

## Week 8

# Solutions

### 8.1 Vapor Pressure Lowering and Consequences

2/28:

- Colligative properties.
  - Vapor pressure lowering.
  - Boiling point elevation for non-volatile solutes.
  - Freezing point depression for solutes (excluding solids).
  - Osmotic pressure.
- **Vapor pressure lowering:** The process of adding less volatile solutes to lower the overall vapor pressure via Raoult's law.
- **Boiling point elevation:** The increase in the normal boiling point of a mixture due to vapor pressure lowering.

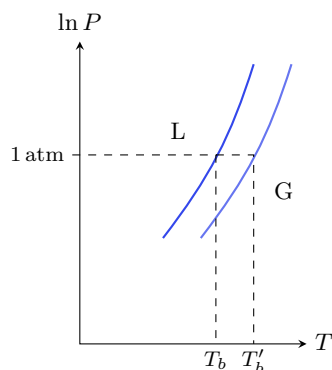


Figure 8.1: Boiling point elevation.

- In Figure 8.1, the dark blue line is the original liquid-gas coexistence curve and the light blue line is the liquid-gas coexistence curve with vapor pressure lowering — notice how at any given temperature, the corresponding pressure represented by the light blue line is lower than that given by the dark blue line.
- However, we still need to achieve a vapor pressure of 1 atm for the liquid to boil.
- We can get to such a pressure with a higher temperature, i.e., by heating the liquid to  $T'_b$  instead of just  $T_b$ .
- Calculating the change in the boiling point  $\Delta T_b$ .

- We can calculate the boiling point elevation from the Clausius-Clapeyron equation.

$$\begin{aligned}
 \frac{\Delta P}{\Delta T_b} &= \frac{\Delta \bar{H}}{T_b \Delta \bar{V}} \\
 \Delta T_b &= P^*(1-x) \frac{T_b \Delta \bar{V}}{\Delta \bar{H}} \\
 &= P^*(1-x) \frac{T_b \bar{V}_g}{\Delta \bar{H}} \\
 &= P^*(1-x) \frac{T_b R T_b}{P^* \Delta \bar{H}} \\
 &= \frac{R T_b^2}{\Delta \bar{H}} (1-x)
 \end{aligned}$$

where  $x$  is the mole fraction of solutes.

- We can also derive the above result from the chemical potential, where we get to the first to the second equation below because (standard) chemical potentials are equal at equilibrium.

$$\begin{aligned}
 \mu_i^\circ(T) + RT \ln x_1 &= \mu_g^\circ(T) + RT \ln \frac{P}{P_0} \\
 RT \ln x_1 &= RT \ln \frac{P}{P_0} + [\mu_g^\circ(T) - \mu_i^\circ(T)] \\
 &= RT \ln \frac{P}{P_0} + [\Delta \bar{H}_{\text{vap}} - T \Delta \bar{S}_{\text{vap}}] \\
 &= RT \ln \frac{P}{P_0} + [\Delta \bar{H}_{\text{vap}} - T_b \Delta \bar{S}_{\text{vap}} + (T_b - T) \Delta \bar{S}_{\text{vap}}] \\
 &= RT \ln \frac{P}{P_0} + \Delta T_b \cdot \frac{\Delta \bar{H}_{\text{vap}}}{T_b} \\
 \Delta T_b &= -\frac{R T_b^2}{\Delta \bar{H}_{\text{vap}}} \ln x_1 \\
 &= -\frac{R T_b^2}{\Delta \bar{H}_{\text{vap}}} \ln(1 - x_2) \\
 &\approx \frac{R T_b^2}{\Delta \bar{H}_{\text{vap}}} x_2
 \end{aligned}$$

- **Freezing point depression:** The decrease in the normal melting point of a mixture due to vapor pressure lowering.

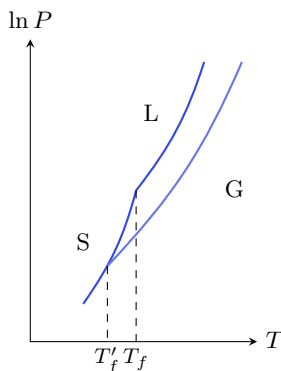


Figure 8.2: Freezing point depression.

- We know that  $\mu_g^\circ(T_f) = \mu_l^\circ(T_f)$ . Thus,

$$\begin{aligned}
 \mu_g^\circ(T) &= \mu_l^\circ(T) + RT \ln x_i \\
 RT \ln x_i &= \mu_g^\circ(T) - \mu_l^\circ(T) \\
 &= \Delta \bar{H}_{\text{fus}}(T) - T \Delta \bar{S}_{\text{fus}} \\
 &= (T_f - T) \Delta \bar{S}_{\text{fus}} \\
 &= (T_f - T) \frac{\Delta \bar{H}_{\text{fus}}}{T_f} \\
 &= -\Delta T_f \cdot \frac{\Delta \bar{H}_{\text{fus}}}{T_f} \\
 \Delta T_f &= -\frac{RT_f^2}{\Delta \bar{H}_{\text{fus}}} \ln x_1 \\
 &\approx \frac{RT_f^2}{\Delta \bar{H}_{\text{fus}}} x_2
 \end{aligned}$$

- The final result should be

$$\Delta T_f = -\frac{RT_f^2}{\Delta \bar{H}_{\text{fus}}} x_2$$

- The freezing point of water as more and more salt is added.

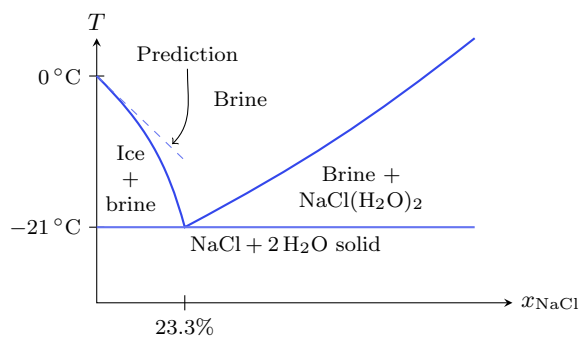


Figure 8.3: Freezing point vs. solute concentration.

- Osmotic pressure.

- Imagine a U-tube with a filter at the bottom that is porous to the solvent but nonporous to the solute.
- We know from Gen Chem that there will be excess pressure on the side with the impurities.
- Let  $\pi = \rho gh$  be the extra pressure where  $h$  is the height difference between the two sides and  $\rho$  is the density of the solvent.

$$\begin{aligned}
 \mu_l^\circ &= \mu_l = \mu_l^\circ + RT \ln x_1 + \pi \bar{V} \\
 0 &= RT \ln x_1 + \pi \bar{V} \\
 \pi &= \frac{RT}{\bar{V}} x_2
 \end{aligned}$$

- Ocean salinity is about 1 M, so  $\pi = 24$  atm. That means that in the tube, the right hand side will rise about as much as the Sears tower. Thus, the minimum amount of pressure/work you need is the height of the Sears tower minus 24 atm. Still, this is far more efficient than distillation.

## 8.2 Nonideal Solutions

3/2: • When solutions are not ideal, we see deviations from Raoult's Law (Figure 7.1).

- However, all solutions follow Raoult's Law when they are nearly pure.
- When the actual partial pressure is higher, that means the substance would rather be in the vapor phase. When the actual partial pressure is lower, that means there is a favorable interaction between particles (they'd rather be in the dissolved state).

• **Henry's Law:** Gives the tangent to the vapor pressure vs. mole percent graph at  $x_1 = 0$ . *Given by*

$$P_1 = k_H x_1$$

as  $x_1 \rightarrow 0$ .

• We know that  $A(g) \rightarrow A(\text{solv})$ .

- At equilibrium  $\Delta \bar{G} = 0 = \Delta \bar{G}_{\text{solv}} + RT \ln x/P$ .
- Thus,

$$P = x e^{\Delta \bar{G}_{\text{solv}}/RT}$$

- $x$  is the mixing entropy,  $P$  is the gas phase entropy.

• Microscopic enthalpy and entropy of solvation contribute to Henry's law, in addition to mixing entropy.

- Larger  $k_H$  means less soluble.

• Temperature dependence.

$$k_{H,cp} = k_{H,cp}^{\Theta} \exp \left[ -C \cdot \left( \frac{1}{T} - \frac{1}{T^{\Theta}} \right) \right]$$

- $\Theta$  indicates reference temperature.
- It follows that as  $T$  increases,  $k_H$  increases.
  - For example,  $\text{O}_2$  is less soluble in water at higher temperatures.
  - This is consistent with solvation being an exothermic process.

• The activity and activity coefficient of a solute. Using Raoult's law as the reference for fully miscible substances.

- We have for an ideal solution that  $\mu_i = \mu_i^* + RT \ln x_i$  and for an ideal gas that  $\mu_i = \mu_i^* + RT \ln \frac{P_i}{P_i^*}$ .
- These two equations together imply Raoult's law.
- Now we want to keep the nice form of the above equations even with nonideality, so we do something similar to defining fugacity by defining the **activity**.
- $a_i \rightarrow x_i$  as  $x_i \rightarrow 1$ .
- As  $x_i \rightarrow 0$ , we have that

$$\begin{aligned} \mu_i^* + RT \ln a_i &= \mu_i^* + RT \ln \frac{P_i}{P_i^*} \\ &= \mu_i^* + RT \ln \frac{k_H}{P_i^*} x_i \end{aligned}$$

i.e.,  $a_i \rightarrow k_H x_i / P_i^*$ .

- As a substance becomes less active, it becomes more reactive.

• **Activity:** A measure of the nonideality of solutions. *Denoted by  $a_i$ . Given by*

$$\mu_i = \mu_i^* + RT \ln a_i$$

- **Activity coefficient:** The following ratio. Denoted by  $\gamma$ . Given by

$$\gamma = \frac{a_i}{x_i}$$

- Example: Carbon disulfide/dimethoxymethane.

$x_{\text{CS}_2}$	$P_{\text{CS}_2}$ (torr)	$P_{\text{CH}_2(\text{OMe})_2}$ (torr)
0	0	587
0.1	109	529
1	514	0

Table 8.1: Pressure data for  $\text{CS}_2$  and  $\text{CH}_2(\text{OMe})_2$ .

- At  $x_{\text{CS}_2} = 0.1$ , we have that  $a_{\text{CS}_2} = 109/514$ .
- As  $x \rightarrow 0$ ,  $k_{H,\text{CS}_2} = 1130$  torr so  $a_{\text{CS}_2} = \frac{1130}{514} x_{\text{CS}_2}$ .
- See McQuarrie and Simon (1997) for using Henry's law as the reference state.
- Nonideality above the Raoult's law diagonal: More "active" than the ideal mixture.
- Nonideality below the Raoult's law diagonal: Less active than at low concentration.

### 8.3 Quantifying Deviations from Raoult's Law

- 3/4: • **Gibbs-Duhem relation:** A relation tying together the partial pressure of one substance to another, regardless of ideality/nonideality.

- We begin with

$$dG = \sum \mu_i dn_i + \sum n_i d\mu_i$$

at constant temperature and pressure.

- We also know from an earlier class that

$$G = \sum \mu_i n_i$$

- Differentiating the above, we get

$$dG = \sum \mu_i dn_i + \sum n_i d\mu_i$$

- It follows by setting the above two equations equal to each other that

$$\sum n_i d\mu_i = 0$$

- We can apply the Gibbs-Duhem relation to our expression for the chemical potential in terms of the activity coefficient.
- From last time,

$$\begin{aligned}\mu_i &= \mu_i^* + RT \ln(\gamma_i x_i) \\ d\mu_i &= RT d(\ln \gamma_i + \ln x_i)\end{aligned}$$

- It follows that

$$\begin{aligned}
 0 &= n_1 d\mu_1 + n_2 d\mu_2 \\
 &= \frac{1}{n_1 + n_2} (n_1 d\mu_1 + n_2 d\mu_2) \\
 &= \frac{n_1}{n_1 + n_2} RT d(\ln \gamma_1 + \ln x_1) + \frac{n_2}{n_1 + n_2} RT d(\ln \gamma_2 + \ln x_2) \\
 &= RT(x_1 d \ln x_1 + x_2 d \ln x_2 + x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2) \\
 &= dx_1 + dx_2 + x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 \\
 &= dx_1 - dx_1 + x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 \\
 &= x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2
 \end{aligned}$$

- Takeaway: If we know the activity coefficient for one component across the whole range, we can find the activity coefficient for the other component.
- In other words, knowing the chemical potential for one component gives us the chemical potential for the other.

- Relating  $P_1, P_2$  with the Gibbs-Duhem relation.

- We assume that we are in phase equilibrium. Thus, the chemical potential of the gas phase equals the chemical potential of the solution. In an equation,

$$\mu_1^* + RT \ln \frac{P_1}{P_1^*} = \mu_1 + RT \ln a_1$$

- Thus, applying the Gibbs-Duhem relation,

$$\begin{aligned}
 0 &= x_1 d \ln P_1 + x_2 d \ln P_2 \\
 &= x_1 \left( \frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} dx_1 + x_2 \left( \frac{\partial \ln P_2}{\partial x_2} \right)_{T,P} dx_2 \\
 &= x_1 \left( \frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} - x_2 \left( \frac{\partial \ln P_2}{\partial x_2} \right)_{T,P}
 \end{aligned}$$

- Takeaway: The slopes of the curves on a pressure-concentration diagram are related, regardless of ideality/nonideality.

- **Margules equation:** An expansion to capture the experimental  $P(x)$  deviation from Raoult's law.

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3 + \dots}$$

- An analytical form that gives us a good representation of experimentally-measured vapor pressures.
- Important features: Follows Henry's law at low concentrations of solute and Raoult's Law at high concentrations of solute.

- Margules equation covers Raoult's law and Henry's law.

- We have by the product rule of derivatives that

$$\frac{dP_1}{dx_1} = P_1^* \left[ e^{\alpha x_2^2 + \beta x_2^3 + \dots} + x_1 (-2\alpha x_2 - 3\beta x_2^2 - \dots) e^{\alpha x_2^2 + \beta x_2^3 + \dots} \right]$$

- As  $x_1 \rightarrow 1$ ,  $dP_1/dx_1 \rightarrow P_1^*$ . This can be seen because the above expression can be rewritten

$$\frac{dP_1}{dx_1} = P_1^* e^{\alpha x_2^2 + \beta x_2^3 + \dots} [1 - 2\alpha x_1 x_2 - 3\beta x_1 x_2^2 - \dots]$$

- Implication: We recover Raoult's law as  $x_1 \rightarrow 1$ .
- Additionally, this explains why there is no linear terms in the exponent: If there were, one of the terms in the sum on the right-hand side above wouldn't go to zero as  $x_1 \rightarrow 1$ , meaning that  $dP_1/dx_1$  would not go to  $P_1^*$ .
- Recovering Henry's law as  $x_1 \rightarrow 0$ : As  $x_1 \rightarrow 0$ ,  $P_1 \rightarrow k_H x_1 = P_1^* e^{\alpha + \beta + \dots} \cdot x_1$ .
- Margules equation parameters fitted for  $P_1$  provide a related equation for  $P_2$  based on Gibbs-Duhem (Problem 24-33).
- To two terms, the Margules equation tells us that

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$$

- As we showed earlier, the Gibbs-Duhem equation implies that

$$x_1 \frac{\partial \ln P_1}{\partial x_1} = x_2 \frac{\partial \ln P_2}{\partial x_2}$$

- Thus, since  $x_2 = 1 - x_1$ ,

$$\begin{aligned} x_1 \frac{\partial \ln P_1}{\partial x_1} &= x_1 \frac{\partial}{\partial x_1} (\ln x_1 + \alpha x_2^2 + \beta x_2^3 + \text{terms not involving } x_1) \\ &= x_1 \left[ \frac{1}{x_1} + (-2\alpha x_2) + (-3\beta x_2^2) \right] \\ &= 1 + x_2(-2\alpha x_1 - 3\beta x_1 x_2) \\ &= 1 + x_2(-2\alpha x_1 - 3\beta x_1(1 - x_1)) \\ &= 1 + x_2(-2\alpha x_1 - 3\beta(x_1 - x_1^2)) \\ &= 1 + x_2[-(2\alpha + 3\beta)x_1 + 3\beta x_1^2] \end{aligned}$$

- Now let

$$P_2 = x_2 P_2^* e^{a x_1^2 + b x_1^3}$$

- It follows as before that

$$x_2 \frac{\partial \ln P_2}{\partial x_2} = 1 + x_2(-2a x_1 - 3b x_1^2)$$

- Direct comparison reveals that

$$\begin{aligned} -2a &= -(2\alpha + 3\beta) & -3b &= 3\beta \\ a &= \alpha + \frac{3}{2}\beta & b &= -\beta \end{aligned}$$

so

$$P_2 = x_2 P_2^* e^{(\alpha + \frac{3}{2}\beta)x_1^2 - \beta x_1^3}$$

- **Regular solution:** A solution for which only  $\alpha \neq 0$  and every other Margules parameter is zero.

- In this case,

$$P_1 = x_1 P_1^* e^{\alpha x_2^2} \qquad P_2 = x_2 P_2^* e^{\alpha x_1^2}$$

- This means that the Raoult's activity of the two solutions is entirely symmetric over the range of compositions.
- This does not necessarily imply that the vapor pressures vary in the same way.
- Mixing Gibbs free energy for a regular solution (24-5).

– We have

$$\begin{aligned}
 \frac{\Delta G_{\text{mix}}}{RT} &= \underbrace{n_1 \mu_1^{\text{sol}} + n_2 \mu_2^{\text{sol}}}_{\text{mixture}} - \underbrace{(n_1 \mu_1^* + n_2 \mu_2^*)}_{\text{pure}} \\
 &= n_1 \ln \frac{P_1}{P_1^*} + n_2 \ln \frac{P_2}{P_2^*} \\
 &= n_1 \ln x_1 + n_2 \alpha x_2^2 + n_2 \ln x_2 + n_2 \alpha x_1^2 \\
 \frac{\Delta G_{\text{mix}}}{RT(n_1 + n_2)} &= x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2^2 + \alpha x_2 x_1^2 \\
 &= x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2 (x_1 + x_2) \\
 \frac{\Delta G_{\text{mix}}}{RT(n_1 + n_2)} &= x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2
 \end{aligned}$$

- The left two terms above represent the entropy of mixing (which does not depend on interaction).
- The right term above is the enthalpy/entropy of mixing which depends *only* on interaction.
- Thus,  $\alpha$  is the microscopic entropy of mixing for a regular solution.
- The upper critical solution temperature (UCST) (critical temperature above which the components of the mixture are miscible in all proportions).

– We have

$$\Delta \bar{G} = RT(x_1 \ln x_1 + x_2 \ln x_2) + \underbrace{RT\alpha x_1 x_2}_{\Omega}$$

- Graphing the above equation will help us determine what extent of mixing will be most energetically favorable.
  - In particular, if we graph the left two terms, that tells us the entropy of mixing, which will be greatest at  $x_1 = x_2$ .
  - Graphing the right term on the other hand yields a parabola.
  - As such, since  $x_1 \ln x_1 + x_2 \ln x_2$  has vertical slope at  $x_1 = 0, 1$  and the other term simply has some positive slope, entropy of mixing will always win at low concentrations of solutes, i.e., when you have a small enough concentration of solute in solvent, you will always observe mixing.
  - However, the overall graph may have minima on the two sides, indicating that forming a fully mixed solution is not energetically favorable, but it is most favorable to separate into substance 1 with a bit of substance 2 and vice versa (think oil and water).
  - At high temperatures, however, this effect goes away and mixing always becomes the most favorable state.
- The temperature at which the overall graph only has one minimum for the first time is the UCST.

## 8.4 Office Hours (PGS)

- Can you go over the spontaneous expansion of an ideal gas from one isolated container to two? Is this an adiabatic process or an isothermal process? How can the gas cool down during the expansion if it ends up at the same final temperature?
  - An isoenthalpic expansion? Only as long as we can neglect the back pressure of the far wall. In this moment,

$$\begin{aligned}
 0 &= \Delta H \\
 &= \Delta U + \Delta KE + \Delta(PV)
 \end{aligned}$$



- The gas shooting out is expanding and picking up a lot of kinetic energy, but we need to conserve enthalpy all together, so that kinetic energy comes from vibrational and spin states.
- After everything comes to equilibrium, though, the temperature is the same.
- It's irreversible, so that means that during the process, you do not have well-defined state variables.
- Note that no work is done even for the intermixing of two gases.
  - Any work done by one gas is canceled by the work on the other gas and no work comes out of the system; it's a pure entropy effect.
  - But work is being done by both gases; just equal and opposite?
- How does the Henry's law we learned relate to the one from Gen Chem (the amount of gas dissolved in solution is proportional to its partial pressure)?
  - The Henry's law of intro chem says that concentration vs. pressure will always be a straight line.
  - We know now that we see deviations at higher concentrations, and that Henry's law is just a good approximation at relatively low pressures.
- Demixing of solutions at lower temperatures?
  - The line connecting all of the two minima with peak at the UCMT is the **spinodal line**.

## 8.5 Chapter 24: Solutions I — Liquid-Liquid Solutions

From McQuarrie and Simon (1997).

- There exist positive and negative deviations from Raoult's Law (see Figure 8.4).

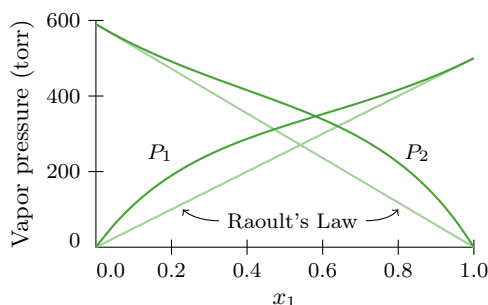


Figure 8.4: Positive deviations from Raoult's law ( $\text{CS}_2/\text{CH}_2(\text{OMe})_2$  at  $25^\circ\text{C}$ ).

- If 1 and 2 denote two substances that are being mixed, positive deviations occur when 1-2 interactions are more repulsive than either 1-1 or 2-2 interactions, and vice versa for negative deviations.
- If one component of a binary solution exhibits positive deviations from Raoult's law, so must the other component.
  - Follows from “Relating  $P_1, P_2$  with the Gibbs-Duhem relation” as in class.
- Molecular structure predicts deviations from Raoult's law.

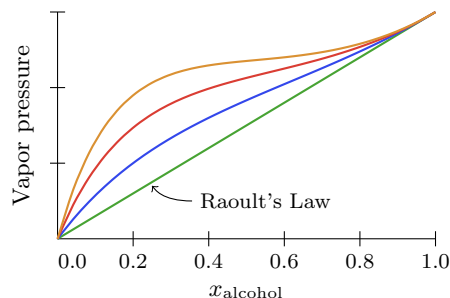


Figure 8.5: Vapor pressure of alcohol/water solutions.

- The blue line represents MeOH, the red line represents EtOH, and the orange line represents PrOH.
- Notice how as molecular structure gets further from that of H<sub>2</sub>O (the solvent), deviations become more exaggerated.
- McQuarrie and Simon (1997) discusses the limiting behavior of  $P_1$  in Figure 8.4, noting the Raoult's law limit as  $x_1 \rightarrow 1$  and introducing **Henry's law**.
- **Henry's law:** The partial pressure of a component in solution approaches the linear function  $k_{H,i}x_i$  as  $x_i \rightarrow 0$ .
- **Henry's law constant:** The constant  $k_{H,i}$  in the above definition.
- For an ideal solution,  $k_{H,i} = P_i^*$ , but this is not true in general (as illustrated by Figure 8.4).
- Example: Finding  $P_1^*$  and  $k_H$  from an equation for  $P_1$ .
  - Let  $P_1 = 180x_1e^{x_2^2 + \frac{1}{2}x_2^3}$ .
  - As  $x_1 \rightarrow 1$ ,  $x_2 \rightarrow 0$ , so  $P_1 \rightarrow 180x_1$ . Since this form should be the Raoult's law limit, we can read off  $P_1^* = 180$  torr.
  - As  $x_1 \rightarrow 0$ ,  $x_2 \rightarrow 1$ , so  $P_1 \rightarrow 180x_1e^{1 + \frac{1}{2}} = 180e^{3/2}x_1$ . Since this form should be the Henry's law limit, we can read off  $k_{H,1} = 180e^{3/2} = 807$  torr.

- McQuarrie and Simon (1997) derives

$$x_1 \left( \frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} = x_2 \left( \frac{\partial \ln P_2}{\partial x_2} \right)_{T,P}$$

as in class.

- In a binary solution, if component 1 obeys Raoult's law as  $x_1 \rightarrow 1$ , then component 2 obeys Henry's law as  $x_2 \rightarrow 0$ .
  - Suppose component 1 satisfies  $P_1 \rightarrow x_1 P_1^*$  as  $x_1 \rightarrow 1$ . Then

$$\begin{aligned} x_2 \left( \frac{\partial \ln P_2}{\partial x_2} \right)_{T,P} &= x_1 \left( \frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} \\ &= x_1 \frac{\partial}{\partial x_1} (\ln x_1 + \ln P_1^*) \\ &= 1 \\ \ln P_2 &= \int \frac{1}{x_2} dx_2 \\ &= \ln x_2 + C \\ P_2 &= k_H x_2 \end{aligned}$$

as desired.

- The vapor pressure curve of WLOG component 1 of a binary solution can often be represented empirically by

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$$

- $\alpha, \beta$  reflect the extent of the nonideality of the solution in some manner because  $P_1 = x_1 P_1^*$  (ideal) for  $\alpha = \beta = 0$ .
- Furthermore, generalizing from the previous example,  $k_{H,1} = P_1^* e^{\alpha + \beta}$  and  $k_{H,2} = P_2^* e^{\alpha + \beta/2}$  (the latter equation will be derived presently).
- Deriving  $P_2 = x_2 P_2^* e^{(\alpha + 3\beta/2)x_1^2 - \beta x_1^3}$  from  $P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$  in an alternate manner to what was presented in class.
  - We are given that  $P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$  and that  $x_2 = 1 - x_1$ .
  - It follows that the chemical potential of component 1 is

$$\begin{aligned}\mu_1 &= \mu_1^\circ + RT \ln P_1 \\ &= \mu_1^\circ + RT [\ln P_1^* + \ln x_1 + \alpha(1 - x_1)^2 + \beta(1 - x_1)^3]\end{aligned}$$

- It follows that the total differential of  $\mu_1(x_1)$  is

$$d\mu_1 = RT \left[ \frac{1}{x_1} - 2\alpha(1 - x_1) - 3\beta(1 - x_1)^2 \right] dx_1$$

- Thus, by the Gibbs-Duhem equation,

$$\begin{aligned}x_1 d\mu_1 + x_2 d\mu_2 &= 0 \\ d\mu_2 &= -\frac{x_1}{x_2} \cdot RT \left[ \frac{1}{x_1} - 2\alpha(1 - x_1) - 3\beta(1 - x_1)^2 \right] dx_1 \\ &= RT \left[ -\frac{1}{x_2} + 2\alpha x_1 + 3\beta x_1(1 - x_1) \right] dx_1\end{aligned}$$

- Substitute  $x_2 = 1 - x_1$  and integrate.

$$\begin{aligned}d\mu_2 &= RT \left[ \frac{1}{x_2} - 2\alpha(1 - x_2) - 3\beta x_2(1 - x_2) \right] dx_2 \\ \int_1^{x_2} d\mu_2 &= RT \int_1^{x_2} \left[ \frac{1}{x'_2} - 2\alpha(1 - x'_2) - 3\beta x'_2(1 - x'_2) \right] dx'_2 \\ \mu_2(x_2) - \mu_2(1) &= RT \left[ \ln x_2 + \alpha(1 - x_2)^2 - \frac{3\beta}{2}(x_2^2 - 1) + \beta(x_2^3 - 1) \right] \\ \mu_2 - \mu_2^* &= RT \left[ \ln x_2 + \alpha x_1^2 + \frac{3\beta}{2} x_1^2 - \beta x_1^3 \right]\end{aligned}$$

- Therefore, since

$$\mu_2 = \mu_2^\circ + RT \ln P_2 \qquad \mu_2^* = \mu_2^\circ + RT \ln P_2^*$$

we have that

$$\begin{aligned}\ln P_2 &= \ln P_2^* + \ln x_2 + \alpha x_1^2 + \frac{3\beta}{2} x_1^2 - \beta x_1^3 \\ P_2 &= x_2 P_2^* e^{(\alpha + 3\beta/2)x_1^2 - \beta x_1^3}\end{aligned}$$

- 3/5:
- **Azeotrope:** A mixture for which there is no change in composition upon boiling.
  - Vapor pressure behavior at various temperatures.

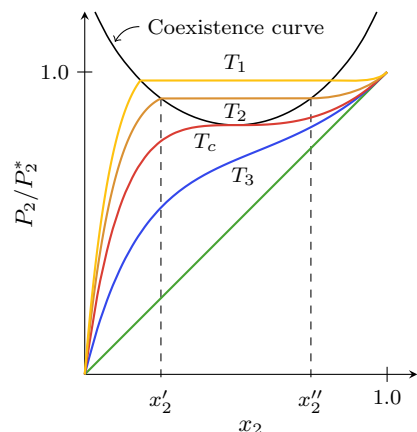


Figure 8.6: The critical behavior of a binary solution.

- In Figure 8.6,  $T_3 > T_c > T_2 > T_1$ . Additionally,  $P_2^*$  denotes the vapor pressure of the pure substance *at each temperature*, and thus serves to “normalize” all of the curves.
- At or above the **consolute temperature**  $T_c$ , component 1 and component 2 will mix to form a homogenous solution regardless of their relative concentrations.
- On the other hand, consider the solution formed at  $T_2 < T_c$ .
  - If  $x_2 < x'_2$  or  $x_2 > x''_2$ , a homogenous solution is formed.
  - However, if  $x_2$  is within this range, the mixture separates into a solution with component 2 concentration  $x'_2$  and a solution with component 2 concentration  $x''_2$ , with the relative proportions dictated by what will give the constant vapor pressure indicated by Figure 8.6.
- “Points inside the **coexistence curve** represent two solution phases, whereas points below the coexistence curve represent one solution phase” (McQuarrie & Simon, 1997, p. 985).
- **Consolute temperature:** The temperature below which two liquids are not miscible in all proportions. *Also known as critical temperature. Denoted by  $T_c$ .*
- A lever rule that gives the relative amounts of the two phases indicated by Figure 8.6.
  - Consider a solution of overall composition  $x_2 \in (x'_2, x''_2)$ . Let  $n'_1, n'_2$  and  $n''_1, n''_2$  be the number of moles of the two components in the phases of composition  $x'_2$  and  $x''_2$ , respectively.
  - By definition, we have the relations

$$x'_2 = \frac{n'_2}{n'_1 + n'_2} \quad x''_2 = \frac{n''_2}{n''_1 + n''_2} \quad x_2 = \frac{n'_2 + n''_2}{n'_1 + n''_1 + n'_2 + n''_2}$$

- It follows that

$$x_2(n'_1 + n''_1 + n'_2 + n''_2) = x'_2(n'_1 + n'_2) + x''_2(n''_1 + n''_2)$$

$$\frac{n'}{n''} = \frac{n'_1 + n'_2}{n''_1 + n''_2} = \frac{x'_2 - x_2}{x_2 - x'_2}$$

- **Activity** (of component  $j$ ): A state function describing the nonideality of the chemical potential of component  $j$  of a solution. *Denoted by  $a_j$ . Given by*

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln a_j$$

- It follows from Raoult’s law that  $a_j \rightarrow x_j$  as  $x_j \rightarrow 1$ .

- We can also represent the activity of component 1 in a binary solution empirically by

$$a_1 = x_1 e^{\alpha x_2^2 + \beta x_2^3 + \dots}$$

- **Activity coefficient** (of component  $j$ ): A measure of the deviation of a solution from ideality. Denoted by  $\gamma_j$ . Given by

$$\gamma_j = \frac{a_j}{x_j}$$

- It should make intuitive sense that  $\gamma_j \rightarrow 1$  as  $x_j \rightarrow 1$ .
- Since activity and chemical potential are directly related, activity is really just another way of expressing chemical potential.
  - It follows that since the chemical potentials of the components of a binary solution are related by the Gibbs-Duhem equation, the activities of said components are related by

$$\begin{aligned} 0 &= x_1 d(\mu_j^* + RT \ln a_1) + x_2 d(\mu_j^* + RT \ln a_2) \\ &= RT x_1 d \ln a_1 + RT x_2 d \ln a_2 \\ &= x_1 d \ln a_1 + x_2 d \ln a_2 \end{aligned}$$

- Consequently, if  $a_1 = x_1$  over the entire composition range, we can use this relation to show that  $a_2 = x_2$ .
- Similarly, if  $a_1 = x_1 e^{\alpha x_2^2}$  over the entire composition range, we can use this relation to show that  $a_2 = x_2 e^{\alpha x_1^2}$ .
- An activity defined by  $a_j = P_j/P_j^*$  is said to be based upon a solvent, or Raoult's law, standard state.
  - This is most convenient for substances that are miscible in all proportions, i.e., when there is no clear "solute" and "solvent."
- If one component is only sparingly soluble in the other, however, picking a standard state based on Henry's law is more convenient.
  - In this case,  $P_j \rightarrow x_j k_{H,j}$  as  $x_j \rightarrow 0$  (we consider  $x_j$  close to zero because component  $j$  is sparingly soluble, so its concentration is naturally low).
  - We thus have that

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln \frac{k_{H,j}}{P_j^*} + RT \ln x_j$$

and must define

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln \frac{k_{H,j}}{P_j^*} + RT \ln a_j$$

- It follows that for these two equations to be the same as  $x_j \rightarrow 0$ , we must take  $a_j = P_j/k_{H,j}$ .
- Additionally, the standard state must be such that

$$\mu_j = \mu_j^* + RT \ln \frac{k_{H,j}}{P_j^*}$$

or  $P_j^* = k_{H,j}$ .

- If such a standard state is not achievable in practice, it is called a **hypothetical standard state**.
- Deriving an expression for the Gibbs energy of mixing of binary solutions in terms of the activity coefficients.
  - We have that

$$\Delta_{\text{mix}} G = n_1 \mu_1^{\text{sln}} + n_2 \mu_2^{\text{sln}} - n_1 \mu_1^* - n_2 \mu_2^*$$

- Since  $\mu_j^{\text{sln}} = \mu_j^* + RT \ln a_j$  for any solution and  $\gamma_j = a_j/x_j$ , it follows that

$$\frac{\Delta_{\text{mix}}G}{RT} = n_1 \ln x_1 + n_2 \ln x_2 + n_1 \ln \gamma_1 + n_2 \ln \gamma_2$$

$$\frac{\Delta_{\text{mix}}\bar{G}}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

- Note that the left two terms above represent the Gibbs energy of mixing of an ideal solution.

- We can use the above result to derive a formula for  $\Delta_{\text{mix}}\bar{G}$  for a binary solution described by

$$P_1 = x_1 P_1^* e^{\alpha x_2^2} \qquad P_2 = x_2 P_2^* e^{\alpha x_1^2}$$

as in class. The final result is

$$\frac{\Delta_{\text{mix}}\bar{G}}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2$$

- Statistical mechanics suggests that  $\alpha$  has the form  $w/RT$ , where  $w$  is a constant. Thus, we can write the above equation as

$$\frac{\Delta_{\text{mix}}\bar{G}}{w} = \frac{RT}{w} (x_1 \ln x_1 + x_2 \ln x_2) + x_1 x_2$$

- Visualizing the Gibbs energy of mixing.

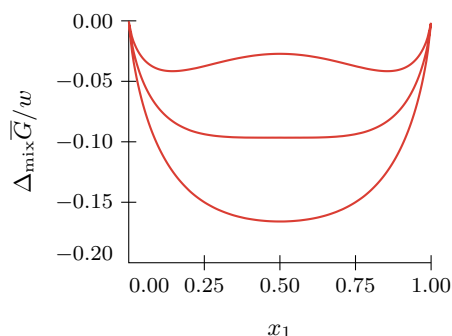


Figure 8.7:  $\Delta_{\text{mix}}\bar{G}$  at various temperatures.

- The curves with a maximum at  $x_1 = 0.5$  have an interesting relation to the extraneous curves in the cubic van der Waals and Redlich-Kwong equations for  $T < T_c$ . In particular, the region between their two minima corresponds to unmixing of the solutions and should be flatter, as per Figure 8.6.
- Note that the three curves plotted are for, from the top down,  $RT/w = 0.4$ ,  $RT/w = 0.5$ , and  $RT/w = 0.6$ .
- By finding the points where  $\partial(\Delta_{\text{mix}}\bar{G}/w)/\partial x_1 = 0$ , we can plot the coexistence curve from Figure 8.6.
  - Note that for  $RT/w \geq 0.5$ ,  $\partial(\Delta_{\text{mix}}\bar{G}/w)/\partial x_1 = 0$  only has one solution ( $x_1 = 0.5$ ), whereas for  $RT/w < 0.5$ ,  $\partial(\Delta_{\text{mix}}\bar{G}/w)/\partial x_1 = 0$  has three solutions ( $x_1 = 0.5$  and two others, corresponding to the other minima as in the plot of  $RT/w = 0.4$  in Figure 8.7).
- **Regular solution:** A solution that can be described by the equation  $\Delta_{\text{mix}}\bar{G}/RT = x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2$ .
- **Excess Gibbs energy of mixing:** The extra Gibbs energy of mixing present in a solution beyond what would be present in an ideal solution. Denoted by  $G^E$ . Given by

$$G^E = \Delta_{\text{mix}}G - \Delta_{\text{mix}}G^{\text{id}}$$

- It follows from the above that

$$\frac{G^E}{RT} = n_1 \ln \gamma_1 + n_2 \ln \gamma_2$$

- **Molar excess Gibbs energy of mixing:** The excess Gibbs energy of mixing for one mole of a solution. Denoted by  $\overline{G}^E$ . Given by

$$\frac{\overline{G}^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

- If the solution in question is described by

$$P_1 = x_1 P_1^* e^{\alpha x_2^2} \qquad P_2 = x_2 P_2^* e^{\alpha x_1^2}$$

then we have that

$$\frac{\overline{G}^E}{RT} = \alpha x_1 x_2$$

## 8.6 Chapter 25: Solutions II — Solid-Liquid Solutions

From McQuarrie and Simon (1997).

3/6:

- **Solute:** The sparingly soluble component in a binary solution.
  - Related quantities are denoted by a subscript 2.
- **Solvent:** The component in excess in a binary solution.
  - Related quantities are denoted by a subscript 1.
- $a_1$  (the activity of the solvent) is defined with respect to a Raoult's law standard state.  $a_2$  (the activity of the solute) is defined with respect to a Henry's law standard state.
  - Note that we still define  $a_2$  with respect to its vapor pressure (even though that quantity may be exceedingly small) because it is still meaningful.
- **Molality:** The number of moles of solute per 1000 g of solvent. Denoted by  $m$ . Units  $\text{mol kg}^{-1}$ . Given by

$$m = \frac{n_2}{1000 \text{ g solvent}}$$

- Relating the mole fraction of solute  $x_2$  and the molality  $m$ .

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{m}{\frac{1000 \text{ g kg}^{-1}}{M_1} + m}$$

- $M_1$  is the molar mass of the solvent.
- $1000 \text{ g kg}^{-1}/M_1$  is the number of moles of solvent  $n_1$  in 1000 g of solvent.
- We convert from the middle equation to the right equation by dividing both the top and bottom of the fraction by 1000 g.
- For  $\text{H}_2\text{O}$ ,
 
$$\frac{1000 \text{ g kg}^{-1}}{M_1} = 55.506 \text{ mol/kg}$$
- We define solute activity in terms of molality by requiring that  $a_2 \rightarrow m$  as  $m \rightarrow 0$ .
- Under this definition, we can reexpress Henry's law in terms of molality with a related set of Henry's law constants. These give us equations like  $P_2 = k_H m$ .

- **Molarity:** The number of moles of solute per 1000 mL of solution. Denoted by  $c$ . Units  $\text{mol L}^{-1}$ . Given by

$$c = \frac{n_2}{1000 \text{ mL solution}}$$

- We can also analogously define solute activity in terms of molarity, requiring  $a_2 \rightarrow c$  as  $c \rightarrow 0$ .
- Relating the solute mole fraction and molarity via the density.

– Consider 1 L of a solution.

– We can find the mass of this quantity of solution via the density  $\rho$ . In particular,

$$\text{mass of the solution per liter} = (1000 \text{ mL L}^{-1})\rho$$

– We can extract from this, the molarity, and the molar mass of the solute  $M_2$  the mass of solvent per liter.

$$\begin{aligned} \text{mass of the solvent per liter} &= \text{mass of the solution per liter} - \text{mass of the solute per liter} \\ &= (1000 \text{ mL L}^{-1})\rho - cM_2 \end{aligned}$$

– Therefore, the number of moles of solvent per liter of solution is

$$\frac{n_1}{1 \text{ L}} = \frac{(1000 \text{ mL L}^{-1})\rho - cM_2}{M_1}$$

so

$$\begin{aligned} x_2 &= \frac{n_2}{n_1 + n_2} \\ &= \frac{n_2}{n_1 + n_2} \cdot \frac{1/1 \text{ L}}{1/1 \text{ L}} \\ &= \frac{c}{\frac{(1000 \text{ mL L}^{-1})\rho - cM_2}{M_1} + c} \\ &= \frac{cM_1}{(1000 \text{ mL L}^{-1})\rho + c(M_1 - M_2)} \end{aligned}$$

- For a nonvolatile solute, an equation of the form  $a_2 = P_2/k_H$  is not practical to use since  $P_2$  is so small. Thus, we invoke the Gibbs-Duhem equation.

– Consider a solution of water with a small amount of a nonvolatile solute.

– Since  $m \ll 55.506 \text{ mol kg}^{-1}$ , we have that

$$x_2 \approx \frac{m}{55.506 \text{ mol kg}^{-1}}$$

– Therefore, since  $a_1 \rightarrow x_1$  as  $x_1 \rightarrow 1$  (as we have at low concentrations), we have that

$$\ln a_1 = \ln x_1 = \ln(1 - x_2) \approx -x_2 \approx -\frac{m}{55.506 \text{ mol kg}^{-1}}$$

– We can now use the form of the Gibbs-Duhem equation relating activities to find  $a_2$ .

– In particular, for 1 kg of solvent,  $n_1 = 55.506 \text{ mol}$  and  $n_2 = m$ , so we have

$$(55.506 \text{ mol kg}^{-1}) d \ln a_1 + m d \ln a_2 = 0$$

– With the definition of the **osmotic coefficient**, we have that  $(55.506 \text{ mol kg}^{-1}) d \ln a_1 = -d(m\phi)$ . Thus,

$$m d \ln(\gamma_{2m} m) = d(m\phi)$$

where  $\gamma_{2m}$  is the molal activity coefficient.



– Therefore,

$$\begin{aligned}
 m \, d\phi + \phi \, dm &= m(d \ln \gamma_{2m} + d \ln m) \\
 d \ln \gamma_{2m} &= d\phi + \frac{\phi - 1}{m} dm \\
 \int_0^m d \ln \gamma_{2m} &= \int_0^m d\phi + \int_0^m \frac{\phi - 1}{m'} dm' \\
 \ln \gamma_{2m} - \ln(1) &= \phi - 1 + \int_0^m \frac{\phi - 1}{m'} dm' \\
 \ln \gamma_{2m} &= \phi - 1 + \int_0^m \frac{\phi - 1}{m'} dm'
 \end{aligned}$$

- **Osmotic coefficient:** A quantity that accounts for the discrepancy between experimental solvent activities and ones predicted by the above equation. Denoted by  $\phi$ . Given by

$$\ln a_1 = -\frac{m\phi}{55.506 \text{ mol kg}^{-1}}$$

- Since  $\phi = 1$  for an ideal dilute solution, the deviation of  $\phi$  from unity is yet another measure of the nonideality of a solution.
- $\phi$  increases as  $m$  increases (this should also make intuitive sense).
- **Colligative property:** A property of a solution that depends (in dilute solutions) upon only the number, not the type, of solute particles.
- Deriving an equation for the activity of the solvent in a solution at the freezing point.
  - At the freezing point,  $\mu_1^s = \mu_1^{\text{sln}}$ . In particular,

$$\begin{aligned}
 \mu_1^s &= \mu_1^l + RT \ln a_1 \\
 \ln a_1 &= \frac{\mu_1^s - \mu_1^l}{RT}
 \end{aligned}$$

- Differentiating the above with respect to  $T$  at constant pressure and concentration, and substituting with the Gibbs-Helmholtz equation, give us

$$\begin{aligned}
 \left( \frac{\partial \ln a_1}{\partial T} \right)_{P, x_1} &= \frac{1}{R} \left[ \frac{\partial}{\partial T} \left( \frac{\mu_1^s}{T} \right) - \frac{\partial}{\partial T} \left( \frac{\mu_1^l}{T} \right) \right]_{P, x_1} \\
 &= \frac{1}{R} \left[ -\frac{\overline{H}_1^s}{T^2} + \frac{\overline{H}_1^l}{T^2} \right] \\
 &= \frac{\Delta_{\text{fus}} \overline{H}}{RT^2}
 \end{aligned}$$

- Integrating the above from pure solvent  $a_1 = 1$ ,  $T = T_{\text{fus}}^*$  to a solution with arbitrary values of  $a_1$ ,  $T_{\text{fus}}$  allows us to calculate the activity  $a_1$  of said solution.
- **Freezing-point depression constant:** The proportionality constant between the change in freezing point  $\Delta T_{\text{fus}}$  from the pure solvent to the given solution and the molality  $m$  of the given solution. Denoted by  $K_f$ . Given by

$$\Delta T_{\text{fus}} = K_f m$$

- Deriving  $K_f$  from our freezing point activity equation.
  - Consider a dilute solution. Assume  $\Delta_{\text{fus}} \overline{H}$  is independent of temperature over the temperature range  $(T_{\text{fus}}, T_{\text{fus}}^*)$ .

- It follows that

$$\begin{aligned}\ln a_1 &= \int_{T_{\text{fus}}^*}^{T_{\text{fus}}} \frac{\Delta_{\text{fus}} \bar{H}}{RT^2} dT \\ \ln x_1 &\approx \frac{\Delta_{\text{fus}} \bar{H}}{R} \int_{T_{\text{fus}}^*}^{T_{\text{fus}}} \frac{dT}{T^2} \\ \ln(1 - x_2) &\approx \frac{\Delta_{\text{fus}} \bar{H}}{R} \left( \frac{1}{T_{\text{fus}}^*} - \frac{1}{T_{\text{fus}}} \right) \\ -x_2 &\approx \frac{\Delta_{\text{fus}} \bar{H}}{R} \left( \frac{T_{\text{fus}} - T_{\text{fus}}^*}{T_{\text{fus}} T_{\text{fus}}^*} \right)\end{aligned}$$

- Now for two more approximations. First, since  $\Delta T_{\text{fus}}$  is small, we can set  $T_{\text{fus}} \approx T_{\text{fus}}^*$  in the denominator of the above equation. Second, since  $m$  is small, we may let

$$x_2 = \frac{m}{\frac{1000 \text{ g kg}^{-1}}{M_1} + m} \approx \frac{M_1 m}{1000 \text{ g kg}^{-1}}$$

- Therefore, making the substitutions and rearranging the above gives us

$$\begin{aligned}-\frac{M_1 m}{1000 \text{ g kg}^{-1}} &= \frac{\Delta_{\text{fus}} \bar{H}}{R} \left( \frac{-\Delta T_{\text{fus}}}{(T_{\text{fus}}^*)^2} \right) \\ \Delta T_{\text{fus}} = T_{\text{fus}}^* - T_{\text{fus}} &= \underbrace{\frac{M_1}{1000 \text{ g kg}^{-1}} \frac{R(T_{\text{fus}}^*)^2}{\Delta_{\text{fus}} \bar{H}}}_{K_f} \cdot m\end{aligned}$$

- **Boiling-point elevation constant:** The proportionality constant between the change in boiling point  $\Delta T_{\text{vap}}$  from the pure solvent to the given solution and the molality  $m$  of the given solution. Denoted by  $K_b$ . Given by

$$\Delta T_{\text{vap}} = K_b m$$

- We can derive an analogous equation to the freezing-point depression result in an analogous way, yielding

$$\Delta T_{\text{vap}} = T_{\text{vap}} - T_{\text{vap}}^* = \underbrace{\frac{M_1}{1000 \text{ g kg}^{-1}} \frac{R(T_{\text{vap}}^*)^2}{\Delta_{\text{vap}} \bar{H}}}_{K_b} \cdot m$$

- **Semipermeable membrane:** A membrane containing pores that allow one substance to pass through but not another.
- **Osmotic pressure:** The hydrostatic pressure head that is built up as solvent molecules pass through a semipermeable membrane from pure solvent to solute-containing solution.
  - Such a process happens to equalize the chemical potentials on the two sides of the semipermeable membrane.
- Deriving an expression for the osmotic pressure.
  - If  $P$  is the pressure exerted on the system and  $\Pi$  is the excess hydrostatic pressure on the solute-containing side, the system seeks  $\Pi$  such that

$$\mu_1^*(T, P) = \mu_1^{\text{sln}}(T, P + \Pi, a_1) = \mu_1^*(T, P + \Pi) + RT \ln a_1$$

- It follows by the Maxwell relation for chemical potential that

$$\begin{aligned} 0 &= \mu_1^*(T, P + \Pi) - \mu_1^*(T, P) + RT \ln a_1 \\ &= \int_P^{P+\Pi} \left( \frac{\partial \mu_1^*}{\partial P'} \right)_T dP' + RT \ln a_1 \\ &= \int_P^{P+\Pi} \bar{V}^* dP' + RT \ln a_1 \end{aligned}$$

- Assuming that  $\bar{V}_1^*$  is invariant under changing pressure, the above equation implies that

$$\begin{aligned} 0 &= \Pi \bar{V}_1^* + RT \ln a_1 \\ \Pi \bar{V}_1^* &= RT x_2 \end{aligned}$$

- Since  $n_2 \ll n_1$ , we may approximate  $x_2 = n_2/(n_1 + n_2) \approx n_2/n_1$  to get

$$\begin{aligned} \Pi &= \frac{n_2 RT}{n_1 \bar{V}_1^*} \\ &= \frac{n_2 RT}{V} \\ \Pi &= cRT \end{aligned}$$

where  $V$  is the total volume of solvent.

- **Van't Hoff equation** (for osmotic pressure): The above equation.
- **Reverse osmosis**: The process of applying pressure to seawater in excess of the osmotic pressure to force it through a rigid semipermeable membrane, resulting in fresh water.
  - The most common such membrane is cellulose acetate.