V$ and $T$. We can hold an analogous argument for $\Delta G$ except that $V$ is not constant so that we have to consider volume work (zero at constant volume) .

$$dG = d(U + PV - TS) = dU - TdS - SdT - PdV + VdP$$

As $dU = TdS + \delta w_{rev}$

$$dG = \delta w_{rev} - SdT + VdP + PdV$$

As the later term is $-\delta w_{volume}$

$$dG = \delta w_{rev} - SdT + VdP - \delta w_{volume}$$

At constant $T$ and $P$ the two middle terms drop out

$$dG = \delta w_{rev} - \delta w_{volume} = \delta w_{otherusefulwork}$$

> **Note**
>
> $\Delta G$ stands for the (maximal) reversible, isobaric isothermal non-$PV$ work that a certain spontaneous change can perform. The volume work may not be zero, but is corrected for.

### 1.8.2.3: Natural variables of G

Because $G \equiv H - TS$ , we can write

$$\begin{aligned} dG &= dH - TdS - SdT \\ &= TdS + VdP - TdS - SdT = VdP - SdT \end{aligned}$$

The natural variables of $G$ are pressure $P$ and temperature $T$. This is what makes this function the most useful of the four $U$, $H$, $A$, and $G$: these are the natural variables of most of your laboratory experiments!

### 1.8.2.4: Summary

We now have developed the basic set of concepts and functions that together form the framework of thermodynamics. Let's summarize four very basic state functions:

| state function | natural variables |
|---|---|
| $dU = -PdV + TdS$ | $U(V,S)$ |
| $dH = +VdP + TdS$ | $H(P,S)$ |
| $dA = -PdV - SdT$ | $A(V,T)$ |
| $dG = +VdP - SdT$ | $G(P,T)$ |

Note:

1. The replacement of $\delta q$ by $TdS$ was based on *reversible* heat. This means that in the irreversible case the expressions for dU and dH become inequalities
2. We only include *volume* work in the above expressions. If other work (elastic, electrical e.g.) is involved extra terms need to be added: $dU = TdS - PdV + xdX$ etc.

We are now ready to begin applying thermodynamics to a number of very diverse situations, but we will first develop some useful partial differential machinery.

---

# 1.8.3: The Maxwell Relations

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

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

for a reversible change, it follows that

$$dq = TdS$$

And since

$$dw = TdS - pdV$$

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

$$dU = TdS - pdV$$

This is an extraordinarily powerful result. This differential for $dU$ can be used to simplify the differentials for $H$, $A$, and $G$. But even more useful are the constraints it places on the variables T, S, p, and V due to the mathematics of exact differentials!

## 1.8.3.1: Maxwell Relations

The above result suggests that the natural variables of internal energy are $S$ and $V$ (or the function can be considered as $U(S, V)$). So the total differential ($dU$) can be expressed:

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

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

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{1.8.3.1}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \tag{1.8.3.2}$$

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

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

By substituting Equations 1.8.3.1and 1.8.3.2, we see that

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

or

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

This is an example of a **Maxwell Relation**. These are very powerful relationship that allows one to substitute partial derivatives when one is more convenient (perhaps it can be expressed entirely in terms of $\alpha$ and/or $\kappa_T$ for example.)

A similar result can be derived based on the definition of $H$.

$$H \equiv U + pV$$

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

$$dH = dU + pdV + Vdp$$

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

$$dH = TdS - \cancel{pdV} + \cancel{pdV} + Vdp$$

This expression can be simplified by canceling the $pdV$ terms.

$$dH = TdS + Vdp \tag{1.8.3.3}$$

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

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dV \tag{1.8.3.4}$$

Comparing Equations 1.8.3.3and 1.8.3.4show that

$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{1.8.3.5}$$

and

$$\left(\frac{\partial H}{\partial p}\right)_S = V \tag{1.8.3.6}$$

It is worth noting at this point that both (Equation 1.8.3.1)

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

and (Equation 1.8.3.5)

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

are equation to $T$. So they are equation to each other

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

Morevoer, the Euler Relation must also hold

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right)_p\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)_S\right]_p$$

so

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

This is the Maxwell relation on $H$. Maxwell relations can also be developed based on $A$ and $G$. The results of those derivations are summarized in Table 6.2.1..

Table 6.2.1: Maxwell Relations

| Function | Differential | Natural Variables | Maxwell Relation |
|---|---|---|---|
| $U$ | $dU = TdS - pdV$ | $S, V$ | $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$ |
| $H$ | $dH = TdS + Vdp$ | $S, p$ | $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$ |

| Function | Differential | Natural Variables | Maxwell Relation |
|---|---|---|---|
| $A$ | $dA = -pdV - SdT$ | $V, T$ | $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$ |
| $G$ | $dG = Vdp - SdT$ | $p, T$ | $\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$ |

The Maxwell relations are extraordinarily useful in deriving the dependence of thermodynamic variables on the state variables of p, T, and V.

**Example 1.8.3.1**

Show that

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

**Solution**

Start with the combined first and second laws:

$$dU = TdS - pdV$$

Divide both sides by $dV$ and constraint to constant $T$:

$$\left.\frac{dU}{dV}\right|_T = \left.\frac{TdS}{dV}\right|_T - p\left.\frac{dV}{dV}\right|_T$$

Noting that

$$\left.\frac{dU}{dV}\right|_T = \left(\frac{\partial U}{\partial V}\right)_T$$

$$\left.\frac{TdS}{dV}\right|_T = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left.\frac{dV}{dV}\right|_T = 1$$

The result is

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

Now, employ the Maxwell relation on $A$ (Table 6.2.1)

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

to get

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

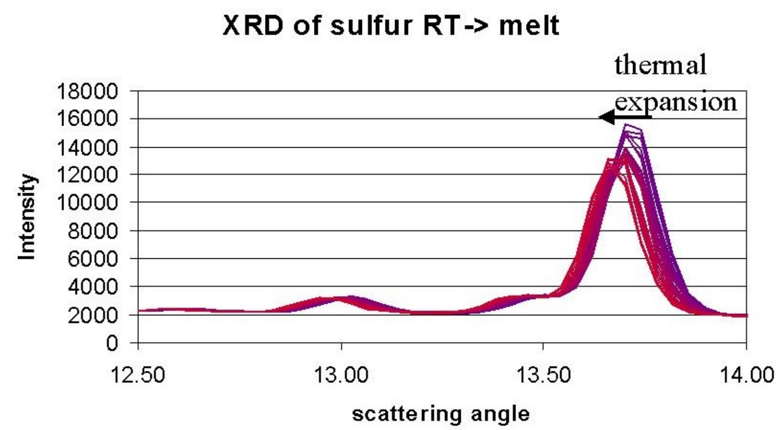
and since

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

It is apparent that

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

*Note*: How cool is that? This result was given without proof in Chapter 4, but can now be proven analytically using the Maxwell Relations!



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# 1.8.4: The Enthalpy of an Ideal Gas is Independent of Pressure

How does pressure affect enthalpy $H$? As we showed above we have the following relations of first and second order for $G$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = -V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

We also know that by definition:

$$G = H - TS \tag{1.8.4.1}$$

Consider an isothermal change in pressure, so taking the partial derivative of each side of Equation 1.8.4.1, we get:

$$\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \tag{1.8.4.2}$$

For an ideal gas

$$\frac{\partial V}{\partial T} = \frac{nR}{P}$$

so Equation 1.8.4.2becomes

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{nR}{P}\right) = 0$$

As we can see for an ideal gas, there is no dependence of $H$ on $P$.

---

# 1.8.5: Thermodynamic Functions have Natural Variables

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

## 1.8.5.1: Introduction

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

## 1.8.5.2: First Law of Thermodynamics

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

$$dU = đq + đw$$

where

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

The "đ" symbol represent **inexact differentials** and indicates that both $q$ and $w$ are path functions. Recall that $U$ is a state function. The first law states that internal energy changes occur only as a result of heat flow and work done.

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

$$w = -\int p dV$$

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

$$dU = đq + đw$$

$$dS = \frac{\delta q_{rev}}{T}$$

we have

$$dU = TdS + \delta w$$

Since only $PV$ work is performed,

$$dU = TdS - pdV \tag{1.8.5.1}$$

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

### 1.8.5.2.1: Principle of Clausius

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

$$dS = \frac{\delta q_{rev}}{T}$$

where

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

### 1.8.5.3: Enthalpy

Mathematically, enthalpy is defined as

$$H = U + pV \tag{1.8.5.2}$$

where $H$ is enthalpy of the system, p is pressure, and V is volume. The fundamental thermodynamic equation for enthalpy follows directly from it deffinition (Equation 1.8.5.2) and the fundamental equation for internal energy (Equation 1.8.5.1) :

$$dH = dU + d(pV)$$

$$= dU + pdV + VdP$$

$$dU = TdS - pdV$$

$$dH = TdS - pdV + pdV + Vdp$$

$$dH = TdS + Vdp$$

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

### 1.8.5.4: Gibbs Energy

The mathematical description of Gibbs energy is as follows

$$G = U + pV - TS = H - TS \tag{1.8.5.3}$$

where $G$ is the Gibbs energy of the system. The fundamental thermodynamic equation for Gibbs Energy follows directly from its definition 1.8.5.3and the fundamental equation for enthalpy 1.8.5.2:

$$dG = dH - d(TS)$$

$$= dH - TdS - SdT$$

Since

$$dH = TdS + VdP$$

$$dG = TdS + VdP - TdS - SdT$$

$$dG = VdP - SdT \tag{1.8.5.4}$$

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

### 1.8.5.5: Helmholtz Energy

Mathematically, Helmholtz energy is defined as

$$A = U - TS \tag{1.8.5.5}$$

where $A$ is the Helmholtz energy of the system, which is often written as the symbol $F$. The fundamental thermodynamic equation for Helmholtz energy follows directly from its definition (Equation 1.8.5.5) and the fundamental equation for internal energy (Equation 1.8.5.1):

$$dA = dU - d(TS)$$

$$= dU - TdS - SdT$$

Since

$$dU = TdS - pdV$$

$$dA = TdS - pdV - TdS - SdT$$

$$dA = -pdV - SdT \tag{1.8.5.6}$$

Equation 1.8.5.6is the fundamental equation for A with natural variables of $V$ and $T$. For the definitions to hold, it is assumed that **only** PV work is done and that **only reversible** processes are used. These assumptions are required for the first law and the principle of Clausius to remain valid. Also, these equations do not account include n, the number of moles, as a variable. When $n$ is included, the equations appear different, but the essence of their meaning is captured without including the n-dependence.

## 1.8.5.6: Chemical Potential

The fundamental equations derived above were not dependent on changes in the amounts of species in the system. Below the n-dependent forms are presented[1,4].

$$dU = TdS - PdV + \sum_{i=1}^{N} \mu_i dn_i$$

$$dH = TdS + VdP + \sum_{i=1}^{N} \mu_i dn_i$$

$$dG = -SdT + Vdp + \sum_{i=1}^{N} \mu_i dn_i$$

$$dA = -SdT - PdV + \sum_{i=1}^{N} \mu_i dn_i$$

where $\mu_i$ is the chemical potential of species i and $dn_i$ is the change in number of moles of substance i.

## 1.8.5.7: Importance/Relevance of Fundamental Equations

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

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

## 1.8.5.8: Maxwell Relations

The fundamental thermodynamic equations are the means by which the Maxwell relations are derived[1,4]. The Maxwell Relations can, in turn, be used to group thermodynamic functions and relations into more general "families"[2,3].

As we said dA is an **exact differential**. Let's write is out in its natural variables (Equation 1.8.5.6) and take a cross derivative. The dA expression in natural variables is

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

The partial derivatives of A of first order can already be quite interesting we see e.g. in step 2 that the first partial of A versus V (at T constant) is the negative of the pressure.

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

Likewise we find the (isochoric) slope with temperature gives us the negative of the entropy. Thus entropy is one of the ***first order derivatives*** of A.

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

When we apply a cross derivative

$$\left(\frac{\partial^2 A}{\partial V \partial T}\right) = \left(\frac{\partial(-S)}{\partial V}\right)_T + \left(\frac{\partial(-P)}{\partial T}\right)_V$$

we get what is known as a ***Maxwell relation***:

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

**Exercise**

What does Equation three mean for the heat capacity? answer

A similar treatment of dG (Equation 1.8.5.4gives:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

and another Maxwell relation

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

## 1.8.5.9: References

1. DOI: 10.1063/1.1749582
2. DOI: 10.1063/1.1749549
3. DOI:10.1103/PhysRev.3.273
4. *A Treatise on Physical Chemistry*, 3rd ed.; Taylor, H. S. and Glasstone, S., Eds.; D. Van Nostrand Company: New York, 1942; Vol. 1; p 454-485.

## 1.8.5.10: Problems

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

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

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

## 1.8.5.11: Answers

1. If it was not assumed that PV-work was the only work done, then the work term in the second law of thermodynamics equation would include other terms (e.g. for electrical work, mechanical work). If reversible processes were not assumed, the Principle of Clausius could not be used. One example of such situations could the movement of charged particles towards a region of like charge (electrical work) or an irreversible process like combustion of hydrocarbons or friction.
2. In general, a closed system of non-reacting components would fit this description. For example, the number of moles would not change for a closed system in which a gas is sealed (to prevent leaks) in a container and allowed to expand/is contracted.
3. See the Maxwell Relations section.

4. $(\frac{\partial H}{\partial P})_{T,n} = 0$ for an ideal gas. Since there are no interactions between ideal gas molecules, changing the pressure will not involve the formation or breaking of any intermolecular interactions or bonds.
5. See the third outside link.

## Contributors and Attributions

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# 1.8.6: The Standard State for a Gas is an Ideal Gas at 1 Bar

Tabulated data are expressed in terms of a pure ideal gas (no mixing) at 1 bar, known as standard state conditions (SSC). Standard states are indicated with the $\circ$ symbol. These values are tabulated at a specific temperature, but that temperature can vary and is not included in the definition of SSC. No real gas has perfectly ideal behavior, but this definition of the standard state allows corrections for non-ideality to be made consistently for all the different gases.

# 1.8.7: The Gibbs-Helmholtz Equation

### 1.8.7.0.1: Ideal gas

For a mole of ideal gas we can use the gas law to integrate volume over pressure and we get

$$\Delta G_{molar} = RT \ln\left(\frac{P_2}{P_1}\right)$$

It is customary to identify one of the pressures (P$_1$} with the *standard state* of **1 bar** and use the plimsoll to indicate the fact that we are referring to a standard state by writing:

$$G_{molar}(P) = G^o_{molar} + RT\ln\left(\frac{P}{1}\right) = G^o_{molar} + RT\ln[P]$$

The fact that we are making the function intensive (per mole) is usually indicated by putting a bar over the $G$ symbol, although this is often omitted for $G^{\ominus}_{molar}$

### 1.8.7.0.1: Solids

For solids the volume does not change very much with pressure (the *isothermal compressibility* $\kappa$ is small), so can assume it more or less constant:

$$G(P_{final}) = G(P_{initial}) + \int V\,dP(\text{from init to final}) \approx G(P_{initial}) + V\int dP(\text{from init to final}) = G(P_{initial}) + V\Delta P$$

## 1.8.7.1: The Gibbs-Helmholtz Expression

$$\frac{G}{T} = \frac{H}{T} - S$$

Take the derivative under constant pressure of each side to get

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2} + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P$$

We make use of the relationship between $C_p$ and $H$ and $C_p$ and $S$

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2} + \cancel{\frac{C_P}{T}} - \cancel{\frac{C_P}{T}} \tag{1.8.7.1}$$

$$= -\frac{H}{T^2} \tag{1.8.7.2}$$

We said before that $S$ is a first order derivative of $G$. As you can see from this derivation the enthalpy $H$ is also a first order derivative, albeit not of $G$ itself, but of $G/T$.

$$\left(\frac{\partial \Delta G/T}{\partial T}\right)_P = -\frac{\triangle H}{T^2}$$

The last step in the derivation simply takes the step before twice -say for the $G$ and $H$ at the begin and end of a *process*- and subtracts the two identical equations leading to a $\Delta$ symbol. In this differential form the Gibbs-Helmholtz equation can be applied to any process.

## 1.8.7.2: Gibbs Energy as a Function of Temperature

If heat capacities are know from 0 K we could determine both enthalpy and entropy by integration:

$$S(T) = S(0) + \int_0^T \frac{C_p}{T}\,dT$$

$$H(T) = H(0) + \int_0^T C_p \, dT$$

As we have seen we must be careful at phase transitions such as melting or vaporization. At these points the curves are *discontinuous* and the derivative $C_p$ is undefined.

$$H(T) = H(0) + \int_0^{T_{fus}} C_p(T)_{solid} dT + \Delta H_{fus} + \int_{T_{fus}}^{T_{boil}} C_p(T)_{liquid} dT + \Delta H_{vap} + etc. \tag{1.8.7.3}$$

$$S(T) \quad = S(0) + \int_0^{T_{fus}} \frac{C_p(T)_{solid}}{T} dT + \Delta S_{fus} + \int_{T_{fus}}^{T_{boil}} \frac{C_p(T)_{liquid}}{T} dT + \Delta S_{vap} + etc. \tag{1.8.7.4}$$

$$= S(0) + \int_0^{T_{fus}} \frac{C_p(T)_{solid}}{T} dT + \frac{\Delta H_{fus}}{T_{fus}} + \int_{T_{fus}}^{T_{boil}} \frac{C_p(T)_{liquid}}{T} dT + \frac{\Delta H_{vap}}{T_{boil}} + etc. \tag{1.8.7.5}$$

with $H(T=0) = \text{undefined}$ and $S(T=0) = 0$ from the third law of thermodynamics.

> We also discussed the fact that the third law allows us to define $S(0)$ as zero in most cases. For the enthalpy we cannot do that so that our curve is with respect to an undefined zero point. We really should plot $H(T) - H(0)$ and leave $H(0)$ undefined.

Because the Gibbs free energy $G = H - TS$ we can also construct a curve for $G$ as a function of temperature, simply by combining the $H$ and the $S$ curves (Equations 1.8.7.3and 1.8.7.5):

$$G(T) = H(T) - TS(T)$$

Interestingly, if we do so, the **discontinuities** at the phase transition points will **drop out** for $G$ because at these points $\Delta_{trs} H = T_{trs} \Delta_{trs} S$. Therefore, $G$ is **always** continuous.

The $H(0)$ problem does not disappear so that once again our curve is subject to an arbitrary offset in the y-direction. The best thing we can do is plot the quantity $G(T) - H(0)$ and leave the offset $H(0)$ undefined.

We have seen above that the derivative of $G$ with temperature is $-S$. As entropy is always positive, this means that the G-curve is always *descending* with temperature. It also means that although the curve is *continuous* even at the phase transitions, the slope of the G curve is not, because the derivative $-S$ makes a jump there. Fig. 22.7 in the book shows an example of such a curve for benzene. Note the kinks in the curve at the mp and the boiling point.

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# 1.8.8: Fugacity Measures Nonideality of a Gas

We have seen that, for a closed system, the Gibbs energy is related to pressure and temperature as follows:

$$dG = VdP - SdT \tag{1.8.8.1}$$

For a constant temperature process:

$$dG = VdP \tag{1.8.8.2}$$

Equation 1.8.8.2can be evaluated for an ideal gas:

$$d\bar{G} = \frac{RT}{P}dP \tag{1.8.8.3}$$

At constant temperature, $T$:

$$d\bar{G} = RT\ d\ln P \tag{1.8.8.4}$$

This expression by itself is strictly applicable to ideal gases. However, Lewis, in 1905, suggested extending the applicability of this expression to all substances by defining a new thermodynamic property called **fugacity**, $f$, such that:

$$d\bar{G} = RT\ d\ln f \tag{1.8.8.5}$$

This definition implies that for ideal gases, $f$ must be equal to $P$. For non ideal gases, $f$ is not equal to $P$. The ratio between fugacity and pressure is:

$$\phi = \frac{f}{P} \tag{1.8.8.6}$$

where $\phi$ is the fugacity coefficient. The fugacity coefficient takes a value of unity when the substance behaves like an ideal gas. Therefore, the fugacity coefficient is also regarded as a *measure of non-ideality*; the closer the value of the fugacity coefficient is to unity, the closer we are to the ideal state. In the zero-pressure limit, fugacity approaches ideal gas behavior:

$$\lim_{P \to 0} d\bar{G} = RT\ d\ln P \tag{1.8.8.7}$$

For mixtures, this expression is written as:

$$d\bar{G}_i = RT\ d\ln f_i \tag{1.8.8.8}$$

where $\bar{G}_i$ and $f_i$ are the partial molar Gibbs energy and fugacity of the i-th component, respectively. Fugacity can be readily related to chemical potential because of the one-to-one relationship of Gibbs energy to chemical potential, which we have discussed previously. Therefore, the definition of fugacity in terms of chemical potential becomes:

$$d\bar{\mu}_i = RT\ d\ln f_i \tag{1.8.8.9}$$

Even though the concept of thermodynamic equilibrium is given in terms of chemical potentials, the above definitions allow us to restate the same principle in terms of fugacity. To do this, previous expressions can be integrated to obtain:

$$\bar{\mu} = \bar{\mu}^\circ + RT\ln\frac{f}{P^\circ} \tag{1.8.8.10}$$

At equilibrium:

$$0 = \bar{\mu}^\circ + RT\ln\frac{f}{P^\circ} \tag{1.8.8.11}$$

$$\bar{\mu}^\circ = -RT\ln\frac{f}{P^\circ} \tag{1.8.8.12}$$

## Contributors and Attributions

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# 1.8.E: Helmholtz and Gibbs Energies (Exercises)

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region $\Delta x$; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position $\Delta x$ and the uncertainty in momentum $\Delta p$.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{1.8.E.1}$$

You can see from Equation 1.8.E.1 that as $\Delta p$ approaches 0, $\Delta x$ must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

### Exercise $1.8.E.1$

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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# 1.9: Phase Equilibria and Mixtures

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In this chapter we extend the concept of the Gibbs energy to phase transitions and mixtures. In the case of mixtures, the number of moles of the different components can change as a result of a chemical reaction or a phase transition. The partial molar Gibbs energy or chemical potential can be used to determine the spontaneity a process. We first derive an expression for the chemical potential. Then we will consider the impacts of pressure and temperature and use that to understand phase transitions, vapor pressure of volatile liquids, and ideal solutions. We then introduce the concept of the activity to write a general expression for the chemical potential.

**Learning Objectives**

- Know the definition of the chemical potential as the partial molar Gibbs energy, and be able to analyze the spontaneity of a phase transition based on the change in chemical potential.
- Be able to use the chemical potential to calculate the change in Gibbs energy for a process involving changing number of moles.
- Understand how to model the shapes of the phase boundaries in a pressure versus temperature phase diagram.
- Understand the definition of the activity and how it can be used to describe both ideal and real solutions.

## 1.9.1: Gibbs energy and phase equilibria

For a phase transition in equilibrium at the phase transition temperature, such as the freezing of liquid water at 0 °C, the process is reversible. At equilibrium, the change in the *molar* Gibbs energy $\Delta G_{molar} = 0$, meaning that if two phases are at equilibrium,

$$G_{molar}(solid) = G_{molar}(liquid) \tag{1.9.1}$$

Notice here that the molar Gibbs energy is the same for the two phases. The molar Gibbs energy is an *intensive* variable (Gibbs energy per mole). We must use the molar Gibbs energy because the phase equilibrium is independent of the amount of substance. For example, we could have a small ice cube in equilibrium with a large volume of water at 0 °C.

If we have multiple species in our system, the intensive variable of interest is the **partial molar Gibbs energy** that is defined for the i$^{th}$ component of the system as:

$$G_{molar,i} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \tag{1.9.2}$$

where $n_i$ is the number of moles of the i$^{th}$ component, and $n_j$ is the number of moles of all the other components in the system. The total Gibbs energy is a function of the number of moles of each species:

$$G = \sum_i n_i G_{molar,i} \tag{1.9.3}$$

The partial molar Gibbs, $G_{molar,i}$ also shows how infinitesimal changes in the Gibbs energy, dG, depend on infinitesimal changes in the number of moles of a component ($n_1$, $n_2$, …):

$$dG = G_{molar,1}dn_1 + G_{molar,2}dn_2 + \ldots \tag{1.9.4}$$

## 1.9.2: The chemical potential

Because the partial molar Gibbs is used so often when considering equilibria, we give this quantity a special name called the **chemical potential** which gets the Greek symbol μ, and we write the chemical potential of the i$^{th}$ component as:

$$\mu_i = G_{molar,i} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \tag{1.9.5}$$

Substituting into Equation 1.9.4 gives:

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \ldots = \sum_i \mu_i dn_i \tag{1.9.6}$$

Consider the spontaneous transfer of some moles of a molecule from state A to state B as shown in figure 1.9.1 .

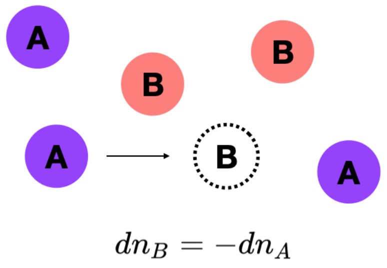

Figure 1.9.1 The conversion of a molecule from state A into state B. The number of moles converted from state A into state B is given by dnB, and is equal and opposite to dnA.

The change in the number of moles in state A, $dn_A$ will be equal and opposite to the change in the number of moles in state B, $dn_B$, so we can write the total change in Gibbs energy from equation 1.9.6 as

$$dG = \mu_A dn_A + \mu_B dn_B = (\mu_B - \mu_A) dn_B \tag{1.9.7}$$

We now ask ourselves, when will the transition from state A into state B become spontaneous? For a spontaneous process dG < 0. Thus, the transition of $dn_B$ moles from state A to state B, will be *spontaneous* if

$$(\mu_B - \mu_A) dn_B < 0 \implies \mu_B < \mu_A \tag{1.9.8}$$

We see that matter flows in the direction of lower chemical potential.

> Key Result: Matter flows spontaneously from high chemical potential to low chemical potential. The flow of matter will continue until the chemical potentials are equal, which is the equilibrium condition.

## 1.9.3: How does changes in conditions change G and thus $\mu$?

In order to determine how the equilibria between phases change as conditions change we need to understand the dependence of G (and thus $\mu$) on state variables such as T and P.

### 1.9.3.1: Changes in pressure

Recall that:

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{1.9.9}$$

or for $\mu$:

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V_{molar} \tag{1.9.10}$$

For an ideal gas $V_{molar}$ depends on P :

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \frac{RT}{P} \tag{1.9.11}$$

For incompressible liquids and solids $V_{molar}$ is a constant.

### 1.9.3.2: Changes in temperature

Recall that the fundamental differential relation for free energy is:

$$dG = VdP - SdT \implies d\mu = V_{molar} dP - S_{molar} dT \tag{1.9.12}$$

If pressure is constant dP = 0 and and equation 1.9.12 becomes:

$$d\mu = -S_{molar} dT \implies \left(\frac{\partial \mu}{\partial T}\right)_P = -S_{molar} \tag{1.9.13}$$

## 1.9.4: Single species phase equilibria

The simplest use of these relations is to understand the shape of the curves in a pressure versus temperature phase diagram for a pure substance. If we have two phases A and B equilibrium is when $\mu_A = \mu_B$. We need to understand how the combinations of P and T where this is true change.

### 1.9.4.1: Impact of changes in P

First, we **consider how P impacts the values of $\mu$ at constant T**. Since matter takes up space $V_{molar} > 0$ (equations 1.9.10 and 1.9.11), $\mu$ increases with pressure (P). The slope of the increase is the constant $V_{molar}$ for solids and liquids, while for gases the slope is steepest at lower pressures. Without knowing actual values of $\mu$ we can sketch a $\mu$ versus P diagram showing when the chemical potential of pairs of phases are equal. At high pressure the most stable phase will be the one with the lowest $V_{molar}$ (highest density, usually the solid phase) because as pressure increases that one will increase the least. In figure 1.9.2 this is indicated by the right most point on the line for $\mu_s$. Likewise the liquid phase will have a slightly higher $\mu_l$ indicated by the right most point on the line for $\mu_l$ in figure 1.9.2. The gas phase has the highest $\mu_g$ at high pressure, with a $\mu$ that drops of more steeply as the pressure drops.

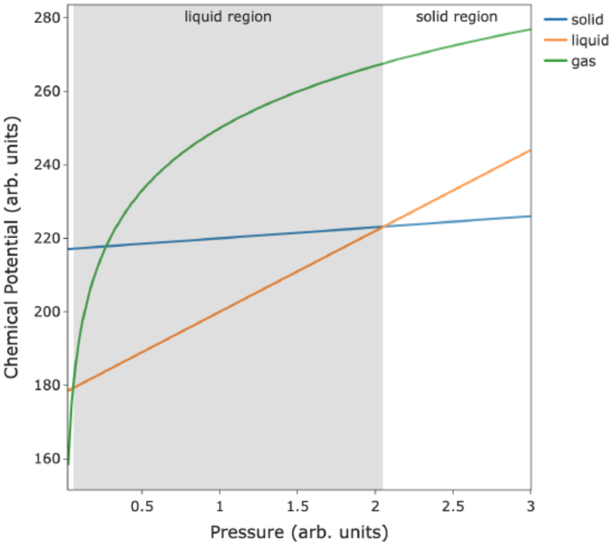

Figure 1.9.2: Variation of $\mu$ for solids, liquids and gases versus pressure. Each phase is stable in the region where $\mu$ of that phase is lowest. In this example only a little sliver near P = 0 favors the gas phase.

As seen in figure 1.9.2, this leads to the lowest pressure equilibrium occurring where the gas and liquid lines cross. The next equilibrium occurs at a slightly higher pressure where the gas and solid lines cross. The final equilibrium occurs at the highest pressure between the liquid and solid. As noted matter flows towards the lowest $\mu$. Thus figure 1.9.2 can be divided into three pressure regions demarcated by the pressures of the equlibriums: 1) the lowest pressure region is where the gas phase is thermodynamically favored; 2) the middle pressure region where the liquid phase is favored; and 3) the high pressure region where the solid phase is favored. Thus, if we started with a sample in the gas phase and increased the pressure it would undergo a phase transition to the liquid phase at the left edge of the liquid region. The chemical potential $\mu$ would then follow the liquid line until reaching the right edge of the liquid region. The material then undergoes a phase transition to the solid phase and follows the solid $\mu$ line as the pressure increase more.

### 1.9.4.2: Impact of changes in T

Second, we **consider how T impacts the values of $\mu$ at constant P**. Since entropy is always greater than zero the slope of $\mu$ (equation 1.9.13) is negative for all phases. As before, we can draw a qualitative diagram showing the relations of the chemical potentials as the temperature is varied. At any temperature $S_{molar}(g) > S_{molar}(l) > S_{molar}(s)$ . Thus at low temperatures the most stable phase will be the the solid; the next most stable the liquid and the least stable the gas. This relationship is indicated by the initial (leftmost) values of the $\mu$ for each phase in figure 1.9.3. Although entropy increases with temperature, so that the slopes of the curves should get more steeply negative, in this diagram we assume the temperature range is small enough that $S_{molar}$ is nearly constant leading to linear behavior over the temperature range plotted. Once again this leads to three places where two of the phases are in equilibrium and three regions of phase stability: 1) solid stable at low temperature; 2) liquid stable in an intermediate range and 3) gas stable at the highest temperatures (see figure 1.9.3).

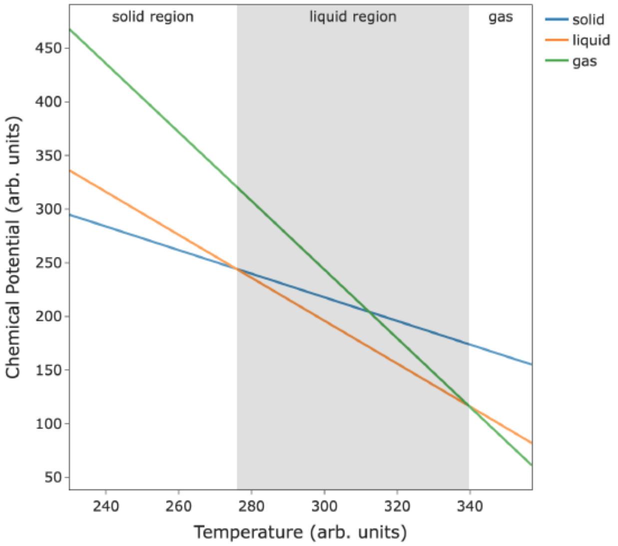

Figure 1.9.3: Variation of $\mu$ for solids, liquids and gases versus temperature. Each phase is stable in the region where $\mu$ of that phase is lowest. We hava assumed that the temperature range of this figure is small enough that the entropies of each phase is nearly constant, leading to a nearly constant slope.

### 1.9.4.3: Pressure versus temperature phase diagrams

Typical phase diagrams for pure substances display curves in P-T space, where the curves indicate the boundaries between the phases. Alternatively, you can think of the curves as representing the combinations of P and T where the neighboring phases A and B are in equilibrium ($\mu_A = \mu_B$ ). To describe the shapes of these curves we require expressions for $\frac{dP}{dT}$ along these boundaries. First we will derive the generic relation and then examine the implications for the shape of each boundary.

Beginning with equation 1.9.12 in its chemical potential form we note that chemical potentials of the two species must stay equal to stay on the boundary. This means the the changes in the two chemical potentials must be equal:

$$d\mu_A = V_{molar,A}dP - S_{molar,A}dT = d\mu_B = V_{molar,B}dP - S_{molar,B}dT \implies V_{molar,A}dP - S_{molar,A}dT = V_{molar,B}dP - S_{molar,B}dT \tag{1.9.14}$$

Rearranging the last expression to get the molar volumes on one side and the molar entropies on the other leads to:

$$S_{molar,B}dT - S_{molar,A}dT = V_{molar,B}dP - V_{molar,A}dP \implies (S_{molar,B} - S_{molar,A})dT = (V_{molar,B} - V_{molar,A})dP \tag{1.9.15}$$

Notice that in equation 1.9.15 the collected differences are just the changes in the molar entropy and volume on shifting phases. So this can be rewritten as:

$$\Delta S_{molar}dT = \Delta V_{molar}dP \tag{1.9.16}$$

Dividing both sides by $\Delta V_{molar}$ and dT yields an expression for the change in P for a change in T:

$$\frac{dP}{dT} = \frac{\Delta S_{molar}}{\Delta V_{molar}} = \frac{\Delta S_{trs}}{\Delta V_{trs}} \tag{1.9.17}$$

where in the final version the subscript 'trs' stands for transition ('vap' for vaporization, 'fus' for melting, 'sub' for sublimation). This is the fundamental form of the Clapyron equation. A very useful alternative form of this equation makes use of the fact that when P and T are constant (at a particular equilibrium point on the boundary) $\Delta S_{trs} = \frac{\Delta H_{trs}}{T_{trs}}$ . Substituting this into equation 1.9.17 yields:

$$\frac{dP}{dT} = \frac{\Delta H_{trs}}{T_{trs}\Delta V_{trs}} \tag{1.9.18}$$

With this expression we can estimate the slope at any point along a phase boundary given enthalpy, temperature and molar volume change or a way to estimate them.

Carbon dioxide exhibits a phase diagram (figure 1.9.4) that is typical of substances that exist as solids, liquids and gases between a 0 and a few hundred atmospheres of pressure and between temperatures that are easily achieved in the lab. Thus it is a good example to keep in mind as we look at the slopes of the phase boundaries.

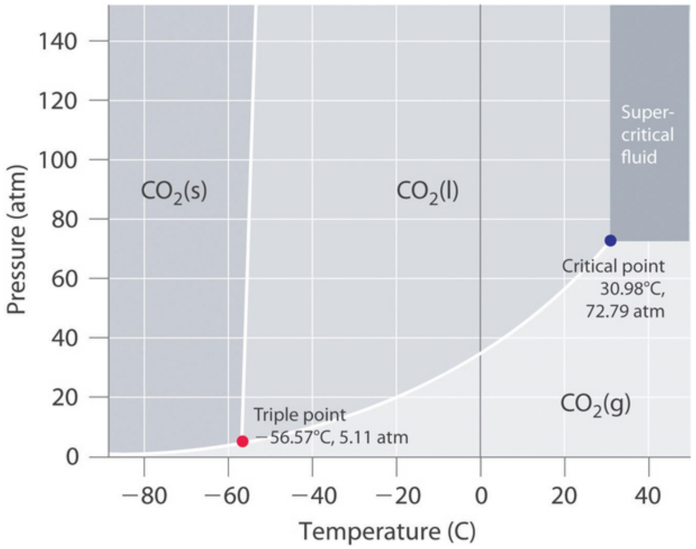

Figure 1.9.4 Phase diagram of $CO_2$. This is an example of a typical phase diagram.

### 1.9.4.4: Solid — liquid phase boundary

In most cases $V_{molar}$(solid) < $V_{molar}$(liquid) so $\Delta V_{trs} > 0$. Also $\Delta H_{trs} > 0$. Since temperature is also positive, equation 1.9.18 implies that the solid - liquid coexistence boundary will have a positive slope. As the enthalpy and volume change are nearly constant with pressure and temperature the slope will slowly decrease as the temperature increases. In the part of the $CO_2$ phase diagram shown in figure 1.9.4 this phase boundary appears to grow linearly. This is because the ratio $\frac{\Delta H}{\Delta V}$ is so large that the temperature changes little in the pressure range considered. We can rearrange 1.9.18 and integrate to get an expression for the change in P for a given change in T assuming $\frac{\Delta H}{\Delta V}$ is constant:

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \implies dP = \frac{\Delta H}{T\Delta V}dT \tag{1.9.19}$$

so, assuming constant enthalpy and volume changes:

$$\int_{P_1}^{P_2} dP = \int_{T_1}^{T_2} \frac{\Delta H}{T\Delta V}dT \implies \Delta P = \frac{\Delta H}{\Delta V}\int_{T_1}^{T_2} \frac{dT}{T} \tag{1.9.20}$$

which integrates to:

$$\Delta P = \frac{\Delta H}{\Delta V} ln\left(\frac{T_2}{T_1}\right) \tag{1.9.21}$$

So given a starting point on the curve we can estimate nearby P and T combinations on the curve.

**Note**

Note that water has a solid - liquid phase boundary with a negative slope because $V_{molar}$(ice) > $V_{molar}$(water); thus $\Delta V < 0$ (see figure 1.9.5).

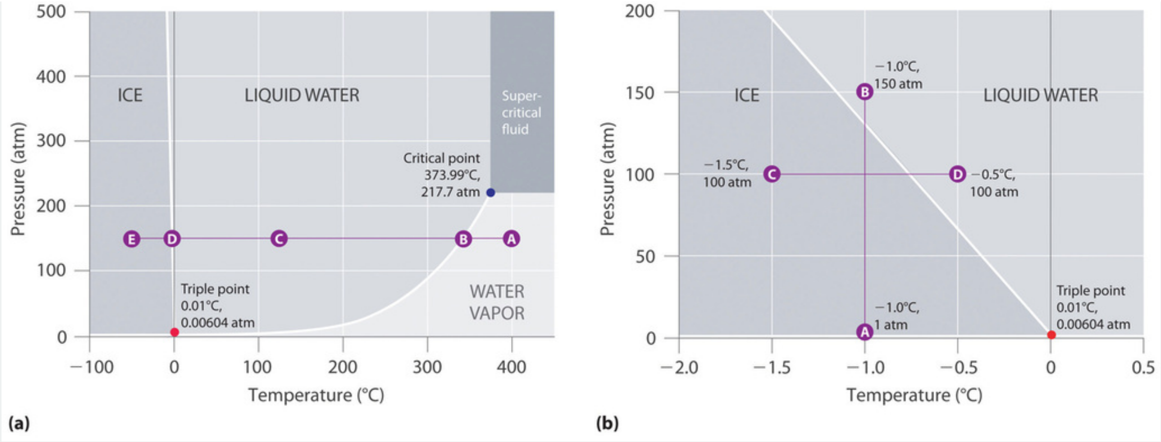

Figure 1.9.5: Two Versions of the Phase Diagram of Water. (a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure.

### 1.9.4.5: Liquid — gas and solid — gas phase boundaries

In this case $V_{molar}(g)$ is much greater than $V_{molar}(l)$ or $V_{molar}(s)$. For example near room temperature the molar volume of liquid water is about 18 mL, while the molar volume of gaseous water is about 800 L. So $V_{molar}(g)$ is around 40000 times larger than that of the liquid or solid. Thus, to within about 1 part in $10^5$:

$$\Delta V_{trs} = V_{molar}(g) - V_{molar}(\text{s or l}) \approx V_{molar}(g) \tag{1.9.22}$$

Substituting this into the Clapyron equation 1.9.18 and assuming the gas behaves ideally, $V_{molar} = \frac{RT}{P}$ , yields:

$$\frac{dP}{dT} = \frac{\Delta H_{trs}}{T_{trs} V_{molar}(g)} = \frac{P \Delta H_{trs}}{RT^2} \tag{1.9.23}$$

Collecting all the Ps on one side and Ts on the other allows us to integrate one side versus P and the other versus T. First consider the indefinite integral:

$$\int \frac{dP}{P} = \int \frac{\Delta H_{trs}}{RT^2} dT \implies lnP = \frac{-\Delta H}{RT} + C \tag{1.9.24}$$

where we have collected the constants of integration from both sides into C. Exponentiating both sides and calling $e^C$ C' gives us an expression for the temperature dependence of P along the phase boundary:

$$P = C' exp\left(\frac{-\Delta H}{RT}\right) = C' e^{\frac{-\Delta H}{RT}} \tag{1.9.25}$$

So, we expect to see exponentially increasing curves. These terminate at the triple and critical points, so do not blow up. We can also do the definite integrals of equation 1.9.23, which yields the most commonly used form of the Clausius-Clapyron equation:

$$ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{1.9.26}$$

**Vapor pressure of a pure substance**

Equations 1.9.25 and 1.9.26 also show how the vapor pressure of a pure substance varies with temperature.

**NOTE**: keep in mind that the assumption that $\Delta H_{vap}$ is constant means that the equation is only valid over relatively small temperature changes. For larger changes the the variation must be taken into account, usually by measuring the values experimentally.

## 1.9.5: Mixtures

For a multi-component system of ideal gases, chemical potential for each component is related to the partial pressure $P_i$ of each species compared to the standard potential at 1 bar. Rearranging and integrating equation 1.9.11 we get:

$$\int_{P^o}^{P_i} d\mu = \int_{P^o}^{P_i} \frac{RT}{P} dP \implies \Delta\mu = RTln\left(\frac{P_i}{P^o}\right) \tag{1.9.27}$$

Adding this to the standard chemical potential of the species $\mu_i^o$ yields:

$$\mu_i = \mu_i^o + RTln\left(\frac{P_i}{P^o}\right) \tag{1.9.28}$$

> Key Result: For a mixture of ideal gases, the chemical potential of the i$^{th}$ species is $\mu_i = \mu^o + RTln\left(\frac{P_i}{P^o}\right)$ where $P_i$ is the partial pressure of the gas and $\mu_i^o$ is the standard chemical potential of component i when its partial pressure is 1 bar.

## 1.9.6: Thermodynamics of mixing volatile liquids

Figure 1.9.6 shows a pure liquid at equilibrium with its vapor in a closed container.

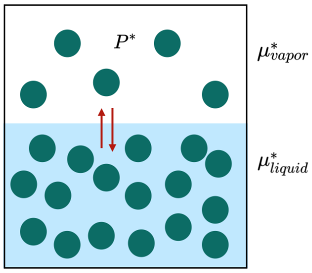

Figure 1.9.6

Since the system is at equilibrium the chemical potentials are equal:

$$\mu^*_{vapor} = \mu^*_{liquid} \tag{1.9.29}$$

where the asterisk (*) indicates a pure substance. From equation 1.9.28 for the gas phase we can write:

$$\mu^*_{vapor} = \mu^*_{liquid} = \mu^o_{vapor} + RTln\left(\frac{P^*}{P^o}\right) \tag{1.9.30}$$

where $P^*$ is the vapor pressure and $\mu^o_{vapor}$ is the chemical potential at $P^o$ = 1 bar.

Now consider a mixture of volatile liquids as shown in figure 1.9.7

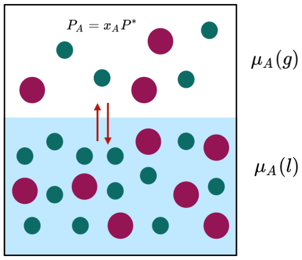

Figure 1.9.7

Since both components are in equilibrium with their vapors, the chemical potential for each component is still equal in the two phases. For example, for component A, we have:

$$\mu_A(l) = \mu_A(g) = \mu_A^o(g) + RTln\left(\frac{P_A}{P^o}\right) \tag{1.9.31}$$

where $P_A$ is the partial pressure of vapor A. Because, $\mu^o_{vapor} = \mu^o_A(g)$, we subtract equation 1.9.30 from equation 1.9.31 to obtain:

$$\mu_A(l) - \mu_A^*(l) = RT\ln\left(\frac{P_A}{P^o}\right) - RT\ln\left(\frac{P^*}{P^o}\right) \implies \mu_A(l) = \mu_A^*(l) + RT\ln\left(\frac{P_A}{P_A^*}\right) \tag{1.9.32}$$

Thus, from equation 1.9.32, the chemical potential of a liquid in a mixture, $\mu_A$(l), is given in terms of the chemical potential of the pure liquid ($\mu_A^*(l)$) and the ratio of the vapor pressure in the pure state over the vapor pressure in the mixture.

The relationship between the two vapor pressures in equation is given by **Raoult’s law** which states that the vapor pressure of a substance in a mixture is the product of its vapor pressure as a pure liquid and its mole fraction:

$$P_A = x_A P_A^* \tag{1.9.33}$$

where $x_A$ is the mole fraction of component A in the mixture. Inserting equation 1.9.33 into equation 1.9.32 gives the final expression for the chemical potential of a liquid in an **ideal** mixture:

$$\mu_A(l) = \mu_A^*(l) + RTln(x_A) \tag{1.9.34}$$

**Raoult's law** is based on a lifetime of work measuring vapor pressures (partial pressures) of liquid vapor above solutions by F. Raoult in the 1800s. It is only valid for solutions that behave ideally or are very dilute ($x_A \approx 1$).

***Very dilute*** conditions are met when the volatile liquid of interest is in large excess (often the case for the solvent in a solution). The closer the mole fraction of the solvent is to 1, the more ideally it behaves. There are some cases where the two species being mixed are similar enough that ideal behavior is seen for all mole fractions. An example where ideal behavior is seen at all concentrations is when mixing benzene and methylbenzene.

**Physical interpretation of Raoult's law**: For an ideal mixture of two substances the fraction of each substance at the surface will be their mole fractions. This means that the chance a molecule of a substance can escape the surface will be reduced from the pure case by a factor of its mole fraction.

**Thermodynamic interpretation of Raoult's law**: A mixture has a higher entropy than a pure substance. This reduces the propensity of liquid molecules escaping into the gas phase to increase their entropy.

See Practice Problems 1.9.4 and 1.9.5.

## 1.9.7: Thermodynamics of ideal solutions

For the case of a solute dissolved in a solvent (liquid), the chemical potential of the solvent is the same as for a mixture of volatile liquids:

$$\mu_{solvent}(l) = \mu^*_{solvent}(l) + RT \ln x_{solvent} \tag{1.9.35}$$

For the case of the solute, it is often more convenient to express the chemical potential in terms of the *molality* m defined as

$$\text{molality} = \frac{\text{moles of solute}}{\text{mass of solvent in kg}}$$

For the solute, the chemical potential is:

$$\mu_{solute}(l) = \mu^\circ_{solute}(l) + RT \ln\left(\frac{m_{solute}}{m^\circ}\right) \tag{1.9.36}$$

Note here the careful choice of the reference state for the solute. The references state is defined as a state of unit molality where $m^o$ = 1 mol kg$^{-1}$.

## 1.9.8: Thermodynamics of real solutions

Under realistic conditions such as inside a cell or in a body of surface water (oceans and most lakes and streams) the conditions are far from that of an ideal solution. To account for more realistic conditions while maintaining the mathematical formulations as clost to what we have derived as possible we write the chemical potential of a species as:

$$\mu_i = \mu_i^\circ + RT \ln a_i \tag{1.9.37}$$

where ai is called the **activity** and μ∘i is a reference state. For real solutions, the activity is given as

$$a_i = \gamma_i (m_i/m^\circ) \tag{1.9.38}$$

where $\gamma_i$ is called the **activity coefficient** that is a measure of the deviation from ideality. For an ideal solution, γ=1 and $a_i = \frac{m_i}{m^o}$. Table 1.9.1 summarizes the expression of the activity and standard state for various substances. Note that for a pure sold and a pure liquid the activity is one.

Table 1.9.1 Activity and standard state for various substances.

| Substance | Standard State ($\mu^o$) | activity (a) |
|---|---|---|
| solid | pure solid, 1 bar | 1 |

| Substance | Standard State ($\mu^o$) | activity (a) |
|---|---|---|
| liquid | pure liquid, 1 bar | 1 |
| gas | pure gas, 1 bar | $P^*$/(1 bar) |
| solvent | pure solvent | mole fraction $x_i$ |
| ideal solute | molality of 1 mol kg$^{-1}$ | $\frac{m_i}{m^o}$ |
| real solution | molality of 1 mol kg$^{-1}$ | $\gamma_i(m_i/m^\circ)$ |

## 1.9.9: Practice Problems

**Problem 1.9.1.** At high pressure, graphite (density ρ=2.25 g/cm$^3$) can be spontaneously converted into diamond (density ρ=3.51 g/cm$^3$) through a solid-to-solid phase transition:

C (graphite) → C (diamond)

At 1 atm of pressure the standard molar Gibbs energy of this reaction is $\Delta G^o$=2.84 kJ/mol. At what pressure does the reaction become spontaneous (i.e. at what pressure does $\Delta G_{molar}$=0)?

**Problem 1.9.2.** Consider the *reversible* freezing of liquid water into ice at a constant temperature of 0 °C and constant pressure of 1 atm.

$H_2O$ (l) ↔ $H_2O$ (g) 0 °C

Show that ΔG for this process is 0. (Hint: use the relation $\Delta G = \Delta H - T\Delta S$).

**Problem 1.9.3.** Which of the following has a higher chemical potential? (If neither, answer “same”)

**(a)** $H_2O$ (l) or $H_2O$ (s) at water’s normal melting point (0 ºC).

**(b)** $H_2O$ (l) or $H_2O$ (s) at -5 ºC and 1 bar.

**Problem 1.9.4.** Which would have the higher chemical potential? Benzene at 25 ºC and 1 bar or benzene in a 0.1 M toluene solution at 25 ºC and 1 bar.

**Problem 1.9.5.** Calculate the chemical potential of ethanol in solution relative to that of pure ethanol when its mole fraction is 0.40 at its boiling point (78.3 ºC.)

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# SECTION OVERVIEW

## 1.10: Extended Explanations - Phase Equilibria

Phase equilibria is the term used to describe with two or more phases co-exist (in equilibrium). The stability of phases can be predicted by the chemical potential, in that the most stable form of the substance will have the minimum chemical potential at the given temperature and pressure. A key tool in exploring phase equilibria is a phase diagram which is used to show conditions (pressure, temperature, volume, etc.) at which thermodynamically distinct phases (such as solid, liquid or gaseous states) occur and coexist at equilibrium.

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# 1.10.1: Phase Diagrams

**Learning Objectives**

- To understand the basics of a one-component phase diagram as a function of temperature and pressure in a closed system.
- To be able to identify the triple point, the critical point, and four regions: solid, liquid, gas, and a supercritical fluid.

The state exhibited by a given sample of matter depends on the identity, temperature, and pressure of the sample. A phase diagram is a graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system.

## Introduction

A typical phase diagram consists of discrete regions that represent the different phases exhibited by a substance (Figure 1.10.1.1). Each region corresponds to the range of combinations of temperature and pressure over which that phase is stable. The combination of high pressure and low temperature (upper left of Figure 1.10.1.1) corresponds to the solid phase, whereas the gas phase is favored at high temperature and low pressure (lower right). The combination of high temperature and high pressure (upper right) corresponds to a supercritical fluid.

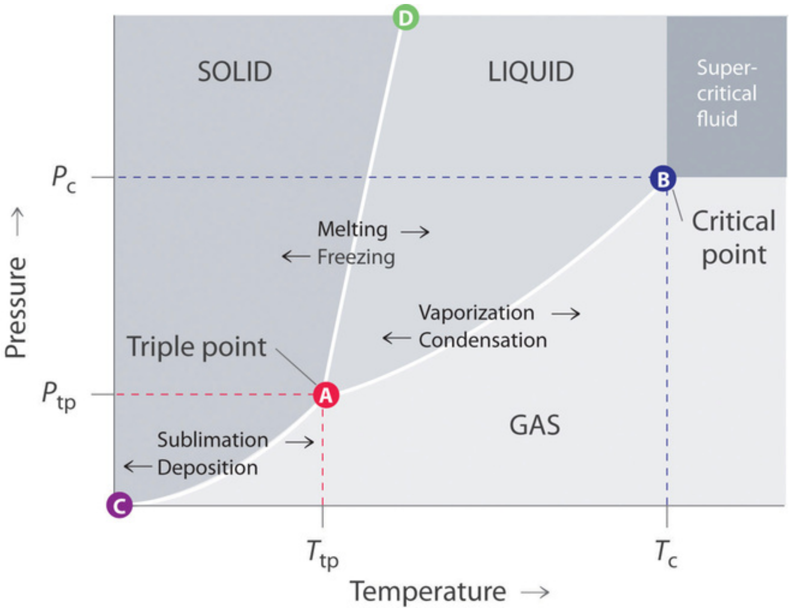

Figure 1.10.1.1: A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region

> The solid phase is favored at low temperature and high pressure; the gas phase is favored at high temperature and low pressure.

The lines in a phase diagram correspond to the combinations of temperature and pressure at which two phases can coexist in equilibrium. In Figure 1.10.1.1, the line that connects points A and D separates the solid and liquid phases and shows how the melting point of a solid varies with pressure. The solid and liquid phases are in equilibrium all along this line; crossing the line horizontally corresponds to melting or freezing. The line that connects points A and B is the vapor pressure curve of the liquid, which we discussed in Section 11.5. It ends at the critical point, beyond which the substance exists as a supercritical fluid. The line that connects points A and C is the vapor pressure curve of the *solid* phase. Along this line, the solid is in equilibrium with the vapor phase through sublimation and deposition. Finally, point A, where the solid/liquid, liquid/gas, and solid/gas lines intersect, is the triple point; it is the *only* combination of temperature and pressure at which all three phases (solid, liquid, and gas) are in equilibrium and can therefore exist simultaneously. Because no more than three phases can ever coexist, a phase diagram can never have more than three lines intersecting at a single point.

Remember that a phase diagram, such as the one in Figure 1.10.1.1, is for a single pure substance in a closed system, not for a liquid in an open beaker in contact with air at 1 atm pressure. In practice, however, the conclusions reached about the behavior of a substance in a closed system can usually be extrapolated to an open system without a great deal of error.

## The Phase Diagram of Water

Figure 1.10.1.2 shows the phase diagram of water and illustrates that the triple point of water occurs at 0.01°C and 0.00604 atm (4.59 mmHg). Far more reproducible than the melting point of ice, which depends on the amount of dissolved air and the atmospheric pressure, the triple point (273.16 K) is used to define the absolute (Kelvin) temperature scale. The triple point also represents the lowest pressure at which a liquid phase can exist in equilibrium with the solid or vapor. At pressures less than 0.00604 atm, therefore, ice does not melt to a liquid as the temperature increases; the solid sublimes directly to water vapor. Sublimation of water at low temperature and pressure can be used to "freeze-dry" foods and beverages. The food or beverage is first cooled to subzero temperatures and placed in a container in which the pressure is maintained below 0.00604 atm. Then, as the temperature is increased, the water sublimes, leaving the dehydrated food (such as that used by backpackers or astronauts) or the powdered beverage (as with freeze-dried coffee).

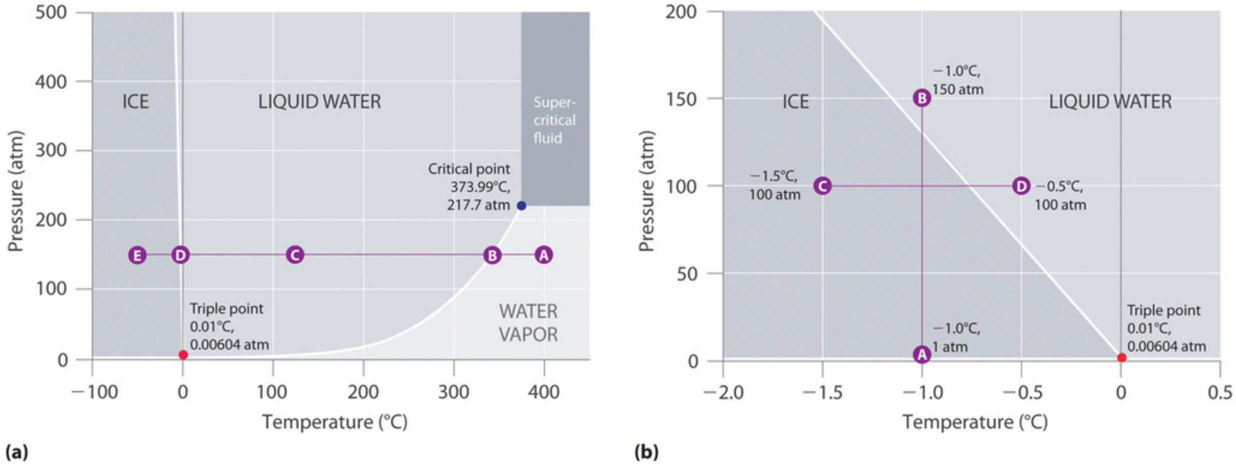

Figure 1.10.1.2: Two Versions of the Phase Diagram of Water. (a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters refer to points discussed in Example 1.10.1.1).

The phase diagram for water illustrated in Figure 1.10.1.2b shows the boundary between ice and water on an expanded scale. The melting curve of ice slopes up and slightly to the left rather than up and to the right as in Figure 1.10.1.1; that is, the melting point of ice *decreases* with increasing pressure; at 100 MPa (987 atm), ice melts at −9°C. Water behaves this way because it is one of the few known substances for which the crystalline solid is *less dense* than the liquid (others include antimony and bismuth). Increasing the pressure of ice that is in equilibrium with water at 0°C and 1 atm tends to push some of the molecules closer together, thus decreasing the volume of the sample. The decrease in volume (and corresponding increase in density) is smaller for a solid or a liquid than for a gas, but it is sufficient to melt some of the ice.

In Figure 1.10.1.2b point A is located at $P$ = 1 atm and $T$ = −1.0°C, within the solid (ice) region of the phase diagram. As the pressure increases to 150 atm while the temperature remains the same, the line from point A crosses the ice/water boundary to point B, which lies in the liquid water region. Consequently, applying a pressure of 150 atm will melt ice at −1.0°C. We have already indicated that the pressure dependence of the melting point of water is of vital importance. If the solid/liquid boundary in the phase diagram of water were to slant up and to the right rather than to the left, ice would be denser than water, ice cubes would sink, water pipes would not burst when they freeze, and antifreeze would be unnecessary in automobile engines.

### Ice Skating: An Incorrect Hypothesis of Phase Transitions

Until recently, many textbooks described ice skating as being possible because the pressure generated by the skater's blade is high enough to melt the ice under the blade, thereby creating a lubricating layer of liquid water that enables the blade to slide across the ice. Although this explanation is intuitively satisfying, it is incorrect, as we can show by a simple calculation.

Pressure from ice skates on ice. from wikihow.com.

Recall that pressure (*P*) is the force (*F*) applied per unit area (*A*):

$$P = \frac{F}{A}$$

To calculate the pressure an ice skater exerts on the ice, we need to calculate only the force exerted and the area of the skate blade. If we assume a 75.0 kg (165 lb) skater, then the force exerted by the skater on the ice due to gravity is

$$F = mg$$

where *m* is the mass and *g* is the acceleration due to Earth's gravity (9.81 m/s$^2$). Thus the force is

$$F = (75.0\ kg)(9.81\ m/s^2) = 736\ (kg \bullet m)/s^2 = 736N$$

If we assume that the skate blades are 2.0 mm wide and 25 cm long, then the area of the bottom of each blade is

$$A = (2.0 \times 10^{-3}\ m)(25 \times 10^{-2}\ m) = 5.0 \times 10^{-4} m^2$$

If the skater is gliding on one foot, the pressure exerted on the ice is

$$P = \frac{736\ N}{5.0 \times 10^{-4}\ m^2} = 1.5 \times 10^6\ N/m^2 = 1.5 \times 10^6\ Pa = 15\ atm$$

The pressure is much lower than the pressure needed to decrease the melting point of ice by even 1°C, and experience indicates that it is possible to skate even when the temperature is well below freezing. Thus pressure-induced melting of the ice cannot explain the low friction that enables skaters (and hockey pucks) to glide. Recent research indicates that the surface of ice, where the ordered array of water molecules meets the air, consists of one or more layers of almost liquid water. These layers, together with melting induced by friction as a skater pushes forward, appear to account for both the ease with which a skater glides and the fact that skating becomes more difficult below about −7°C, when the number of lubricating surface water layers decreases.

### ✓ Example 1.10.1.1: Water

Referring to the phase diagram of water in Figure $1.10.1.2$

a. predict the physical form of a sample of water at 400°C and 150 atm.
b. describe the changes that occur as the sample in part (a) is slowly allowed to cool to −50°C at a constant pressure of 150 atm.

**Given:** phase diagram, temperature, and pressure

**Asked for:** physical form and physical changes

**Strategy:**

A. Identify the region of the phase diagram corresponding to the initial conditions and identify the phase that exists in this region.
B. Draw a line corresponding to the given pressure. Move along that line in the appropriate direction (in this case cooling) and describe the phase changes.

**Solution:**

a. **A** Locate the starting point on the phase diagram in part (a) in Figure $1.10.1.2$ The initial conditions correspond to point A, which lies in the region of the phase diagram representing water vapor. Thus water at *T* = 400°C and *P* = 150 atm is a gas.

b. **B** Cooling the sample at constant pressure corresponds to moving left along the horizontal line in part (a) in Figure 1.10.1.2. At about 340°C (point B), we cross the vapor pressure curve, at which point water vapor will begin to condense and the sample will consist of a mixture of vapor and liquid. When all of the vapor has condensed, the temperature drops further, and we enter the region corresponding to liquid water (indicated by point C). Further cooling brings us to the melting curve, the line that separates the liquid and solid phases at a little below 0°C (point D), at which point the sample will consist of a mixture of liquid and solid water (ice). When all of the water has frozen, cooling the sample to −50°C takes us along the horizontal line to point E, which lies within the region corresponding to solid water. At $P$ = 150 atm and $T$ = −50°C, therefore, the sample is solid ice.

### Exercise 1.10.1.2

Referring to the phase diagram of water in Figure 1.10.1.2, predict the physical form of a sample of water at −0.0050°C as the pressure is gradually increased from 1.0 mmHg to 218 atm.

**Answer**

The sample is initially a gas, condenses to a solid as the pressure increases, and then melts when the pressure is increased further to give a liquid.

## The Phase Diagram of Carbon Dioxide

In contrast to the phase diagram of water, the phase diagram of $CO_2$ (Figure 1.10.1.3) has a more typical melting curve, sloping up and to the right. The triple point is −56.6°C and 5.11 atm, which means that liquid $CO_2$ cannot exist at pressures lower than 5.11 atm. At 1 atm, therefore, solid $CO_2$ sublimes directly to the vapor while maintaining a temperature of −78.5°C, the normal sublimation temperature. Solid $CO_2$ is generally known as dry ice because it is a cold solid with no liquid phase observed when it is warmed.

Dry ice ($CO_2(s)$) sublimed in air under room temperature and pressure. from Wikipedia.

Also notice the critical point at 30.98°C and 72.79 atm. Supercritical carbon dioxide is emerging as a natural refrigerant, making it a low carbon (and thus a more environmentally friendly) solution for domestic heat pumps.

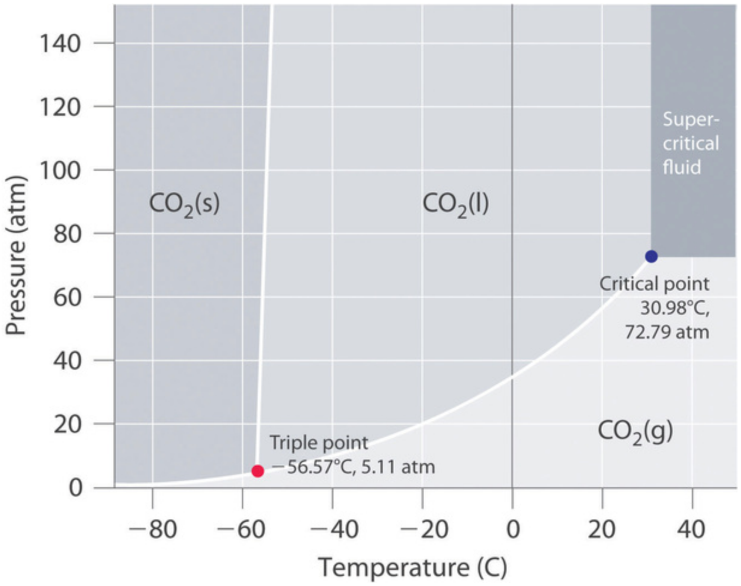

Figure 1.10.1.3: The Phase Diagram of Carbon Dioxide. Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

The triple point is at -57.57 degrees C and 5.11 atm. The critical point is at 30.98 degree C and 72.79 atm.

## The Critical Point

As the phase diagrams above demonstrate, a combination of high pressure and low temperature allows gases to be liquefied. As we increase the temperature of a gas, liquefaction becomes more and more difficult because higher and higher pressures are required to overcome the increased kinetic energy of the molecules. In fact, for every substance, there is some temperature above which the gas can no longer be liquefied, regardless of pressure. This temperature is the critical temperature ($T_c$), the highest temperature at which a substance can exist as a liquid. Above the critical temperature, the molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase. Instead, the substance forms a single phase that completely occupies the volume of the container. Substances with strong intermolecular forces tend to form a liquid phase over a very large temperature range and therefore have high critical temperatures. Conversely, substances with weak intermolecular interactions have relatively low critical temperatures. Each substance also has a critical pressure ($P_c$), the minimum pressure needed to liquefy it at the critical temperature. The combination of critical temperature and critical pressure is called the critical point. The critical temperatures and pressures of several common substances are listed in Figure 1.10.1.1.

Figure 1.10.1.1: Critical Temperatures and Pressures of Some Simple Substances

| Substance | $T_c$ (°C) | $P_c$ (atm) |
|---|---|---|
| $NH_3$ | 132.4 | 113.5 |
| $CO_2$ | 31.0 | 73.8 |
| $CH_3CH_2OH$ (ethanol) | 240.9 | 61.4 |
| He | −267.96 | 2.27 |
| Hg | 1477 | 1587 |
| $CH_4$ | −82.6 | 46.0 |
| $N_2$ | −146.9 | 33.9 |
| $H_2O$ | 374.0 | 217.7 |

> High-boiling-point, nonvolatile liquids have high critical temperatures and vice versa.

## Supercritical Fluids

A Video Discussing Phase Diagrams. Video Source: Phase Diagrams(opens in new window) [youtu.be]

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# 1.10.2: A Phase Diagram Summarizes the Solid-Liquid-Gas Behavior of a Substance

A good map will take you to your destination with ease, provided you know how to read it. A map is an example of a *diagram*, a pictorial representation of a body of knowledge. In science they play a considerable role. Next to plots and tables *diagrams* are an important means of making information and/or theoretical knowledge accessible.

Constructing them takes quite a bit of thought. You want to represent as much of what you know and give as accurate a picture of it without conveying anything incorrect. If the drawing can be made to scale that makes it quite a bit more powerful, but this is not strictly necessary. A remark like *not to scale* or *schematically* does need to be given if applicable. A good caption or description is essential.

## 1.10.2.1: Thermodynamic Stability and Fluctuations

There are different kinds of equilibrium, besides the ***stable*** equilibrium that represents an absolute minimum in the $G$ function. Of course $G$ is potentially a function of a great number of variables, but let us look at a *diagram* in which $G$ is shown as a function of only one unspecified variable. You could think of the density, the mole fraction of one of the components of a mixture or an applied electrical field or whatever, but the argument is general.

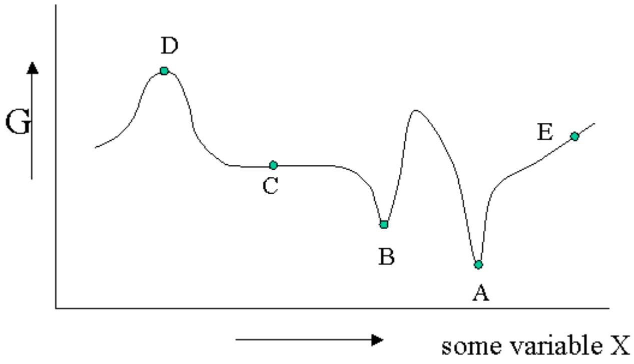


Figure 23.1.1 : A schematic $G$ curve showing various Points of stability. Due to statistical fluctuations the value of $G$ is not quite constant over time, because less likely realizations of the ensemble (having a slightly less favorable value of $G$) do occur from time to time. After all, the Boltzmann distribution is simply the most likely one, not the only one possible. The fluctuations have drastically different consequences depending on whether the system is in an unstable ($E$), labile ($D$) , indifferent ($C$), metastable ( $B$) or stable ($A$) state. Notice that $A$ and $B$ just wobble around a bit. $C$ fluctuates wildly in the value of $X$, while both $E$ and $D$ eventually vanish because the system transits to a more favorable state. For $E$ this starts immediately, for $D$ it starts once fluctuation has caused it to move from its peak sufficiently.

Figure 23.1.1 is helpful to point out that besides a stable equilibrium ($A$) there can also be an ***metastable*** equilibrium (B) or an ***indifferent*** equilibrium ($C$). The local derivatives of $G$ (versus *all* variables of which we only show one) are zero in all three cases, which means that changes in the variables are *not spontaneous*. For a ***labile*** equilibrium ($D$) the opposite is true. Any small deviation will make the system role down hill. (Note that the second derivative has the opposite sign compared to cas A) and B)) A labile equilibrium is seldom or never observed except in a circus where artists delight in balancing objects on their heads (because you pay for it).. This usually requires continuous small corrections to maintain the precarious balance. All other points in our diagram represent state of ***instability*** because locally $dG$ is not zero and a spontaneous process can take place.

The fact that $dG = 0$ in the equilibrium points does not mean small deviations from the minimum cannot happen at times. We have seen e.g. that the Boltzmann distribution was simply *the most likely* distribution. The most likely one is the one that has the highest number of realizations W. Another way of saying that is that it is the one with the highest entropy S. A slightly less likely distribution may occur from time to time by chance. It will have a little less entropy, but the same $\langle E\rangle$. That means it will have a slightly higher $G$ ($G = H - TS$ ). From time to time therefore $G$ will fluctuate a bit. Such fluctuations are very small for large systems, but they are of greater relative importance for small systems (like a nanoparticle). (Statistical averaging works best on large ensembles.)

The fluctuations in $G$ mean that small fluctuations in its variables like density etc. can also occur. They are usually kept in check, because $dG$ is no longer zero when moving away from the equilibrium state. This drives the system back to the minimum spontaneously. You could picture the system wobbling a bit around in its G-well. This holds for stable and metastable equilibria alike.

In the indifferent case ($C$) however the derivative is zero (or very close to zero) for a *range* of neighboring values of some variable. In contrast to $A$ and $B$ also the *second derivative* is zero. This means that there is little penalty to much larger deviations in the variable. If this variable is the density the system becomes milky and shows *opalescence* a strong scattering of light because the refractive index depends on the strongly fluctuating density. This is observed near critical points and is called *critical opalescence*.

## 1.10.2.2: Unary Phase Diagrams

A unary phase diagram summarizes the equilibrium states of a single pure substance. We will see that we can also look at mixtures of two components (binary diagrams) or more (ternary, quaternary, quinary, senary etc.). Usually a phase diagram only maps out stable equilibria, but occasionally metastable ones may be given too (e.g., with a dashed line).

### 1.10.2.2.0.1: Liquid-Vapor Equilibrium Curve

We have seen that the Gibbs function $G$ depends strongly (logarithmically) on pressure for a gas, but only slightly (and linearly) for a liquid. The two curves intersect in a point representing the *equilibrium vapor pressure* of the liquid. At lower pressures the vapor is more stable, at higher ones the liquid. (For a solid the same holds as for the liquid). This means that except at the intersection point we only will observe one phase.

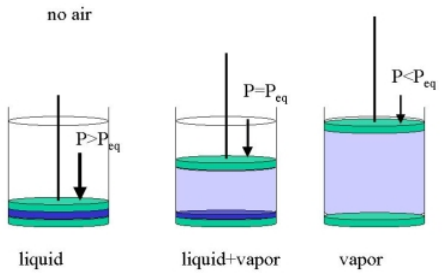


***Figure 23.1.2** : A cylinder with one substance*

It is important to stress that this holds *in the absence of other matter*, e.g., when we put only water into an evacuated cylinder (Figure 23.1.2 ). We may get three cases:

- we compress the cylinder until it only contains the liquid under hydrostatic pressure ($P > P_{eq}$ )
- we expand the cylinder until all water has vaporized ($P < p_{eq}$ )>
- we let part of the water evaporate, just enough so that the space above the liquid is filled with an equilibrium vapor pressure ( $P = P_{eq}$ )

At room temperature $P_{eq}$ for water is only about 15 Torr. If we apply 1 bar -or let the atmosphere do the job- we will only have liquid water. If other gases are present, e.g., air, we must distinguish between the total pressure (e.g., 1 bar) and the equilibrium vapor pressure which will now be the *partial* pressure. In a cylinder with water and one bar of air just enough water will evaporate to establish equilibrium. The evaporation will be limited to the gas-liquid interface unless the partial pressure equals the total pressure. Then the liquid will *boil*.

> *(Do allow the volume to expand, though., why? If the volume is constant the pressure builds up and boiling will stop.*

If we consider the set of equilibrium pressures as a function of temperature and plot that in a P vs. T diagram we have one component of our phase diagram.

### 1.10.2.2.0.1: Gas-solid Equilibrium Curve

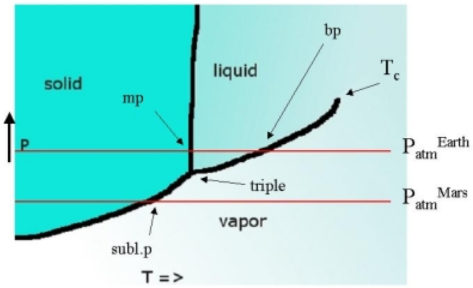
For solids the situation is similar as the $G(P)$ curve is once again an almost flat straight line. The intersection with the logarithmic curve for the gas will define an equilibrium pressure for gas-solid co-existence. Generally vapor pressures above solids are quite small, but not negligible. As for liquids we can construct a line representing the equilibrium pressures for sublimation as function of temperature and add it to the phase diagram.

### 1.10.2.2.0.1: Liquid-solid Equilibrium Curve

The $\text{solid} \rightleftharpoons \text{liquid}$ equilibrium is known as **melting** or **freezing** is not very dependent on pressure. Usually melting points increase a little bit with pressure, although water is a peculiar exception. It expands upon freezing and the melting point goes down (a bit) with pressure. In our diagram this will represent an almost vertical line leaning a little forwards for most substances, but backwards for water and a few others.

### 1.10.2.2.1: Putting the Curve Together

The three lines come together in the *triple point*, the only point where all three phases are at equilibrium with each other. For water, its temperature is only 0.01 K different from the normal melting point (273.16 K) and its pressure is only 4.58 Torr. The intersection points with a line representing atmospheric pressure give the melting and boiling points at that pressure.



*A typical unary diagram*

If the triple point lies above the line that represents atmospheric pressure this implies that a liquid is never observed. On earth $CO_2$ is such a substance. The intersection of the solid-vapor equilibrium line with the 1 bar line represents a state where the solid will *'boil'* (evaporate from inside out). This is known as the *sublimation point*. The melting points at P=1 bar are known as the *standard melting point*, the only slightly different one at 760 Torr = 1 atm is called *normal melting point*. The same goes for boiling and sublimation points.

There is *nothing magical* about $P = 1\, bar$. It just happens to be the pressure of our home planet. On a planet with higher atmospheric pressures $CO_2$ may well be a liquid and on such a planet, all boiling points will be quite different (higher than on earth). The melting points will also differ, but only slightly so. On Mars where atmospheric pressure is much lower water can not occur in liquid form, much like carbon dioxide on earth - it sublimes.

> We should also realize that in a *closed container* (glass ampoule, hermetically sealed DSC pan), we can observe melting points at only very slightly different temperature values, but we will ***not*** see a boiling effect. Why?
>
> To see a boiling point the container must be open to the (*constant!*) 1 bar pressure of the earths atmosphere that ***defines*** it and causes the boiling phenomenon. If the ampoule is sealed it will generate its *own* (autogenous) pressure, depending on what you put in, how much of it in relation to the volume, how volatile it is and the temperature. The autogenous pressure does not interfere with the melting point much (the melting line is almost vertical), but as $P$ changes with temperature you may never reach boiling conditions.
>
> In DSC experiments it is possible to observe boiling points only if the pan has been carefully *perforated* with a hole of known size. It must be big enough that the pressure inside the pan does not build up above atmospheric, but small enough that it does not cause premature loss of mass during the run. The latter spoils the calculation of the intensive value (per mole, per gram) of the heat of vaporization.
>
> The liquid evaporation line ends in a point that we have encountered before: the critical point $T_C$. As temperature increases the liquid and vapor phases in equilibrium with each other start to resemble each other more and more and at $T_c$ they coalesce. At this point the liquid-gas equilibrium becomes indifferent with respect to density and large fluctuations occur leading to critical opalescence.
>
> Notice that there is a relationship of dimensionality between the objects in the diagram and the number of phases present:
>
> - 2 D planes: one phase
> - 1 D curves: two phases

> - 0 D point: three phases
>
> As you see the sum is always three.

## 1.10.2.3: Number of moles

So far we have typically considered one substance at the time, but for chemists it is imperative to deal with more than one because we are typically changing one into the other in our reactions. This means that the number of moles $n$, that we often simply set equal to one now becomes an important variable in its own right. Besides we will actually have two (or more) of them: the number of moles of component one and the one for the other component. This makes n a much less trivial variable.

This is already the case at a simple melting point, say when ice melts, because we are dealing with changing quantities of ice and water:

$$n_{ice} + n_{water} = n_{total}$$

If all we do is turn water into ice or vice versa, we have $dn_{total} = 0$, so that:

$$dn_{ice} = -dn_{water}$$

To deal with changing n's, we need to expand our mathematical notation a bit.

### 1.10.2.3.1: Partial variables

So far we have simply divided our thermodynamic functions if they were extensive by the number of moles and arrived at intensive molar values:

$$G_{molar} = \frac{G}{n}$$

$$V_{molar} = \frac{V}{n}$$

We have written such intensive molar values by writing a bar over the symbol G or V. We should note that scaling the function this way departs from the assumption that the function $G$ depends on the variable n as a straight line that passes through the origin.

If we have the same pure compound in two phases, like ice and water we can still apply this principle and write:

$$G^{ice}_{molar} = \frac{G^{ice}}{n^{ice}}$$

$$V^{ice}_{molar} = \frac{V^{ice}}{n^{ice}}$$

$$G^{water}_{molar} = \frac{G^{water}}{n^{water}}$$

$$V^{water}_{molar} = \frac{V^{water}}{n^{water}}$$

If we have a ***mixture*** of two substances present as $n_1$ and $n_2$ moles the dependency need not be linear on either if the two substances interact with each other. This is also true for function like the volume of a liquid mixture. In the presence of interactions volumes do *not* have to be linearly additive. We can define a partial molar value of e.g. for the volume:

$$V_{partialmolar,1} = \frac{\partial V}{\partial n_1}$$

at $n_2$ = constant

$$V_{partialmolar,2} = \frac{\partial V}{\partial n_2}$$

at $n_1$ = constant

The notation of putting a bar over the $V$ symbol is used for these partial quantities as well. Partial molar volumes have been measured for many binary systems. They are functions of the composition (mole fraction) as well as the temperature and to a lesser extent the pressure.

**The partial molar Gibbs free energy**

The partial molar Gibbs free energy ( $\left(\frac{\partial G}{\partial n_i}\right)_{P,T}$ , all other n's) is denoted with $\mu$ and is called the thermodynamic potential.

When numbers of moles can change we can write the corresponding change in $G$ as:

$$dG = -SdT + VdP + \sum_i^N \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_{j\neq i}} dn_i$$

$$dG = -SdT + VdP + \sum_i^N \mu_i dn_i$$

over $N$ phases in the system. As you can see we are adding a set of conjugate variables $\mu_i n_i$ for each phase $i$. If we are considering a *pure* component (but in different modifications, like ice and steam), we can still write:

$$\mu_i = \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_{j\neq i}} = \frac{G_i}{n_i}$$

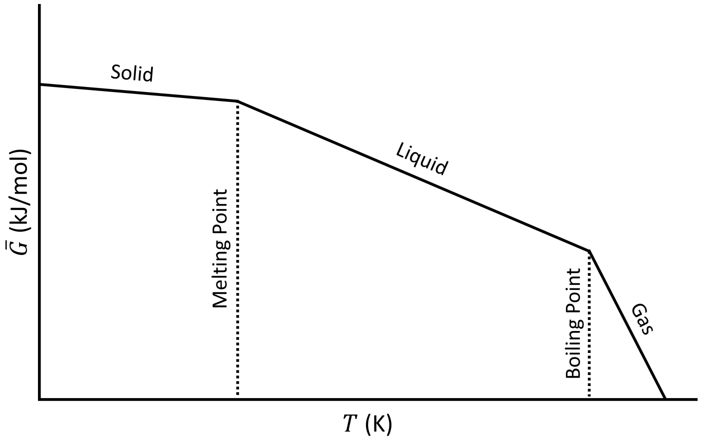
As soon as we are dealing with mixtures we really do have derivatives.

---

# 1.10.3: Gibbs Energies and Phase Diagrams

## 1.10.3.1: First Order Transitions

The following plot shows the Gibbs energy as a function of temperature, including phase changes from solid to liquid (melting) and liquid to gas (boiling).



*Gibbs energy ($\bar{G}$) as a function of temperature ($T$).*

Although the $G$ curve is continuous, its first order derivatives ($-S$) is discontinuous at the phase changes. This is why this transition it called a *first order transition*. We could say that:

- $G$ is continuous but has a kink
- The first order derivatives ($H$,$S$,..) are discontinuous (have a jump)
- The second order derivatives ($C_P$, ..) have a singularity (go to ∞)

## 1.10.3.2: Second Order Transitions

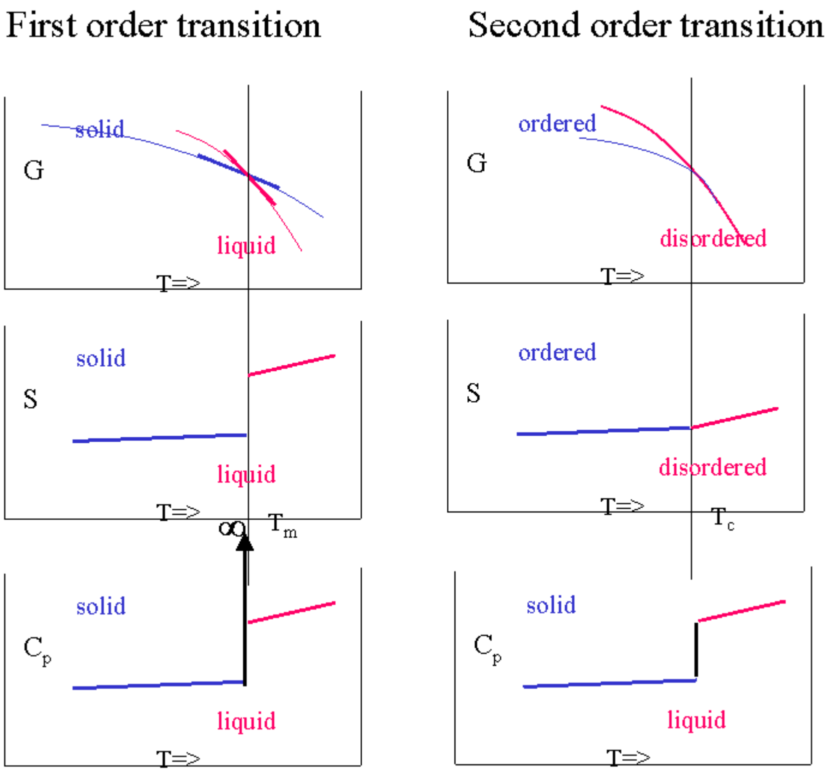
More subtle transitions where $G$ is continuous, $H$ and $S$ are also continuous but have a kink and the discontinuity is only found in the second order derivatives (such as $C_P$) also exist. They are called *second order transitions*. In such a case:

- $G$ is continuous and has no kink
- The first order derivatives ($H$,$S$,..) are continuous (but have a kink)
- The second order derivatives ($C_P$, ..) are discontinuous (have a jump)

Table 23.2.1: Properties of Phase Transitions

| **Transition Order** | **Function** | **1$^{st}$ Order** | **2$^{nd}$ Order** |
|---|---|---|---|
| 0 | G,A | kink | smooth |
| 1 | H,S,V,.. | jump | kink |
| 2 | CP,CV,α,κ | sing. ∞ | jump |

This classification goes back to Ehrenfest. Obviously it based on the question: what order derivative is the first to go discontinuous? Of course we could extend this principle and define *third order transitions* but there are reasons to be doubtful that such things exist. Another problem is that it is assumed that the order must be integer: 1,2, etc. Is it possible to have a transition of intermediate non-integer order, say 1.3? Although derivatives of fractional order are beyond the scope of the chemistry curriculum the mathematics does exist (Liouville).



*Schematic comparison of $G$, $S$ and $C_P$ for 1st and 2nd order transitions*

The Gibbs free energy is a particularly important function in the study of phases and phase transitions. The behavior of $G(N, P, T)$, particularly as a function of $P$ and $T$, can signify a phase transition and can tell us some of the thermodynamic properties of different phases.

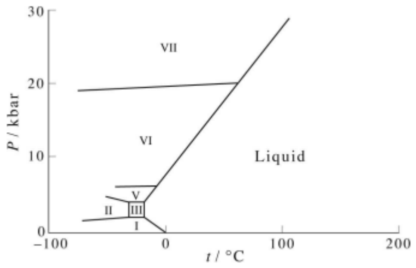


Figure 13.4: Some of the ice polymorphs.

Consider, first, the behavior of $G$ vs. $T$ between the solid and liquid phases of benzene: We immediately notice several things. First, although the free energy is continuous across the phase transition, its first derivative, $\partial G/\partial T$ is not: The slope of $G(T)$ in the solid region is different from the slope in the liquid region. When the first derivative of the free energy with respect to one of its dependent thermodynamic variables is discontinuous across a phase transition, this is an example of what is called a *first order phase transition*. The solid-liquid-gas phase transition of most substances is first order. When the free energy exhibits continuous first derivatives but discontinuous second derivatives, the phase transition is called *second order*. Examples of this type of phase transition are the order-disorder transition in paramagnetic materials.

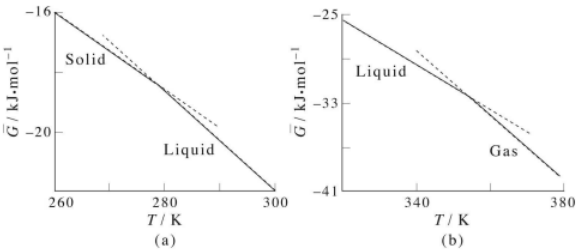


Figure 13.5: Behavior of the Gibbs free energy across the solid-liquid phase (left) and liquid-gas (right) transitions for benzene.

Now, recall that

$$S = -\frac{\partial G}{\partial T} \tag{1.10.3.1}$$

Consider the slopes in the solid and liquid parts of the graph:

$$\frac{\partial G^{(\text{solid})}}{\partial T} = -S^{(\text{solid})}, \qquad \frac{\partial G^{(\text{liquid})}}{\partial T} = -S^{(\text{liquid})} \tag{1.10.3.2}$$

However, since

$$\frac{\partial G^{(\text{liquid})}}{\partial T} < \frac{\partial G^{(\text{solid})}}{\partial T} \tag{1.10.3.3}$$

(*note that the slopes are all negative, and the slope of the liquid line is more negative than that of the solid line*), it follows that $-S^{(\text{liquid})} < -S^{(\text{solid})}$ or $S^{(\text{liquid})} > S^{(\text{solid})}$. This is what we might expect considering that the liquid phase is higher in entropy than the solid phase. The same argument can be made with regards to the gaseous phase.

Similarly, if we consider the dependence of $G$ on pressure, we obtain a curve like that shown in the figure below:

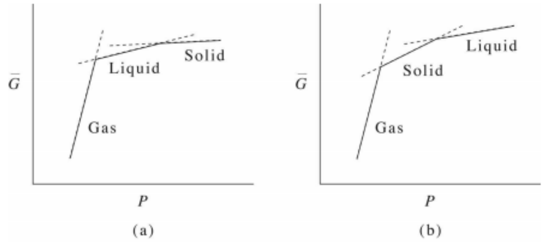


Figure 13.6: Dependence of the Gibbs free energy as a function of pressure for benzene (left) and water (right). For benzene, the temperature is above the triple point, whereas for water, it is set below triple point.

As noted previously, here again, we see that the first derivative of $\bar{G}(P)$ is discontinuous, signifying a first-order phase transition. Recalling that the average molar volume is

$$\bar{V} = \frac{\partial \bar{G}}{\partial P} \tag{1.10.3.4}$$

From the graph, we see that the slopes obey

$$\bar{V}^{(\text{gas})} \gg \bar{V}^{(\text{liquid})} > \bar{V}^{(\text{solid})} \tag{1.10.3.5}$$

as one might expect for a normal substance like benzene at a temperature above its triple point. Because the temperature is above the triple point, the free energy follows a continuous path (even though it is not everywhere differentiable) from gas to liquid to solid.

On the other hand, for water, we see something a bit different, namely, that

$$\bar{V}^{(\text{gas})} \gg \bar{V}^{(\text{solid})} > \bar{V}^{(\text{liquid})} \tag{1.10.3.6}$$

at a temperature below the triple point. This, again, indicates, the unusual property of water that its solid phase is less dense than its liquid phase in the coexistence region.

Interestingly, if we look at how the plot of $G(P)$ changes with $T$, we obtain a plot like that shown below: Below the triple point, it is easy to see from the benzene phase diagram that the system proceeds directly from solid to gas. There is a liquid curve on this plot that is completely disconnected from the gas-solid curve, suggesting that, below the triple point, the liquid state can exist metastably if at all. AT the triple point, the solid can transition into the liquid or gas phases depending on the value of the free energy. Near the critical temperature, we see the liquid-gas transition line, while the solid line is disconnected. Above the critical temperature, the system exists as a supercritical fluid, which is shown on the lower line, and this line now shows derivative discontinuity.

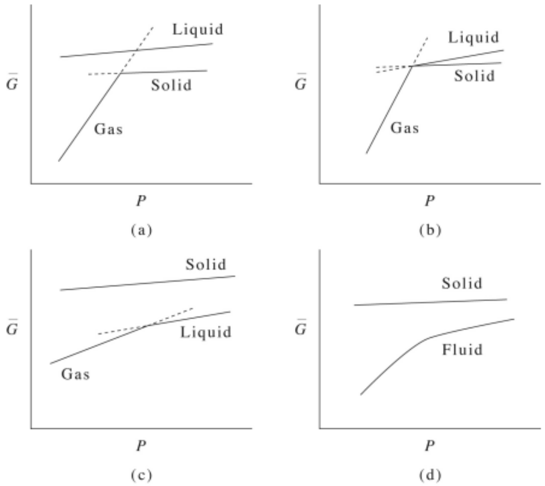


Figure 13.7: Behavior of the Gibbs free energy as a function of $P$ across different phases at different temperatures for benzene. (a): Temperature is less than the triple point; (b): Temperature is equal to the triple point; (c): Temperature is just below the critical temperature; (d): Temperature is greater than the critical temperature.

## 1.10.3.3: Conjugate Variables

As discussed before there are many other forms of work possible, such as electrical work, magnetic work or elastic work. These they are commonly incorporated in the formalism of thermodynamics by adding other terms, e.g:

$$dG = -SdT + VdP + \mathcal{E}de + MdH + FdL + \gamma dA$$

1. $\mathcal{E}de$ stands for the electromotoric force $\mathcal{E}$ and $de$ the amount of charge transported against it.
2. $MdH$ stand for magnetization and (change in) magnetic field.
3. $F$ stands for the elastic force of e.g. a rubber band $dL$ for the length it is stretched
4. $\gamma$ stands for the surface tension (e.g. of a soap bubble), $A$ for its surafce area.

The terms always appear in a pair of what is known as conjugate variables. That is even clearer if we write out the state function rather than its differential form:

$$G = U + PV - TS + \mathcal{E}e + MH + FL + \gamma A + \ldots$$

The PV term can also be generalized -and needs to be so- for a viscous fluid to a stress-strain conjugate pair. It then involves a stress tensor. We will soon encounter another conjugate pair: μdn that deals with changes in composition (n) and the thermodynamic potential μ.

# 1.10.4: The Chemical Potentials of a Pure Substance in Two Phases in Equilibrium

## 1.10.4.1: Chemical Potential of Two Phases in Equilibrium

Equilibrium between two phases, e.g. water ice ($ice$) and liquid water ($water$), is at constant $T$ and $P$. Therefore:

$$dG = \cancel{-SdT + VdP} + \mu_{ice} dn_{ice} + \mu_{water} dn_{water}$$

There is a relationship between the amount of ice and water:

$$dn_{ice} = -dn_{water}$$

From this, we get:

$$0 = [\mu_{ice} - \mu_{water}] dn_{water} = \Delta\mu \; dn_{water}$$

As $dn_{water}$ is not zero, this means that $\Delta\mu$ must be zero! This must hold true for any set of points where ice and water are in equilibrium. The statement is not just for liquid and solid water, but for any two phases in equilibrium. That is, any two phases in equilbrium will always have the same chemical potential.

## 1.10.4.2: The Clapeyron Equation

That is the almost vertical line in the diagram. Its points are not at the same $P$ and $T$, but we can find out where they should be by considering the thermodynamic potential $\mu$ as a *function* of $T$ and $P$:

$$d\mu = \left(\frac{\partial \mu}{\partial P}\right)_T dT + \left(\frac{\partial \mu}{\partial T}\right)_P dP$$

Because $\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} = \bar{G}$ , it is not hard to identify the partial derivatives:

$$\left(\frac{\partial \mu}{\partial P}\right) = \left(\frac{\partial \bar{G}}{\partial P}\right) = \bar{V}$$

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

This is true for both water and ice, or any two phases in equilibrium. As the $\Delta\mu = 0$, we can equate the $d\mu$ expressions for both water and ice:

$$\left(\frac{\partial \mu_{ice}}{\partial P}\right)_T dT + \left(\frac{\partial \mu_{ice}}{\partial T}\right)_P dP = \left(\frac{\partial \mu_{water}}{\partial P}\right)_T dT + \left(\frac{\partial \mu_{water}}{\partial T}\right)_P dP$$

Rearranging and identifying the partials gives:

$$\bar{V}_{ice} dP - \bar{S}_{ice} dT = \bar{V}_{water} dP - \bar{S}_{water} dT$$

Solving for $dP/dT$ we get:

$$\frac{dP}{dT} = \frac{\Delta\bar{S}}{\Delta\bar{V}}$$

As $\Delta\bar{G} = \Delta\bar{H} - T\Delta\bar{S} = 0$ , we have:

$$\Delta\bar{S} = \frac{\Delta\bar{H}}{T_m}$$

So:

$$\frac{dP}{dT} = \frac{\Delta\bar{H}}{T\Delta\bar{V}}$$

This expression should be valid for all points along a phase boundary, such as the melt line. In fact, it tells use that the phase boundary is **defined** by $\Delta\bar{H}/T\Delta\bar{V}$. For water and ice, we immediately see why the melt line runs a little to the left: exceptionally $\Delta\bar{V}$ is negative for ice, because water is actually a little denser that ice.

The above expression(s) are named after ***Clapeyron.*** The values of $\Delta\bar{H}$ and $\Delta\bar{V}$ do not change much with pressure and can often be considered *constants* for the melting line. When gases are involved that is not really true.

---

## 1.10.5: The Clausius-Clapeyron Equation

### 1.10.5.1: Evaporation

In Section 23.3, the Clapeyron Equation was derived for melting points.

$$\frac{dP}{dT} = \frac{\Delta H_{molar}}{T\Delta V_{molar}}$$

However, our argument is actually quite general and should hold for vapor equilibria as well. The only problem is that the molar volume of gases are by no means so nicely constant as they are for condensed phases. (i. e., for condenses phases, both $\alpha$ and $\kappa$ are pretty small).

We can write:

$$\frac{dP}{dT} = \frac{\Delta H_{molar}}{T\Delta V_{molar}} = \frac{\Delta H_{molar}}{T}\left[V^{gas}_{molar} - V^{liquid}_{molar}\right]$$

as

$$V^{gas}_{molar} \gg V^{liquid}_{molar}$$

we can approximate

$$V^{gas}_{molar} - V^{liquid}_{molar}$$

by just taking $V^{gas}_{molar}$. Further more if the vapor is considered an ideal gas, then

$$V^{gas}_{molar} = \frac{RT}{P}$$

We get

$$\frac{1}{P}.\frac{dP}{dT} = \frac{d\ln P}{dT} = \frac{\Delta H^{vap}_{molar}}{RT^2} \tag{1.10.5.1}$$

Equation 1.10.5.1is known as the **Clausius-Clapeyron** equation. We can further work our the integration and find the how the equilibrium vapor pressure changes with temperature:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H^{vap}_{molar}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Thus if we know the molar enthalpy of vaporization we can predict the vapor lines in the diagram. Of course the approximations made are likely to lead to deviations if the vapor is not ideal or very dense (e.g., approaching the critical point).

### 1.10.5.2: The Clapeyron Equation

The Clapeyron attempts to answer the question of what the shape of a two-phase coexistence line is. In the $P-T$ plane, we see the a function $P(T)$, which gives us the dependence of $P$ on $T$ along a coexistence curve.

Consider two phases, denoted $\alpha$ and $\beta$, in equilibrium with each other. These could be solid and liquid, liquid and gas, solid and gas, two solid phases, et. Let $\mu_\alpha(P,T)$ and $\mu_\beta(P,T)$ be the chemical potentials of the two phases. We have just seen that

$$\mu_\alpha(P,T) = \mu_\beta(P,T) \tag{1.10.5.2}$$

Next, suppose that the pressure and temperature are changed by $dP$ and $dT$. The changes in the chemical potentials of each phase are

$$d\mu_\alpha(P,T) = d\mu_\beta(P,T) \tag{1.10.5.3}$$

$$\left(\frac{\partial \mu_\alpha}{\partial P}\right)_T dP + \left(\frac{\partial \mu_\alpha}{\partial T}\right)_P dT = \left(\frac{\partial \mu_\beta}{\partial P}\right)_T dP + \left(\frac{\partial \mu_\beta}{\partial T}\right)_P dT \tag{1.10.5.4}$$

However, since $G(n,P,T) = n\mu(P,T)$, the *molar* free energy $\bar{G}(P,T)$, which is $G(n,P,T)/n$, is also just equal to the chemical potential

$$\bar{G}(P,T) = \frac{G(n,P,T)}{n} = \mu(P,T) \tag{1.10.5.5}$$

Moreover, the derivatives of $\bar{G}$ are

$$\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}, \qquad \left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S} \tag{1.10.5.6}$$

Applying these results to the chemical potential condition in Equation 1.10.5.4 we obtain

\[\begin{align} \left( \dfrac{\partial \bar{G}_\alpha}{\partial P} \right)_T dP + \left( \dfrac{\partial \bar{G}_\alpha}{\partial T} \right)_P dT &= \left( \dfrac{\partial \bar{G}_\beta}{\partial P} \right)_T dP + \left( \dfrac{\partial \bar{G}_\beta}{\partial T} \right)_P dT \\

5pt] \bar{V}_\alpha dP - \bar{S}_\alpha dT &= \bar{V}_\beta dP - \bar{S}_\beta dT \end{align} \label{14.5}

Dividing through by $dT$, we obtain

\[\begin{align} \bar{V}_\alpha \dfrac{\partial P}{\partial T} - \bar{S}_\alpha &= \bar{V}_\beta \dfrac{\partial P}{\partial T} - \bar{S}_\beta \\

\[5pt] (\bar{V}_\alpha - \bar{V}_\beta) \dfrac{\partial P}{\partial T} &= \bar{S}_\alpha - \bar{S}_\beta \\

5pt] \dfrac{dP}{dT} &= \dfrac{\bar{S}_\alpha - \bar{S}_\beta}{\bar{V}_\alpha - \bar{V}_\beta} \end{align} \label{14.6}

The importance of the quantity $dP/dT$ is that is represents the slope of the coexistence curve on the phase diagram between the two phases. Now, in equilibrium $dG = 0$, and since $G = H - TS$, it follows that $dH = T\,dS$ at fixed $T$. In the narrow temperature range in which the two phases are in equilibrium, we can assume that $H$ is independent of $T$, hence, we can write $S = H/T$. Consequently, we can write the molar entropy difference as

$$\bar{S}_\alpha - \bar{S}_\beta = \frac{\bar{H}_\alpha - \bar{H}_\beta}{T} \tag{1.10.5.7}$$

and the pressure derivative $dP/dT$ becomes

$$\frac{dP}{dT} = \frac{\bar{H}_\alpha - \bar{H}_\beta}{T(\bar{V}_\alpha - \bar{V}_\beta)} = \frac{\Delta_{\alpha\beta}\bar{H}}{T\Delta_{\alpha\beta}\bar{V}} \tag{1.10.5.8}$$

a result known as the **Clapeyron equation**, which tells us that the slope of the coexistence curve is related to the ratio of the molar enthalpy between the phases to the change in the molar volume between the phases. If the phase equilibrium is between the solid and liquid phases, then $\Delta_{\alpha\beta}\bar{H}$ and $\Delta_{\alpha\beta}\bar{V}$ are $\Delta\bar{H}_{\text{fus}}$ and $\Delta\bar{V}_{\text{fus}}$, respectively. If the phase equilibrium is between the liquid and gas phases, then $\Delta_{\alpha\beta}\bar{H}$ and $\Delta_{\alpha\beta}\bar{V}$ are $\Delta\bar{H}_{\text{vap}}$ and $\Delta\bar{V}_{\text{vap}}$, respectively.

For the liquid-gas equilibrium, some interesting approximations can be made in the use of the Clapeyron equation. For this equilibrium, Equation 1.10.5.8becomes

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{\text{vap}}}{T(\bar{V}_g - \bar{V}_l)} \tag{1.10.5.9}$$

In this case, $\bar{V}_g \gg \bar{V}_l$ , and we can approximate Equation 1.10.5.9as

$$\frac{dP}{dT} \approx \frac{\Delta\bar{H}_{\text{vap}}}{T\bar{V}_g} \tag{1.10.5.10}$$

Suppose that we can treat the vapor phase as an ideal gas. Certainly, this is not a good approximation so close to the vaporization point, but it leads to an example we can integrate. Since $PV_g = nRT$ , $P\bar{V}_g = RT$ , Equation 1.10.5.10becomes

\[\begin{align} \dfrac{dP}{dT} &= \dfrac{\Delta \bar{H}_\text{vap} P}{RT^2} \

\[5pt] \dfrac{1}{P} \dfrac{dP}{dT} &= \dfrac{\Delta \bar{H}_\text{vap}}{RT^2} \

5pt] \dfrac{d \: \text{ln} \: P}{dT} &= \dfrac{\Delta \bar{H}_\text{vap}}{RT^2} \end{align} \label{14.11}

which is called the ***Clausius-Clapeyron equation***. We now integrate both sides, which yields

$$\ln P = -\frac{\Delta\bar{H}_{\text{vap}}}{RT} + C \tag{1.10.5.11}$$

where $C$ is a constant of integration. Exponentiating both sides, we find

$$P(T) = C' e^{-\Delta\bar{H}_{\text{vap}}/RT} \tag{1.10.5.12}$$

which actually has the wrong curvature for large $T$, but since the liquid-vapor coexistence line terminates in a critical point, as long as $T$ is not too large, the approximation leading to the above expression is not that bad.

If we, instead, integrate both sides, the left from $P_1$ to $P_2$, and the right from $T_1$ to $T_2$, we find

\[\begin{align} \int_{P_1}^{P_2} d \: \text{ln} \: P &= \int_{T_1}^{T_2} \dfrac{\Delta \bar{H}_\text{vap}}{RT^2} dT \

\[5pt] \text{ln} \: \left( \dfrac{P_2}{P_1} \right) &= -\dfrac{\Delta \bar{H}_\text{vap}}{R} \left( \dfrac{1}{T_2} - \dfrac{1}{T_1} \right) \

5pt] &= \dfrac{\Delta \bar{H}_\text{vap}}{R} \left( \dfrac{T_1 - T_1}{T_1 T_2} \right) \end{align} \label{14.12}

assuming that $\Delta\bar{H}_{\text{vap}}$ is independent of $T$. Here $P_1$ is the pressure of the liquid phase, and $P_2$ is the pressure of the vapor phase. Suppose we know $P_2$ at a temperature $T_2$, and we want to know $P_3$ at another temperature $T_3$. The above result can be written as

$$\ln\left(\frac{P_3}{P_1}\right) = -\frac{\Delta\bar{H}_{\text{vap}}}{R}\left(\frac{1}{T_3} - \frac{1}{T_1}\right) \tag{1.10.5.13}$$

Subtracting the two results, we obtain

$$\ln\left(\frac{P_2}{P_3}\right) = -\frac{\Delta\bar{H}_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_3}\right) \tag{1.10.5.14}$$

so that we can determine the vapor pressure at any temperature if it is known as one temperature.

In order to illustrate the use of this result, consider the following example:

**✓ Example 1.10.5.1**

At 1 bar, the boiling point of water is $373\text{ K}$. At what pressure does water boil at $473\text{ K}$? Take the heat of vaporization of water to be $40.65\text{ kJ/mol}$

**Solution**

Let $P_1 = 1\text{ bar}$ and $T_1 = 373\text{ K}$. Take $T_2 = 473\text{ K}$, and we need to calculate $P_2$. Substituting in the numbers, we find

\[\begin{align} \text{ln} \: P_2(\text{bar}) &= -\dfrac{(40.65 \: \text{kJ/mol})(1000 \: \text{J/kJ})}{8.3145 \: \text{J/mol} \cdot \text{K}} \left( \dfrac{1}{473 \: \text{K}} - \dfrac{1}{373 \: \text{K}} \right) = 2.77 \

5pt] P_2(\text{bar}) &= (1 \: \text{bar}) \: e^{2.77} = 16 \: \text{bar} \end{align}

## 1.10.5.3: The Clapeyron Equation

The Clapeyron attempts to answer the question of what the shape of a two-phase coexistence line is. In the $P - T$ plane, we see the a function $P(T)$, which gives us the dependence of $P$ on $T$ along a coexistence curve.

Consider two phases, denoted $\alpha$ and $\beta$, in equilibrium with each other. These could be solid and liquid, liquid and gas, solid and gas, two solid phases, et. Let $\mu_\alpha(P,T)$ and $\mu_\beta(P,T)$ be the chemical potentials of the two phases. We have just seen that

\mu_\alpha (P, T) = \mu_\beta (P, T) \label{14.1}

Next, suppose that the pressure and temperature are changed by $dP$ and $dT$. The changes in the chemical potentials of each phase are

d \mu_{\alpha} (P, T) = d \mu_{\beta} (P, T) \label{14.2a}

\left( \dfrac{\partial \mu_{\alpha}}{\partial P} \right)_T dP + \left( \dfrac{\partial \mu_{\alpha}}{\partial T} \right)_P dT = \left( \dfrac{\partial \mu_{\beta}}{\partial P} \right)_T dP + \left( \dfrac{\partial \mu_{\beta}}{\par

However, since $G(n,P,T) = n\mu(P,T)$, the *molar* free energy $\bar{G}(P,T)$, which is $G(n,P,T)/n$, is also just equal to the chemical potential

\bar{G} (P, T) = \dfrac{G(n, P, T)}{n} = \mu (P, T) \label{14.3}

Moreover, the derivatives of $\bar{G}$ are

\left( \dfrac{\partial \bar{G}}{\partial P} \right)_T = \bar{V}, \: \: \: \: \: \: \: \left( \dfrac{\partial \bar{G}}{\partial T} \right)_P = -\bar{S} \label{14.4}

Applying these results to the chemical potential condition in Equation 1.10.5.4, we obtain

$$\left(\frac{\partial \bar{G}_\alpha}{\partial P}\right)_T dP + \left(\frac{\partial \bar{G}_\alpha}{\partial T}\right)_P dT = \left(\frac{\partial \bar{G}_\beta}{\partial P}\right)_T dP + \left(\frac{\partial \bar{G}_\beta}{\partial T}\right)_P dT \tag{1.10.5.15}$$

$$\bar{V}_\alpha dP - \bar{S}_\alpha dT = \bar{V}_\beta dP - \bar{S}_\beta dT \tag{1.10.5.16}$$

Dividing through by $dT$, we obtain

$$\bar{V}_\alpha \frac{\partial P}{\partial T} - \bar{S}_\alpha = \bar{V}_\beta \frac{\partial P}{\partial T} - \bar{S}_\beta \tag{1.10.5.17}$$

$$(\bar{V}_\alpha - \bar{V}_\beta)\frac{\partial P}{\partial T} = \bar{S}_\alpha - \bar{S}_\beta \tag{1.10.5.18}$$

$$\frac{dP}{dT} = \frac{\bar{S}_\alpha - \bar{S}_\beta}{\bar{V}_\alpha - \bar{V}_\beta} \tag{1.10.5.19}$$

The importance of the quantity $dP/dT$ is that is represents the slope of the coexistence curve on the phase diagram between the two phases. Now, in equilibrium $dG = 0$, and since $G = H - TS$, it follows that $dH = T\,dS$ at fixed $T$. In the narrow temperature range in which the two phases are in equilibrium, we can assume that $H$ is independent of $T$, hence, we can write $S = H/T$. Consequently, we can write the molar entropy difference as

\bar{S}_\alpha - \bar{S}_\beta = \dfrac{\bar{H}_\alpha - \bar{H}_\beta}{T} \label{14.7}

and the pressure derivative $dP/dT$ becomes

\dfrac{dP}{dT} = \dfrac{\bar{H}_\alpha - \bar{H}_\beta}{T (\bar{V}_\alpha - \bar{V}_\beta)} = \dfrac{\Delta_{\alpha \beta} \bar{H}}{T \Delta_{\alpha \beta} \bar{V}} \label{14.8}

a result known as the **Clapeyron equation**, which tells us that the slope of the coexistence curve is related to the ratio of the molar enthalpy between the phases to the change in the molar volume between the phases. If the phase equilibrium is between the solid and liquid phases, then $\Delta_{\alpha\beta}\bar{H}$ and $\Delta_{\alpha\beta}\bar{V}$ are $\Delta\bar{H}_{\text{fus}}$ and $\Delta\bar{V}_{\text{fus}}$, respectively. If the phase equilibrium is between the liquid and gas phases, then $\Delta_{\alpha\beta}\bar{H}$ and $\Delta_{\alpha\beta}\bar{V}$ are $\Delta\bar{H}_{\text{vap}}$ and $\Delta\bar{V}_{\text{vap}}$, respectively.

For the liquid-gas equilibrium, some interesting approximations can be made in the use of the Clapeyron equation. For this equilibrium, Equation 1.10.5.8becomes

\dfrac{dP}{dT} = \dfrac{\Delta \bar{H}_\text{vap}}{T (\bar{V}_g - \bar{V}_l)} \label{14.9}

In this case, $\bar{V}_g \gg \bar{V}_l$, and we can approximate Equation 1.10.5.9as

\dfrac{dP}{dT} \approx \dfrac{\Delta \bar{H}_\text{vap}}{T \bar{V}_g} \label{14.10}

Suppose that we can treat the vapor phase as an ideal gas. Certainly, this is not a good approximation so close to the vaporization point, but it leads to an example we can integrate. Since $PV_g = nRT$, $P\bar{V}_g = RT$, Equation 1.10.5.10becomes

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{\text{vap}} P}{RT^2} \tag{1.10.5.20}$$

$$\frac{1}{P}\frac{dP}{dT} = \frac{\Delta\bar{H}_{\text{vap}}}{RT^2} \tag{1.10.5.21}$$

$$\frac{d\ln P}{dT} = \frac{\Delta\bar{H}_{\text{vap}}}{RT^2} \tag{1.10.5.22}$$

which is called the ***Clausius-Clapeyron equation***. We now integrate both sides, which yields

$$\ln P = -\frac{\Delta\bar{H}_{\text{vap}}}{RT} + C$$

where $C$ is a constant of integration. Exponentiating both sides, we find

$$P(T) = C' e^{-\Delta\bar{H}_{\text{vap}}/RT}$$

which actually has the wrong curvature for large $T$, but since the liquid-vapor coexistence line terminates in a critical point, as long as $T$ is not too large, the approximation leading to the above expression is not that bad.

If we, instead, integrate both sides, the left from $P_1$ to $P_2$, and the right from $T_1$ to $T_2$, we find

$$\int_{P_1}^{P_2} d\ln P = \int_{T_1}^{T_2} \frac{\Delta\bar{H}_{\text{vap}}}{RT^2} dT \tag{1.10.5.23}$$

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta\bar{H}_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{1.10.5.24}$$

$$= \frac{\Delta\bar{H}_{\text{vap}}}{R}\left(\frac{T_1 - T_1}{T_1 T_2}\right) \tag{1.10.5.25}$$

assuming that $\Delta\bar{H}_{\text{vap}}$ is independent of $T$. Here $P_1$ is the pressure of the liquid phase, and $P_2$ is the pressure of the vapor phase. Suppose we know $P_2$ at a temperature $T_2$, and we want to know $P_3$ at another temperature $T_3$. The above result can be written as

\text{ln} \: \left( \dfrac{P_3}{P_1} \right) = -\dfrac{\Delta \bar{H}_\text{vap}}{R} \left( \dfrac{1}{T_3} - \dfrac{1}{T_1} \right) \label{14.13}

Subtracting the two results, we obtain

\text{ln} \: \left( \dfrac{P_2}{P_3} \right) = -\dfrac{\Delta \bar{H}_\text{vap}}{R} \left( \dfrac{1}{T_2} - \dfrac{1}{T_3} \right) \label{14.14}

so that we can determine the vapor pressure at any temperature if it is known as one temperature.

In order to illustrate the use of this result, consider the following example:

### ✓ Example 1.10.5.1

At 1 bar, the boiling point of water is 373 K. At what pressure does water boil at 473 K? Take the heat of vaporization of water to be $40.65\ \text{kJ/mol}$

**Solution**

Let $P_1 = 1\ \text{bar}$ and $T_1 = 373\ \text{K}$. Take $T_2 = 473\ \text{K}$, and we need to calculate $P_2$. Substituting in the numbers, we find

$$\ln P_2(\text{bar}) = -\frac{(40.65\ \text{kJ/mol})(1000\ \text{J/kJ})}{8.3145\ \text{J/mol}\cdot\text{K}}\left(\frac{1}{473\ \text{K}} - \frac{1}{373\ \text{K}}\right) = 2.77 \tag{1.10.5.26}$$

$$P_2(\text{bar}) = (1\ \text{bar})\, e^{2.77} = 16\ \text{bar} \tag{1.10.5.27}$$

### Learning Objectives

- Apply the Clausius-Clapeyron equation to estimate the vapor pressure at any temperature.
- Estimate the heat of phase transition from the vapor pressures measured at two temperatures.

The *vaporization curves* of most liquids have similar shapes with the vapor pressure steadily increasing as the temperature increases (Figure 1.10.5.1).

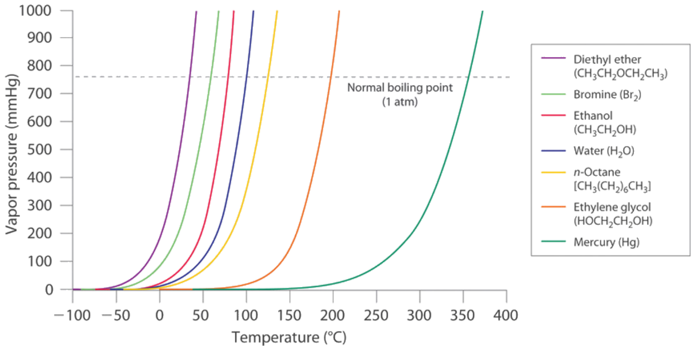


Figure 1.10.5.1: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the *P* = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC 3.0; Anonymous)

A good approach is to find a mathematical model for the pressure increase as a function of temperature. Experiments showed that the vapor pressure $P$ and temperature $T$ are related,

$$P \propto \exp\left(-\frac{\Delta H_{vap}}{RT}\right) \tag{1.10.5.28}$$

where $\Delta H_{vap}$ is the Enthalpy (heat) of Vaporization and $R$ is the gas constant (8.3145 J mol$^{-1}$ K$^{-1}$).

A simple relationship can be found by integrating Equation 1.10.5.28between two pressure-temperature endpoints:

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{1.10.5.29}$$

where $P_1$ and $P_2$ are the vapor pressures at two temperatures $T_1$ and $T_2$. Equation 1.10.5.29is known as the **Clausius-Clapeyron Equation** and allows us to estimate the vapor pressure at another temperature, if the vapor pressure is known at some temperature, and if the enthalpy of vaporization is known.

### Alternative Formulation

The order of the temperatures in Equation 1.10.5.29matters as the Clausius-Clapeyron Equation is sometimes written with a negative sign (and switched order of temperatures):

$$\ln\left(\frac{P_1}{P_2}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{1.10.5.30}$$

### ✓ Example 1.10.5.1: Vapor Pressure of Water

The vapor pressure of water is 1.0 atm at 373 K, and the enthalpy of vaporization is 40.7 kJ mol$^{-1}$. Estimate the vapor pressure at temperature 363 and 383 K respectively.

**Solution**

Using the Clausius-Clapeyron equation (Equation 1.10.5.30), we have:

$$\begin{aligned} P_{363} &= 1.0 \exp\left[-\left(\frac{40,700}{8.3145}\right)\left(\frac{1}{363\ K} - \frac{1}{373\ K}\right)\right] \\ &= 0.697\ atm \\ P_{383} &= 1.0 \exp\left[-\left(\frac{40,700}{8.3145}\right)\left(\frac{1}{383\ K} - \frac{1}{373\ K}\right)\right] \\ &= 1.409\ atm \end{aligned}$$

Note that the increase in vapor pressure from 363 K to 373 K is 0.303 atm, but the increase from 373 to 383 K is 0.409 atm. The increase in vapor pressure is not a linear process.

**Discussion**

We can use the Clausius-Clapeyron equation to construct the entire vaporization curve. There is a deviation from experimental value, that is because the enthalpy of vaporization varies slightly with temperature.

The Clausius-Clapeyron equation can be also applied to sublimation; the following example shows its application in estimating the heat of sublimation.

### ✓ Example 1.10.5.2: Sublimation of Ice

The vapor pressures of ice at 268 K and 273 K are 2.965 and 4.560 torr respectively. Estimate the heat of sublimation of ice.

**Solution**

The enthalpy of sublimation is $\Delta H_{sub}$. Use a piece of paper and derive the Clausius-Clapeyron equation so that you can get the form:

$$\begin{aligned} \Delta H_{sub} &= \frac{R\ln\left(\frac{P_{273}}{P_{268}}\right)}{\frac{1}{268\ K}-\frac{1}{273\ K}} \\ &= \frac{8.3145\ln\left(\frac{4.560}{2.965}\right)}{\frac{1}{268\ K}-\frac{1}{273\ K}} \\ &= 52,370\ J\ mol^{-1} \end{aligned}$$

Note that the heat of sublimation is the sum of heat of melting (6,006 J/mol at 0°C and 101 kPa) and the heat of vaporization (45,051 J/mol at 0 °C).

**? Exercise 1.10.5.2**

Show that the vapor pressure of ice at 274 K is higher than that of water at the same temperature. Note the curve of vaporization is also called the curve of evaporization.

**✓ Example 1.10.5.3: Vaporization of Ethanol**

Calculate $\Delta H_{vap}$ for ethanol, given vapor pressure at 40 ºC = 150 torr. The normal boiling point for ethanol is 78 ºC.

**Solution**

Recognize that we have TWO sets of $(P,T)$ data:

- Set 1: (150 torr at 40+273K)
- Set 2: (760 torr at 78+273K)

We then directly use these data in Equation 1.10.5.30

$$\begin{aligned} \ln\left(\frac{150}{760}\right) &= \frac{-\Delta H_{vap}}{8.314}\left[\frac{1}{313}-\frac{1}{351}\right] \\ \ln 150-\ln 760 &= \frac{-\Delta H_{vap}}{8.314}\left[\frac{1}{313}-\frac{1}{351}\right] \\ -1.623 &= \frac{-\Delta H_{vap}}{8.314}[0.0032-0.0028] \end{aligned}$$

Then solving for $\Delta H_{vap}$

$$\begin{aligned} \Delta H_{vap} &= 3.90\times 10^4 \text{ joule/mole} \\ &= 39.0 \text{ kJ/mole} \end{aligned}$$

**Advanced Note**

It is important to not use the Clausius-Clapeyron equation for the solid to liquid transition. That requires the use of the more general **Clapeyron equation**

$$\frac{dP}{dT}=\frac{\Delta\bar{H}}{T\Delta\bar{V}}$$

where $\Delta\bar{H}$ and $\Delta\bar{V}$ is the molar change in enthalpy (the enthalpy of fusion in this case) and volume respectively between the two phases in the transition.

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# 1.10.6: Chemical Potential Can be Evaluated From a Partition Function

The chemical potential can be given in terms of a partition function. Internal energy can be defined as:

$$U = RT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{n,V}$$

And entropy can be defined as:

$$S = RT \left( \frac{\partial \ln Q}{\partial T} \right)_{n,V} + R \ln Q$$

We know that Helmholtz energy is:

$$A = U - TS$$

Using our two equations above, we obtain:

$$A = -RT \ln Q$$

Now, let's change gears a bit to show how Helmholtz energy is related to chemical potential. The total differential for Helmholtz energy is:

$$dA = \left( \frac{\partial A}{\partial T} \right)_{n,V} + \left( \frac{\partial A}{\partial V} \right)_{n,T} + \left( \frac{\partial A}{\partial n} \right)_{V,T}$$

And the fundamental equation is:

$$dA = -SdT - PdV + \left( \frac{\partial A}{\partial n} \right)_{V,T} dn$$

Using the relationship between Helmholtz energy and Gibbs energy:

$$G = A + PV$$

We obtain:

$$\begin{aligned} dG &= dA + d(PV) \\ &= -SdT + VdP + \left( \frac{\partial A}{\partial n} \right)_{V,T} dn \end{aligned}$$

We know that the change in Gibbs energy is:

$$\begin{aligned} dG &= -SdT + VdP + \left( \frac{\partial G}{\partial n} \right)_{P,T} dn \\ &= -SdT + VdP + \mu dn \end{aligned}$$

Inspecting these equations, we see that:

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

This shows us that, as long as the natural variables for each thermodynamic potential are held constant, the partial derivatives of Gibbs energy and Helmholtz energy with respect to the number of moles, $n$ are equal to the chemical potential. We can now plug in our expression above for Helmholtz energy in terms of the partition function:

$$\mu = -RT \left( \frac{\partial \ln Q}{\partial n} \right)_{V,T}$$

We now have chemical potential written in terms of the partition function, $Q$.

# 1.10.E: Phase Equilibria (Exercises)

# 1.11: Colligative Properties

Colligative properties are important properties of **solutions** as they describe how the properties of the **solvent** will change as **solute** (or solutes) is (are) added. Before discussing these important properties, let us first review some definitions.

- **Solution** – a homogeneous mixture.
- **Solvent** – The component of a solution with the largest mole fraction
- **Solute** – Any component of a solution that is not the solvent.

Solutions can exist in solid (alloys of metals are an example of solid-phase solutions), liquid, or gaseous (aerosols are examples of gas-phase solutions) forms. For the most part, this discussion will focus on liquid-phase solutions.

## 1.11.1: Freezing Point Depression

The empirically it is found that the change in freezing point is proportional to the molality of the solute:

$$\Delta T_f = K_f m_B \tag{1.11.1}$$

where $\Delta T$ gives the magnitude of the reduction of freezing point for the solution, $K_f$ is is the **cryoscopic constant** for the solvent and $m_B$ is the molality of the solute.

**Caution**

$m_B$ is the **molality of particles dissolved** not molality of empirical formula units. If the solute is NaCl than $m_B \approx$ 2(molality of NaCl). This is often indicated by including the van 't Hoff factor (usually represented by i): $\Delta T_f = K_f i m_B$. Because many salts do not dissociate completely except at very low concentrations the van 't Hoff factor is an additional empirically determined quantity.

In equation 1.11.1 $K_f$ is a negative value. However, many tabulations record $K_f$ as a positive value. You must remember that $\Delta T$ for freezing point depression is < 0 and change the sign of tabulated $K_f$ values accordingly.

Notice that this result is independent of the identity of the solute.

The solute particles do not dissolve in the solid. This means that adding solute to the liquid phase increases its entropy relative to the solid phase, favoring the liquid phase. Thus, the temperature must drop to a lower value to favor the solid phase. It is important to keep in mind that for a real solution, freezing of the solvent changes the composition of the solution by decreasing the mole fraction of the solvent and increasing that of the solute. As such, the magnitude of $\Delta T$ will change as the freezing process continually removes solvent from the liquid phase of the solution.

**Demonstration of why the dependence on concentration is expected to be nearly linear.**

In general a liquid will freeze when

$$\mu_s \leq \mu_l$$

The key is that the solute remains in the liquid solvent. As such, the freezing point of the solvent in a solution will be affected by anything that changes the chemical potential of the solvent, while the chemical potential of the solid will only be impacted by the temperature change. In a mixture, the chemical potential of component $A$ can be calculated by

$$\mu_A = \mu_A^o + RT\ln x_A \tag{1.11.2}$$

And because $x_A$ is always less than (or equal to) 1, the chemical potential is always reduced by the addition of another component.

We also know how temperature impacts chemical potential, which will effect both phases:

$$\left(\frac{\partial\mu}{\partial T}\right)_P = -S_{molar} \implies \Delta\mu = -S_{molar}\Delta T \tag{1.11.3}$$

The condition under which the solvent will freeze is

$$\mu_s = \mu_l$$

If we start at the standard freezing point of the pure solvent we can call the chemical potential $\mu^{fp}$. For the solid phase when we reach the new equilibrium this is only impacted by the temperature change, while the solvent chemical potential is changed by both dissolving the solute and the temperature change. Thus, at the new equilibrium we have new chemical potentials for the two phases:

$$\mu_s(T_2) = \mu^{fp} - S_{molar}(s)\Delta T \tag{1.11.4}$$

$$\mu_l(T_2) = \mu^{fp} - S_{molar}(l)\Delta T + RT_2 ln(x_A) \tag{1.11.5}$$

Setting these equal to each other:

$$\cancel{\mu^{fp}} - S_{molar}(s)\Delta T = \cancel{\mu^{fp}} - S_{molar}(l)\Delta T + RT_2 ln(x_A) \implies -S_{molar}(s)\Delta T = -S_{molar}(l)\Delta T + RT_2 ln(x_A) \tag{1.11.6}$$

Collecting the entropy terms on one side and recognizing that $x_A = 1 - x_B$ yields:

$$S_{molar}(l)\Delta T - S_{molar}(s)\Delta T = RT_2 ln(x_A) \implies \Delta S_{fus}\Delta T = RT_2 ln(1 - x_B) \tag{1.11.7}$$

For small $x_B$, $ln(1 - x_B) \approx -x_B$ :

$$\Delta S_{fus}\Delta T = -RT_2 x_B \tag{1.11.8}$$

which can be rearranged to:

$$\Delta T = -\frac{RT_2}{\Delta S_{fus}} x_B \tag{1.11.9}$$

Since we have assumed a relatively small $x_B$ the temperature change will be small meaning $\Delta S$ will be nearly constant. Thus, everything in the fraction on the right-hand-side of equation 1.11.9 can be identified as the constant $K_f$. As molality is proportional to mole fraction this justifies the form of the freezing point depression equation.

## 1.11.2: Boiling Point Elevation

Boiling point elevation is similar to freezing point depression. In short, the introduction of a solute into a liquid solvent lowers the chemical potential of the solvent, causing it to favor the liquid phase over the vapor phase. As such, the temperature must be increased to increase the chemical potential of the solvent in the liquid solution until it is equal to that of the vapor-phase solvent. The increase in the boiling point can be expressed as

$$\Delta T = K_b m_B$$

$K_b$ is called the **ebullioscopic constant** and, like the cryoscopic constant, is a property of the solvent that is independent of the solute or solutes.

**Caution**

As with freezing point depression $m_B$ is the molality of dissolved particles.

Some values of $K_f$ and $K_b$ are shown in the table below.

| Substance | $K_f$ (°C kg mol-1) | $T_f^o$ (°C) | $K_b$ (°C kg mol-1) | $T_b^o$ (°C) |
|---|---|---|---|---|
| **Water** | 1.86 | 0.0 | 0.51 | 100.0 |
| **Benzene** | 5.12 | 5.5 | 2.53 | 80.1 |
| **Ethanol** | 1.99 | -114.6 | 1.22 | 78.4 |
| **$CCl_4$** | 29.8 | -22.3 | 5.02 | 76.8 |

**Example 1.11.1:**

The boiling point of a solution of 3.00 g of an unknown compound in 25.0 g of $CCl_4$ raises the boiling point to 81.5 °C. What is the molar mass of the compound?

### Solution

The approach here is to find the number of moles of solute in the solution. First, find the concentration of the solution:

$$(85.5\,^\circ C - 76.8\,^\circ C) = (5.02\,^\circ C\; Kg/mol)\, m$$

$$m = 0.936\, mol/kg$$

Using the number of kg of solvent, one finds the number for moles of solute:

$$\left(0.936\, mol/\ \cancel{kg}\right)(0.02\ \ \cancel{kg}) = 0.0234\, mol$$

The ratio of mass to moles yields the final answer:

$$\frac{3.00\, g}{0.0234} = 128 g/mol$$

## 1.11.3: Vapor Pressure Lowering

For volatile solutes we have noted that Raoult's Law $P_A = x_A P_A^*$ is usually only valid at low solute concentrations. The derivation below (note it use 'p' instead of 'P' for pressure) shows that for non-volatile solutes Raoult's law can be expected to work over a much larger mole fraction range.

For much the same reason as the lowering of freezing points and the elevation of boiling points for solvents into which a solute has been introduced, the vapor pressure of a volatile solvent will be decreased due to the introduction of a solute. The magnitude of this decrease can be quantified by examining the effect the solute has on the chemical potential of the solvent.

In order to establish equilibrium between the solvent in the solution and the solvent in the vapor phase above the solution, the chemical potentials of the two phases must be equal.

$$\mu_{vapor} = \mu_{solvent}$$

If the solute is not volatile, the vapor will be pure, so (assuming ideal behavior)

$$\mu_{vap}^o + RT \ln \frac{p'}{p^o} = \mu_A^o + RT \ln \chi_A \tag{1.11.10}$$

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

$$\mu_A^o = \mu_{vap}^o + RT \ln \frac{p_A}{p^o} \tag{1.11.11}$$

where $p^o$ is the standard pressure of 1 atm, and $p_A$ is the vapor pressure of the pure solvent. Substituting Equation 1.11.11into Equation 1.11.10yields

$$\cancel{\mu_{vap}^o} + RT \ln \frac{p'}{p^o} = \left(\cancel{\mu_{vap}^o} + RT \ln \frac{p_A}{p^o}\right) + RT \ln \chi_A$$

The terms for $\mu_{vap}^o$ cancel, leaving

$$RT \ln \frac{p'}{p^o} = RT \ln \frac{p_A}{p^o} + RT \ln \chi_A$$

Subtracting $RT \ln(P_A/P^o)$ from both side produces

$$RT \ln \frac{p'}{p^o} - RT \ln \frac{p_A}{p^o} = RT \ln \chi_A$$

which rearranges to

$$RT \ln \frac{p'}{p_A} = RT \ln \chi_A$$

Dividing both sides by $RT$ and then exponentiating yields

$$\frac{p'}{p_A} = \chi_A$$

or

$$p' = \chi_A p_A \tag{1.11.12}$$

This last result is Raoult’s Law. A more formal derivation would use the fugacities of the vapor phases, but would look essentially the same. Also, as in the case of freezing point depression and boiling point elevations, this derivation did not rely on the nature of the solute! However, unlike freezing point depression and boiling point elevation, this derivation did not rely on the solute being dilute, so the result should apply the entire range of concentrations of the solution.

**Example 1.11.2:**

Consider a mixture of two volatile liquids A and B. The vapor pressure of pure A is 150 Torr at some temperature, and that of pure B is 300 Torr at the same temperature. What is the total vapor pressure above a mixture of these compounds with the mole fraction of B of 0.600. What is the mole fraction of B in the vapor that is in equilibrium with the liquid mixture?

**Solution**

Using Raoult's Law (Equation 1.11.12)

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

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

$$P_{tot} = P_A + P_B = 240\,Torr$$

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

$$x_A = \frac{P_A}{P_{tot}} = \frac{60.0\,Torr}{240\,Torr} = 0.250$$

$$x_B = \frac{P_B}{P_{tot}} = \frac{180.0\,Torr}{240\,Torr} = 0.750$$

And, of course, it is also useful to note that the sum of the mole fractions is 1 (as it must be!)

$$x_A + x_B = 1$$

## 1.11.4: Osmotic Pressure and Osmotic Virial Coefficients

In dealing with solutions (either solutions of small molecule solutes or macromolecules in solution), an important colligative property is the **osmotic pressure**. The osmotic pressure is given by the symbol $\Pi$ and is different from the pressure of a gas (P) because it does not arise from collisions of molecules against the wall of a container. The osmotic pressure is a *hydrostatic* pressure that arises when solvent molecules pass through a semipermeable membrane to the more concentrated side of the membrane as shown in figure 1.11.1. The flow of solvent across the semipermeable membrane is called **osmosis**. Consider the osmotic pressure ($\Pi$) that develops on the more concentrated side of the membrane due to solvent molecules moving from the dilute to the concentrated side of the membrane. This situation illustrated in figure 1.11.1.

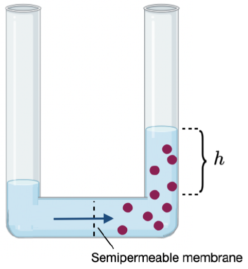


Figure 1.11.1: Definition of osmotic pressure. The difference in concentration across the membrane causes a chemical potential. Solvent flows from the dilute to the concentrated side in an attempt to equalize the chemical potential. As water flows from the dilute to concentrated side, the water level will rise on the concentrated side. At equilibrium, the pressure differential is equal to the osmotic pressure.

As the pressure builds up on the high concentration side, the solvent level will rise by a height, $h$. The hydrostatic pressure is the difference between the pressure on the two sides of the semipermeable membrane and is given as

$$\Pi = \rho g h \tag{1.11.13}$$

where $\rho$ is the solvent density, and $g$ is the acceleration due to gravity. For an **ideal solution**, the osmotic pressure, $\Pi$, resembles the form of the ideal gas law:

$$\Pi V = nRT \tag{1.11.14}$$

Using the fact that $n/V$ is the **concentration** (i.e. number of moles per unit volume of solution), we can rewrite Equation 1.11.14 in terms of the **molarity** ($\underline{M}$):

$$\Pi = \underline{M}RT \tag{1.11.15}$$

If we define the **mass concentration** (C) of the solute (in units of g • L$^{-1}$), then we can rewrite 1.11.15 as:

$$\frac{\Pi}{RTC}=\frac{1}{M_w} \tag{1.11.16}$$

where $M_w$ is the molar mass of the solute molecule (in units of g • mol$^{-1}$), and $C$ is the mass concentration of the solute ($C=nM_w/V$).

Equation 1.11.16 assumes we are dealing with an ideal solution in which the solute particles are non-interacting. Instead, if we want to consider a *non-ideal* solution of weakly interacting molecules, we can expand Equation 1.11.16in powers of $C$ to obtain a virial equation of state for the osmotic pressure of a real solution:

$$\frac{\Pi}{RTC}=\frac{1}{M_w}\left[1+B_2'C+B_3'C^2+B_4'C^3+\ldots\right] \tag{1.11.17}$$

where $B_2', B_3', B_4'\ldots$ are the second, third, and fourth osmotic virial coefficients.

In the dilute limit ($C$ << 1), we can truncate the expansion at the second virial coeffient:

$$\frac{\Pi}{RTC}=\frac{1}{M_w}\left[1+B_2'C\right] \tag{1.11.18}$$

The second virial coefficient $B'$ is related to the interactions between atoms. The second virial coefficent may be positive or negative depending on the nature of the particle-particle interactions. A negative coefficient corresponds to net attractive interactions, and a positive coefficient correspond to repulsive interactions.

Osmotic pressure plays an important role in biology. For example, trees use osmotic pressure to transport water from the roots to the upper branches. The effect of osmotic pressure on the cell is illustrated in figure 1.11.2. When red blood cells are placed in a salt solution having a lower concentration than the intracellular fluid, the solution is **hypotonic**, and the cell will gain water through osmosis in an attempt to equalize the osmotic pressure. This situation is illustrated in figure 1.11.2(a). The cells will swell and potentially burst. When red blood cells are placed in a salt solution with the same osmotic pressure as the intracellular fluid, the solution is **isotonic** with respect to the cytoplasm. This situation is illustrated in See figure 1.11.2(b). Finally, when red blood cells are placed in a solution with a higher salt concentration than the intracellular fluid, the solution is **hypertonic** and water inside the cell flows outside the cell in an attempt to equalize the osmotic pressure, causing the cell to shrink. This is the situation illustrated in figure 1.11.2(c).

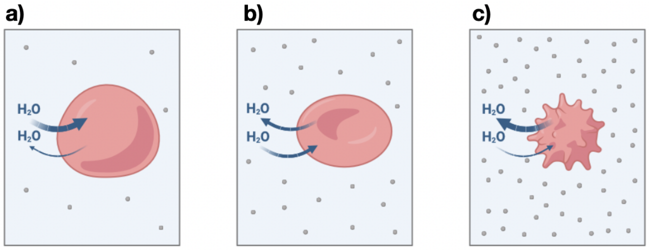
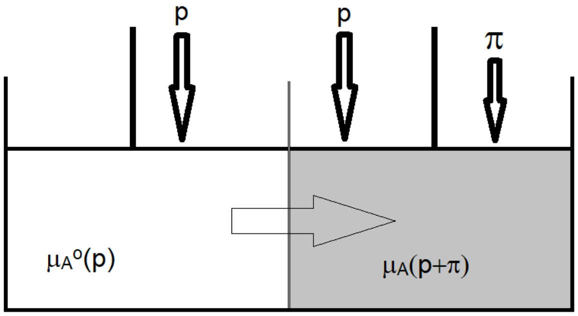


Figure 1.11.2: a) When red blood cells are placed in a hypotonic solution whose osmotic pressure is less than that of the intracellular fluid, water flows into the cells and the cell swells and eventually bursts. b) When red blood cells are placed in an isotonic salt solution having the same osmotic pressure as the intracellular fluid, the rate of flow of water into and out of the cells is the same and the cell does not change shape. c) When red blood cells are placed in a hypertonic solution, the osmotic pressure is greater outside than that of the intracellular fluid, and water flows out of the cells. The cells shrink.

## 1.11.5: Derivation of osmotic pressure equation form

**Osmosis** is a process by which solvent can pass through a semi-permeable membrane (a membrane through which solvent can pass, but not solute) from an area of low solute concentration to a region of high solute concentration. The **osmotic pressure** is the pressure that when exerted on the region of high solute concentration will halt the process of osmosis.



The nature of osmosis and the magnitude of the osmotic pressure can be understood by examining the chemical potential of a pure solvent and that of the solvent in a solution. The chemical potential of the solvent in the solution (before any extra pressure is applied) is given by

$$\mu_A = \mu_A^o + RT \ln x_A$$

And since $x_A < 1$, the chemical potential is of the solvent in a solution is always lower than that of the pure solvent. So, to prevent osmosis from occurring, something needs to be done to raise the chemical potential of the solvent in the solution. This can be accomplished by applying pressure to the solution. Specifically, the process of osmosis will stop when the chemical potential solvent in the solution is increased to the point of being equal to that of the pure solvent. The criterion, therefore, for osmosis to cease is

$$\mu_A^o(p) = \mu_A(x_b, +\pi)$$

To solve the problem to determine the magnitude of p, the pressure dependence of the chemical potential is needed in addition to understanding the effect the solute has on lowering the chemical potential of the solvent in the solution. The magnitude, therefore, of the increase in chemical potential due to the application of excess pressure p must be equal to the magnitude of the reduction of chemical potential by the reduced mole fraction of the solvent in the solution. We already know that the chemical potential of the solvent in the solution is reduced by an amount given by

$$\mu_A^o - \mu_A = RT \ln x_A$$

And the increase in chemical potential due to the application of excess pressure is given by

$$\mu(p+\pi) = \mu(p) + \int_p^\pi \left(\frac{\partial \mu}{\partial p}\right)_T dp$$

The integrals on the right can be evaluated by recognizing

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

where $V$ is the molar volume of the substance. Combining these expressions results in

$$-RT \ln x_A = \int_p^{p+\pi} V\, dp$$

If the molar volume of the solvent is independent of pressure (has a very small value of $\kappa_T$ – which is the case for most liquids) the term on the right becomes.

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

Also, for values of $\chi_A$ very close to 1

$$\ln \chi_A \approx -(1-\chi_A) = -\chi_B$$

So, for dilute solutions

$$\chi_B RT = V\pi$$

Or after rearrangement

$$\pi \frac{\chi_B RT}{V}$$

again, where $V$ is the molar volume of the solvent. And finally, since $\chi_B/V$ is the concentration of the solute $B$ for cases where $n_B \ll n_A$. This allows one to write a simplified version of the expression which can be used in the case of very dilute solutions

$$\pi = [B]RT$$

When a pressure exceeding the osmotic pressure $\pi$ is applied to the solution, the chemical potential of the solvent in the solution can be made to exceed that of the pure solvent on the other side of the membrane, causing reverse osmosis to occur. This is a very effective method, for example, for recovering pure water from a mixture such as a salt/water solution.

Colligative properties are properties that depend on the *number* of particles rather than their total mass. This implies that these properties can be used to measure molar mass. Colligative properties include:

- melting point depression
- boiling point elevation

- osmotic pressure

## 1.11.6: Problems

**Problem 1.11.1.** The osmotic pressure of a protein in solution at 298 K (under crystallization conditions) was measured at the following concentrations:

| Concentration (g $L^{-1}$) | osmotic pressure ($10^{-2}$ kPa) |
|---|---|
| 0.50 | 1.85 |
| 1.00 | 3.68 |
| 1.50 | 5.48 |
| 2.00 | 7.25 |
| 2.50 | 9.00 |

Assuming that the osmotic virial equation of state can be truncated after the second virial coefficient,

**a)** What is the molar mass of the protein?

**b)** What is the value of the second osmotic virial coefficient in units of L/g?

**c)** Based on the sign of the second virial coefficient, what might you speculate about the average contribution of intermolecular interactions under crystallization conditions? (For reference see: A. George and W.W. Wilson, "Predicting Protein Crystallization from Dilute Solution Property," *Acta Cryst.* (1994). D50, 361-365).

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# 1.12: Osmotic Pressure can Determine Molecular Masses

Some membrane materials are permeable for some molecules, but not for others. This is often a matter of the *size* of the molecules, but it can also be a question of *solubility* of the molecule in the barrier material. Many biological membranes have semipermeable properties and osmosis is therefore an important biological process. Figure 25.4.1 shows a simple osmotic cell. Both compartments contain water, but the one on the right also contains a solute whose molecules (represented by green circles) are too large to pass through the membrane. Many artificial and natural substances are capable of acting as semi-permeable membranes. For example, the walls of most plant and animal cells fall into this category.

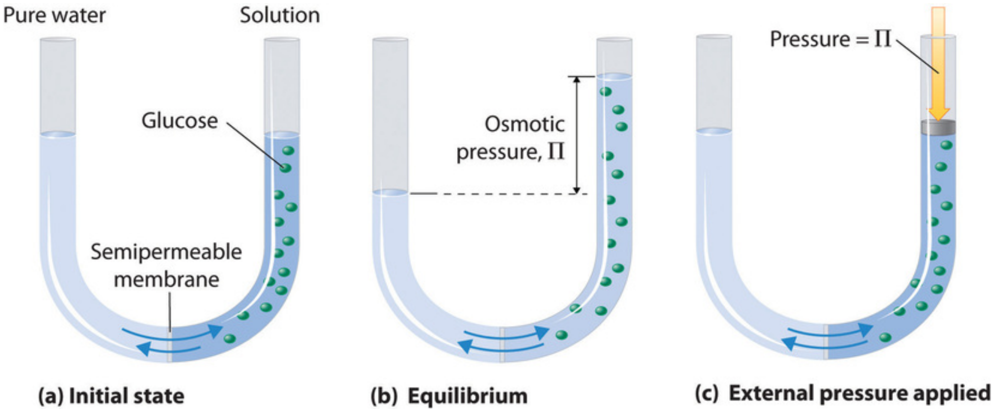

Figure 25.4.1 : Osmotic Pressure. (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution ( $\Pi_{soln}$), equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation.

If solvent molecules can pass through the membrane, but solute molecules (or ions) cannot, solvent molecules will spontaneously migrate across the membrane to increase the solution's volume and thus reduce its concentration. If the solution is ideal, this process is in many ways analogous to the spontaneous increase in volume of a gas allowed to expand against vacuum. Of course the volume of the 'solute-gas' is limited by the availability of solvent and, if done under gravity in a U-shaped tube, by the build up of hydrostatic pressure. This pressure is known as the *osmotic pressure* $\Pi$. At equilibrium we can write:

$$\mu^*(T,P) = \mu^{sln}(T,P+\Pi,a_1)$$

$$\mu^*(T,P) = \mu^*(T,P+\Pi) + RT\ln a_1$$

From Gibbs energy $(dG)$ in its natural variables $(P,T)$ we know that:

$$\left(\frac{\partial G}{\partial P}\right)_{T,x} = V$$

Taking the partial versus $x_1$ we get:

$$\left(\frac{\partial \mu^*}{\partial P}\right)_{T,x_j} = \bar{V}_1^*$$

This means we can integrate over the molar volume to convert $\mu^*(T,P+\Pi)$ to a different pressure:

$$\mu^*(T,P+\Pi) = \mu^*(T,P) + \int_P^{P+\Pi} \bar{V}_1^* dP$$

Thus we get:

$$\mu^*(T,P) = \mu^*(T,P+\Pi) + RT\ln a_1$$

$$\mu^*(T,P) = \mu^*(T,P) + \Pi\bar{V}_1^* + RT\ln a_1$$

Once again using the ideal approximation:

$$\ln a_1 \ln x_1 \approx -x_2$$

we get:

$$RTx_2 = \Pi \bar{V}_1^*$$

$$x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1}$$

The combination gives an expression involving the molarity:

$$\Pi = RTc$$

Where $c$ is the molar concentration. Osmosis can be used in reverse, if we apply about 30 bar to sea water we can obtain fresh water on the other side of a suitable membrane. This process is used in some places, but better membranes would be desirable and they easily get clogged. The resulting water is not completely salt-free and this means that if used for agriculture the salt may accumulate on the field over time.

## 1.12.1: Determining Molar Masses

Both melting point depression and boiling point elevation only facilitate the determination of relatively *small* molar weights. The need for such measurements is no longer felt because we now have good techniques to determine the structure of most small to medium size molecules. For polymers this is a different matter. They usually have a molecular weight (mass) *distribution* and determining it is an important topic of polymer science.

Osmometry is still of some practical usefulness. It is also colligative and able to measure up to about 8000 daltons. Many polymers are much bigger than that. Their mass distribution is usually determined by different means. The polymers is dissolved and led over a chromatographic column usually based on size-exclusion. The effluent is then probed as function of the elution time by a combination of techniques:

1. UV absorption (determine the monomer concentration)
2. Low Angle Laser Light Scattering (LALLS) and/or Viscometry

The latter two provide information on the molar mass distribution but they give a different moment of that distribution. The combination of techniques gives an idea not only of how much material there is of a given molar mass but also of the linearity or degree of branching of the chains.

### Purity analysis

Nevertheless melting point depression is still used in a somewhat different application. When a slightly impure solid is melted its melting point in depressed. Also the melting process is not sudden but takes place over the whole trajectory from typically a lower eutectic temperature up to the depressed melting point (the liquid line in the phase diagram). In organic synthesis the melting behavior is often used as a first convenient indication of purity. In a differential scanning calorimetry (DSC) experiment the melting peak becomes progressively skewed towards lower temperatures at higher impurity levels. The shape of the curve can be modeled with a modified version of the melting point depression expression. This yields a value for the total impurity level in the solid. This technique is used in the pharmaceutical industry for quality control purposes.

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# CHAPTER OVERVIEW

## 2: Extended Explanations - Solutions I - Volatile Solutes

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# 2.1: A Mixture is a Combination of Two or More Substances

So far, we have only discussed systems that are comprised of one component. Because a lot of chemistry occurs in mixtures or produces a mixture, chemists need to consider the thermodynamics of mixtures. A mixture can consist of many different components, however, for the sake of simplicity, we will restrict ourselves for now to two-component mixtures. Two-component mixtures can consist of two gases, two liquids, two solids, or even a liquid and a gas.

## 2.1.1: Partial Quantities and Scaling

Let's consider a two-component system where the volume and number of moles are changing. For example, we could have a system of a certain size of 1 and reduce its size stepwise in successive steps by taking half of it and throwing the other half away. The number of moles of each component, $n_1$ and $n_2$, will change as the volume of the system, $V$, changes:

$$dn_1 = n_1 dV$$

$$dn_2 = n_2 dV$$

The extensive Gibbs free energy will be affected the same way:

$$dG = GdV$$

At constant $T$ and $P$ we can write:

$$dG = -\cancel{SdT} + V\cancel{dP} + \mu_1 dn_1 + \mu_2 dn_2$$

So:

$$dG = \mu_1 dn_1 + \mu_2 dn_2$$

$$GdV = \mu_1 n_1 dV + \mu_2 n_2 dV$$

If we integrate this from the original size, 1, down to 0 (or 0 to 1, it does not matter). We get:

$$\int_0^1 GdV = \int_0^1 \mu_1 n_1 dV + \int_0^1 \mu_2 n_2 dV$$

$$G\int_0^1 dV = \mu_1 n_1 \int_0^1 dV + \mu_2 n_2 \int_0^1 dV$$

$$G = \mu_1 n_1 + \mu_2 n_2$$

By the same argument we have:

$$V = \bar{V}_1 n_1 + \bar{V}_2 n_2$$

where $\bar{V}_i$ is the partial molar volume for component $i$. These partial molar volumes are generally a function of composition (and $P$, $T$) and have been tabulated for a number of liquid systems. They allow us to calculate the real volume of a binary mixture. Volumes are generally speaking ***not strictly additive***. This fact is typically ignored in volumetric analysis and the use of molarities. Fortunately the deviations are often negligible in dilute solutions.

For phase diagrams, molarity (moles per liter) is not a very suitable quantity to use for concentration due to its volume dependence. Usually we work with mole fractions or molalities (moles per kilogram), where there are no volume dependencies.

## 2.1.2: Gaseous Mixtures

Gases can always mix in any ratio and mixtures typically act close to ideal unless heavily compressed or brought to low temperatures. The only exception is if the gases react (e.g, HCl and $NH_3$). Gas molecules experience little interaction with each other and, therefore, it does not matter much whether the molecules are different or the same. The total pressure can be computed by adding the partial pressures of the two components (Dalton's Law of Partial Pressures):

$$P_{total} = P_1 + P_2 \tag{2.1.1}$$

## 2.1.3: Liquid Mixtures

There are binary liquid systems that are fully miscible and are said to act as *ideal solutions*. Liquid molecules typically experience *strong* interactions with their neighbors. For the solution to be ideal, the interactions must remain *equally strong* even when the neighboring substance is different. This means they must be chemically similar. For this reason, liquid binaries are often *not* ideal. The next nearest thing are **regular solutions**. Even these systems can display phase segregation and limited mutual solubilities at low temperatures. Many liquid-liquid binaries diverge from ideality even more than the regular solutions and many of them are hardly miscible at all.

Table 24.1.1: Solutions

| Solution/mixture | Interactions | Miscibility |
|---|---|---|
| Ideal gas | none | complete |
| Ideal liquid | strong but similar | complete |
| Regular liquid | strong, modestly dissimilar | not always complete |
| Real liquid | often strongly dissimilar | partial or none |

## 2.1.4: Solid Mixtures

Solid binaries tend to be even less miscible than liquid binaries to the point that immiscibility is the rule and miscibility is the exception. Even totally miscible systems like electrum (the alloys of silver and gold) are far from ideal.

Figure 24.1.1: Electrum coin of the Byzantine Emperor Alexius I Comnenus. (CC-BY-SA-3.0; Classical Numismatic Group, Inc. http://www.cngcoins.com)

Another point of practical (kinetic rather than thermodynamic) importance is that even if two compounds are able to form a homogeneous solid solution, it usually takes heating for prolonged periods to get them to mix because solid diffusion is typically very slow. Nevertheless, solid solubility is an important issue for many systems, particularly for metal alloys. Two molecular solid substances that differ vastly in shape, size, polarity and or hydrogen bonding (e.g. organic compounds) typically have *negligible* mutual solid solubility. The latter fact is frequently exploited in organic chemistry to purify compounds through recrystallization.

Note

Solid solutions are relatively infrequent and never ideal.

## 2.1.5: Ideal liquid/Ideal Gas Phase Diagrams

Let's mix two liquids together. Liquids typically have different boiling points, with one being more volatile than the other. The vapor pressure of a component scales simply with the equilibrium vapor pressure of the pure component. In the gas phase, ***Dalton's law*** is applicable:

$$y_i = \frac{P_i}{P_{total}} \tag{2.1.2}$$

This is a consequence of the fact that ideal gases do not interact. The latter implies that the total pressure is simply the sum of the partial ones:

$$P_{total} = \sum_i^N P_i$$

If the liquid solution is ideal, then the vapor pressure of both components follow ***Raoult's law***, which states that the equilibrium vapor pressure above the mixture is the equilibrium pressure of the pure component times the mole fraction:

$$P_i = x_i P_i^* \tag{2.1.3}$$

- $P_i$ is the vapor pressure of component $i$ in the mixture
- $P_i^*$ is equilibrium vapor pressure of the pure component $i$.
- $x_i$ is the mole fraction of $i^{th}$ component in the liquid phase.

Note that values for pure components are typically indicated by adding an asterisk * superscript.

The idea behind Raoult's law is that if the interactions are similar, it is a matter of random chance which component sits at the interface at any given moment. The equilibrium vapor pressure has to do with the probability that a molecule escapes from the interface into the gas phase and is dependent on both the substances volatility and the number that cover the surface. This leads to Raoult's Law, where we must multiply the vapor pressure of the pure liquid (volatility) by the mole fraction (number on the surface).

**Note: Applicability of Raoult's Law**

Raoult's law seldom holds completely, which is more applicable if the two components are almost chemically identical like two isomers, e.g., 1-propanol and 2-propanol.

## 2.1.6: The Pressure Phase Diagram

If we assume that temperature is constant, we can plot the total pressure for both Dalton and Raoult's laws versus composition (of gas: $y_1$ and liquid: $x_1$ on the same axis).

**Liquid Phase:**

$$P_{total} = P_1 + P_2 = x_1 P_1^* + x_2 P_2^* = x_1 P_1^* + (1 - x_1) P_2^* = P_2^* - x_1 (P_2^* - P_1^*) \tag{2.1.4}$$

Clearly this is a straight line going from $P_2^*$ at $x = 0$ to $P_1^*$ at $x = 1$.

However the composition of the vapor in equilibrium with a liquid at a given mole fraction $x$ is *different* than that of the liquid. So $y$ is not $x$. If we take Dalton's law (Equation 2.1.2) and substitute Raoult's Law (Equation 2.1.3) in the numerator and the straight line in the denominator we get:

$$y_1 = \frac{x_1 P_1^*}{P_2^* - x_1 (P_2^* - P_1^*)} \tag{2.1.5}$$

**Exercise**

Suppose $P_1^* = 50$ Torr and $P_2^* = 25$ Torr. If (X_1= 0.6\) what is the composition of the vapor?

We can rearrange Equations 2.1.4 and 2.1.5 to plot the total pressure as function of $y_1$:

$$P_{total} = \frac{P_1^* P_2^*}{P_1^* + (P_2^* - P_1^*) y_1} \tag{2.1.6}$$

This is *not* a straight line.

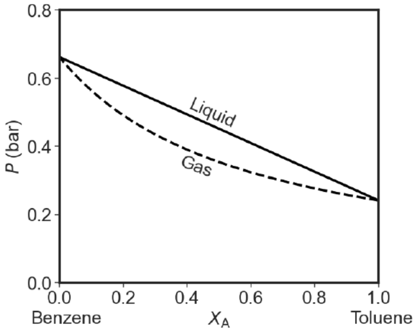

Figure 24.1.1: an ideal-ideal phase diagram for the binary system of toluene (A) and benzene (B). The curves are calculated from Equations 2.1.4 and 2.1.6.

As you can see when we plot both lines we get a diagram with three regions. At high pressures we just have a liquid. At low pressures we just have a gas. In between we have a ***phase gap*** or ***two phase region***. Points inside this region represent states that the system cannot achieve homogeneously. The horizontal ***tie-line*** shows which *two* phases coexists. I used the same 25 and 50 Torr values for the pure equilibrium pressures as in the question above. If you try to make a system with *overall* composition x and impose a pressure that falls in the forbidden zone you get two phases: a gaseous one that is richer in the more volatile component and a liquid one that is poorer in the volatile component than the overall composition would indicate.

## 2.1.7: The Temperature Phase Diagram

Note that the question: *what phase do we have when?* is really a function of ***both*** $\boldsymbol{P}$ ***and*** $\boldsymbol{T}$, so that if we want to represent *all* our knowledge in a diagram we should make it a three dimensional picture. This is not so easy to draw and not easy to comprehend visually either. This is why we usually look at a 2D cross section of the 3D space.

The above diagram is *isothermal*: we vary $P$, keeping $T$ constant. It is, however, more usual (and easier) to do it the other way around. We keep pressure constant (say 1 bar, that's easy) and start heating things up isobarically.

The boiling points of our mixtures can also be plotted against $x$ (the liquid composition) and $y$ (the gaseous one) on the same horizontal axis. Again because in general $y$ is not equal $x$ we get two different curves. Neither of them are straight lines in this case and we end up with a lens-shaped two phase region:

binary T-X diagram showing the lever rule

binary T-X diagram showing the lever rule

What happens to a mixture with a given overall composition x(=x$_1$) when it is brought to a temperature where it boils can be seen at the intersection of a vertical line (an isopleth) at $x_{overall}$ and a horizontal one (an isotherm) at $T_{boil}$. If the intersection points in inside the two phase region a vapor phase and a liquid phase result that have a different composition from the overall one. The vapor phase is always richer in the more volatile component (the one with the lowest boiling point, on the left in the diagram). The liquid phase is enriched in the less volatile one.

### 2.1.7.1: The Lever Rule

How much of each phase is present is represented by the arrows in the diagram. The amount of liquid is proportional to the left arrow, the amount of gas to the right one (i.e. it works crosswise). The composition of the liquid in equilibrium with the vapor is:

$$x_2 = \frac{n_2^{liq}}{n_{1+2}^{liq}}$$

$$x_2^* n_{1+2}^{liq} = n_2^{liq}$$

The composition of the vapor is:

$$y_2 = \frac{n_2^{gas}}{n_{1+2}^{gas}}$$

$$y_2^* n_{1+2}^{gas} = n_2^{gas}$$

The overall composition is:

$$x_{all} = \frac{n_2^{liq+gas}}{n_{1+2}^{liq+gas}}$$

$$x_{all}^* n_{1+2}^{liq+gas} = n_2^{gas} + n_2^{liq}$$

$$x_{all}^* n_{1+2}^{liq+gas} = y_2^* n_{1+2}^{gas} + x_2^* n_{1+2}^{liq}$$

$$x_{all}^* n_{1+2}^{gas} + x_{all}^* n_{1+2}^{liq} = y_2^* n_{1+2}^{gas} + x_2^* n_{1+2}^{liq}$$

Thus:

$$\frac{n_{1+2}^{liq}}{n_{1+2}^{gas}} = \frac{y_2 - x_{all}}{x_{all} - x_2}$$

### 2.1.7.2: Distillation

The difference in composition between the gas and the liquid can be exploited to separate the two components, at least partially. We could trap the vapor and cool it down to form a liquid with a different composition. We could then boil it again and repeat the process. Each time the vapor will be more enriched in the volatile phase whereas the residual liquid is more enriched in the less volatile one. This process is known as ***distillation***. In practice the process is done one a fractionation column which makes it possible to have a series of vapor-liquid equilibria at once.

A good degree of purity can be reached this way, although 100% purity would take an infinite number of distillation steps.

---

# 2.2: The Gibbs-Duhem Equation Relates Chemical Potential and Composition at Equilibrium

At **equilibrium**, there is no change in chemical potential for the system:

$$\sum_i n_i d\mu_i = 0 \tag{2.2.1}$$

This is the Gibbs-Duhem relationship and it places a compositional constraint upon any changes in the chemical potential in a mixture at constant temperature and pressure for a given composition. This result is easily derived when one considers that $\mu_i$ represents the partial molar Gibbs function for component $i$. And as with other partial molar quantities:

$$G_{\text{tot}} = \sum_i n_i \mu_i \tag{2.2.2}$$

Taking the derivative of both sides yields:

$$dG_{\text{tot}} = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i \tag{2.2.3}$$

But $dG$ can also be expressed as:

$$dG = Vdp - sdT + \sum_i \mu_i dn_i \tag{2.2.4}$$

Setting these two expressions equal to one another:

$$\sum_i n_i d\mu_i + \cancel{\sum_i \mu_i dn_i} = Vdp - sdT + \cancel{\sum_i \mu_i dn_i} \tag{2.2.5}$$

And after canceling terms, one gets:

$$\sum_i n_i d\mu_i = Vdp - sdT \tag{2.2.6}$$

For a system at constant temperature and pressure:

$$V\,dp - s\,dT = 0 \tag{2.2.7}$$

Substituting Equation 2.2.7 into 2.2.6 results in the **Gibbs-Duhem equation** (Equation 2.2.1). This expression relates how the chemical potential can change for a given composition while the system maintains equilibrium.

## 2.2.1: **Gibbs-Duhem for** Binary Systems

For a binary system consisting of components two components, $A$ and $B$:

$$n_B d\mu_B + n_A d\mu_A = 0 \tag{2.2.8}$$

Rearranging:

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A \tag{2.2.9}$$

Consider a Gibbs free energy that only includes $\mu_n$ conjugate variables as we obtained it from our scaling experiment at $T$ and $P$ constant:

$$G = \mu_A n_A + \mu_B n_B$$

Consider a change in $G$:

$$dG = d(\mu_A n_A) + d(\mu_B n_B)$$

$$dG = n_A d\mu_A + \mu_A dn_A + n_B d\mu_B + \mu_B dn_B$$

However, if we simply write out a change in $G$ due to the number of moles we have:

$$dG = \mu_A dn_A + \mu_B dn_B$$

Consequently the other terms must add up to zero:

$$0 = n_A d\mu_A + n_B d\mu_B$$

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

$$d\mu_A = -\frac{x_B}{x_A} d\mu_B$$

In the last step we have simply divided both denominator and numerator by the total number of moles. This expression is the Gibbs-Duhem equation for a 2-component system. It relates the change in one thermodynamic potential ($d\mu_A$) to the other ($d\mu_B$).

> *The Gibbs-Duhem equation relates the change in one thermodynamic potential ($d\mu_A$) to the other ($d\mu_B$).*

## 2.2.2: Gibbs-Duhem in the Ideal Case

In the ideal case we have:

$$\mu_B = \mu_B^* + RT \ln x_B$$

Gibbs-Duhem gives:

$$d\mu_A = -\frac{x_B}{x_A} d\mu_B$$

As:

$$d\mu_B = 0 + \frac{RT}{x_B}$$

with $x_B$ being the only active variable at constant temperature, we get:

$$d\mu_A = -\frac{x_B}{x_A}\frac{RT}{x_B} = \frac{RT}{x_A}$$

If we now wish to find $\mu_A$ we need to integrate $d\mu_A$, e.g. form pure 1 to $x_A$. This produces:

$$\mu_A = \mu_A^* + RT \ln x_A$$

This demonstrates that Raoult's law can only hold over the whole range for one component ***if*** it also holds for the other over the whole range.

---

# 2.3: Chemical Potential of Each Component Has the Same Value in Each Phase in Which the Component Appears

In much the same fashion as the partial molar volume is defined, the **partial molar Gibbs function** is defined for compound $i$ in a mixture:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j \neq i} \tag{2.3.1}$$

The partial molar function is of particular importance and is called the **chemical potential**. The chemical potential tells how the Gibbs function will change as the composition of the mixture changes. Since systems tend to seek a minimum aggregate Gibbs function, the chemical potential will point to the direction the system can move in order to reduce the total Gibbs function and reach equilibrium. In general, the total change in the Gibbs function ($dG$) can be calculated from:

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,n_j \neq i} dn_i \tag{2.3.2}$$

Or, by substituting the definition for the chemical potential, and evaluating the pressure and temperature derivatives:

$$dG = VdP - SdT + \sum_i \mu_i dn_i \tag{2.3.3}$$

But as it turns out, the chemical potential can be defined as the partial molar quantity of any of the four major thermodynamic functions $U$, $H$, $A$, or $G$:

Table 2.3.1: Chemical potential can be defined as the partial molar derivative any of the four major thermodynamic functions

| | |
|---|---|
| $dU = TdS - PdV + \sum_i \mu_i dn_i$ | $\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j \neq i}$ |
| $dH = TdS - VdT + \sum_i \mu_i dn_i$ | $\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j \neq i}$ |
| $dA = -PdV - TdS + \sum_i \mu_i dn_i$ | $\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_j \neq i}$ |
| $dG = VdP - SdT + \sum_i \mu_i dn_i$ | $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j \neq i}$ |

The last definition, in which the chemical potential is defined as the partial molar Gibbs function, is the most commonly used, and perhaps the most useful (Equation 2.3.1). As the partial most Gibbs function, it is easy to show that:

$$d\mu = VdP - SdT \tag{2.3.4}$$

where $V$ is the molar volume, and $S$ is the molar entropy. Using this expression, it is easy to show that:

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V \tag{2.3.5}$$

and so at constant temperature:

$$\int_{\mu^o}^{\mu} d\mu = \int_{P^o}^{P} V\, dP \tag{2.3.6}$$

So that for a substance for which the molar volume is fairly independent of pressure at constant temperature (i. e., $\kappa_T$ is very small), therefore Equation 2.3.6 becomes:

$$\int_{\mu^o}^{\mu} d\mu = V \int_{P^o}^{P} dP \tag{2.3.7}$$

$$\mu - \mu^o = V(P - P^o) \tag{2.3.8}$$

or:

$$\mu = \mu^o + V(P - P^o) \tag{2.3.9}$$

Where $P^o$ is the standard state pressure (1 bar) and $\mu^o$ is the chemical potential at the standard pressure. If the substance is highly compressible (such as a gas) the pressure dependence of the molar volume is needed to complete the integral. If the substance is an ideal gas:

$$V = \frac{RT}{P} \tag{2.3.10}$$

So at constant temperature, Equation 2.3.6 then becomes:

$$\int_{\mu^o}^{\mu} d\mu = RT int_{P^o}^{P} \frac{dP}{P} \tag{2.3.11}$$

or:

$$\mu = \mu^o + RT \ln\left(\frac{P}{P^o}\right) \tag{2.3.12}$$

A lot of chemistry takes place in solution and therefore this topic is of prime interest for chemistry.

## 2.3.1: Thermodynamic potentials of solutions

The Gibbs free energy of an ideal gas depends logarithmically on pressure:

$$G = G^o + RT \ln \frac{P}{P^o}$$

$P^{\ominus}$ is *is often dropped out of the formula.* and we write:

$$G = G^o + RT \ln P$$

> Notice however that although $P$ and $P/P^o$ have the same numerical value, the dimensions are different. $P$ usually has dimensions of bar, but $P/P^o$ is *dimensionless*.

If we have a gas mixture we can hold the same logarithmic argument for each partial pressure as the gases do not notice each other. We do need to take into account the number of moles of each and work with (partial) molar values, i.e. the thermodynamic potential:

$$\mu_j = \mu_j^o + RT \ln \frac{P_j}{P^o} \tag{2.3.13}$$

If we are dealing with an equilibrium over an ideal liquid solution the situation in the gas phase gives us a probe for the situation in the liquid. The equilibrium must hold for each of *all* components j (say two in binary mixture). That means that for each of them the thermodynamic potential in the liquid and in the gas must be equal:

$$\mu_j^{sln} = \mu_j^{gas}$$

for all $j$. Consider what happens to a pure component, e.g. $j = 1$ in equilibrium with its vapor. We can write:

$$\mu_1^{pure\ liq} = \mu_1^{pure\ vapor} = \mu_1^o + RT \ln \frac{P_1^*}{P^o}$$

The asterisk in $P_1^*$ denotes the equilibrium vapor pressure of pure component 1 and we will use that to indicate the thermodynamic potential of pure compounds too:

$$\mu_1^{*liq} = \mu_1^o + RT \ln \frac{P_1^*}{P^o} \tag{2.3.14}$$

Combining Equations 2.3.14 and 2.3.13 we find a relationship between the solution and the pure liquid:

$$\mu_j^{sln} = \mu_j^* + RT \ln \frac{P_j}{P_j^*}$$

Notice that the *gas* and its pressure is used to link the mixture and the pure compound.

---

# 2.4: Ideal Solutions obey Raoult's Law

Liquids tend to be volatile, and as such will enter the vapor phase when the temperature is increased to a high enough value, provided they do not decompose first. A volatile liquid is one that has an appreciable vapor pressure at the specified temperature. An ideal mixture containing at least one volatile liquid can be described using **Raoult's Law:**

$$P_j = x_j P_j^*$$

Raoult's law can be used to predict the total vapor pressure above a mixture of two volatile liquids. As it turns out, the composition of the vapor will be different than that of the two liquids, with the more volatile compound having a larger mole fraction in the vapor phase than in the liquid phase. This is summarized in the following diagram for an ideal mixture of two compounds, water and ethanol at 75 °C. At this temperature, water a pure vapor pressure of 384 Torr and ethanol has a pure vapor pressure of 945 Torr. In Figure 24.4.1, the composition of the liquid phase is represented by the solid line and the composition of the vapor phase is represented by the dashed line.

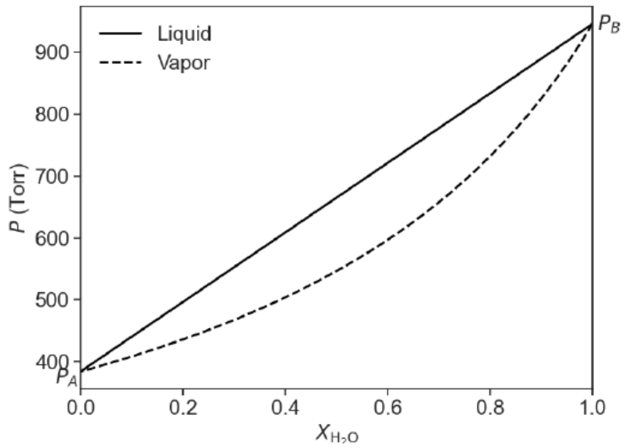

Figure 24.4.1: The composition of the liquid phase (solid line) and the vapor phase (dashed lined) as a function of mole fraction according to Raoult's law. The solution is a mixture of water and ethanol. $P_A$ is the vapor pressure of pure water and $P_B$ is the vapor pressure of pure ethanol at 75 °C

Often, it is desirable to depict the phase diagram at a single pressure so that temperature and composition are the variables included in the graphical representation. In such a diagram, the vapor, which exists at higher temperatures) is indicated at the top of the diagram, while the liquid is at the bottom. A typical temperature vs. composition diagram is depicted in Figure 24.4.2 for an ideal mixture of two volatile liquids.

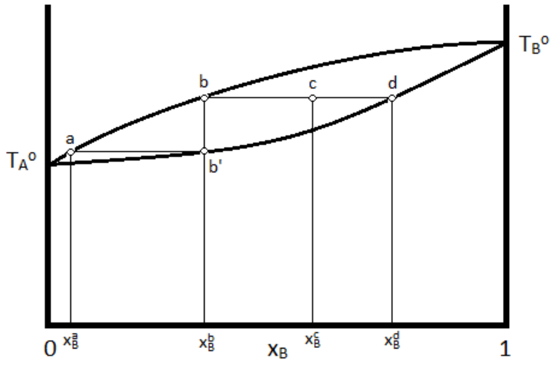

Figure 24.4.2: A typical temperature vs. composition diagram.

In this diagram, $T_A$ and $T_B$ represent the boiling points of pure compounds $A$ and $B$. If a system having the composition indicated by $\chi_B^c$ has its temperature increased to that indicated by point $c$, The system will consist of two phases, a liquid phase, with a composition indicated by $\chi_B^d$ and a vapor phase indicated with a composition indicated by $\chi_B^b$. The relative amounts of material in each phase can be described by the lever rule, as described previously.

Further, if the vapor with composition $\chi_B^b$ is condensed (the temperature is lowered to that indicated by point b') and re-vaporized, the new vapor will have the composition consistent with $\chi_B^a$. This demonstrates how the more volatile liquid (the one with the lower boiling temperature, which is $A$ in the case of the above diagram) can be purified from the mixture by collecting and re-evaporating fractions of the vapor. If the liquid was the desired product, one would collect fractions of the residual liquid to achieve the desired result. This process is known as distillation.

## 2.4.1: The Gibbs energy of mixing is always negative

When we add $n_A$ moles of component $A$ and $n_B$ moles of component $B$ to form an ideal liquid solution, this is generally a spontaneous process. Let us consider the Gibbs free energy change of that process:

$$\Delta_{mix} G = n_1 \mu_1^{sln} + n_2 \mu_2^{sln} - (n_1 \mu_1^* + n_2 \mu_2^*) \tag{2.4.1}$$

Using:

$$\mu_i^{sln} \equiv \mu_i^* + nRT x_i \ln x_i \tag{2.4.2}$$

his expression simplifies to:

$$\Delta_{mix} G = nRT x_A \ln x_A + nRT x_B \ln x_B \tag{2.4.3}$$

where $n$ is the total moles. Mole fraction, $x_i$, is always less than one, so the Gibbs energy of mixing is always negative; mixing is always spontaneous. We can generalize this to mixtures with more than two components:

$$\Delta_{mix} G = nRT \sum_i x_i \ln x_i \tag{2.4.4}$$

This expression looks suspiciously familiar. Apart from a factor of $-T$, it is just like the **entropy of mixing**:

$$\Delta_{mix} S = -nR \sum_i x_i \ln x_i \tag{2.4.5}$$

Recalling the relationship between Gibbs energy and entropy:

$$\Delta_{mix} G = \Delta_{mix} H - T \Delta_{mix} S \tag{2.4.6}$$

This leaves no room at all for an enthalpy effect:

$$\Delta_{mix} H = 0 \tag{2.4.7}$$

Even though there are strong interactions between neighboring particles in liquids, there is no enthalpy change. This implies that it does not matter what the neighboring molecules are. If we represent the average interaction energy between molecule $i$ and $j$ by $U_{ij}$, we are assuming that $U_{ij}$ is always the same. In practice, this is *seldom* the case. It usually does matter and then the enthalpy term is not zero. As this affects the thermodynamics of the liquid solution, it should also affect the vapor pressures that are in equilibrium with it.

## 2.4.2: In the ideal case, volumes are additive

From the change of $G$ in its natural variables, we know that:

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

This means that if we take

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V_{mix}$$

In the ideal case we get:

$$\left(\frac{\partial \Delta G^{ideal}}{\partial P}\right)_T = \Delta V_{mix}^{ideal}$$

$$\left(\frac{\partial RT(n_1 \ln x_1 + n_2 \ln x_2)}{\partial P}\right)_T = \Delta V_{mix}^{ideal} = 0$$

In the ideal case, volumes are *additive* and we need not worry about how the partial molar volumes change with composition.

# 2.5: Most Solutions are Not Ideal

If we plot the partial pressure of one component, $P_1$, above a mixture with a mole fraction $x_1$, we should get a straight line with a slope of $P_1^*$ (Raoult's law). Above non-ideal solutions the graph will no longer be a straight line but a curve. However towards $x_1 = 1$ the curve typically approaches the Raoult line. On the other extreme, there often is a more or less linear region as well, ***but with a different slope*** (Figure 24.5.1 ). This means that we can identify two *limiting* laws:

- For $x \rightarrow 0$: **Henry's law**:

$$P_1 = K_H x_1$$

- For $x \rightarrow 1$: **Raoult's law**:

$$P_1 = P_1^* x_1$$

This implies that the straight line that indicates the Henry expression will intersect the y-axis at $x = 1$ (pure compound) at a ***different*** point than $P^*$. For $x \rightarrow 0$ (low concentrations) we can speak of component 1 being the *solute* (the minority component). At the other end $x \rightarrow 1$ it plays the role of the *solvent* (majority component).

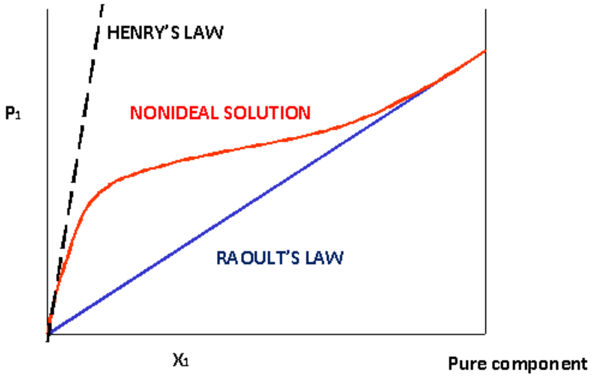

Figure 24.5.1 : Vapor pressure above an ideal and a non-ideal solution

> Another thing to note is that $P^*$ is a property of *one pure component*, the value of $K_H$ by contrast is a property of the *combination of two components*, so it needs to be measured for each solute-solvent combination.

As you can see we have a description for both the high and the low end, but not in the middle. In general, the more modest the deviations from ideality the larger the range of validity of the two limiting laws. The way to determine $K_H$ would be to actually determine vapor pressures. How about the other component? Do we need to measure them too? Fortunately we can use thermodynamics to answer this question with no. There is a handy expression that saves us the trouble.

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# 2.6: Vapor Pressures of Volatile Binary Solutions

The behaviors of ideal solutions of volatile compounds follow Raoult's Law. Henry's Law can be used to describe the deviations from ideality. Henry's law states:

$$P_B = k_H P_B^o \tag{2.6.1}$$

For which the Henry's Law constant ($k_H$) is determined for the specific compound. Henry's Law is often used to describe the solubilities of gases in liquids. The relationship to Raoult's Law is summarized in Figure 2.6.1.

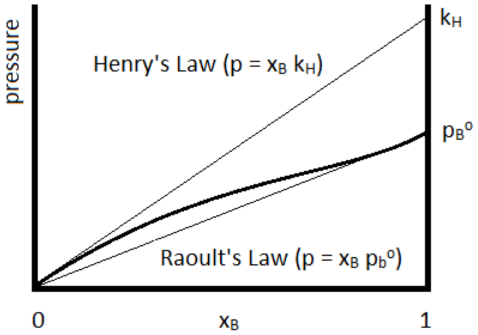


Figure 2.6.1: The relationship between Raoult's Law and Henry's Law for a binary mixture.

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

## Example 2.6.1: Solubility of Carbon Dioxide in Water

The solubility of $CO_2(g)$ in water at 25 $^oC$ is 3.32 x $10^{-2}$ M with a partial pressure of $CO_2$ over the solution of 1 bar. Assuming the density of a saturated solution to be 1 kg/L, calculate the Henry's Law constant for $CO_2$.

**Solution**:

In one L of solution, there is 1000 g of water (assuming the mass of $CO_2$ dissolved is negligible.)

$$(1000\,g)\left(\frac{1\,mol}{18.02\,g}\right) = 55\,mol\,H_2O \tag{2.6.2}$$

The solubility of $CO_2$ can be used to find the number of moles of $CO_2$ dissolved in 1 L of solution also:

$$\frac{3.32 \times 10^{-2} mol}{L} \cdot 1\,L = 3.32 \times 10^{-2} mol\,CO_2 \tag{2.6.3}$$

and so the mol fraction of $CO_2$ is

$$\chi_b = \frac{3.32 \times 10^{-2} mol}{55.5\,mol} = 5.98 \times 10^{-4} \tag{2.6.4}$$

And so

$$10^5\,Pa = 5.98 \times 10^{-4} k_H \tag{2.6.5}$$

or

$$k_H = 1.67 \times 10^9\,Pa \tag{2.6.6}$$

## 2.6.1: Azeotropes

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

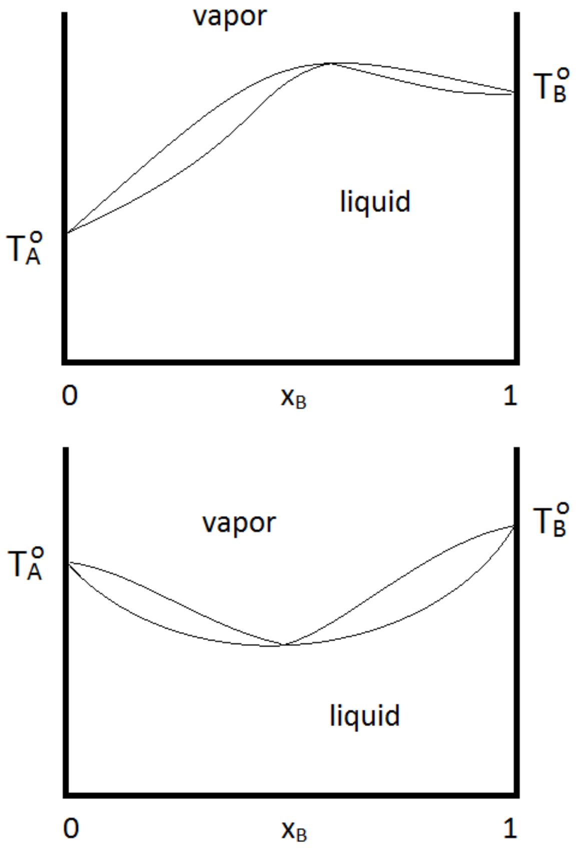


Figure $2.6.2$: Phase diagrams for (left) a maximum boiling point azeotrope and (right) Ta maximum boiling point azeotrope.

Azeotropes can be either maximum boiling or minimum boiling, as show in Figure $2.6.2; left$. Regardless, distillation cannot purify past the azeotrope point, since the vapor and the liquid phases have the same composition. If a system forms a minimum boiling azeotrope and has a range of compositions and temperatures at which two liquid phases exist, the phase diagram might look like Figure $2.6.2; right$.

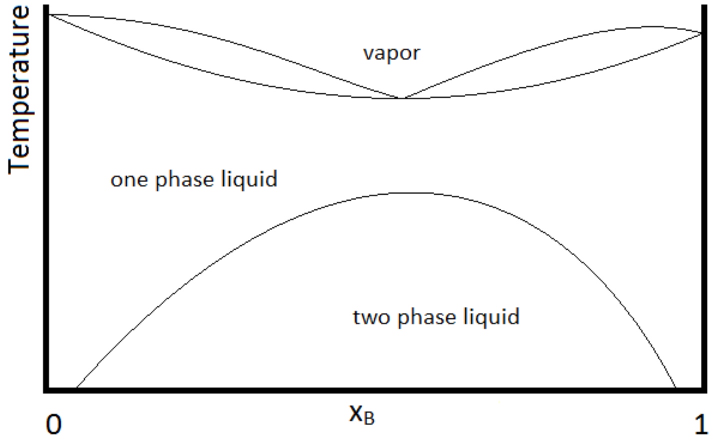
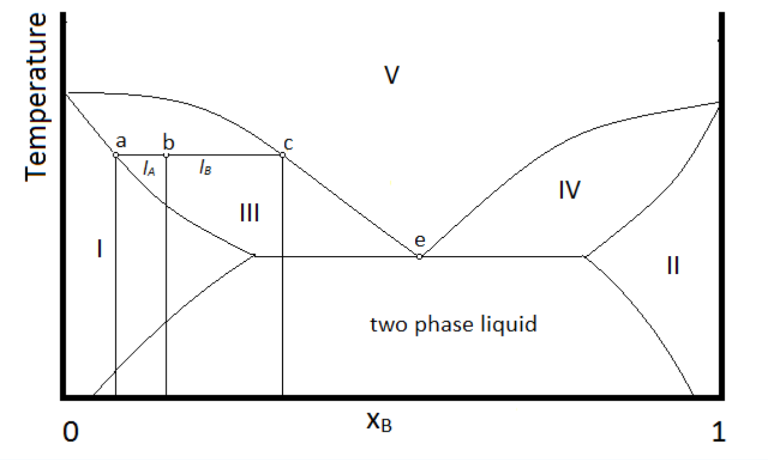


Figure $2.6.3$: *Phase diagram for a binary solution with the boiling point of a minimum boiling azeotrope that is higher that when components are miscible (single phase).*

Another possibility that is common is for two substances to form a two-phase liquid, form a minimum boiling azeotrope, but for the azeotrope to boil at a temperature below which the two liquid phases become miscible. In this case, the phase diagram will look like Figure $2.6.3$.

**Example 2.6.1:**

In the diagram, make up of a system in each region is summarized below the diagram. The point e indicates the azeotrope composition and boiling temperature.



I. Single phase liquid (mostly compound A)
II. Single phase liquid (mostly compound B)
III. Single phase liquid (mostly A) and vapor
IV. Single phase liquid (mostly B) and vapor
V. Vapor (miscible at all mole fractions since it is a gas)

**Solution**

Within each two-phase region (III, IV, and the two-phase liquid region, the lever rule will apply to describe the composition of each phase present. So, for example, the system with the composition and temperature represented by point b (a single-phase liquid which is mostly compound A, designated by the composition at point a, and vapor with a composition designated by that at point c), will be described by the lever rule using the lengths of tie lines $l_A$ and $l_B$.

### 2.6.1.1: Gibbs-Duhem and Henry's law

What happens when Raoult does *not* hold over the whole range? Recall that in a gas:

$$\mu_j = \mu_j^o + RT \ln \frac{P_j}{P^o} \tag{2.6.7}$$

or

$$\mu_j = \mu_j^o + RT \ln P_j$$

after dropping $P^o = 1\ bar$ out of the notation. Note that numerically this does not matter, since $P_j$ is now *assumed* to be dimensionless.

Let's consider $d\mu_1$ at constant temperature:

$$d\mu_1 = RT \left(\frac{\partial \ln P_1}{\partial x_1}\right) dx_1$$

likewise:

$$d\mu_2 = RT \left(\frac{\partial \ln P_2}{\partial x_2}\right) dx_2$$

If we substitute into the Gibbs-Duhem expression we get:

$$x_1\left(\frac{\partial \ln P_1}{\partial x_1}\right)dx_1 + x_2\left(\frac{\partial \ln P_2}{\partial x_2}\right)dx_2 = 0$$

Because $dx_1 = -dx_2$ :

$$x_1\left(\frac{\partial \ln P_1}{\partial x_1}\right) = x_2\left(\frac{\partial \ln P_2}{\partial x_2}\right)$$

(This is an alternative way of writing Gibbs-Duhem).

If in the limit for $x_1 \rightarrow 1$ Raoult Law holds then

$$P_1 \rightarrow x_1 P_1^*$$

Thus:

$$\frac{\partial \ln P_1}{\partial x_1} = \frac{1}{x_1}$$

and

$$\begin{aligned}\frac{x_1}{x_1} &= x_2\frac{\partial \ln P_2}{\partial x_2} \\ 1 &= x_2\frac{\partial \ln P_2}{\partial x_2} \\ \frac{1}{x_2} &= \frac{\partial \ln P_2}{\partial x_2}\end{aligned} \tag{2.6.8}$$

We can integrate Equation 2.6.8 to form a logarithmic impression, but it will have an integration constant:

$$\ln P_2 = \ln x_2 + constant$$

This constant of integration can be folded into the logarithm as a multiplicative constant, $K$

$$\ln P_2 = \ln(Kx_2)$$

So for $x_1 \rightarrow 1$ (i.e., $x_2 \rightarrow 0$), we get that

$$P_2 = Kx_2$$

where $K$ is *some* constant, but not necessarily $P^*$. What this shows is that when one component follows Raoult the other *must* follow Henry and vice versa. (Note that the ideal case is a subset of this case, in that the value of $K$ then becomes $P^*$ and the linearity must hold over the whole range.)

## 2.6.2: Margules Functions

Of course a big drawback of the Henry law is that it only describes what happens at the two extremes of the phase diagram and not in the middle. In cases of moderate non-ideality, it is possible to describe the whole range (at least in good approximation) using a **Margules function**:

$$P_1 = (x_1 P_1^*)\, f_{Mar}$$

The function $f_{Mar}$ has the shape:

$$f_{Mar} = \exp\left[\alpha x_2^2 + \beta x_2^3 + \delta x_2^3 + \ldots\right]$$

Notice that the Margules function involves the mole fraction of the *opposite* component. It is an exponential with a series expansion. with the constant and linear term missing. As you can see the function has a number of parameters $\alpha$, $\beta$, $\delta$ etc. that need to be determined by experiment. In general, the more the system diverges from ideality, the more parameters you need. Using Gibbs-Duhem is is possible to translate the expression for $P_1$ into the corresponding one for $P_2$.

---

# 2.7: Activities of Nonideal Solutions

The bulk of the discussion in this chapter dealt with ideal solutions. However, real solutions will deviate from this kind of behavior. So much as in the case of gases, where fugacity was introduced to allow us to use the ideal models, **activity** is used to allow for the deviation of real solutes from limiting ideal behavior. The activity of a solute is related to its concentration by

$$a_B = \gamma \frac{m_B}{m^o}$$

where $\gamma$ is the **activity coefficient**, $m_B$ is the molaliy of the solute, and $m^o$ is unit molality. The activity coefficient is unitless in this definition, and so the activity itself is also unitless. Furthermore, the activity coefficient approaches unity as the molality of the solute approaches zero, insuring that dilute solutions behave ideally. The use of activity to describe the solute allows us to use the simple model for chemical potential by inserting the activity of a solute in place of its mole fraction:

$$\mu_B = \mu_B^o + RT \ln a_B$$

The problem that then remains is the measurement of the activity coefficients themselves, which may depend on temperature, pressure, and even concentration.

## 2.7.1: Activity Coefficients for Ionic Solutes

For an ionic substance that dissociates upon dissolving

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

the chemical potential of the cation can be denoted $\mu_+$ and that of the anion as $\mu_-$. For a solution, the total molar Gibbs function of the solutes is given by

$$G = \mu_+ + \mu_-$$

where

$$\mu = \mu^* + RT \ln a$$

where \(\mu^*\) denotes the chemical potential of an ideal solution, and $a$ is the activity of the solute. Substituting his into the above relationship yields

$$G = \mu_+^* + RT \ln a_+ + \mu_-^* + RT \ln a_-$$

Using a molal definition for the activity coefficient

$$a_i = \gamma_i m_i$$

The expression for the total molar Gibbs function of the solutes becomes

$$G = \mu_+^* + RT \ln \gamma_+ m_+ + \mu_-^* + RT \ln \gamma_- m_-$$

This expression can be rearranged to yield

$$G = \mu_+^* + \mu_-^* + RT \ln m_+ m_- + RT \ln \gamma_+ \gamma_-$$

where all of the deviation from ideal behavior comes from the last term. Unfortunately, it impossible to experimentally deconvolute the term into the specific contributions of the two ions. So instead, we use a geometric average to define the **mean activity coefficient**, $\gamma_\pm$.

$$\gamma_\pm = \sqrt{\gamma_+ \gamma_-}$$

For a substance that dissociates according to the general process

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

the expression for the mean activity coefficient is given by

$$\gamma_\pm = (\gamma_+^x \gamma_-^y)^{1/x+y}$$

### 2.7.1.1: Debeye-Hückel Law

In 1923, Debeye and Hückel (Debye & Hückel, 1923) suggested a means of calculating the mean activity coefficients from experimental data. Briefly, they suggest that

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

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

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

For a solution in water at 25 $^o$C,

As seen before activities are a way to account for deviation from ideal behavior while still keeping the formulism for the ideal case intact. For example in a ideal solution we have:

$$\mu^{sln} = \mu^* + RT\ln x_i$$

is replaced by

$$\mu^{sln} = \mu^* + RT\ln a_i$$

The relationship between $a_i$ and $x_i$ is often written using an activity coefficient $\gamma$:

$$a_i = \gamma_i x_i$$

## 2.7.2: Raoult versus Henry

Implicitly we have made use of Raoult's law here because we originally used

$$x_i = \frac{P_i}{P_i^*}$$

In the case of a solvent this makes sense because Raoult's law is still valid in the limiting case, but for the solute it would make more sense to use Henry's law as a basis for the definition of activity:

$$a_{solute,H} \equiv \frac{P_{solute}}{K_{x,H}}$$

This does mean that the $\mu^*$ now becomes a $\mu^{*Henry}$ because the extrapolation of the Henry law all the way to the other side of the diagram where $x_{solute} = 1$ points to a point that is not the equilibrium vapor pressure of this component. In fact it represents a virtual state of the system that cannot be realized. This however does not affect the usefulness of the convention.

## 2.7.3: Various concentration units

The subscript X was added to the K value because we are still using mole fractions. However Henry's law is often used with other concentration measures. The most important are:

- molarity
- molality
- mole fraction

Both the numerical values and the dimensions of K will differ depending on which concentration measure is used. In addition the pressure units can differ. For example for oxygen in water we have:

$K_{x,H}$= 4.259 $10^4$ atm
$K_{cp,H}$= 1.3 $10^{-3}$ mol/lit.atm
$K_{pc,H}$= 769.23 lit.atm/mol

As you can see $K_{cp,H}$ is simply 1/$K_{pc,H}$, both conventions are used..

Note that in this case a choice based on Raoult is really not feasible. At room temperature we are far above the critical point of oxygen which make the equilibrium vapor pressure a non-existent entity. Returning to activities we could use each of the versions of K as a basis for the activity definition. This means that when using activities it must be specified what scale we are using. Activities and Henry coefficients of dissolved gases in water (both fresh and salt) are quite important in geochemistry, environmental chemistry etc.

## 2.7.4: Non-volatile solutes

A special case arises if the vapor pressure of a solute is negligible. For example if we dissolve sucrose in water. In that case we can still use the Henry based definition

$$a_{solute,H} \equiv \frac{P_{solute}}{K_{x,H}}$$

Even though both $K$ and $P$ will be exceedingly small their ratio is still finite. However how do we determine either?

The answer lies in the solvent. Even if the vapor pressure of sucrose is immeasurably small, the water vapor pressure above the solution can be measured. The Gibbs-Duhem equation can then be used to translate one into the other. We can use Raoult Law to define the activity of the solvent:

$$a_1 = \frac{P_1}{P_1^*}$$

We can measure the pressures as a function of the solute concentrations. At low concentrations

$$\ln a_1 \ln x - 1 \approx -x - 2$$

At higher concentrations we will get deviations, we can write:

$$\ln \frac{P_1}{P_1^*} = \ln a_1 \approx -x_2 \varphi$$

The 'fudge factor' $\varphi$ is known as the *osmotic coefficient* and can thus be determined as a function of the solute concentration from the pressure data. What we are really interested in is $a_2$, not $a_1$:

$$a_2 = \gamma_2 x_2$$

Using Gibbs-Duhem we can convert $\varphi$ into $\gamma_2$. Usually this is done in terms of molalities rather than mole fractions and it leads to this integral:

$$\ln \gamma_{2,m} = \varphi - 1 + \int_{m'=0}^{m} \frac{\varphi - 1}{m'} dm'$$

# 2.8: Activities are Calculated with Respect to Standard States

Need to define a new variable. The thermodynamic activity, $a$, is the effective concentration of a species in a mixture. It is a dimensionless quantity that are calculated with respect to standard states. For a gas, this would be related to the fugacity and for a solution, to the concentration. The activity for a real gas:

$$a_i = \frac{f_i}{P^\circ} = \frac{\phi_i P_i}{P^\circ} = \frac{\phi_i (y_i P)}{P^\circ} \tag{2.8.1}$$

For systems where we treat the gases as ideal:

$$\phi_i = 1 \tag{2.8.2}$$

$$a_i = \frac{P_i}{P^\circ} = y_i \frac{P}{P^\circ} \tag{2.8.3}$$

The activity for a solution:

$$a_i = \gamma i \frac{[\text{A}]}{1 \ \underline{\text{M}}} \tag{2.8.4}$$

General chemistry and organic chemistry use ideal reactants where $\gamma_i = 1$:

$$a_i = \frac{[\text{A}]}{1 \ \underline{\text{M}}} \tag{2.8.5}$$

The activity for a solid or liquid:

$$a_i = 1 \tag{2.8.6}$$

# 2.9: Gibbs Energy of Mixing of Binary Solutions in Terms of the Activity Coefficient

## 2.9.0.1: Activity and activity coefficients

In the ideal case, we have seen that the thermodynamic potential for species $i$ can be written as:

$$\mu_i^{sln} = \mu_i^o + RT\ln x_i = \mu_2^o + RT\ln\left(\frac{P_i}{P^o}\right)$$

One approach to non-ideality is to simply ***redefine*** the problem and say:

$$\mu_i^{sln} \equiv \mu_i^o + RT\ln a_i$$

≡ indicates this is actually a definition. The newly defined variable $a_2$ is known as the **activity**. Alternatively we can define it as:

$$[a_i] \equiv \frac{P_i}{P^o}$$

As at high enough values of the mole fraction we know that we can still apply Raoult law. So $a_i$ must approach $x_i$ in this limit, but for other concentrations this will no longer hold. Often this is expressed in terms of an ***activity coefficient*** $\gamma$:

$$[a_i] = \gamma_i x_i$$

For high values of $x_i$, $\gamma_i$ will approach unity. If we model the non-ideality with a Margules function we see that:

$$P_i = x_i P^o f_{Mar} \tag{2.9.1}$$

$$[a_i] = \left[\frac{P_i}{P^0}\right] = \left[\frac{x_i P^0 f_{Mar}}{P^0}\right] = [x_i f_{Mar}] \tag{2.9.2}$$

The activity coefficient and the Margules function are the same thing in this description.

## 2.9.0.1: Regular solutions

A special and simplest case of a Margules function is the case where all but one Margules parameters $(a)$ can be neglected. Such a system is called a ***regular solution***. In this case, we can write:

$$a_1 = x_1 e^{ax_2^2} \tag{2.9.3}$$

We can use Gibbs-Duhem to show that this *implies*:

$$a_2 = x_2 e^{ax_1^2} \tag{2.9.4}$$

# Gibbs free energy of regular solutions

Consider the change in Gibbs free energy when we mix two components to form a regular solution:

$$\Delta G_{mix} = n_1\mu_1^{sln} + n_2\mu_2^{sln} - (n_1\mu_1^* + n_2\mu_2^*) \tag{2.9.5}$$

Dividing by the total number of moles, we get:

$$\Delta_{mix} G = x_1\mu_1^{sln} + x_2\mu_2^{sln} - (x_1\mu_1^* + x_2\mu_2^*) \tag{2.9.6}$$

Using:

$$\mu_i^{sln} \equiv \mu_i^* + RT\ln a_i \tag{2.9.7}$$

and:

$$[a_i] = \gamma_i x_i \tag{2.9.8}$$

We get:

$$\frac{\Delta_{mix} G}{RT} = x_1\ln x_1 + x_2\ln x_2 + x_1\ln\gamma_1 + x_2\ln\gamma_2 \tag{2.9.9}$$

For a regular solution:

$$\ln \gamma_1 = \ln f_{Mar} = a x_2^2 \tag{2.9.10}$$

$$\ln \gamma_2 = \ln f_{Mar} = a x_1^2 \tag{2.9.11}$$

This gives:

$$\begin{aligned} \frac{\Delta_{mix} G}{RT} &= x_1 \ln x_1 + x_2 \ln x_2 + x_1 a x_2^2 + x_2 a x_1^2 \\ &= x_1 \ln x_1 + x_2 \ln x_2 + a[x_1 + x_2] x_1 x_2 \\ &= x_1 \ln x_1 + x_2 \ln x_2 + a x_1 x_2 \end{aligned}$$

Since:

$$x_1 + x_2 = 1 \tag{2.9.12}$$

In this expression we see that we have an additional term to the entropy of mixing term we had seen before. Its coefficient $a$ is dimensionless but represents the fact that the (strong!) interactions between the molecules are different depending on who is the neighbor. In general. $a$ can be written as $W/RT$, where $W$ represents an energy (enthalpy) that brings the difference in interaction energies into account. $W$ does not depend strongly on temperature. We could look at $W$ as the difference in average interaction energies:

$$W = 2U_{12} - U_{11} - U_{22} \tag{2.9.13}$$

Rearranging we get:

$$\frac{\Delta_{mix} G}{W} = \frac{RT}{W} [x_1 \ln X_1 + x_2 \ln x_2] + x_1 x_2 \tag{2.9.14}$$

The two terms will ***compete*** as a function of temperature. The mixing entropy will be more important at high temperatures, the interaction enthalpy at low temperatures. The entropy term has a *minimum* at $x_1$=0.5, the enthalpy term a *maximum* if W is positive. So, one tends to favor mixing, the other segregation and we will get a compromise between the two. Depending on the value of $RT/W$ (read: temperature), we can either get one or two minima. This means that at low temperatures there will be a solubility limit of 1 into 2 and *vice versa*. At higher temperatures the two components can mix completely. At the transition between these two regimes we will have ***critical or consolute point***.

Notice that even though we used the vapor pressures of the gas to develop our theory, they are conspicuously absent from the final result. The same thing we said about melting points hold true here. Because we are dealing with the miscibility behavior of two condensed phases, the outcome should not depend very strongly on the total pressure of our experiment.

Although in regular solutions the consolute point is predicted to be a maximum in temperature, we can find them as minima as well in practice. The nicotine-water system even has two consolute points, an upper and a lower one. When heating up a mixture of these we first observe mixing, then segregation and then mixing again. Obviously this behavior is far more complicated than we can describe with just one Margules parameter.

### 2.9.0.0.1: Partial molar volumes

What we said above about volumes simply being additive in the ideal case is no longer true here.

$$\left( \frac{\partial \Delta G_{mix}}{\partial P} \right)_T = \Delta V_{\text{regular}} \tag{2.9.15}$$

$$\left( \frac{\partial \Delta H_{mix} + RT(n_1 \ln [x_1] + n_2 \ln [x_2])}{\partial P} \right)_T = \Delta V_{\text{mix}} \tag{2.9.16}$$

$$\left( \frac{\partial \Delta H_{mix}}{\partial P} \right)_T = \Delta V_{\text{mix}} \tag{2.9.17}$$

In general the enthalpy of mixing does depend on pressure as it is related to the interactions between the molecules in solution. ($W$ depends on the distance between them). This means that partial molar volumes now become a function of composition and volume is no longer simply additive.

### 2.9.1: Real solutions

Notice that the curves are *symmetrical* around $x = 0.5$. This implies that it is as easy (or not) dissolving A into B as vice versa. In many cases this is not realistic. Many systems diverge more seriously from ideal behavior that the regular one. Up to a point we can model that by adding more terms to the Margules function. For example, adding a β-term undoes the symmetry (see example 24-7). However, many systems are so non-ideal that the Margules expression become unwieldy with too many parameters.

### 2.9.2: Boiling non-ideal solutions

#### 2.9.2.1: Azeotropes

For ideal solutions we have seen that there is a lense shaped two-phase region between the gas and the liquid phase. For non-ideal systems the two-phase region can attain different shapes. In many cases there is either a minimum or a maximum. As such a point the phase gap closes to a point that is known as an *azeotrope*. It represents a composition of the liquid that boils *congruently*. That means that the vapor and the liquid have the same composition for a change. Azeotropes impose an important limitation unto distillation: they represent the end point of a distillation beyond which we can not purify by this method.

#### 2.9.2.2: Eutectics

Another point to be made is that in the diagram with the consolute point we are assuming the pressure to be constant. If we lower the pressure this would affect the boiling points strongly: the whole gas-liquid gap would come down in temperature (see animation). The mixing behavior is only weakly affected. (The reason is that one involves the volume term of the gas, the other only of the liquid(s)). At lower pressures it is possible therefore that the consolute point is *above* the gas-liquid gap. In other words: the mixtures will boil before they get a chance to mix. The boiling points will be lower there than for the pure compounds. There will be a composition for which the boiling point is at a minimum and where the mixture boils congruently (i.e. to a vapor with the same (overall) composition).

The mutual solubility limits increase as temperature increases, just as happens in the critical mixing case, but that due to the competition from the vapor phase this process comes to an end at the eutectic temperature. At this temperature one liquid boils always completely, the other one in part. At the eutectic composition they both boil away simultaneously.

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# 2.E: Solutions I- Liquid-Liquid Solutions (Exercises)

TBA

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CHAPTER OVERVIEW

# 3: Extended Explanations - Solutions II - Nonvolatile Solutes

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# 3.1: Standard State of Nonvolatile Solutions

The activity is a relative measure as it measures equilibrium relative to a standard state. The standard state is defined by the International Union of Pure and Applied Chemistry (IUPAC) and followed systematically by chemists around the globe. The standard state for a solution is defined in terms of the infinite-dilution behavior. This is in contrast to the standard state concentration of 1 mol/L. This can be reconciled by considering that the standard state is a hypothetical solution of 1 mol/L in which the solute has infinite-dilution properties, e.g. solute particles do not interact with each other. This means that the activity coefficient describes all non-ideal behavior when the value is not equal to 1.

# 3.2: The Activities of Nonvolatile Solutes

For non-ideal gases, we introduced in chapter 11 the concept of *fugacity* as an *effective pressure* that accounts for non-ideal behavior. If we extend this concept to non-ideal solution, we can introduce the *activity* of a liquid or a solid, $a$, as:

$$\mu_{\text{non-ideal}} = \mu^{-\ominus} + RT \ln a, \tag{3.2.1}$$

where $\mu$ is the chemical potential of the substance or the mixture, and $\mu^{-\ominus}$ is the chemical potential at standard state. Comparing this definition to Equation 11.4.2, it is clear that the activity is equal to the fugacity for a non-ideal gas (which, in turn, is equal to the pressure for an ideal gas). However, for a liquid and a liquid mixture, it depends on the chemical potential at standard state. This means that the activity is not an absolute quantity, but rather a relative term describing how "active" a compound is compared to standard state conditions. The choice of the standard state is, in principle, arbitrary, but conventions are often chosen out of mathematical or experimental convenience. We already discussed the convention that standard state for a gas is at $P^{-\ominus} = 1 \text{ bar}$, so the activity is equal to the fugacity. The standard state for a component in a solution is the pure component at the temperature and pressure of the solution. This definition is equivalent to setting the activity of a pure component, $i$, at $a_i = 1$.

For a component in a solution we can use Equation 11.4.2 to write the chemical potential in the gas phase as:

$$\mu_i^{\text{vapor}} = \mu_i^{-\ominus} + RT \ln \frac{P_i}{P^{-\ominus}}. \tag{3.2.2}$$

If the gas phase is in equilibrium with the liquid solution, then:

$$\mu_i^{\text{solution}} = \mu_i^{\text{vapor}} = \mu_i^*, \tag{3.2.3}$$

where $\mu_i^*$ is the chemical potential of the pure element. Subtracting Equation 3.2.3 from Equation 3.2.2, we obtain:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln \frac{P_i}{P_i^*}. \tag{3.2.4}$$

For an ideal solution, we can use Raoult's law, Equation 13.1.1, to rewrite Equation 3.2.4 as:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln x_i, \tag{3.2.5}$$

which relates the chemical potential of a component in an ideal solution to the chemical potential of the pure liquid and its mole fraction in the solution. For a non-ideal solution, the partial pressure in Equation 3.2.4 is either larger (positive deviation) or smaller (negative deviation) than the pressure calculated using Raoult's law. The chemical potential of a component in the mixture is then calculated using:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln(\gamma_i x_i), \tag{3.2.6}$$

where $\gamma_i$ is a positive coefficient that accounts for deviations from ideality. This coefficient is either larger than one (for positive deviations), or smaller than one (for negative deviations). The activity of component $i$ can be calculated as an *effective mole fraction*, using:

$$a_i = \gamma_i x_i, \tag{3.2.7}$$

where $\gamma_i$ is defined as the **activity coefficient**. The partial pressure of the component can then be related to its vapor pressure, using:

$$P_i = a_i P_i^*. \tag{3.2.8}$$

Comparing Equation 3.2.8 with Raoult's law, we can calculate the activity coefficient as:

$$\gamma_i = \frac{P_i}{x_i P_i^*} = \frac{P_i}{P_i^{\text{R}}}, \tag{3.2.9}$$

where $P_i^{\text{R}}$ is the partial pressure calculated using Raoult's law. This result also proves that for an ideal solution, $\gamma = 1$. Equation 3.2.9 can also be used experimentally to obtain the activity coefficient from the phase diagram of the non-ideal solution. This is achieved by measuring the value of the partial pressure of the vapor of a non-ideal solution. Examples of this procedure are reported for both positive and negative deviations in Figure 3.2.1.

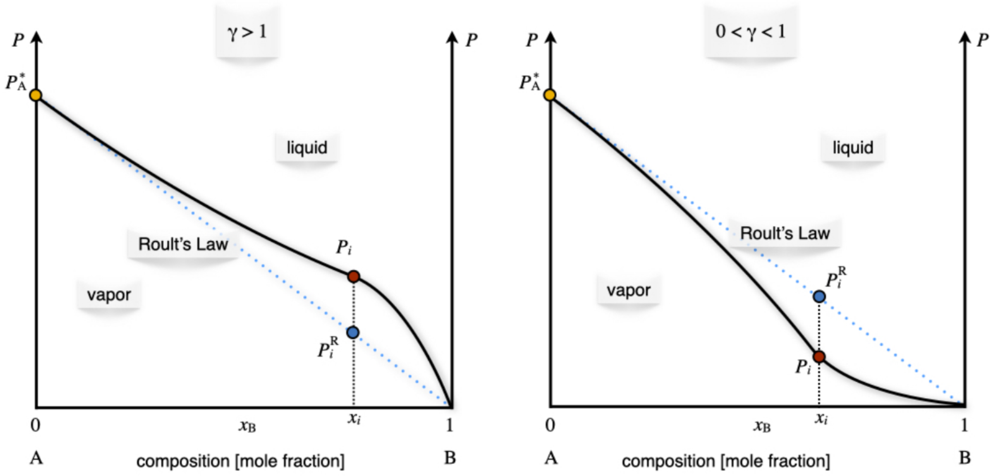

Figure 3.2.1: Positive and Negative Deviation from Raoult's Law in the Pressure–Composition Phase Diagram of Non-Ideal Solutions at Constant Temperature.

- As we already discussed in chapter 10, the activity is the most general quantity that we can use to define the equilibrium constant of a reaction (or the reaction quotient). The advantage of using the activity is that it's defined for ideal and non-ideal gases and mixtures of gases, as well as for ideal and non-ideal solutions in both the liquid and the solid phase.[1]

---

1. Notice that, since the activity is a relative measure, the equilibrium constant expressed in terms of the activities is also a relative concept. In other words, it measures equilibrium relative to a standard state. This fact, however, should not surprise us, since the equilibrium constant is also related to $\Delta_{\text{rxn}}G^{-\ominus}$ using Gibbs' relation. This is why the definition of a universally agreed-upon standard state is such an essential concept in chemistry, and why it is defined by the International Union of Pure and Applied Chemistry (IUPAC) and followed systematically by chemists around the globe.

---

# 3.3: Electrolytes Solutions are Nonideal at Low Concentrations

A solution with a strong electrolyte, such as NaCl in water, is perhaps one of the most obvious systems to consider but, unfortunately, is also one of the more difficult ones. The reason is that the electrolyte produces two ***charged*** solutes, $Na^+$ and $Cl^+$ (both in hydrated form), in solution. We need to consider the dissociation process and stoichiometry as we are bringing more than one solute species into solution. We also need to consider electrostatic interactions between solutes. The charges introduce a strong interaction that falls off with $r^{-1}$, as opposed to $\sim r^{-6}$ if only neutral species are present. This causes a very serious divergence from ideality even at very low concentrations. Consider a salt going into solution:

$$C_{\nu_+}A_{\nu_-} \rightarrow \nu_+ C^{z+} + \nu_- A^{z-} \tag{3.3.1}$$

where $\nu_+$ and $\nu_-$ are the ***stoichiometric coefficients*** and $z_+$ and $z_-$ are the formal charges of the cation and anion, respectively. As we shall see, the stoichiometric coefficients involved in the dissociation process are important for a proper description of the thermodynamics of strong electrolytes. Charge neutrality demands:

$$\nu_+ z_+ + \nu_- z_- = 0 \tag{3.3.2}$$

## 3.3.1: Thermodynamic potentials versus the dissociation

For the salt, we can write:

$$\mu_2 = \mu_2^o + RT\ln a_2 \tag{3.3.3}$$

However, we need to take into account the dissociation of the salt. To do so, we write:

$$\mu_2 = \nu_+\mu_+ + \nu_-\mu_- \tag{3.3.4}$$

This implies:

$$\mu_2^o = \nu_+\mu_+^o + \nu_-\mu_-^o \tag{3.3.5}$$

where

$$\mu_+ = \mu_-^o + RT\ln a_+ \tag{3.3.6}$$

$$\mu_- = \mu_-^o + RT\ln a_- \tag{3.3.7}$$

Usually Henry's law is taken as standard state for both type of ions. However, we cannot measure the activities of the ions separately as it is impossible to add one without adding the other. Nevertheless, we can derive a useful formalism that takes into account the dissociation process. If we substitute the last two equations in the ones above we get:

$$\nu_+\ln a_+ + \nu_-\ln a_- = \ln a_2 \tag{3.3.8}$$

Taking the exponent of either side of Equation 3.3.8, we get:

$$a_2 = a_+^{\nu_+} a_-^{\nu-} \tag{3.3.9}$$

Notice that the stoichiometric coefficients (Equation 3.3.1) are *exponents* in Equation 3.3.9. We now introduce the sum of the stoichiometric coefficients:

$$\nu_+ + \nu_- = \nu \tag{3.3.10}$$

and *define* the ***mean ionic activity*** $a_\pm$ as:

$$a_\pm^\nu \equiv a_2 = a_+^{\nu+} a_-^{\nu-}$$

**Note**

The mean ionic activity $a_\pm$ and the activity of the salt are closely related but the relationship involves *exponents* due to stoichiometric coefficients involved in the dissociation process. For example:

- For $Na_1Cl_1$: ν= 1+1 = **2**: $a_\pm{}^2 = a_{NaCl}$
- For $Al_2(SO_4)_3$: ν= 2+3 = **5**: $a_\pm{}^5 = a_{Al_2(SO_4)_3}$

## 3.3.2: Activity coefficients

All this remains a formality unless we find a way to relate it back to the concentration of the salt. Usually *molality* is used as a convenient concentration measure rather than molarity because we are dealing with pretty strong deviations from ideal behavior and that implies that volume may not be an additive quantity. Molality does not involve volume in contrast to molarity. Working with molalities, we can define activity coefficients for both ions, even though we have no hope to determine them separately:

$$a_+ = \gamma_+ m_+ \tag{3.3.11}$$

$$a_- = \gamma_- m_- \tag{3.3.12}$$

Stoichiometry dictates the molalities of the individual ions must be related to the ***molality of the salt*** $m$ by:

$$m_- = \nu_- m \tag{3.3.13}$$

$$m_+ = \nu_+ m \tag{3.3.14}$$

**Note**

We cannot measure the activities of the ions separately because it is impossible to add one without adding the other

Analogous to the mean ionic activity, we can define a **mean ionic molality** as:

$$m_\pm^\nu \equiv m_+^{\nu+} m_-^{\nu-} \tag{3.3.15}$$

We can do the same for the **mean ionic activity coefficient**:

$$\gamma_\pm^\nu = \gamma_+^{\nu+} \gamma_-^{\nu-} \tag{3.3.16}$$

Using this definitions we can rewrite:

$$a_2 = a_\pm^\nu = a_+^{\nu+} a_-^{\nu-} \tag{3.3.17}$$

as:

$$a_2 = a_\pm^\nu = \gamma_\pm^\nu m_\pm^\nu \tag{3.3.18}$$

**Note**

Note that when preparing a salt solution of molality $m$, we should ***substitute****:*

$$m_- = \nu_- m$$

$$m_+ = \nu_+ m$$

into:

$$m_\pm^\nu \equiv m_+^{\nu+} m_-^{\nu-}$$

**✓ Example 25.5.1: Aluminum Sulfate**

For $Al_2(SO_4)_3$ we get:

- $\nu = 2+3 = \mathbf{5}$
- $a_\pm{}^{\mathbf{5}} = a_{Al_2(SO_4)_3}$
- $m_- = 3m$
- $m_+ = 2m$

So:

$$m_\pm{}^{\nu} = m_+{}^{\nu_+} m_-{}^{\nu_-} = (2m)^2 (3m)^3 = \mathbf{108} m^{\mathbf{5}}$$

$$a_{Al_2(SO_4)_3} = a_\pm{}^{\mathbf{5}} = \mathbf{108} m^{\mathbf{5}} \gamma_\pm{}^5$$

> As you can see the stoichiometry enter *both* into the exponents *and* into the calculation of the molality. Notice that the activity of the salt now goes as the fifth power of its overall molality (on top of the dependency of $\gamma_\pm$ of exp(√m) as shown below).

## 3.3.3: Measuring mean ionic activity coefficients

In contrast to the individual coefficients, the ***mean ionic activity coefficient*** $\gamma_\pm$ is a quantity that ***can be determined***. In fact we can use the same Gibbs-Duhem trick we did for the sucrose problem to do so. We simply measure the water vapor pressure above the salt solution and use:

$$\ln \gamma_\pm = \varphi - 1 + \int_{m'=0}^{m} [\varphi - 1] m' \, dm'$$

The fact that the salt itself has a negligible vapor pressure does not matter. Particularly for ions with high charges, the deviations from ideality are very strong even at tiny concentrations. Admittedly doing these vapor pressure measurements in pretty tedious, there are some other procedures involving electrochemical potentials. However, they too are tedious.

---

# 3.4: The Debye-Hückel Theory

As ionic solutions are very common in chemistry, having to measure all activity coefficients ($\gamma_\pm$) for all possible solute-solvent combinations is a pretty daunting task, even though in times past extensive tabulation has taken place. We should be grateful for the rich legacy that our predecessors have left us in this respect (it would be hard to get any funding to do such tedious work today). Of course, it would be very desirable to be able to *calculate* $\gamma_\pm$ values from first principles or if that fails by semi-empirical means. Fortunately, considerable progress has been made on this front as well. We can only scratch the surface of that topic in this course and will briefly discuss the simplest approach due to Debye and Hückel

Debye and Hückel came up with a theoretical expression that makes is possible to predict mean ionic activity coefficients as *sufficiently* dilute concentrations. The theory considers the vicinity of each ion as an atmosphere-like cloud of charges of opposite sign that cancels out the charge of the central ion (Figure $3.4.1$). From a distance the cloud looks neutral. The quantity $1/\kappa$ is a measure for the size of this cloud and $\kappa$ is the ***Debye-length***. Its size depends on the concentration of all other ions.

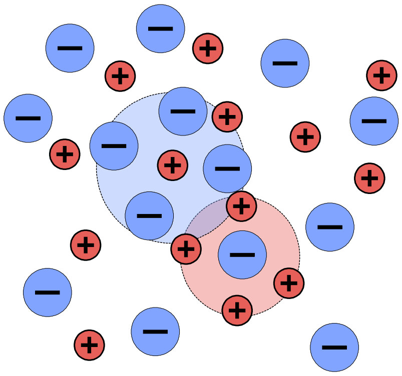

Figure $3.4.1$: An idealized representation of a solution of a 1:1 electrolyte. (CC BY-SA 3.0 unported; Roland1952 via Wikipedia)

## 3.4.1: Ionic Strength

To take the effect from all other ions into account, it is useful to define the ***ionic strength*** ($I$) as:

$$I = \frac{1}{2} \sum m_i z_i^2$$

where $m_i$ is the molality of ion $i$ and $z_i$ is its charge coefficient. Note that highly charged ions (e.g. $z = 3+$) contribute strongly (nine times more than +1 ions), but the formula is *linear* in the molality. Using the ionic strength the Debye-length becomes:

$$\kappa^2 = constant\, I$$

The constant contains $kT$ and $\varepsilon_r \varepsilon_o$ in the denominator and the number of Avogadro $N_A$ and the square of the charge of the electron $e$ in the numerator:

$$constant = 2000 \frac{e^2 N_A}{\varepsilon_r \varepsilon_o kT}$$

The Debye length and the logarithmic mean ionic activity coefficient are proportional:

$$\ln \gamma_\pm \propto \kappa$$

Again there are a number of factors in the proportionality constant:

$$\ln \gamma_\pm = -|q_+ q_-| \frac{\kappa}{8\pi \varepsilon_r \varepsilon_o kT}$$

**Note**

The factors $\varepsilon_r$ and $\varepsilon_o$ are the relative permittivity of the medium and the permittivity of vacuum, respectively. Note that the factor $8\pi\varepsilon_r\varepsilon_o$ is *specific* to the SI system of units. In cgs units the expression would look different, because the permittivities are defined differently in that system

If there is only one salt being dissolved, the ionic strength depends linearly on its concentration, the Debye length κ and $\ln \gamma_\pm$, therefore, go as the *square root of concentration* (usually molality):

$$\ln \gamma_\pm \propto \sqrt{m}$$

If there are other ions present the ionic strength involves *all* of them. This fact is sometimes used to keep ionic strength constant while changing the concentration of one particular ion. Say we wish to lower the concentration of $Cu^{2+}$ in a redox reaction but we want to keep activity coefficients the same as much as possible. We could then *replace* it by an ion of the same charge say $Zn^{2+}$ that does not partake in the reaction. A good way to do that is to dilute the copper solution with a zinc solution of the same concentration instead of with just solvent. The mean activity coefficient is given by the logarithm of this quantity as follows:

$$\log_{10} \gamma_\pm = -A z_j^2 \frac{\sqrt{I}}{1 + B a_0 \sqrt{I}} \tag{3.4.1}$$

with:

$$A = \frac{e^2 B}{2.303 \times 8\pi\epsilon_0\epsilon_r k_B T} \tag{3.4.2}$$

$$B = \left(\frac{2e^2 N}{\epsilon_0 \epsilon_r k_B T}\right)^{1/2} \tag{3.4.3}$$

where $I$ is the ionic strength and $a_0$ is a parameter that represents the distance of closest approach of ions. For aqueous solutions at 25 °C $A = 0.51\, mol^{-1}/2dm^{3/2}$ and $B = 3.29 nm^{-1} mol^{-1}/2dm^{3/2}$.

Unfortunately this theory only works at very low concentrations and is therefore also known as the **Debye limiting law** (Figure $3.4.2$). There are a number of refinements that aim at extending the range of validity of the theory to be able to work at somewhat higher concentrations. These are discussed in the next section.

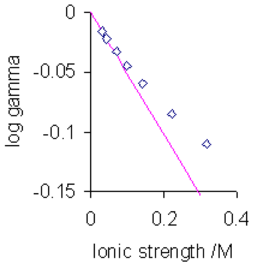

Figure $3.4.2$: Experimental $\log \gamma_\pm$ values for KBr at 25°C (points) and Debye–Hückel limiting law (coloured line) (Public Domain; Petergans via Wikipedia)

The most significant aspect of Equation 3.4.1 is the prediction that the mean activity coefficient is a function of *ionic strength* rather than the electrolyte concentration. For very low values of the ionic strength the value of the denominator in the expression above becomes nearly equal to one. In this situation the mean activity coefficient is proportional to the square root of the ionic strength.

### Importance for Colloids

When a solid is formed by a reaction from solution it is sometimes possible that it remains dispersed as very small particles in the solvent. The sizes typically range in the nanometers This is why it has become fashionable to call them *nanoparticles*, although they had been known as *colloidal particles* since the mid nineteenth century. They are smaller than the wavelength of the visible reason. This causes liquids that contain them to remain *clear*, although they can at times be beautifully colored. A good example is the reduction of $AuCl_4^-$ with citrate to metallic gold. This produces clear wine red solutions, even at tiny gold concentrations.

$$2\,\mathrm{nAuCl_4(aq)^-} + \mathrm{n\,citrate^{3-}(aq)} + 2\,\mathrm{n\,H_2O(l)} \rightarrow$$
$$2\,\mathrm{n\,Au(colloid)} + 3\,\mathrm{n\,CH_2O(aq)} + 3\,\mathrm{n\,CO_2(g)} + 8\,\mathrm{n\,Cl^-(aq)} + 3\,\mathrm{n\,H^+(aq)}$$

The reason the gold does not precipitate completely is typically that the nanoparticle (AuNP) formed during the reaction are *charged* by the attachment of some of the ionic species in solution to its surface. This results in an charged particle with an atmosphere with a certain Debye length around it (Figure $3.4.3$). This charged cloud prevents the particle form coalescing with other particles by electrostatic repulsion.

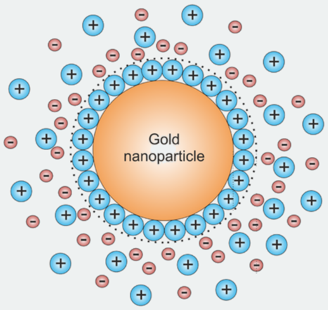

Figure $3.4.3$: Potential difference as a function of distance from gold nanoparticle surface. (CC-SA-BY-3.0; Larryisgood)

Such a system is called a ***colloid.*** Of course these systems are ***metastable***. Often they have a pretty small threshold to crashing to a real precipitate under influence of the strong van der Waals interactions that the particles experience once they manage to get in close contact. Under the right conditions colloids can survive for a long time. Some gold colloids prepared by Faraday in the 1850's are still stable today.

It will be clear from the above that addition of a salt -particularly containing highly charged ions like 3+ or 3-- may destabilize the colloid because the ionic strength will changed drastically and this will affect the Debye length.

---

# 3.5: Extending Debye-Hückel Theory to Higher Concentrations

The equation for $\log \gamma_{\pm}$ predicted from Debye–Hückel limiting law is:

$$\log_{10} \gamma_{\pm} = -A z_j^2 \frac{\sqrt{I}}{1 + B a_0 \sqrt{I}} \tag{3.5.1}$$

It gives satisfactory agreement with experimental measurements for low electrolyte concentrations, typically less than $10^{-3} mol/L$. Deviations from the theory occur at higher concentrations and with electrolytes that produce ions of higher charges, particularly asymmetrical electrolytes. These deviations occur because the model is oversimplified, so there is little to be gained by making small adjustments to the model. Instead, we must challenge the individual assumptions of the model:

- **Ions do not interact with each other**. Ion association may take place, particularly with ions of higher charge. This was followed up in detail by Niels Bjerrum. The Bjerrum length is the separation at which the electrostatic interaction between two ions is comparable in magnitude to $kT$.
- **Complete dissociation**. A weak electrolyte is one that is not fully dissociated. As such it has a dissociation constant. The dissociation constant can be used to calculate the extent of dissociation and hence, make the necessary correction needed to calculate activity coefficients.
- **Ions are spherical point charges that cannot be polarizable**. Ions, as all other atoms and molecules, have a finite size. Many ions, such as the nitrate ion $\mathrm{NO_3^-}$, are not spherical. Polyatomic ions are polarizable.
- **The solvent composition does not matter**. The solvent is not a structureless medium but is made up of molecules. The water molecules in aqueous solution are both dipolar and polarizable. Both cations and anions have a strong primary solvation shell and a weaker secondary solvation shell. Ion–solvent interactions are ignored in Debye–Hückel theory.
- **Ionic radius is negligible**. At higher concentrations, the ionic radius becomes comparable to the radius of the ionic atmosphere.

Most extensions to the Debye–Hückel theory are empirical in nature. They usually allow the Debye–Hückel equation to be followed at low concentration and add further terms in some power of the ionic strength to fit experimental observations. Several approaches have been proposed to extend the validity of the Debye–Hückel theory.

## 3.5.1: Extended Debye-Hückel Equation

One such approach is the Extended Debye-Hückel Equation:

$$-\log(\gamma) = \frac{A|z_+ z_-|\sqrt{I}}{1 + B a \sqrt{I}} \tag{3.5.2}$$

where $\gamma$ is the activity coefficient, $z$ is the integer charge of the ion $\mu$ is the ionic strength of the aqueous solution, and $a$, is the size or effective diameter of the ion in angstrom. The effective hydrated radius of the ion, $a$ is the radius of the ion and its closely bound water molecules. Large ions and less highly charged ions bind water less tightly and have smaller hydrated radii than smaller, more highly charged ions. Typical values are 3 Å for ions such as H+,Cl-,CN-, and HCOO-. The effective diameter for the hydronium ion is 9 Å. \ (A\) and $B$ are constants with values of respectively 0.5085 and 0.3281 at 25°C in water.

Other approaches include the Davies equation, Pitzer equations and specific ion interaction theory.

## 3.5.2: Davis Equation

The Davies equation is an empirical extension of Debye–Hückel theory which can be used to calculate activity coefficients of electrolyte solutions at relatively high concentrations at 25 °C. The equation, originally published in 1938, was refined by fitting to experimental data. The final form of the equation gives the mean molal activity coefficient f± of an electrolyte that dissociates into ions having charges z1 and z2 as a function of ionic strength I:

$$-\log f_{\pm} = 0.5 z_1 z_2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.30 I \right). \tag{3.5.3}$$

The second term, 0.30 $I$, goes to zero as the ionic strength goes to zero, so the equation reduces to the Debye–Hückel equation at low concentration. However, as concentration increases, the second term becomes increasingly important, so the Davies equation can be used for solutions too concentrated to allow the use of the Debye–Hückel equation. For 1:1 electrolytes the difference between measured values and those calculated with this equation is about 2% of the value for 0.1 M solutions. The calculations become less precise for electrolytes that dissociate into ions with higher charges. Further discrepancies will arise if there is association between the ions, with the formation of ion pairs, such as $\mathrm{Mg^{2+}SO_4^{2-}}$.

Plot of activity coefficients calculated using the Davies equation.

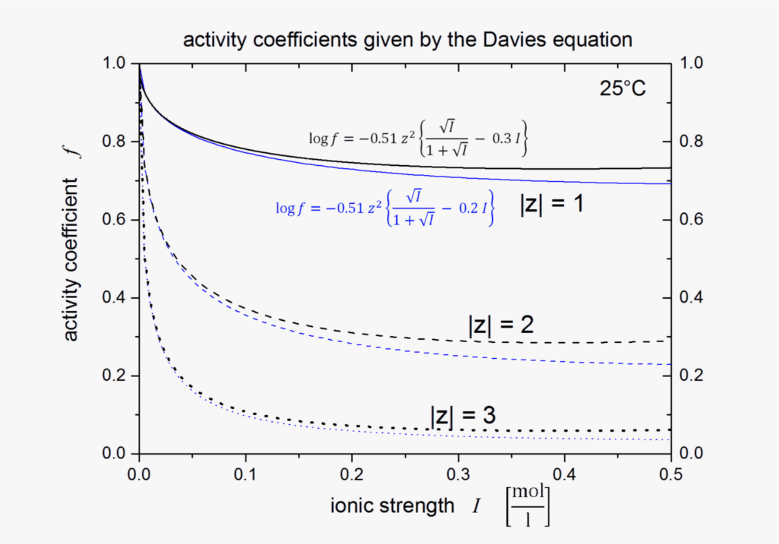

Figure 3.5.1: Semi-log plot of activity coefficients calculated using the Davies equation. (CC BY-SA 4.0; PChemiker via Wikipedia)

## 3.5.3: Pitzer Equations

Pitzer equations are important for the understanding of the behaviour of ions dissolved in natural waters such as rivers, lakes and sea-water. They were first described by physical chemist Kenneth Pitzer. The parameters of the Pitzer equations are linear combinations of parameters, of a virial expansion of the excess Gibbs free energy, which characterize interactions amongst ions and solvent. The derivation is thermodynamically rigorous at a given level of expansion. The parameters may be derived from various experimental data such as the osmotic coefficient, mixed ion activity coefficients, and salt solubility. They can be used to calculate mixed ion activity coefficients and water activities in solutions of high ionic strength for which the Debye–Hückel theory is no longer adequate.

An expression is obtained for the mean activity coefficient.

$$\ln \gamma_{\pm} = \frac{p \ln \gamma_M + q \ln \gamma_X}{p+q} \tag{3.5.4}$$

$$\ln \gamma_{\pm} = |z^+ z^-| f^{\gamma} + m \left( \frac{2pq}{p+q} \right) B^{\gamma}_{MX} + m^2 \left[ 2 \frac{(pq)^{3/2}}{p+q} \right] C^{\gamma}_{MX} \tag{3.5.5}$$

These equations were applied to an extensive range of experimental data at 25 °C with excellent agreement to about 6 mol kg−1 for various types of electrolyte. The treatment can be extended to mixed electrolytes and to include association equilibria. Values for the parameters β(0), β(1) and C for inorganic and organic acids, bases and salts have been tabulated. Temperature and pressure variation is also discussed.

## 3.5.4: Specific ion interaction theory

Specific ion Interaction Theory (SIT theory) is a theory used to estimate single-ion activity coefficients in electrolyte solutions at relatively high concentrations. It does so by taking into consideration interaction coefficients between the various ions present in solution. Interaction coefficients are determined from equilibrium constant values obtained with solutions at various ionic strengths. The determination of SIT interaction coefficients also yields the value of the equilibrium constant at infinite dilution.

The activity coefficient of the jth ion in solution is written as $\gamma_j$ when concentrations are on the molal concentration scale and as yj when concentrations are on the molar concentration scale. (The molality scale is preferred in thermodynamics because molal concentrations are independent of temperature). The basic idea of SIT theory is that the activity coefficient can be expressed as

$$\log \gamma_j = -z_j^2 \frac{0.51\sqrt{I}}{1+1.5\sqrt{I}} + \sum_k \epsilon_{jk} m_k \tag{3.5.6}$$

where z is the electrical charge on the ion, $I$ is the ionic strength, $\varepsilon$ and $b$ are interaction coefficients and $m$ are concentrations. The summation extends over the other ions present in solution, which includes the ions produced by the background electrolyte. The first term in these expressions comes from Debye-Hückel theory. The second term shows how the contributions from "interaction" are dependent on concentration. Thus, the interaction coefficients are used as corrections to Debye-Hückel theory when concentrations are higher than the region of validity of that theory.

---

## 3.6: Homework Problems

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region $\Delta x$; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position $\Delta x$ and the uncertainty in momentum $\Delta p$.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{3.6.1}$$

You can see from Equation 3.6.1 that as $\Delta p$ approaches 0, $\Delta x$ must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

### Exercise 3.6.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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