

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.

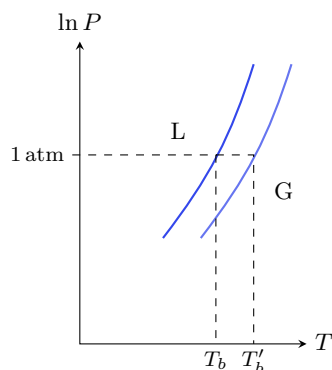


Figure 8.1: Boiling point elevation.

- 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 ΔT_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.

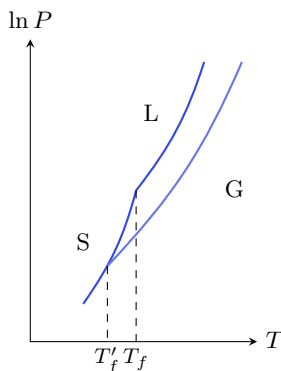


Figure 8.2: Freezing point depression.

- 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.

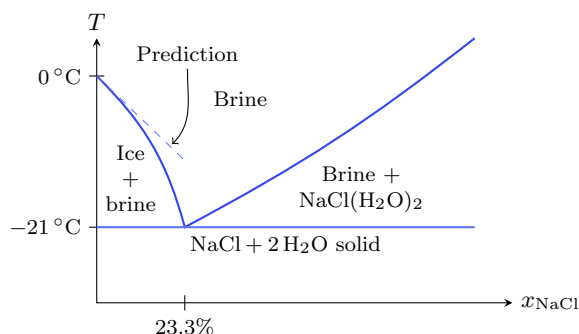


Figure 8.3: Freezing point vs. solute concentration.

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

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

- 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.

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

- Θ indicates reference temperature.
- It follows that as T increases, k_H increases.
 - For example, 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 γ . Given by

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

- Example: Carbon disulfide/dimethoxymethane.

x_{CS_2}	P_{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 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, α 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.