Chapter 7

Phase Equilibria

In this chapter, we will examine phase equilibria. We will first use the equilibrium condition derived in Ch. 5 to study equilibria involving different phases of a single substance. Later, we will extend this to examine phase equilibria involving mixtures.

7.1 Phase Diagrams of Single-Component Systems

While applying the thermodynamics we have developed in the last few chapters to the case of phase equilibrium is actually quite straightforward, one of the most obtuse concepts in the study of phase equilibrium is the phase diagram. The phase diagram is a plot on the pressure-temperature ($P$-$T$) plane showing the coexistence between two adjacent phases. This deserves some explanation.

In general, a single-component system has three distinct phases: solid (S), liquid (L) and vapor (V). An example of a phase diagram is shown in Fig. 7.1 for water. Inside each of the regions marked solid, liquid and vapor, the substance is in a single phase. We know, for example, that near room temperature, water is a liquid under 1 atm pressure, so we see that the point $(T,P) = (25 \degree C, 1 \text{ atm})$ is indeed located inside the liquid region. The low-$P$, high-$T$ end (bottom) of the phase diagram is always the vapor. The high-$P$, low-$T$ end (top left) is always the solid. In between, we have the liquid. Sometimes, a certain phase, e.g. the solid, may also exist in several distinct phases characterized by different structures. An example is solid carbon which may exist in either the graphite or the diamond structure depending on $T$ and $P$, as shown in Fig. 7.2. You may wonder why the carbon we encounter in daily life can be found in two different phases at room temperature and 1 atm pressure (e.g. graphite in our pencils and the precious stones used for jewelries), whereas the phase diagram suggests that only of these phases is the proper thermodynamics phase. This is because the interconversion rate between diamond and graphite is extremely slow. Even though graphite is the proper thermodynamic phase for solid carbon at normal
conditions, you would literally never see the spontaneous conversion of diamond back into graphite.

![Phase diagram of water.](image)

Figure 7.1: Phase diagram of water.

The solid lines in the diagram show where the coexistence between the two adjacent phases are. For instance, the line between the solid and the liquid phases (the S-L line) shows at what values of \(P\) and \(T\) the solid and the liquid phases are in equilibrium with each other. We know, for example, that at 0°C and 1 atm pressure, water and ice are at equilibrium with each other. Therefore, the point \((T, P) = (0^\circ\text{C}, 1 \text{ atm})\) is on the S-L line. Similarly, we know that at 100°C and 1 atm, water and steam are at equilibrium with each other. Therefore, the point \((T, P) = (100^\circ\text{C}, 1 \text{ atm})\) is on the L-V line.

We need to be more precise about the concept of “coexistence”. While thermodynamics tells us at what \((T, P)\) are the two phases in equilibrium, it does not dictate how much of each phase we should have. For example, if you mix 0.9 mole of steam at \((T, P) = (100^\circ\text{C}, 1 \text{ atm})\) with 0.1 mole of liquid water at the same \((T, P)\), this mixture is at equilibrium. But a mixture with 0.3 mole of steam and 0.7 mole of liquid water at \((T, P) = (100^\circ\text{C}, 1 \text{ atm})\) is also at equilibrium. Of course, the 0.9:0.1 steam:water mixture has a larger molar volume than the 0.3:0.7 mixture. In fact, at \((T, P) = (100^\circ\text{C}, 1 \text{ atm})\), there are an infinite number of possible combinations of steam:water mixtures, all of which are at equilibrium. The molar volume of these mixtures ranges from a 0:1 steam:water mixture being the smallest to a 1:0 steam:water mixture being the largest. If we look at the possible values of \(V\) on the equation of state (EOS) surface shown in Fig. 7.3, we indeed see that for a single value of \((T, P)\) on the coexistence line in the phase diagram, where are many different values of \(V\) that are possible. These values of \(V\) form parallel lines on the EOS surface. In this sense, the coexistence region on the EOS surface resembles the sheer faces of
the Half Dome in Yosemite National Park (see photo in Ch.1). If you happen to look at the EOS surface from the $P$-$T$ plane, you are looking directly down these lines. So the projection of the EOS surface on the $P$-$T$ plane is what gives you the kind of phase diagrams that are shown in Fig. 7.1 or 7.2.

On the phase diagram, there may exist a single point where all three phases are in equilibrium with each other. This point is called the **triple point**. In addition, the L-V coexistence line ends at the **critical point** ($T_c, P_c$). We have encountered the critical point in Ch. 1. Above the critical temperature $T_c$, there is no physical distinction between the liquid and its vapor. While there is an “end” to the coexistence between the liquid and the vapor, it is believed that the S-L coexistence line goes on forever. Of course, this is difficult to verify experimentally, since we can never go to infinite $P$. But so far, a termination point on the S-L coexistence line has never been observed for any real substance.

### 7.2 The Solid-Liquid Coexistence

After we have understood the phase diagram, the rest of our task is to simply use thermodynamics to either determine or explain the coexistence lines. Using the equilibrium condition we obtained in the last two chapters, this is either easy or very easy. We will start with the S-L coexistence line.

The stoichiometry of a solid-liquid transition is 1:1, so the equilibrium condition requires that

$$
\mu_L - \mu_S = (\mu^0_L + RT \ln a_L) - (\mu^0_S + RT \ln a_S).
$$

But because the solid and the liquid are both pure phases and have no activities, the equilibrium condition for a S-L coexistence is just

$$
\Delta G^0_{S-L} = \mu^L_L - \mu^L_S = 0.
$$
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Clearly, $\Delta G^\circ_{S\leftrightarrow L}$ depends on $T$ and $P$; therefore, the S-L coexistence will move with $T$ and $P$.

Let’s say we already know that a certain point $(T, P)$ is on the S-L coexistence line, e.g. $(0^\circ, 1 \text{ atm})$ for ice and liquid water, and we want to know where the new coexistence pressure $P$ is when we move $T$ slightly. We can once again make use of the differential of $G$:

$$d\Delta G^\circ_{S\leftrightarrow L} = -\Delta S^\circ_{S\leftrightarrow L}dT + \Delta V^\circ_{S\leftrightarrow L}dP.$$  \(7.3\)

If we move $T$ by $dT$, we want to find the corresponding change in $dP$ which will keep $\Delta G^\circ_r$ at the new $T$ and $P$ unchanged and equal to 0. Setting $d\Delta G^\circ_r = 0$ gives the Clapeyron equation:

$$dP \over dT = \Delta S^\circ_{S\leftrightarrow L} \over \Delta V^\circ_{S\leftrightarrow L} = \Delta H^\circ_{S\leftrightarrow L} \over T \Delta V^\circ_{S\leftrightarrow L},$$  \(7.4\)

where the second equality comes from $\Delta H_{S\leftrightarrow L} - T \Delta S_{S\leftrightarrow L} = \Delta G_{S\leftrightarrow L} = 0$.

The Clapeyron equation essentially gives the derivative of the S-L line on the phase diagram. $\Delta S^\circ_{S\leftrightarrow L}$ is almost always positive; therefore, the sign of $\Delta V^\circ_{S\leftrightarrow L}$ alone will determine whether the S-L line has a positive or negative
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slopes. Most liquids contract when they freeze, so \( \Delta V_{S \rightarrow L} \) is usually > 0 and the S-L line usually has a positive slope. Water is an exception, since it expands upon freezing. Therefore, the S-L line has a negative slope as shown in Fig. 7.1.

### 7.3 The Liquid-Vapor and Solid-Vapor Coexistence

The only difference between the S-L coexistence and the L-V or S-V coexistence is that the vapor’s chemical potential has a fugacity dependence. For example, for the L-V coexistence, the equilibrium condition becomes:

\[
(\mu^\circ_V - \mu^\circ_L) + RT \ln a_V = \Delta G^\circ_{L \rightarrow V} + RT \ln a_V = 0,
\]

where \( \mu^\circ_V \) is the chemical potential of the pure vapor at the reference pressure \( P_0 \) of either 1 atm or 1 bar. If we assume that the vapor is ideal, \( a_V = P_V / P_0 \), where \( P_V \) is the pressure of the vapor that is in equilibrium with the liquid at temperature \( T \). Comparing this to the expression for the equilibrium constant in Ch. 6, we see that \( P_V / P_0 \) plays the role of an equilibrium constant for a liquid to vapor transition:

\[
\ln \left( \frac{P_V}{P_0} \right) = -\frac{\Delta G^\circ_{L \rightarrow V}}{RT} = -\frac{\Delta H^\circ_{L \rightarrow V}}{RT} + \frac{\Delta S^\circ_{L \rightarrow V}}{R}.
\]

A similar equation exists for the solid to vapor transition. With the known temperature-dependence of \( \Delta H^\circ \) and \( \Delta S^\circ \), it is easy to calculate the vapor pressure of a liquid or a solid at any temperature.

One may further simplify Eq. (7.6) by assuming \( \Delta H^\circ \) and \( \Delta S^\circ \) are independent of \( T \). This assumption is usually acceptable within a narrow temperature range. This allows us to express the vapor pressure \( P_2 \) of a liquid (or a solid) at a temperature \( T_2 \) relative to its vapor pressure \( P_1 \) at temperature \( T_1 \) as:

\[
\ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta H^\circ_{vap}}{R} \times \left( \frac{1}{T_1} - \frac{1}{T_2} \right),
\]

where \( \Delta H^\circ_{vap} \) is the enthalpy of vaporization of the liquid (or the enthalpy of sublimation if we are dealing with a solid to vapor transition).

### 7.4 Liquid-Vapor Coexistence of a Binary Mixture

In separation science, one often exploits the preference of a substance for one phase over another to separate a mixture. This is the principle behind distillation. We will describe this briefly in this section.

We have seen in Ch. 5 that under ideal condition, the vapor pressure of a volatile liquid obeys Raoult’s law. Say we have a liquid mixture containing two
components 1 and 2. Let the mole fraction of 1 in the liquid be \( x_1 \) and the mole fraction of 2 be \( x_2 \). \( x_1 + x_2 = 1 \) necessarily. If at some temperature \( T \), the vapor pressure of the pure component 1 is \( P^*_1 \) and that of the pure component 2 is \( P^*_2 \), then the partial pressures of the two substances in the vapor phase are described by Raoult’s law if the solution is ideal:

\[
P_1 = x_1 P^*_1, \quad P_2 = x_2 P^*_2.
\]  

(7.8)

The total pressure of the two vapors is

\[
P = P_1 + P_2 = x_1 P^*_1 + x_2 P^*_2 = P^*_2 - x_1(P^*_2 - P^*_1).
\]  

(7.9)

This is plotted as the red curve in Fig. 7.4 and clearly it is just a linear function of \( x_1 \). To produce this total pressure, the mole fraction of component 1 in the liquid must be \( x_1 \). But what is the mole fraction of component 1 in the vapor? To find out what it is, we simply divide the vapor pressure of 1 by the total pressure and get:

\[
\frac{x_1 P^*_1}{P^*_2 - x_1(P^*_2 - P^*_1)} = y_1.
\]  

(7.10)

To distinguish this from the mole fraction of component 1 in the liquid phase, we denote the mole fraction of component 1 in the vapor phase \( y_1 \). This is certainly not equal to \( x_1 \) (except if coincidentally \( P^*_1 = P^*_2 \)). Therefore, when a liquid evaporates, the composition of its vapor is necessarily different from the composition of the liquid. This is easy to rationalize in terms of Raoult’s law: the more volatile component should become enriched in the vapor phase. Using Eq.(7.10), we can solve for \( x_1 \) in terms of \( y_1 \) and re-express the total pressure in Eq.(7.9) as a function of \( y_1 \):

\[
P = \frac{P^*_1 P^*_2}{P^*_1 + (P^*_2 - P^*_1)y_1}
\]  

(7.11)

This equation is also plotted in Fig. 7.4 as the blue curve.

Eqs.(7.9) and (7.10) relate the total pressure \( P \) of the vapor mixture to the mole fraction of component 1 in the liquid and the vapor, respectively. Notice that so far we have not used any thermodynamics, except the empirical assumption that Raoult’s law applies to both components of the ideal mixture. So the results in Eqs. (7.9) and (7.10) should work equally well for a constant-volume or a constant-pressure experiment. Let’s see how they apply to each experiment.

In a constant-volume experiment, we prepare a liquid mixture of the two components and seal it inside a closed vessel. Before we close it, we make sure that it has some space above the liquid for the vapor to go into. We then attach a pressure gauge and measure the total pressure when the vapor and the liquid come into equilibrium. Of course, to have an equilibrium between the two phases, we must have at least some of each. The experiment would not be valid if, for example, the entire liquid mixture completely evaporates. This experiment is depicted in Fig. 7.5(a). To construct the graph in Fig. 7.4, we can
analyze the compositions of the equilibrium liquid and vapor separately. But to get a different point on the plot, we will have to open up the vessel and repeat the experiment with a number of different liquid mixtures having various initial compositions.

On the other hand, the constant-pressure version of the same experiment is depicted in Fig. 7.5(b). In this experiment, we put in some initial liquid mixture and use a piston to control the pressure. We make sure that the space above the liquid is completely evacuated initially so that no gas other than the two component are in the system. We wait for the equilibrium to be established between the liquid and the vapor at the pressure $P$. We can then measure the compositions of the vapor and the liquid to construct the plot in Fig. 7.4.

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get a different point on the graph, we only need to change the applied pressure on the pistol. There are, however, limits to the range of \( x_1 \) and \( y_1 \) we can get. For example, if both components are present in the initial mixture, the point \( x_1 \) or \( y_1 = 0 \) is obviously impossible to get. Therefore, to obtain the entire curve, the mixture will eventually have to be changed.

For the constant-pressure experiment, not only do the red and blue lines in Fig. 7.4 have significance, the other regions convey useful information too. Above the red line, the mixture is entirely liquid. This is the situation where the applied pressure \( P \) is too large for the vapor to be formed. In this region, the mixture has only one phase, i.e., there is only liquid under the piston. On the other hand, below the blue curve, the mixture is entirely vapor. In this region, the applied pressure \( P \) is too small for the liquid to be present, so there is only vapor under the piston. The space between the red and blue curves marks the coexistence region between the liquid and the vapor. If \( P \) happens to be inside this region, the two components will partition themselves according to the equilibrium. The liquid portion will necessarily have mole fraction \( x_1(P) \). The vapor portion will necessarily have mole fraction \( y_1(P) \). This is shown in Fig. 7.6(a). Since the compositions of the liquid and the vapor at a certain \( P \) inside the the coexistence region are fixed by the equilibrium, the quantities of liquid and vapor are also fixed. To illustrate this, we define the total mole fraction of component 1 to be \( z_1 \). \( z_1 \) is the number of moles of component 1 in both the liquid and the vapor, divided by the total number of moles of everything inside the system. \( z_1 \) is of course completely determined by whichever you put into the reaction mixture. At a certain pressure \( P \), \( z_1 \) has to be between \( y_1(P) \) and \( x_1(P) \) in order for the system to be able to go inside the L-V coexistence region. If \( z_1 \) is closer to \( y_1(P) \), the equilibrium mixture will be mostly vapor. On the other hand, if \( z_1 \) is closer to \( x_1(P) \), the equilibrium mixture will be mostly liquid. In between, the equilibrium quantities of liquid and vapor will be determined by where \( z_1 \) is between \( y_1(P) \) and \( x_1(P) \). It is easy to show that the ratio of the quantity (number of moles) of vapor, \( n_V \), to the quantity of liquid, \( n_L \), is equal to the ratio of the distance between \( z_1 \) and \( x_1(P) \) to the distance between \( z_1 \) and \( y_1(P) \):

\[
\frac{n_V}{n_L} = \frac{|z_1 - x_1(P)|}{|z_1 - y_1(P)|}
\]  

(7.12)

This is illustrated in Fig. 7.6(b), which is a closeup of (a). This equation is known as the “lever rule”.

So far, we have used nothing but Raoult’s law to analyze the phase equilibrium of a two-component system. Of course, we can also use thermodynamics to arrive at the same equations and the same picture as the above. This would involve invoking the ideal solution assumption for both the liquid and the vapor to express the chemical potential of each component in the two phases, and then we would use the equilibrium condition to determine the equilibrium position. We will not repeat the calculations here.

Before we close this section, we will quickly consider one more experiment. Notice that in the constant-pressure experiment above, we have fixed the tem-
Figure 7.6: (a) The mole fraction $x_1(P)$ of the liquid and the mole fraction $y_1(P)$ of the vapor for a pressure $P$ in the coexistence region. (b) The lever rule: the distance between $z_1$ and $y_1(P)$ is proportional to the quantity of liquid and the distance between $z_1$ and $x_1(P)$ is proportional to the quantity of vapor in the equilibrium mixture.

perature $T$ and vary the pressure $P$ to map out the boundaries of the coexistence region. If we have a certain $P$ and composition $z_1$ that is inside the coexistence region, we can think of $T$ as the boiling point $T_b$ of this mixture, because at this temperature the vapor is in equilibrium with the liquid. We can turn this around. Instead of varying $P$ at some fixed $T$, we can varying $T$ at some fixed $P$. If we repeat the same experiment in Fig. 7.5(b) under these conditions, we will be able to map out the boiling temperature $T_b$ as a function of the composition of the mixture at pressure $P$. The resulting graph will give us a boiling temperature plot of a binary mixture. An example is shown in Fig. 7.7. The proper way to interpret this plot is this: if the system is inside the coexistence region at a certain temperature $T_b$, the composition of the liquid must be $x_1(T_b)$ and the composition of the vapor must be $y_1(T_b)$.

7.5 Henry’s Law and Activity Coefficients

Most real binary solutions are nonideal, so they do not obey Raoult’s law throughout the entire concentration range. An example is shown in Fig. 7.8. Even though Raoult’s law does not apply to most real solutions, it is always correct in the limit when the mole fraction of one of the component approaches one, i.e. when this component is nearly pure. This limiting behavior is observed in the acetone-chloroform system in Fig. 7.8. When the mole fraction of chloroform $x_1 \to 1$, the vapor pressure of the mixture is a linear function of $(1 - x_1)$: $P \approx P_1^* (1 - x_1)$.

While Raoult’s law is the correct limiting behavior for the most concentrated component when it is nearly pure, it is certainly not correct for the other component at this limit. For example, in the limit where the mole fraction of
chloroform \( x_1 \to 1 \), the vapor pressure of the other component, acetone, does not follow Raoult’s law. In particular, the slope of the acetone partial pressure in this limit is clearly not equal to the vapor pressure of pure acetone. So while Raoult’s law works for the concentrated component, it fails for the dilute component, i.e. \( P_2 \neq P_2^* x_2 \) when \( x_2 \to 0 \), where \( P_2^* \) is the vapor pressure of the pure dilute component 2. While Raoult’s law is not true for the dilute component 2, its vapor pressure is actually linear with \( x_2 \): \( P_2 \approx K_2 x_2 \) when \( x_2 \) is small, except the coefficient \( K_2 \neq P_2^* \). This limiting behavior for the dilute component is called Henry’s law, and the coefficient \( K_2 \) is the Henry’s law coefficient for component 2 in the dilute limit.

If we have a binary solution, the concentrated component is the solvent and the dilute component is the solute. Since the concentrated component obeys Raoult’s law, it is natural to take the standard state of the solvent to be the pure solvent. We showed in Ch. 5 that this leads to the definition of the chemical potential of solvent as

\[
\mu_1^{(l)} = \mu_1^{(l)\circ} + RT \ln x_1,
\]

where \( \mu_1^{(l)\circ} \) is the chemical potential of the pure solvent. We saw that this comes from the equilibrium requirement that \( \mu_1^{(l)} = \mu_1^{(g)} \), and

\[
\mu_1^{(g)} = \mu_1^{(g)\circ} + RT \ln \frac{x_1 P_1^*}{P_0}.
\]

But for the solute, its chemical potential in the vapor is

\[
\mu_2^{(g)} = \mu_2^{(g)\circ} + RT \ln \frac{x_2 K_2}{P_0},
\]

where \( K_2 \) is its Henry’s law coefficient. Therefore, for the solute in the liquid phase:

\[
\mu_2^{(l)} = \mu_2^{(g)\circ} + RT \ln \frac{K_2}{P_0} + RT \ln x_2
\]
\[ \mu = \mu^* \ln x + RT \ln x, \]  

Figure 7.8: The vapor pressure of an acetone-chloroform mixture as a function of the liquid composition.

\[ \mu^* \ln x + RT \ln x, \]  

where \( \mu^* \) is the chemical potential of the (hypothetical) pure component 2 that obeys Henry’s law. Notice that for the standard state of the solute, we use a * instead of a ◦.

In a real solution, the dependence of the chemical potential of the solvent in Eq.(7.13) on its mole fraction \( x_1 \) and of the chemical potential of the solute in Eq.(7.16) on its mole fraction \( x_2 \) should be replaced by their activities:

\[ \mu_1 = \mu_1^\circ + RT \ln a_1 = \mu_1^\circ + RT \ln \gamma_1 a_1, \]  

\[ \mu_2 = \mu_2^* + RT \ln a_2 = \mu_2^* + RT \ln \gamma_2 a_2, \]  

where the activity coefficient \( \gamma_1 \) for the solvent is defined as \( a_1 = \gamma_1 x_1 \), and \( \gamma_2 \) for the solute is defined as \( a_2 = \gamma_2 x_2 \).

### 7.6 Colligative Properties

The phenomena of freezing point depression, boiling point elevation and osmotic pressure are collectively called the “colligative properties”. All of them have to do with the change in the chemical potential of the solvent in the liquid phase when a dilute nonvolatile solute is added to it.

When a nonvolatile solute is dissolved in a liquid, its boiling point generally increases while its freezing point generally decreases. This is the reason why salt can be used to unfreeze icy roadways in winter. These two effects are easy to explain using Eq.(7.13). When solute is added, the mole fraction of the solvent is
lowered below 1. But when a liquid freezes, it crystalizes into its pure solid state by “squeezing” out the solute, so the solid is essentially pure and its chemical potential is unmodified by the solute. Similarly, when the liquid vaporizes, the nonvolatile solute does not go into the vapor, so the vapor is also essentially pure and its chemical potential is not modified by the solute either. Given these facts, the lowering of the chemical potential of the solvent in the liquid will necessarily shift the equilibrium position of the S-L and L-V coexistence.

For the S-L coexistence, the equilibrium position is given by:

$$
\mu_s^{(s)} = \mu_l^{(l)} + RT \ln x_1,
$$

(7.19)

where \(x_1\) is the mole fraction of the solvent, \(\mu_s^{(s)}\) and \(\mu_l^{(l)}\) are the chemical potentials of the pure solid and liquid, respectively. When \(x_1 = 1\), \(\mu_s^{(s)} = \mu_l^{(l)}\) at \(T_f\), the normal freezing temperature. When \(x_1 < 1\), \(\mu_s^{(s)}\) and \(\mu_l^{(l)}\) are no longer exactly equal to each other at \(T_f\). To find out how \(T_f\) will shift, we rewrite \(\mu_l^{(l)} - \mu_2^{(2)}\) as \(\Delta H_{\text{fus}} - T \Delta S_{\text{fus}}\), where \(\Delta H_{\text{fus}}\) and \(\Delta S_{\text{fus}}\) are the changes in enthalpy and entropy going from pure solid to pure liquid, and set this equal to \(RT \ln x_1\). Solving for the new temperature at which the two phases are in equilibrium, we obtain the ratio of the new freezing temperature to the normal \(T_f\):

$$
\frac{T'_f}{T_f} = \left[ 1 - \frac{RT_f}{\Delta H_{\text{fus}}} \ln x_1 \right]^{-1},
$$

(7.20)

where we have used the relationship \(\Delta H_{\text{fus}} - T_f \Delta S_{\text{fus}}\) in favor of \(T_f\), the normal freezing point. Since \(\Delta H_{\text{fus}} > 0\) and \(\ln x_1 < 0\), the new freezing point \(T'_f\) is lower than \(T_f\), resulting in a freezing point depression. By replacing \(x_1\) by \(1 - x_2\), where \(x_2\) is the mole fraction of the solute and expanding the right hand side of Eq.(7.20) to first order in \(x_2\), we obtain the change in the freezing point as:

$$
T'_f - T_f \approx \left( \frac{RT_f}{\Delta H_{\text{fus}}} \right) x_2,
$$

(7.21)

which is linear in \(x_2\), the mole fraction of the solute. The analysis for the boiling point in the case of L-V coexistence is similar, leading to the ratio of the new boiling temperature \(T'_b\) to the normal one \(T_b\) as:

$$
\frac{T'_b}{T_b} = \left[ 1 + \frac{RT_b}{\Delta H_{\text{vap}}} \ln x_1 \right]^{-1},
$$

(7.22)

where \(\Delta H_{\text{vap}}\) is now the enthalpy change of vaporization. We see that in the case of vaporization, the boiling point is elevated instead.

The osmotic pressure of a solution is measured in an experiment depicted in Fig. 7.9. The solution is separated from the pure solvent by a semipermeable membrane, which allows the solvent to pass through but not the solute. The solution is open on the top to atmospheric pressure through a tube. The pure solvent from the outside spontaneously enters the solution through the membrane and the extra volume of the solution rises up the tube, developing an
additional pressure on the liquid below due to the height of the column. This pressure is called the osmotic pressure $\Pi$. The solution inside has a chemical potential:

$$\mu_1(T, P + \Pi) = \mu_1^o(T, P + \Pi) + RT \ln x_1,$$

where $x_1$ is the mole fraction of the solvent, $P$ is the atmospheric pressure and $\Pi$ is the osmotic pressure, whereas the chemical potential of the pure solvent outside is just $\mu_1^o(T, P)$. The solution inside must be in equilibrium with the solvent outside, and we can equate the two chemical potentials to find the equilibrium position, yielding:

$$\mu_1^o(T, P + \Pi) - \mu_1^o(T, P) = -RT \ln x_1.$$  

(7.24)

for small $\Pi$, we can expand the difference on the left hand side to first order in $\Pi$:

$$\frac{d\mu_1^o}{dP} \Pi = \bar{V^o} \Pi = -RT \ln x_1,$$

(7.25)

where $\bar{V^o}$ is the standard state molar volume of the pure solvent. Again, using the solute’s mole fraction $x_2 = 1 - x_1$ and expanding the right hand side of this equation to first order in $x_2$, we obtain the result:

$$\Pi \approx \left(\frac{RT}{\bar{V}}\right) x_2,$$

(7.26)

which indicates that the osmotic pressure is simply proportional to the mole fraction of the solute in the dilute limit.

**Appendix: Interacting Lattice Gas and the Bragg-Williams Approximation**