

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.

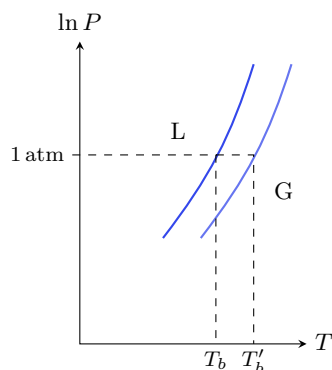


Figure 8.1: Boiling point elevation.

- 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.

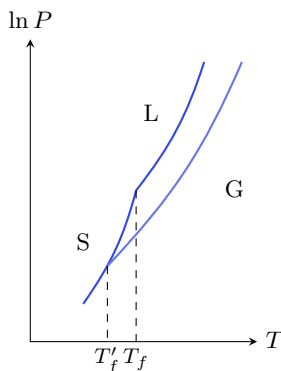


Figure 8.2: Freezing point depression.

- 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.

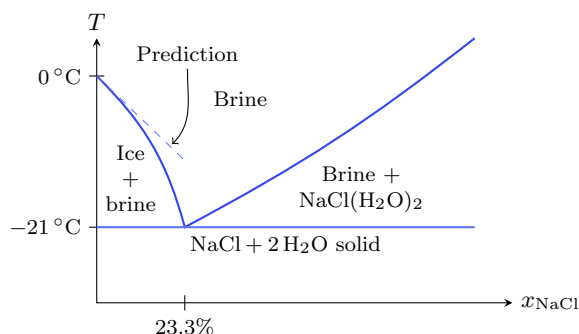


Figure 8.3: Freezing point vs. solute concentration.

- 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). *picture: Figure 24.7*
 - 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.