IV. Phase Equilibria and Non-Electrolyte Solutions

A. Phase equilibria

1. Introduction

We have concentrated so far on single-phase, one-component systems. We now consider multi-phase, one-component systems, mostly two-phase systems such as liquid-gas or solid-liquid systems. We use our just-developed apparatus involving the Gibbs free energy.

As already mentioned, the appearance of a well-defined surface is evidence for the establishment of a new phase. Sometimes, however, the same phase may appear fragmented in the system. Thus, a container with a few drops of water in equilibrium with water vapor is a two-phase system, even though the liquid phase is fragmented into drops. Similarly, several chunks of Dry Ice in equilibrium with carbon dioxide gas is a two-phase system, even though the solid carbon dioxide is fragmented into chunks. If surface effects are taken into account, it is found that there is a small, but often measurable difference in the equilibrium properties of drops of liquid or chunks of solid that have different surface areas.

It is also possible to have two different solids or liquids in the system. Thus, a mixture of sodium chloride and sucrose crystals is a two-phase system. Oil floating on water is a two-phase system (or three-phase if there is some vapor present).

2. Equilibrium between distinct phases

a. General

A fundamental rule about equilibrium between two distinct phases may be derived by consideration of the process,

\[ X(1) = X(2) \]

in which \( X(1) \) and \( X(2) \) are the same substance in two different phases. For example,

\[ \text{H}_2\text{O}(l) = \text{H}_2\text{O}(g) \]

We imagine an infinitesimal process in which, at equilibrium, \( d\xi \) moles of phase (1) of \( X \) becomes \( d\xi \) moles of phase (2) of \( X \). Then, for this process,

\[ dn_1 = -d\xi \quad \text{while} \quad dn_2 = d\xi \]

Now,

\[ dG(1) = \overline{G}(1)dn_1 = -\overline{G}(1)d\xi \]

and

\[ dG(2) = \overline{G}(2)dn_2 = +\overline{G}(2)d\xi \]
Therefore, 
\[ dG = dG(1) + dG(2) = (\overline{G}(2) - \overline{G}(1))d\xi \]

But, for an infinitesimal process away from equilibrium, \( dG = 0 \). Since \( d\xi \) is arbitrary (but small) and non-zero, it must be that \( \overline{G}(1) = \overline{G}(2) \). In words, the partial molar Gibbs free energy values must be equal for the same substance in two different phases in equilibrium with one another.

From expressions given above for \( d\overline{G} \),

\[-\bar{S}(1)dt + \bar{V}(1)dp = -\bar{S}(2)dt + \bar{V}(2)dp\]

or

\[ [\bar{S}(2) - \bar{S}(1)]dt = [\bar{V}(2) - \bar{V}(1)]dp \]

b. Liquid-vapor equilibria

For,

\[ X(l) = X(g) \]

we have just shown that

\[ [\bar{S}(g) - \bar{S}(l)]dt = [\bar{V}(g) - \bar{V}(l)]dp \]

Now,

\[ [\bar{V}(g) - \bar{V}(l)] \equiv \bar{V}(g) \]

because the molar volume of the liquid form of a substance is so much smaller than the volume of the gaseous form of the substance at ordinary pressures.

Also, from before,

\[ \bar{S}(g) - \bar{S}(l) = \frac{\Delta H_{vap}}{T} \quad (\Delta H_{vap} = \text{enthalpy of vaporization}) \]

Therefore, for a vapor that is an ideal gas,

\[ \Delta H_{vap} \frac{dT}{T} = \bar{V}(g)dp = RT \frac{dp}{p} \]

or

\[ \Delta H_{vap} \frac{dT}{T^2} = R \frac{dp}{p} \]

We integrate both sides of this equation between state 1 where \( T = T_1 \) and \( V = V_1 \), and state 2 where \( T = T_2 \) and \( V = V_2 \). If the enthalpy of vaporization is assumed constant between the two temperatures (a good approximation, if the temperatures are not too different), the result is
\[
\Delta H_{vap} \left[ -\frac{1}{T_2} + \frac{1}{T_1} \right] = R \left[ \ln p_2 - \ln p_1 \right]
\]
or
\[
\ln \left( \frac{p_2}{p_1} \right) = \frac{\Delta H_{vap}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]
which is known as the Clausius-Clapeyron equation. This equation can also be written

\[
\ln p = -\frac{\Delta H_{vap}}{R} \left( \frac{1}{T} \right) + C
\]

where \( C \) is an integration constant. This form of the equation shows that if the logarithm of the equilibrium vapor pressure of a liquid is plotted on the \( y \) axis and \( T^{-1} \) is plotted on the \( x \) axis, the slope of the plot is \(-\Delta H_{vap} / R\). This is a practical way to measure the enthalpy of vaporization.

For example, the following is a plot of \( \ln p \) vs. \( T^{-1} \) for water vapor.

\[c. \quad \text{Equilibrium between two condensed phases}\]

For \( X(s) = X(l) \) at equilibrium at constant temperature and pressure,

\[ d\bar{G}(s) = d\bar{G}(l) \]
for an infinitesimal process away from equilibrium. Therefore,

\[
\left[ S(l) - S(s) \right]dT = \left[ V(l) - V(s) \right]dp
\]

or

\[
\frac{\Delta H_{\text{fus}}}{T}dT = \Delta V dp \quad \text{where} \quad \Delta V = V(l) - V(s)
\]

If \( \Delta H_{\text{fus}} \) and \( \Delta V \) are assumed to be independent of \( T \) and \( p \),

\[
\frac{dp}{dT} = \frac{\Delta H_{\text{fus}}}{T\Delta V}
\]

which is known as the Clapeyron equation.

An interesting and unusual example of the Clapeyron equation involves water, for which the densities of the liquid and solid are

\[
\rho(\text{H}_2\text{O}(l)) = 1.000 \text{ g cm}^{-3} \quad \text{and} \quad \rho(\text{H}_2\text{O}(s)) = 0.917 \text{ g cm}^{-3}
\]

so that

\[
\Delta V = V(l) - V(s) = \frac{18.015 \text{ g mol}^{-1}}{1.000 \text{ g cm}^{-3}} - \frac{18.015 \text{ g mol}^{-1}}{0.917 \text{ g cm}^{-3}} = -1.631 \text{ cm}^3 \text{ mol}^{-1}
\]

An interesting feature is that water is unusual in that it is one of a small number of liquids for which \( \Delta V = V(l) - V(s) \) is negative. This leads to a negative value for \( dp/dT \), which means that the melting point of water decreases with increasing pressure, in contrast to most substances for which the melting point increases with increasing pressure.

Insertion of the value for the enthalpy of fusion leads to

\[
\frac{dp}{dT} = \frac{\Delta H_{\text{fus}}}{T\Delta V} = \frac{7080 \text{ J mol}^{-1}}{(273.15 \text{ K})(-1.613 \text{ cm}^3 \text{ mol}^{-1})} = -159 \text{ J K}^{-1} \text{ cm}^{-3}
\]

\[
= -1.59 \times 10^7 \text{ J K}^{-1} \text{ m}^{-3} = -1.59 \times 10^7 \text{ Pa K}^{-1} = -157 \text{ atm K}^{-1}
\]

Another interesting feature is that it requires application of 157 atm pressure to decrease the melting point of water by 1 °C.

3. \textit{Phase diagrams for one-component systems}

One form of a phase diagram for a system that contains only one substance consists of plots of the equilibrium vapor pressure for the solid and liquid forms of the substance vs. temperature as
well as a plot of the equilibrium pressure vs. melting point of the solid. A rough drawing for water is as follows:

The three solid lines in the diagram meet at a point called the **triple point**, at which all three phases exist in equilibrium. For water, the triple point occurs at 0.01 °C and 4.6 Torr.

The lines in the phase diagram divide the temperature-pressure plot into three regions. If the system is at a pressure and temperature that intersect in one of the regions, the system will exist in a single phase. This is compatible with the Gibbs phase rule mentioned earlier, which says that the number of degrees of freedom \((F)\) is related to the number of components \((C)\) and the number of phases \((P)\), as follows:

\[
F = C - P + 2
\]

In a one-phase, one-component system, there are 2 degrees of freedom \((F = 2)\), which are the temperature and the pressure in our phase diagram. For example, at point \(A\) in the diagram, the system consists of solid water (ice). There are two degrees of freedom in the sense that the pressure and the temperature can be adjusted independently, within reason, and the system will still consist of solid water.

By contrast, at point \(B\) on the solid-liquid line, the system consists of two phases: solid and liquid water. At this point, in order to maintain a two-phase system in equilibrium, the pressure and temperature can not be varied independently, because they have to be varied in such a way that their intersection lies on the solid-liquid line. A choice of one of these variables determines the other. This is consistent with the Gibbs phase rule, which says that a two-phase, one-component system has only one degree of freedom.

At the triple point, three phases - solid, liquid, and gas - are all in equilibrium. The Gibbs phase rule predicts that for \(P = 3\), \(C = 1\), \(F = 0\). There are no degrees of freedom, which is consistent with the triple point being a single point on the diagram.

If the sample is heated at constant pressure starting at the point \(A\) in the diagram and the temperature is monitored for constant rate of heat input, a *melting-point diagram* is produced.
This is the opposite of the *cooling curve* shown in the Atkins text. A melting point diagram may appear as follows:

![Melting Point Diagram](image)

At first the constant rate of heat input raises the temperature of the solid almost linearly. At the fusion temperature $T_f$ the temperature rise ceases while the heat input supplies the heat of fusion to melt the solid. After the solid is all melted, the temperature rises nearly linearly again until the vaporization temperature $D$ is reached. At this point the temperature rise stops again while the heat input supplies the heat of vaporization to vaporize the liquid. Finally, when all of the liquid is vaporized, the temperature again begins its nearly linear rise. The slopes of the linear portions of the curve are related to the heat capacities of the different phases of the substance. For water, the specific heat of ice (2.1 J K$^{-1}$ g$^{-1}$) and water vapor (2.0 J K$^{-1}$ g$^{-1}$) are about the same and about half that of liquid water (4.2 J K$^{-1}$ g$^{-1}$). The lengths of the flat portions of the diagram are directly proportional to the values of the heat of fusion and the heat of vaporization. The enthalpy of vaporization of water (40,656 J K$^{-1}$ mol$^{-1}$) at the normal boiling point is almost seven times the enthalpy of fusion of water (6,008 J K$^{-1}$ mol$^{-1}$) at the normal freezing point.

The *normal boiling point* is the temperature at which the equilibrium vapor pressure of the liquid is equal to 1 atm, while the *normal freezing point* is the temperature at which the liquid freezes at 1 atm pressure. Finally, the critical point is the highest temperature and pressure point on the liquid-vapor line. As mentioned earlier, the critical temperature is the highest temperature at which the substance can be liquified by the application of pressure. The equilibrium vapor pressure of the liquid at the critical temperature is the critical pressure.

The slope of the liquid-solid line for water was calculated above to be -157 atm K$^{-1}$. The fact that this number is negative, which has profound consequences for life on earth, is a result of the fact that ice has a lower density than liquid water. A much more common behavior for liquid and solid forms of the same substance is for the solid to have the greater density. When this is the case, the liquid-solid line has a positive slope. An example is CO$_2$, whose phase diagram looks roughly like the following:
An unusual characteristic of this phase diagram is that the triple point occurs at a pressure that is greater than one bar. As a consequence, observation of liquid carbon dioxide is rather rare. At usual atmospheric temperatures and pressures, solid carbon dioxide converts directly to gaseous carbon dioxide; it *sublimes*. The liquid can exist only at pressures above 5.11 bar, the triple-point pressure. The normal sublimation temperature, at which the equilibrium vapor pressure of the solid is 1 bar, is 194.7 K, which is −78.5 °C.

**B. Non-electrolyte solutions: concentrations**

1. **Molarity**

The *molar concentration*, or *molarity*, of a substance is the number of moles of the substance in one liter (1 L = 1 dm³) of solution. Molarity is symbolized by placing the name or symbol for the substance between square brackets. Thus, \([\text{NaCl}]\) is the molarity of NaCl, usually, but not always, in water. Thus,

\[
[X] = \frac{n_X}{V_{\text{solution}}}
\]

in which \(n_X\) is the number of moles of substance X in a sample of the solution whose volume in liters is \(V_{\text{solution}}\). The molarity is also symbolized by writing the numerical value of the molarity followed by \(M\). For example, if 90 g of glucose (molar mass = 180) is dissolved in 2.0 L of water,

\[
[\text{glucose}] = \frac{0.5 \text{ mol}}{2.0 \text{ L}} = 0.25 \text{ mol L}^{-1} = 0.25 \text{ M}
\]

Molarity, or moles per liter, is a concentration expressed as an amount of substance per unit volume. This is a very useful construct, especially for theoretical purposes. Unfortunately, because the volumes of substances change when the temperature changes, the molarity of a solution is temperature dependent. For precise work, a small change in the temperature can alter the molarity significantly.
2. **Molality**

To provide a temperature-independent concentration unit, the *molality* was invented. The molality is defined as

\[ m_X = \frac{n_X}{M_{\text{solvent}}} \]

where \( n_X \) is the number of moles of \( X \) in the solution and \( M_{\text{solvent}} \) is the mass of the solvent in kg. The symbol for molality is usually \( m \). Thus, a solution of 1.0 mol sucrose in 2.0 kg of water is 0.5 \( m \).

Conversion between molarity and molality requires information about the density of the solution. The two quantities are almost equal for very dilute water solutions. For example, a solution of NaCl that is 0.01709 M is 0.01713 \( m \). To see how this works, we assume a solution of 1.000 g NaCl (mol. mass = 58.44 g mol\(^{-1}\)) in 999.0 g of water. This solution has a density of 0.9989 g cm\(^{-3}\) (according to the Handbook of Chemistry and Physics), which is 0.9989 kg L\(^{-1}\). Then,

\[ n_{\text{NaCl}} = 1.000 \text{ g/58.44 g mol}\(^{-1}\) = 0.01711 \text{ mol} \]

\[ m_{\text{NaCl}} = 0.01711 \text{ mol solute/0.999 kg solvent} = 0.01713 \text{ mol kg}\(^{-1}\) \]

1.000 kg of solution = 1.000 kg/0.9989 kg L\(^{-1}\) = 1.0011 L

so that \( M_{\text{NaCl}} = 0.01711 \text{ mol solute/1.0011 L solution} = 0.01709 \text{ mol L}\(^{-1}\) \)

For more concentrated solutions, the values of the molarity and the molality can be rather different. For example, 5% by weight NaCl solution has a density of 1.0340 g cm\(^{-3}\) (Handbook of Chemistry and Physics). For this solution, \( m = 0.9006 \text{ mol kg}\(^{-1}\) \) and \( M = 0.8847 \text{ mol L}\(^{-1}\) .

3. **Mole fraction**

The concentration unit known as the *mole fraction* is defined as follows:

\[ x_A = \frac{n_A}{n} \]

Here, \( x_A \) is the mole fraction of component \( A \) in the solution, \( n_A \) is the number of moles of \( A \) in a sample of solution containing \( n \) total moles of all of the components. We will see that the mole fraction is very useful in the discussion of non-electrolyte solutions, i.e., solutions that do not conduct electricity. It is worth noting that the mole fraction is also the particle fraction; it is the fractional number of particles in the solution of a given type.

An important property of mole fraction solution concentrations is that the sum of the mole fractions of all of the components in solution is one. Thus, if
\[ x_i = \frac{n_i}{n} \quad \text{and} \quad n = \sum_i n_i \quad \text{then} \quad \sum_i x_i = 1 \]

In particular, for a binary solution of the substances A and B,

\[ x_A = \frac{n_A}{n_A + n_B} ; x_B = \frac{n_B}{n_A + n_B} ; x_A + x_B = 1 \]

C. Non-electrolyte solutions: thermodynamics

1. Chemical potentials in different phases

The partial molar Gibbs free energy of substance \( i \) in a solution is known as the chemical potential (\( \mu_i \)) of substance \( i \); i.e.,

\[ \mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n'} = \overline{G}_i \]

To see why this is called the chemical potential, we imagine two systems (A and B) that can exchange particles. We imagine that \( dn \) particles of substance \( i \) are transferred from A to B. Then,

\[ dn_i^A = -dn \quad , \quad dn_i^B = +dn \quad , \]

\[ dG_A = \left( \frac{\partial G_A}{\partial n_i} \right)_{T,P,n'} \quad dn_i^A = \mu_i^A (-dn) \quad , \]

and

\[ dG_B = \left( \frac{\partial G_B}{\partial n_i} \right)_{T,P,n'} \quad dn_i^B = \mu_i^B (+dn) \quad , \]

so that

\[ dG = dG_A + dG_B = (\mu_i^B - \mu_i^A)dn \]

Now, we assume \( dn > 0 \), and consider three possibilities:

a) \[ \mu_i^B < \mu_i^A \]

Then, \( dG < 0 \) and the transfer of \( dn \) moles of substance \( i \) from system A to system B is spontaneous. Substance \( i \) moves from a system of higher chemical potential (system A) to a system of lower chemical potential (system B) (we assumed \( \mu_i^B < \mu_i^A \)).
b) \( \mu^B_i > \mu^A_i \)

Then, \( dG > 0 \) and the transfer of \( dN \) moles of substance \( i \) from system \( A \) to system \( B \) is forbidden. Apparently, substance \( i \) cannot go uphill in chemical potential.

c) \( \mu^B_i = \mu^A_i \)

Then, \( dG = 0 \), which means that system \( A \) and system \( B \) are in equilibrium with respect to substance \( i \).

The conclusion is that the chemical potential is similar to a mechanical potential in the sense that molecules tend to move from regions of high chemical potential to regions of low chemical potential. And, regions with the same chemical potential for a substance are in equilibrium for that substance.

If \( \mu^B_i = \mu^A_i \) for all \( i \), then systems \( A \) and \( B \) are in complete thermodynamic equilibrium. (All of the preceding discussion is for constant temperature and pressure.)

2. Chemical potentials in the gas phase

In part III of these notes we showed that the Gibbs free energy per mole for a pure gas obeys the following relation:

\[
\bar{G} - \bar{G}^o = RT \ln \left( \frac{p}{p^o} \right) = RT \ln(a), \quad \text{where} \quad a = \frac{p}{p^o}
\]

Here, \( p \) is the pressure of the gas and \( p^o \) is the pressure of the gas in its standard state, usually taken to be 1 bar. The ratio of these two pressures, \( a \), is called the activity of the gas in the state of interest. It turns out that for an ideal gas mixture, these equations hold for each component gas in the mixture if we take the gas pressures to be partial pressures. Thus,

\[
\bar{G}_i - \bar{G}_i^o = RT \ln \left( \frac{p_i}{p_i^o} \right) = RT \ln(a_i), \quad \text{where} \quad a_i = \frac{p_i}{p_i^o}
\]

In addition, \( \bar{G}_i = \mu_i \) and \( \bar{G}_i^o = \mu_i^o \), so

\[
\mu_i - \mu_i^o = RT \ln \left( \frac{p_i}{p_i^o} \right) = RT \ln(a_i)
\]

We will use this equation, or one like it, repeatedly, so it would be well to pay particular attention to its structure. Note, especially, that in the state in which the partial pressure of the gas is \( p_i \) the
chemical potential of the gas is $\mu_i$, while in the state in which the partial pressure of the gas is $p_i^0$ the chemical potential of the gas is $\mu_i^0$.

The units for the chemical potential (partial molar Gibbs free energy or Gibbs free energy per mole) are energy/mole, usually kJ mol$^{-1}$. By contrast, the activity is unitless, since it is a ratio of pressures. Sometimes, the activity of a gas in a gas mixture will be said to be its partial pressure in bar. What is meant by this is that the activity of the gas is the numerical value of its pressure in bar. This is because the standard pressure is usually 1 bar and division of a pressure in bar by 1 bar simply strips the pressure of its units.

For real gases, all of the equations above hold if the partial pressures are replaced by fugacities. Therefore, strictly speaking, the activity of a gas in a gas mixture is the ratio of its fugacity in the mixture to its fugacity in its standard state (usually again taken to be 1 bar). There exist well-defined ways of determining the fugacities of gases in various situations, but for this course, we will always assume ideal gases, in which case the fugacity is just equal to the partial pressure.

### 3. Chemical potentials in condensed phases

For a substance with a measurable vapor pressure, we can relate the chemical potential in a condensed phase, such as a liquid solution, to the chemical potential in the gas phase. We showed earlier that for two phases at equilibrium, the chemical potential of a substance in one phase must be the same as the chemical potential of the substance in the other phase. Thus, we would conclude that the chemical potential of a vapor in equilibrium with a solution is the same as the chemical potential of the substance in the solution.

There are two common conventions for the choice of standard state for substances in solution, neither of which is equivalent to the choice for pure gases. One of these is chosen for substances in high concentration, while the other is chosen for substances in low concentration. So, one of these conventions is referred to as the **solvent standard state**, while the other is referred to as the **solute standard state**.

**a) Solvent standard state**

In the **solvent standard state** convention, the standard state of the component in the solution is taken to be the pure component. In this case the activity of the substance becomes

$$a_A = \frac{p_A}{p_A^*}$$

Here, $p_A$ is the equilibrium partial vapor pressure of substance $A$ over the solution and $p_A^*$ is the equilibrium partial vapor pressure of substance $A$ when pure. In this case,

$$\mu_A = \mu_A^* + RT \ln a_A$$
where $\mu_A$ is the chemical potential of substance $A$ in the solution and $\mu_A^*$ is the chemical potential of pure $A$. The activity of $A$ in the solution is $a_A$.

The difference in chemical potential of $A$ in the solvent and gas phase standard states is given by the expression

$$\mu_A^* - \mu_A^o = RT \ln \frac{p_A^*}{p_A^o}$$

There are at least two reasons for the choice of pure liquid for the standard state for the solvent in a solution. One is that the solvent concentration is often near the concentration when pure, in which case the difference between $\mu_A$ and $\mu_A^*$ is not large. The other reason is that for many solutions, Raoult’s law holds for the solvent. This law states in words:

*The vapor pressure of a component in a solution is equal to the product of the vapor pressure of the substance when pure and the mole fraction of the substance in the solution.*

The mathematical statement of Raoult’s Law is

$$p_A = x_A p_A^*$$

From the form of this expression, one can see that the activity of a substance that obeys this law is equal to the mole fraction of the substance in the solution, if the solvent standard state is assumed. Thus, for the solvent standard state, $a_A = x_A$ for any substance that obeys Raoult's Law.

Raoult’s Law holds for many solvents in dilute solutions. In fact, it is believed that for every solvent in sufficiently dilute solution, Raoult's Law is valid. It turns out that Raoult's Law also holds approximately across the entire range of composition for all of the components of solutions of chemically related species. This gives rise to the concept of an *ideal solution*, which is defined to be a solution in which Raoult's Law is valid for all substances for all concentrations. As an example, solutions of benzene in toluene are almost ideal.
In this diagram the partial vapor pressures of benzene and toluene are shown as a function of composition as dashed lines. The (straight) liquid line is a plot of the total vapor pressure over the solution as a function of composition of the liquid, while the (curved) vapor line is a plot of the total pressure of the vapor as a function of the composition of the vapor. Straight lines for the plots of partial and total vapor pressure as a function of composition of the liquid are hallmarks of Raoult's Law.

b) **Solute standard state**

The nature of a solute standard state is suggested by the existence of Henry's Law, which relates the partial vapor pressure of a solute in dilute solution to the mole fraction of the solute. In words, Henry's Law says:

*The partial vapor pressure of a solute over a dilute solution is directly proportional to the mole fraction of the solute. The proportionality constant, known as the Henry's Law constant, depends on both the solute and the solvent.*

The mathematical statement of Henry's law is

$$p_B = x_B K_B$$

Here, $p_B$ is the partial vapor pressure of substance $B$ over a solution in which $x_B$ is the mole fraction of $B$. The constant $K_B$ is the Henry's Law constant. There is a superficial resemblance of Henry's Law to Raoult's Law, but there is an important difference: the Henry's Law constant is normally not equal to the partial vapor pressure of pure B.
There is an alternate form of Henry's Law that is commonly used for solutions of gases in liquids. This new form depends on the fact that in very dilute solution the molality of a substance and the mole fraction are almost proportional to one another. The alternate form is

\[ p_B = m_B K'_B \]

where \( m_B \) is the molality (moles of solute per kilogram of solvent) and \( K'_B \) is a modified Henry's Law constant that may be shown to be related to the original constant, as follows:

\[ K'_B = K_B \frac{M_A}{1000 \text{ g/kg}} \]

where \( M_A \) is the molar mass of the solvent in g/mol.

As an example of the use of the alternate form, we calculate the solubility of \( N_2 \) in water at 298 K in air. The modified Henry's Law constant is 1610 atm mol\(^{-1}\) kg and the pressure of \( N_2 \) in air is 0.78 atm.

\[ m_{N_2} = \frac{p_{N_2}}{K'_B} = \frac{0.78 \text{ atm}}{1610 \text{ atm mol}^{-1} \text{ kg}} = 4.8 \times 10^{-4} \text{ mol kg}^{-1} \]

In the solute standard state, the activity of the solute \( B \) is given by

\[ a_B = \frac{p_B}{K_B} \]

so that for a substance that obey's Henry's Law, \( a_B = x_B \); i.e., the activity is the mole fraction.

The Henry's Law constant has units of pressure, so the activity is still unitless. The partial vapor pressure and the Henry's Law constant must be expressed in the same units, however.

It is possible to provide a simple explanation for the fact that the Henry's law constant and the vapor pressure of the pure solute are different, i.e., a rationale for the difference between Henry's law and Raoult's Law. In a dilute solution, most of the interactions are solvent-solvent with only an occasional solvent-solute interaction. For this reason, Raoult's Law for the solvent is independent of the solute; only the solvent matters. By contrast, the solute molecules in dilute solution are almost surrounded by solvent molecules. Therefore, the Henry's Law constant is indicative of solute-solvent interaction and the Henry's Law constant for a given solute depends strongly on both the solute and the solvent.
c) *Vapor pressure diagrams*

As an example, we consider solutions of acetone and chloroform, for which the *vapor pressure diagram* appears, as follows:

In this plot of the pressure of the vapor at equilibrium over the solution it is apparent that for both substituents the Henry’s Law constant $K$ is smaller than the vapor pressure of the pure component. This is the case of *negative deviations from Raoult’s law*.

Solutions of acetone in carbon disulfide show positive deviations from Raoult's Law, as follows:

The vapor in equilibrium with a binary solution normally has a different composition from that of the liquid, even if the solution is ideal. The only exception would be if the two components of the solution have the same vapor pressure when pure. If we let $y_A$ and $y_B$ be the mole fractions of $A$ and $B$ in the vapor over the solution, then we can develop the following sequence of expressions:
Then, 

\[ y_A = \frac{p_A}{p} = x_A \frac{p_A^*}{p} \quad \text{and} \quad y_B = \frac{p_B}{p} = x_B \frac{p_B^*}{p} \]

d) Activity coefficients

At intermediate concentrations, in many cases neither Raoult’s Law nor Henry’s Law holds for either the solvent or solute. In these cases, if the solvent standard state is assumed, the activity is determined by the vapor pressure, as before, but is not equal to the mole fraction. It is the product of the mole fraction and a quantity called the activity coefficient \( \gamma_A \), as follows:

\[ a_A = \frac{p_A}{p_A^*} = \gamma_A x_A \]

If the solute standard state is assumed, the activity expression is as follows:

\[ a_B = \frac{p_B}{K_B} = \gamma_B x_B \]

In some applications of the solute standard state the activity is related to the molality, as follows:

\[ a_B = \frac{p_B}{K_B} = \gamma_B' m_B \]

It is important to realize that all of the activity coefficients, \( \gamma_A \), \( \gamma_B \), and \( \gamma_B' \), are different, even for the same substance in the same solution.

4. Activities: summary

We have thus far considered activities for a variety of chemical systems. In general the activity of a component in a chemical system is the ratio of the vapor pressure (or more precisely, the fugacity) of the substance to its vapor pressure (or fugacity) in its standard state. Two rules about activities in general are as follows:

i) The chemical potential of a substance increases as the activity of the substance increases.

ii) The activity of a substance in its standard state is 1.

A summary of standard states and activities developed so far is as follows (for the following, the gases (or vapors) are assumed ideal; if they are not, the pressures should be replaced with fugacities):
a)  \textit{Gases}

For gases, the standard state is the hypothetical state in which the gas behaves ideally at 1 bar pressure. For ideal gases, it is the gas at 1 bar pressure. The activity of a substance $X$ in the gas phase is then

$$a_X = \frac{p_X}{1 \text{ bar}}$$

where $p_X$ is the partial pressure of $X$ in the gas mixture.

b)  \textit{Pure liquids and solids}

The standard states of pure liquids and solids are the pure liquid or pure solid at 1 bar pressure. Since it is very difficult to change the chemical potential of a pure liquid or solid by application of pressure, for most situations, the activity of a pure liquid or pure solid may be taken to be 1. If it is necessary to obtain a more precise activity for a pure liquid or solid, equations given earlier show how to calculate the change in chemical potential that results from application of a pressure other than 1 bar. The calculated change in chemical potential can be set equal to $RT \ln a$ and the activity calculated.

c)  \textit{Solutions: solvent standard state}

The solvent standard state for a component (not necessarily just the solvent) of a solution is the pure component at 1 bar pressure. If the vapor pressure of the pure component $A$ is $p_A^*$ and the vapor pressure of $A$ above the solution is $p_A$, then the activity of $A$ in the solution is

$$a_A = \frac{p_A}{p_A^*} = \gamma_A x_A$$

If component $A$ obeys Raoult's Law, then the activity coefficient $\gamma_A = 1$.

d)  \textit{Solutions: solute standard state}

The standard state for a component of a solution that is referred to the solute standard state is the hypothetical state in which the pure component has an equilibrium vapor pressure equal to the Henry's Law constant. If this constant is $K_B$ for substance $B$ in the particular solvent (we recall that $K_B$ depends on both solute and solvent), and if the equilibrium vapor pressure of $B$ over the solution is $p_B$, then the activity of $B$ is

$$a_B = \frac{p_B}{K_B} = \gamma_B x_B$$
If component $B$ obeys Henry’s Law, then the activity coefficient $\gamma_B = 1$.

5. Colligative properties

The colligative properties are properties of solutions of non-volatile solutes in volatile solvents (non-volatile means very low vapor pressure, while volatile means at least moderate vapor pressure). The colligative properties for a given solvent depend only on the concentration of the solute and not on the nature of the solute. This characteristic can be exploited to learn something about the solute. Most commonly, it is used to determine the molecular mass of the solute. The colligative properties that we will discuss include the vapor pressure lowering, the boiling point elevation, the freezing point depression, and the osmotic pressure.

a) Vapor pressure lowering

Consider a solution of a non-volatile solute ($p_B^* \equiv 0$) in a volatile solvent. Then,

$$p = x_A p_A^* + x_B p_B^* \equiv x_A p_A^* = (1 - x_B) p_A^*$$

Therefore,

$$\Delta p = (p_A^* - p) \equiv x_B p_A^* = \text{vapor pressure lowering.}$$

The vapor pressure lowering is apparently proportional to the mole fraction of the solute (no matter what it is, as long as it is non-volatile). And, the proportionality constant ($p_A^*$) depends only on the solvent.

b) Boiling point elevation

The boiling point elevation is the boiling point of a solution minus the boiling point of the pure solvent at the same applied pressure. We can show that

$$\Delta T_b \equiv (T_b - T_b^0) = K_b m_B$$

where $\Delta T_b$ is the boiling point elevation, $T_b$ is the boiling point of the solution, $T_b^0$ is the boiling point of the pure solvent, $K_b$ is the boiling point elevation constant (ebullioscopic constant), which depends only on the solvent, and $m_B$ is the molality of the solute $B$. Apparently, the elevation of the boiling point depends only on the concentration of the solute and not on the identity of the solute. By measurement of the boiling point of the pure solvent and the boiling point of the solution, the molality of the solution can be determined. Usually the measurement of the two boiling points is made with the same thermometer, because the difference may not be large. Then, even if the thermometer is not absolutely precise, it may be sufficiently accurate to record differences to high precision.

A proof of the boiling point elevation expression may be made, as follows:
The **boiling point** of a solution is the temperature at which the equilibrium vapor pressure of the solution is equal to the applied pressure. If the applied pressure is 1 bar, then we have the so-called **normal boiling point** at which the equilibrium vapor pressure is 1 bar, which is the pressure in the standard state of the gas. Therefore, at the normal boiling point for the pure liquid \( T_b^o \),

\[
\mu^o\left(A(g), T_b^o\right) = \mu^o\left(A(l), T_b^o\right)
\]

while at the normal boiling point \( T_b \) for the solution (assumed ideal),

\[
\mu^o\left(A(g), T_b\right) = \mu^o\left(A(l), T_b\right) + RT_b \ln x_A
\]

If we subtract the first equation from the second, we get

\[
\mu^o\left(A(g), T_b\right) - \mu^o\left(A(g), T_b^o\right) = \mu^o\left(A(l), T_b\right) - \mu^o\left(A(l), T_b^o\right) + RT_b \ln x_A
\]

From the result obtained in part III of these lecture notes,

\[
\left(\frac{\partial \bar{G}}{\partial T}\right)_p = -\bar{S}
\]

and the fact that the partial molar Gibbs free energy is the chemical potential, we can show that

\[
\mu^o\left(A(g), T_b\right) - \mu^o\left(A(g), T_b^o\right) = -\bar{S}_A^o\left(g\right)\left(T_b - T_b^o\right)
\]

To derive this equation, it is necessary to assume that the entropy does not vary significantly between the two temperatures. A similar equation can be derived for the difference in chemical potentials of the liquid. With these two expressions in the equation above, we obtain

\[
-\bar{S}_A^o\left(g\right)\left(T_b - T_b^o\right) = -\bar{S}_A^o\left(l\right)\left(T_b - T_b^o\right) + RT_b \ln x_A
\]

Now, we showed earlier that

\[
\bar{S}_A^o\left(g\right) - \bar{S}_A^o\left(l\right) = \frac{\Delta H_{vap}}{T_b^o}
\]

where \( \Delta H_{vap} \) is the enthalpy of vaporization. So,
\[ \ln x_A = - \frac{\Delta \bar{H}_{vap}}{R} \left( \frac{T_b - T_b^o}{T_b T_b^o} \right) \equiv - \frac{\Delta \bar{H}_{vap}}{R T_b^o} \Delta T_b \]

In the last equality we have made use of the fact that the boiling points of the pure solvent and the solution are not much different. The next step is to realize that

\[ \ln x_A = \ln(1 - x_B) \equiv -x_B \]

where the last equality makes use of the fact that \( x_B \ll 1 \) for a dilute solution. Also, for a dilute solution,

\[ x_B = \frac{n_B}{n_A + n_B} \equiv \frac{n_B}{n_A} = \frac{n_B}{W_A / M_A} = n_B \frac{M_A / 1000}{W_A / 1000} \]

In this equation \( n_A \) and \( n_B \) are the numbers of moles of \( A \) and \( B \), respectively, and \( W_A \) and \( M_A \) are the number of grams of \( A \) in the solution and the molecular mass of \( A \), respectively.

Now, \( \frac{n_B}{W_A / 1000} = m_B \) the molality of \( B \).

If we put all of this together, we find

\[ \Delta T_b = \frac{RT_b^o}{1000 \Delta \bar{H}_{vap}} \frac{M_A}{m_B} = K_b m_B \]

where

\[ K_b = \frac{RT_b^o}{1000 \Delta \bar{H}_{vap}} = \frac{RT_b^o}{1000 \Delta h_{vap}} \]

in which \( \Delta h_{vap} \) is the enthalpy of vaporization of the solvent per gram. These equations can be used to calculate the boiling point elevation constant if desired. Many workers prefer, however, to determine the constant empirically by measuring the boiling point of the pure solvent and the boiling points of several solutions of different concentrations of a solute with a known molecular weight.

c. Freezing point depression

Almost the same derivation as that just given for the boiling point elevation gives

\[ \Delta T_f = T_f^o - T_f = K_f m_B \]
In which

\[ K_f = \frac{RT_f^0 M_A}{1000 \Delta H_{fus}} = \frac{RT_f^0}{1000 \Delta h_{fus}} \]

is the freezing point depression constant (cryoscopic constant) and \( \Delta T_f \) is the freezing point depression; \( \Delta h_{fus} \) is the enthalpy of fusion per gram of solvent. The only difference is that the freezing point depression is the freezing point of the pure solvent minus the freezing point of the solution, whereas the boiling point elevation is the boiling point of the solution minus the boiling point of the pure solvent. As a final point, because the names are not the best, it is worth saying silently boiling temperature when reading boiling point and freezing temperature when reading freezing point. Also, as with the boiling point elevation constant, many workers prefer to determine the cryoscopic constant empirically rather than calculate it from these equations.

As an application of the equation for freezing point depression, we calculate the expected freezing point of a solution of 20 g of sucrose (\( M = 342 \text{ g mol}^{-1} \)) in 100 g (0.100 kg) water. The cryoscopic constant for water is 1.86 K kg mol\(^{-1}\). The molality of the solution is

\[ m_{sucrose} = \frac{n_{sucrose}}{W_{water}} = \frac{20 \text{g} / 342 \text{g mol}^{-1}}{0.100 \text{kg}} = 0.585 \text{ mol kg}^{-1} \]

The resulting freezing point depression is

\[ \Delta T_f = K_f m_{sucrose} = (1.86 \text{ K kg mol}^{-1}) (0.585 \text{ mol kg}^{-1}) = 1.09 \text{ K} \]

Since

\[ \Delta T_f = T_f^0 - T_f = 0 \text{ °C} - T_f, \quad T_f = -1.09 \text{ °C}. \]

d. **Osmotic pressure**

We have seen that for the solvent in the solvent standard state

\[ \mu_A = \mu_A^* + RT \ln a_A \]

Here, \( \mu_A \) is the chemical potential of the solvent \( A \) in the solution, \( \mu_A^* \) is the chemical potential of \( A \) when it is pure, and \( a_A \) is the activity of \( A \) in the solution. If the solvent obeys Raoult’s law, \( a_A = x_A < 1 \). Consequently, the chemical potential of \( A \) in the solution is less than the chemical potential of pure \( A \). This means that if a sample of pure \( A \) comes in contact with a solution in which \( A \) is a component, there will be tendency for \( A \) to diffuse from the pure solvent into the solution; i.e., to go from a region of high chemical potential to a region of low chemical potential.

It turns out to be possible to prepare a semipermeable membrane that allows passage of solvent molecules, but which greatly inhibits the passage of solute molecules. If the solvent and the
solution are separated by such a semipermeable membrane, the passage of solvent across the membrane from pure solvent to solution is called \textit{osmosis}.

It also turns out to be possible, by application of sufficient additional pressure to the solution to stop the flow of solvent across the membrane. The minimum necessary additional pressure is called the \textit{osmotic pressure}. We have the following schematic experimental arrangement:

We let the pressure applied to the pure solvent be $p_{atm}$ and the pressure applied to the solution be $p_{atm} + \Pi$, where $\Pi$ is the \textit{osmotic pressure}. The mole fraction of $A$ in the solution is $x_A$. Then, if we recall that the chemical potential of $A$ on each side of the membrane must be the same at equilibrium, we have the following relations between the chemical potentials at equilibrium:

\[
\mu_A(solv, p_{atm}) = \mu_A(solv', n, p_{atm} + \Pi)
\]

\[
\mu_A(solv', n, p_{atm} + \Pi) = \mu_A(solv, p_{atm} + \Pi) + RT \ln x_A
\]

\[
\mu_A(solv, p_{atm} + \Pi) = \mu_A(solv, p_{atm}) + V_A^* \left[ p_{atm} + \Pi - p_{atm} \right]
\]

For the second of these three equations, we assumed that Raoult's Law holds for any applied pressure and for the last of these equations, we recalled that the chemical potential of a pure substance is the Gibbs free energy per mole and that the pressure dependence of this quantity is as shown.

Now, we substitute from the third of the equations into the second and then for the second into the first to obtain

\[
\mu_A(solv, p_{atm}) = \mu_A(solv, p_{atm}) + RT \ln x_A + V_A^* \Pi
\]

or

\[
\Pi V_A^* = -RT \ln x_A = -RT \ln (1 - x_B) = RT x_B
\]

For the last of these equations, we assumed that the mole fraction of the solute is very much less than 1. We now make two further approximations that require this same assumption,
Substitution from these equations into the previous equation gives the \textit{van't Hoff equation for osmotic pressure}:

\[ \Pi V = n_B RT \]

Since \( n_B V \) is the molarity of \( B \) in the solution, the van't Hoff equation can be written in the form of a colligative property equation,

\[ \Pi = RT [B] \]

which shows that the osmotic pressure is directly proportional to the molarity of the solute and that the proportionality constant is \( RT \).

There are a number of approximations in the derivation of the van't Hoff equation that lead to the conclusion that this must be just the first term in a kind of virial expansion in which the osmotic pressure is proportional to a power series in the molarity of the solute. Also, one common application of the measurement of osmotic pressures is to the determination of molecular weights. For this purpose, we make use of the fact that the concentration of \( B \) in the solution in g L\(^{-1}\) (\( c_B \)) is the molecular mass of \( B \) (\( M_B \)) times the molarity of \( B \). Therefore,

\[ \Pi = RT \frac{c_B}{M_B} \]

or

\[ \frac{\Pi}{c_B} = \frac{RT}{M_B} \]

To apply this equation, the ratio of the osmotic pressure to the concentration is plotted against the concentration. The intercept of this plot at \( c_B = 0 \) is \( RT / M_B \). An example of the use of this equation to determine molecular weight is shown below with a plot of the osmotic pressure divided by the concentration of the polymer for a solution of polyisobutylene in benzene against the concentration of the polymer.
The intercept of this plot at \(c_B = 0\) is \(0.960 \times 10^{-4} \text{ atm L g}^{-1}\). Therefore,

\[
0.960 \times 10^{-4} \text{ atm L g}^{-1} = \frac{RT}{M} = \left(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}\right)(298 \text{ K})
\]

or

\[
M = 2.55 \times 10^5 \text{ g mol}^{-1}.
\]

6. **Boiling point diagrams**

The *boiling point* of a liquid is the temperature at which the equilibrium vapor pressure of the liquid equals the applied pressure. Thus, any liquid, pure or not, that is confined without any additional gases to a volume that is larger than the liquid volume comes to equilibrium at its boiling point. The more common situation is a liquid that is open to the atmosphere so that it feels the pressure of permanent gases in addition to the vapor pressures of its components. In this case the liquid reaches its boiling point only when the temperature is raised sufficiently to allow the equilibrium vapor pressure to equal the applied pressure.

The equilibrium vapor pressure and therefore the boiling point of a solution depends on its composition. A plot of the boiling point of a binary solution vs. its composition is called a *boiling point diagram*. As we have already seen, the composition of the vapor over a solution at equilibrium has a different composition from the liquid. Therefore, a complete boiling point diagram will normally show the vapor composition as a function of boiling point as well. A typical boiling point diagram for a binary solution that is nearly ideal has the following appearance.
The compositions of the liquid and vapor at any temperature are connected by a horizontal line called a **tie line**. If the vapor is condensed immediately, the liquid formed will have the same composition as the vapor. For the example shown here, the liquid that has \( x(\text{toluene}) = 0.6 \) boils at 367 K and is in equilibrium with vapor that has \( x(\text{toluene}) = 0.32 \). When this vapor is condensed, it forms a liquid that boils at 360 K and produces a vapor that has \( x(\text{toluene}) = 0.12 \). Thus, the condensed liquid at each step has a composition that is richer in benzene than the original liquid. This is the basis for the process of **distillation** that is used to purify a liquid. The use of successive distillation to purify a substance is known as **fractional distillation**. Each step in the distillation is known as a **theoretical plate**. It should be clear that for the example shown here, a **distillation column** with a great many theoretical plates could in principle produce almost pure benzene. As the distillation proceeds in this case, removal of nearly pure benzene from the top of the column leaves the solution in the pot richer in toluene, so that a nearly complete separation of the two liquids is obtained.

When the vapor pressure of a solution shows marked deviations from Raoult's Law, boiling point diagrams may show that a solution has a boiling point that is either lower or higher than the boiling points of the pure components. When the vapor pressure diagram shows negative deviations from Raoult's Law, it means that the \( A-B \) attractions are stronger than the \( A-A \) or \( B-B \) attractions. Solutions of this kind may show a maximum in the boiling point as a function of composition. An example is provided by solutions of chloroform in acetone.
By following the tie lines for a fractional distillation, it should be seen that distillation of a solution whose composition is richer in chloroform than the maximum boiling composition leads to a distillate that is nearly pure chloroform. The composition in the pot tends to the maximum boiling mixture. By contrast, distillation of a solution that is richer in acetone than the maximum boiling mixture leads to a distillate that is nearly pure acetone, but the composition of the liquid left in the pot again tends to the maximum boiling mixture. In either case, when the composition in the pot is the maximum boiling mixture, the liquid and the vapor have the same composition and no further separation is possible. Because the ultimate composition of the solution left in the pot is the maximum boiling mixture, complete separation of A and B can not be achieved by simple distillation for a mixture that has a maximum boiling mixture. The maximum boiling mixture is referred to as a high-boiling azeotrope.

The situation is different for solutions that show a minimum in the boiling point diagram. This is the case for solutions in which the A-B attractions are substantially smaller than the mean of the A-A and B-B attractions. A typical diagram for this case is shown here.

It should be evident from an examination of the tie lines in this case that distillation of a solution that is richer in ethanol than the minimum boiling azeotrope leads to a distillate that has the azeotropic composition and ultimately to nearly pure ethanol in the pot. By contrast, distillation of a solution that is richer in benzene than the minimum boiling mixture also leads to a distillate that has the azeotropic composition, but the ultimate composition in the pot is pure benzene.
7. *Steam distillation*

When the temperature of a mixture is raised to the point where the equilibrium vapor pressure of the mixture is equal to the applied pressure, the phenomenon of boiling (*ebullition*) takes place. If the liquid mixture contains two liquid phases, as it would if the two components are only partially soluble in each other, then the vapor pressure of the mixture is the sum of the vapor pressures of the two components. The total vapor pressure is then greater than that of either of the components. This situation suggests the possibility of distillation of a substance at atmospheric pressure at a temperature that is considerably lower than the normal boiling point of the liquid. If the liquid is one that suffers decomposition at temperatures near its boiling point, this could be and is a promising route to purification of a mixture without decomposition.

The principle just described is widely used in the process of *steam distillation* in which mixtures that contain water and a high-boiling immiscible liquid are distilled. The reason why this process is so common with water as one of the liquids is that the composition of the vapor produced follows Avogadro's principle in that the number of moles of water and the number of moles of the second liquid are proportional to their vapor pressures; that is,

\[
\frac{n_A}{n_B} = \frac{p_A}{p_B}
\]

In most practical examples, the vapor pressure of the water is much higher than the vapor pressure of the second liquid, so the number of moles of water is much larger than the number of moles of the second liquid. However, water has an unusually low molecular mass, so even a large number of moles of water may be a relatively small number of grams. It is therefore not impossible to have a distillate that includes 50% by weight of the second liquid, even when the vapor pressure of the second liquid is much smaller than the vapor pressure of water at the distillation temperature (which is always < 100 °C if water is one of the liquids).