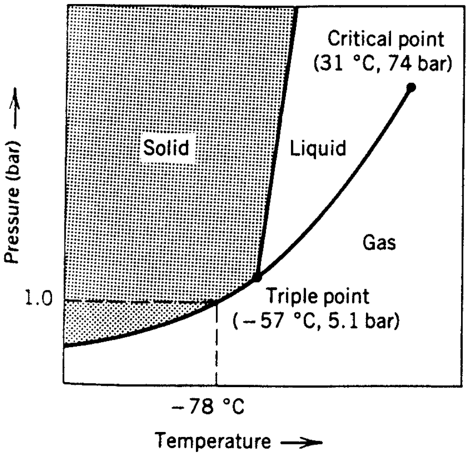
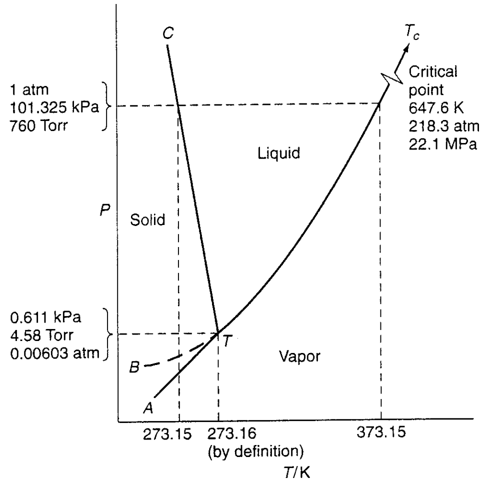
CHAPTER 5 LECTURE NOTES

Phases and Solutions

Phase diagrams for two one component systems, CO_2 and H_2O, are shown below.





The main items to note are the following:

- The lines represent equilibria between two phases.
- The regions “interior” to these lines represent regions where only one phase is present.
- The triple point is a unique, invariant point for each system where three phases are simultaneously in equilibrium.

Thermodynamic condition for equilibrium between two phases *a* and *b* is $G_a = G_b$, so that during an equilibrium phase change, $\Delta G_{ab} = G_a - G_b = 0$.

Note that the slope of the line separating the solid from the liqid region for CO_2 has a positive slope. This is typical of most substances and is indicative of the fact that the solid is denser than the liquid (how?).

On the other hand, the slope of the solid-liquid boundary for water is negative, indicating that the liquid is denser than the solid. This is by far the exception.

The Clapeyron Equation

If we confine ourselves to conditions where two phases, say vapor and liquid, are in equilibrium, we effectively limit ourselves to a one-dimensional world defined by the line separating the liquid region from the vapor region. Under those conditions, the Maxwell relation

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T, \tag{3.124}$$

(3.124) can be modified as follows:

$$\frac{dP}{dT} = \frac{dS}{dV} \simeq \frac{S_{m,v} - S_{m,l}}{V_{m,v} - V_{m,l}} = \frac{\Delta_{vap} S_m}{\Delta_{vap} V_m} \tag{5.8}$$

Substituting the definition of entropy change for a phase change, we obtain

$$\frac{dP}{dT} = \frac{\Delta_{vap} H_m}{T \Delta_{vap} V_m}. \tag{5.9}$$

This is called the **Clapeyron equation**.

Similar equations can be written for the solid-vapor boundary (enthalpy of sublimation!) and the solid-liquid boundary (enthalpy of fusion!). Note that, since enthalpy is a state function,

$$\Delta_{sub} H_m = \Delta_{fus} H_m + \Delta_{vap} H_m. \tag{5.10}$$

The Clausius-Clapeyron Equation:

Eq. (5.9) may be written as

$$\frac{dP}{dT} = \frac{\Delta_{vap} H_m}{T\left(V_{m,g} - V_{m,l}\right)} \approx \frac{\Delta_{vap} H_m}{T V_{m,g}} \simeq \frac{\Delta_{vap} H_m}{R T^2} P, \tag{5.11}$$

where we have assumed that the vapor behaves ideally to get the last equality. This equation may be rearranged and integrated to give

$$\ln P^u = \frac{-\Delta_{vap} H_m}{RT} + C, \text{ or} \tag{5.14}$$

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_{vap} H_m}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \tag{5.16}$$

The Clausius-Clapeyron equation is applicable to solid-vapor equilibrium as well. The pressure plotted in the phase diagrams and used in these relationships is the *vapor pressure* of the substance under consideration, not the total pressure. Eq. (5.14) gives the *P*-*T* relationship required to plot the lines in the phase diagrams.

Therefore, Eq. (5.14) for the liquid-vapor and the solid-vapor equilibria can be used to find the triple point for a one-component system.

Examples 5.2, 5.3, Problems 5.1–5.4, 5.7–5.10, 5.12, 5.15, 5.18, 5.20.

The Gibbs Equation:

By definition,

$$dG = VdP - SdT.$$

At constant temperature, the second term vanishes and we get

$$dG = VdP.$$

For the liquid vapor equilibrium considered earlier, under these circumstances, we have

$$dG_{m,v} = dG_{m,l}$$

or

$$V_{m,v}dP = V_{m,l}dP_t,$$

where the pressure term on the vapor side is the <u>vapor</u> <u>pressure</u> of the substance while on the liquid side, it is the <u>total</u> <u>pressure</u> acting on the liquid surface. Now, using ideal gas law for the vapor, we get

$$\frac{RT}{P}dP = V_{m,l}dP_t \text{ or}$$

$$\frac{dP}{P} = \frac{V_{m,l}}{RT}dP_t.$$

Now consider a situation where, initially, the total pressure acting on a liquid surface is the total pressure. Let us denote this pressure by P_v. The pressure is then changed by the addition of an inert gas, keeping the temperature fixed, to get a final total pressure P_t. We wish to find the new value of the equilibrium vapor pressure P. For this situation, we may integrate this equation above to get

$$\ln\left(\frac{P}{P_v}\right) = \frac{V_{m,l}}{RT}(P_t - P_v), \tag{5.23}$$

where we have assumed that the liquid volume does not change with applied pressure.

This is called the **Gibbs Equation**.

Problems 5.5, 5.17

5.4. Ideal Solutions: Raoult's Law:

Consider a solution formed by two miscible liquids A and B. An ideal solution is one for which

- $V_{\text{soln}} = V_A + V_B$.
- $\Delta H_{\text{soln}} = 0$.
- $\Delta S_{m,\text{soln}} = -R(x_A \ln x_A + x_B \ln x_B)$.
- $\Delta G_{m,\text{soln}} = RT(x_A \ln x_A + x_B \ln x_B)$.

Ideal solutions obey Raoult's law exactly. To state Raoult's law, let us denote the mole fractions in the liquid phase by x and the mole fractions in the vapor phase by y. Also, we denote the vapor pressure of pure A as P_A^* and that of B as P_B^*. Raoult's law can now be written as

$$P_A = x_A P_A^* \text{ and } P_B = x_B P_B^*.$$

In other words, the partial pressure of a substance in the vapor phase is determined by its mole fraction in the liquid phase. Compare this to the Dalton's law of partial pressures, which states

$$P_A = y_A P \text{ and } P_B = y_B P,$$

where the total pressure is denoted as P. If only A and B are present in the gas phase above the solution, we have

$$P = x_A P_A^* + x_B P_B^*.$$

Since A and B are the only substances present in solution, we may re-write this as

$$P = x_A P_A^* + (1 - x_A)\mathrm{P}_B^*,$$

which gives the variation of total pressure as a function of x_A

Problems 5.19, 5.21, 5.28.

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Henry's Law:

Henry's Law may be written in terms of molality, molarity or mole fractions as

$$P_B = k_B m_B \approx k_B'' c_B \approx k_B' x_B.$$

In the limit of infinite dilution, solvents usually follow Raoult's law and solutes usually follow Henry's law.

The form of Henry's law preferred by the authors of the textbook is:

$$P_B = k_B' x_B, \tag{5.28}$$

where B refers to the component present in small amounts in the solution.

One place where Henry's law finds useful application is in estimating the concentration of gases dissolved in a solution at a given partial pressure of the gas.

Example: Problem 5.38

The total pressure above the solution is 750 torr, which consists of the partial pressure of methane and benzene. In other words,

$$P = P_{CH_4} + P_{Bz}.$$

This question actually presents a "catch-22" situation. We have no way of calculating the actual partial pressure of benzene, P_{Bz} (for which we would use Raoult's law since benzene is present in large quantities and can be considered the solvent), without knowing the mole fraction of benzene in the solution, x_{Bz}, which we cannot know until we find the mole fraction of methane in solution. But the whole purpose of the question is to find the mole fraction of methane in solution!

So, since methane obviously cannot have a high concentration, we assume that $x_{Bz} \approx 1$ and, therefore, $P_{Bz} \approx P_{Bz}$*. Then we have

$$P_{CH_4} = P - P_{Bz}^* = 750 - 94.6 = 655.4 \text{ tor}$$

Now we can use Henry's law for methane to get

$$P_{CH_4} = k'_{CH_4} x_{CH_4},$$

and solve for the mole fraction of methane.

We should verify that this indeed is a small number so that the assumption made regarding the partial pressure of benzene is valid.

Problem 5.36.

Non-ideal solutions:

Non-ideal solutions are those that deviate from Raoult's law.

Positive deviation from Raoult's law:

$$P > x_A P_A{}^* + (1 - x_A)P_B{}^*.$$

Negative deviation from Raoult's law:

$$P < x_A P_A{}^* + (1 - x_A)P_B{}^*.$$

In many solutions, both components show the same type of deviation (positive or negative) from Raoult's law so that we have either

$$P_A > x_A P_A{}^* \text{ and } P_B > x_B P_B{}^*$$

or

$$P_A < x_A P_A{}^* \text{ and } P_B < x_B P_B{}^*.$$

However, there are exceptions to this behavior, as seen in Fig. 5.9 (ethanol).

When dealing with non-ideal solutions, it is convenient to define activity of a component as

$$a_A = \frac{P_A}{P_A^*}. \tag{5.75}$$

Obviously, for an ideal solution, Raoult's Law is obeyed and, therefore, $a_A = x_A$. However, for a non-ideal solution, the activity will not be equal to the mole fraction. In such cases, the activity can be related to the mole fraction through the activity coefficient γ_A:

$$\gamma_A = \frac{a_A}{x_A}, \text{ or } a_A = \gamma_A x_A.$$

Note that the textbook uses the symbol f_A for activity coefficient of A. This causes confusion with fugacity, which is also denoted by f. Therefore, I have chosen to denote this quantity by the Greek letter γ (gamma).

Example 5.8, Problems: 5.34, 5.35.

5.5. Partial Molar Quantities

Partial Molar quantities are required to deal with open systems, i.e., systems that permit mass transfer between themselves and surroundings.

Consider an open system with n_1 moles of component 1, n_2 moles of component 2, n_3 moles of component 3, etc.. We would write the free energy change dG for such a system as

$$\begin{aligned} dG &= \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,\ldots} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,\ldots} dT + \left(\frac{\partial G}{\partial n_1}\right)_{P,T,,n_2,\ldots} dn_1 + \ldots \\ &= VdP - SdT + G_1 dn_1 + G_2 dn_2 + \ldots \end{aligned}$$

In the second equality, the quantities G_1, G_2, etc.. are called *partial molar free energies*. Similarly, we may define partial molar volumes, partial molar enthalpies, internal energies, and entropies:

$$V_1 = \left(\frac{\partial V}{\partial n_1}\right)_{P,T,,n_2,\ldots} ; H_1 = \left(\frac{\partial H}{\partial n_1}\right)_{P,T,,n_2,\ldots} ; \text{etc..}$$

Because of their great importance in the thermodynamics of solutions, we discuss partial molar volumes and partial molar free energies further.

Partial Molar Volume:

The total volume of a solution of, say, two miscible liquids is given by

$$\boxed{V = n_1 V_1 + n_2 V_2.} \tag{5.33}$$

The units of partial molar volumes are the same as molar volumes. The relationship between the two, i.e., partial molar volume and the molar volume is a subtle but important one.

- In the case of ideal solutions, the partial molar volume of each component will be identical to the molar volume of the pure substance in the absence of the other component.
- However, in the case of non-ideal solutions, the presence of the second component has a measurable influence on the molar volume of the first component and vice versa. Therefore, in general,

$$V_1 \neq V_1^* \text{ and } V_2 \neq V_2^*$$

The standard state for defining partial molar quantities is a 1 **molal** solution, i.e., a solution that contains 1 mol of the substance in 1.0 kg of solvent.

Physical Interpretation of partial molar quantities:

It may appear that there is something "not quite right" about the following two equations:

$$V = n_1 V_1 + n_2 V_2, \text{ where}$$

$$V_1 = \left(\frac{\partial V}{\partial n_1} \right)_{P,T,n_2}, \text{and } V_2 = \left(\frac{\partial V}{\partial n_2} \right)_{P,T,n_1}.$$

Based on what we have seen so far, the first equation should be $dV = V_1 dn_1 + V_2 dn_2$,which is simply another application of the chain rule in partial differentiation.

However, Eq. (5.33) can indeed be justified on physical grounds as follows. Consider a large volume of solution containing ethanol (E) and water (W). We now add a small amount of water, say, Δn_W moles of water, to this solution. We would want to express the new volume of the solution as

$$V_{new} = V_{old} + \Delta n_W V^*_{W,m},$$

where $V^*_{W,m}$ is the molar volume of pure water. However, this will give us the final volume only in the case of an ideal solution. In the ethanol-water solution, the *effective* molar volumes of both substances are different from their molar volumes in the absence of the other substance. Designating the actual molar volume of water in the presence of ethanol as $V_{W,m}$, the change of volume of the solution is

$$\Delta V = \Delta n_W V_{W,m}$$

Therefore, we get

$$V_{W,m} = \frac{\Delta V}{\Delta n_W}.$$

The partial molar volume of water, V_W, is defined as the value of the fraction on the right hand side in the limit of an infinitesimal change in the number of moles of water. Mathematically, we write

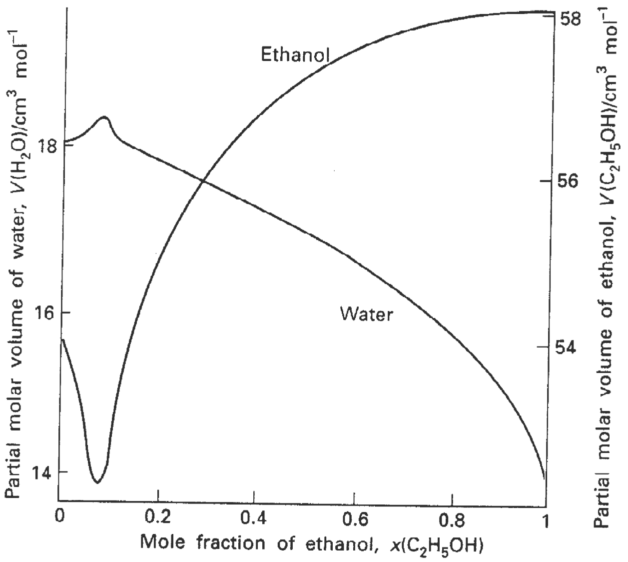
$$V_W = \lim_{\Delta n_W \to 0} \frac{\Delta V}{\Delta n_W} = \frac{dV}{dn_W}.$$

Once we impose the conditions that temperature, pressure and the number of moles of ethanol, n_E, are to be held constant, the derivative on the right hand side becomes identical to the definition of the partial molar volumes used above and in Eq. (5.33):

$$V_W = \left(\frac{\partial V}{\partial n_W} \right)_{T,P,n_E}$$

An example of the applications of Eq. (5.33):

Consider a 40% by mass ethanol solution of ethanol in water at 25°C. From the figure of partial molar volumes of ethanol and water in the presence of each other, estimate the volume of 1000 g of the solution. Compare this to the volume that would have resulted if the solution was ideal. Density of ethanol = 0.785 g mL^{-1} and pure water = 0.997 g mL^{-1} , at this temperature.



In 1000 g of solution, we have 400 g ethanol (*E*) and 600 g water (*W*).

$$n_E = \frac{400\text{ g}}{46.07\text{ g mol}^{-1}} = 8.68\text{ mol.}$$

$$n_W = \frac{600\text{ g}}{18.02\text{ g mol}^{-1}} = 33.30\text{ mol.}$$

$$x_E = 0.207;\ x_W = 0.793.$$

From the figure, we estimate that at these mole fractions, the partial molar volumes are

$$V_E = 55.0\text{ mL mol}^{-1};$$

$$V_W = 17.5\text{ mL mol}^{-1}.$$

Therefore, using Eq. (5.33), we get

$$V = n_E V_E + n_W V_W = 8.68 \times 55.0 + 33.30 \times 17.$$

$$= 1060\text{ mL.}$$

If the solution was ideal, we would use the molar volumes of the pure substances to obtain

$$V = 8.68\text{ mol} \times \frac{46.07\text{ g mol}^{-1}}{0.785\text{ g mL}^{-1}} + 33.30\text{ mol} \times \frac{18.02\text{ g mol}^{-}}{0.997\text{ g mL}^{-1}}$$

$$= 1111\text{ mL.}$$

Therefore, we see that the non-ideal nature of the solution is reflected in a contraction of volume by 51 mL.

Another example of applying Eq. (5.33):

Density of a 50% by mass solution of ethanol in water at 25°C is 0.914 g mL^{-1}. Given that the partial molar volume of water at this composition is 17.4 mL mol^{-1},what is the partial molar volume of ethanol?

No. of moles of ethanol in 100 g of solution: 50 g/46.07 g mol^{-1} = 1.085 mol.
No. of moles of water in 100 g of solution: 50 g/18.02 g mol^{-1} = 2.775 mol.
Now, since $V = n_E V_E + n_W V_W$,we get

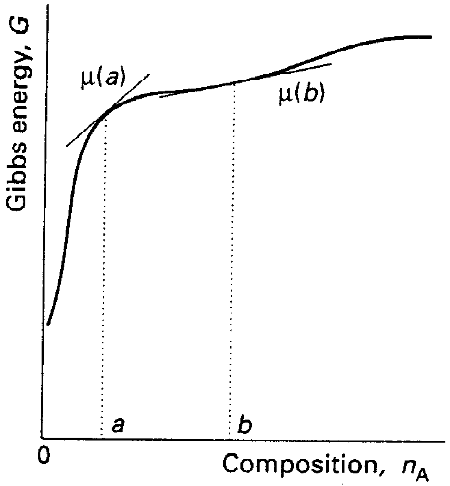
$$\begin{aligned} V_E &= \frac{V - n_W V_W}{n_E} \\ &= \frac{\left(100\ \text{g}/0.914\ \text{g mL}^{-1}\right) - 2.775\ \text{mol} \times 17.4\ \text{mL mol}^{-}}{1.085\ \text{mol}} \\ &= 56.33\ \text{mL mol}^{-1}. \end{aligned}$$

A third example of using Eq. (5.33) is provided in Homework Assignment # 6.

Partial molar Free Energy:

Partial molar free energy is commonly refered to as the “chemical potential,” and denoted by the letter μ:

$$\boxed{\begin{aligned} \mu_A = G_A = \left(\frac{\partial G}{\partial n_A}\right)_{P,T,n_B} \\ \mu_B = G_B = \left(\frac{\partial G}{\partial n_B}\right)_{P,T,n_A} \end{aligned}}\ .$$



The figure shows that the partial molar free energy changes with composition, just as partial molar volume.

If we were to plot μ as a function of composition, we would get a plot that is the exact analog of the plot of partial molar volume we discussed earlier.

If *A* and *B* are present in two phases α and β, the phase equilibrium condition is:

$$\boxed{G_A^\alpha = G_A^\beta \text{ (or } \mu_A^\alpha = \mu_A^\beta\text{) and } G_B^\alpha = G_B^\beta \text{ (or } \mu_B^\alpha = \mu_B^\beta\text{).}}$$

5.7. Raoult's Law and Activities

Consider a binary system consisting of a solution and a vapor phase, each containing components *A* and *B*. The equilibrium condition is:

$$\boxed{G_A^{sol} = G_A^{vap} \text{ (or } \mu_A^{sol} = \mu_A^{vap}\text{) and } G_B^{sol} = G_B^{vap} \text{ (or } \mu_B^{sol} = \mu_B^{vap}\text{).}}$$

If the vapor phase behaves ideally, we may write

$$G_A^{vap} = G_A^{\circ,vap} + n_A RT\ln\left(\frac{P_A}{P^\circ}\right), \text{ and } G_B^{vap} = G_B^{\circ,vap} + n_B RT\ln\left(\frac{P_B}{P^\circ}\right).$$

Now, at equilibrium, we may write

$$\begin{gathered} G_A^{sol} = G_A^{\circ,vap} + n_A RT\ln\left(\frac{P_A}{P^\circ}\right), \text{and } G_B^{sol} = G_B^{\circ,vap} + n_B RT\ln\left(\frac{P_B}{P^\circ}\right), \text{or} \\ \mu_A^{sol} = \mu_A^{\circ,vap} + RT\ln\left(\frac{P_A}{P^\circ}\right) \text{and } \mu_B^{sol} = \mu_B^{\circ,vap} + RT\ln\left(\frac{P_B}{P^\circ}\right). \end{gathered} \tag{5.70,5.71}$$

For the pure liquids in equilibrium with their vapors, we write

$$\mu_A^* = \mu_A^{\circ,vap} + RT\ln\left(\frac{P_A^*}{P^\circ}\right) \text{and } \mu_B^* = \mu_B^{\circ,vap} + RT\ln\left(\frac{P_B^*}{P^\circ}\right) \tag{5.72}$$

From the last two equations, we write (all equations written for component *A* can also be written for *B*):

$$\mu_A^{sol} - \mu_A^* = RT\ln\left(\frac{P_A}{P^\circ}\right) - RT\ln\left(\frac{P_A^*}{P^\circ}\right), \text{ or}$$

$$\mu_A^{sol} = \mu_A^* + RT\ln\left(\frac{P_A}{P_A^*}\right). \tag{5.73}$$

If the solution behaves ideally (i.e., obeys Raoult's law), then $P_A/P^*_A = x_A$. Therefore, we get

$$\mu_A^{sol} = \mu_A^* + RT\ln x_A.$$

For non-ideal solutions, the ratio P_A/P^*_A is called the *activity* of *A*, a_A. In this case, we write

$$\mu_A^{sol} = \mu_A^* + RT\ln a_A.$$

As P_A approaches P^*_A, it is clear that the activity approaches unity. This is the basis for assigning the value of 1 to the activities of all pure substances.

See problem 5.34.

5.8. Colligative Properties

Let us consider the consequence of dissolving a nonvolatile solute B in a solvent A. Since the solute cannot be present in the vapor phase, this immediately leads to a lowering of vapor pressure, because $x_A < 1$ and, therefore, $P_A = x_A P^*_A < P^*_A$. This lowering of vapor pressure is responsible for both lowering the freezing point as well as raising the boiling point of the solvent.

Freezing Point Depression:

For the equilibrium between the liquid and solid phases, we require $\mu^l_A = \mu^s_A$, or $\mu^{*,l}_A + RT\ln x_A = \mu^s_A$, from which we get

$$\ln x_A = \frac{\mu^s_A - \mu^{*,l}_A}{RT} = \frac{-\Delta_{fus}G_{A,m}}{RT}, \text{ at constant } T \text{ and } P.$$

Differentiating both sides with respect to T, we get

$$\frac{d\ln x_A}{dT} = \frac{-1}{R}\left[\frac{\partial\left(\Delta_{fus}G_{A,m}/T\right)}{\partial T}\right]_P = \frac{\Delta_{fus}H_m}{RT^2}, \text{ at the equilibrium temperature.}$$

Now we rearrange and integrate both sides, the LHS from a mole fraction of $x_A = 1$ (pure solvent) to the solvent mole fraction in solution, $x_A < 1$, and correspondingly, the RHS from a liquid-solid equilibrium temperature of T^*_f (freezing point of the pure solvent) to T, the freezing point of the solution. This yields

$$\ln x_A = \frac{\Delta_{fus}H_m}{R}\left(\frac{1}{T^*_f} - \frac{1}{T}\right). \tag{5.115}$$

We may re-write this as

$$\ln(1 - x_B) = \frac{\Delta_{fus}H_m}{R}\left(\frac{T - T^*_f}{T^*_f T}\right). \tag{5.116}$$

We now make two simplifications: for small x_B, $\ln(1-x_B) \approx -x_B$ (see Eq. 5.117) and $T^*_f T_f \approx T^{*2}_f$. This gives

$$x_B = \frac{\Delta_{fus}H_m}{R}\left(\frac{\Delta T_f}{T^{*2}_f}\right),$$

which can be further simplified to yield (see the text above Eq. 5.119)

$$\Delta T_f = \frac{RT^{*2}_f M_A}{\Delta_{fus}H_m} m_B \text{ or } \Delta T_f = K_f m_B, \tag{5.119, 5.120}$$

where K_f is called the *cryoscopic constant* of the solvent.

Boiling Point Elevation:

By considering the liquid-vapor equilibrium in which the vapor contains only the component A, we can derive an expression analogous to that obtained above:

$$\Delta T_b = \frac{RT_b^{*2}M_A}{\Delta_{vap}H_m}m_B \text{ or } \Delta T_b = K_b m_B \tag{5.126}$$

where K_b is called the *ebullioscopic constant* of the solvent.

The elevation of boiling point is a rather weak effect compared to the depression of freezing point. Therefore, the latter property is overwhelmingly used for the practical applications of colligative properties.

Practical Applications:

- Problems 5.39, 5.40, 5.46
- These equations are useful to determine the freezing points or boiling points of various solutions of nonvolatile solutes.

  Problem 5.56
- A somewhat "liberal" interpretation of Eq. (5.115) or (5.116) can be used to calculate the solubility of various solutes at temperature T in a solvent whose enthalpy of fusion and freezing point are known.

  Problem 5.48
- The "simplified" forms are also useful to determine the molar masses of unknown solutes using Eq. (5.122).

  Problems 5.52, 5.55

Colligative properties depend on number of "particles" in solution rather than actual "concentration." For instance, a 1 *m* solution of NaCl leads to a 2 *m* solution of ions (Na^+ and Cl^-). Such a solution, therefore, will yield twice the expected ΔT_f. This effect must be taken into account when dealing with ionic substances (See problem 5.26).