IDEAL SOLUTIONS

→ DEFINITION: A solution of 2 or more components, \( \xi \), whose partial vapor pressures are given by

Raoult's Law

\[ P_i = x_i P_i^* \]

- Real solutions do not obey Raoult's law
  - it's a limiting law, like the ideal gas law

MORE EXPLICITLY,

\[ P_i = x_i P_i^* \text{ in limit } x_i \to 1 \]

and

\[ P_i = x_i P_i^* \text{ for all } x_i \text{ iff } \]

there are identical interactions between all components, i.e.,

ALL COMPONENTS INTERACT WITH ONE ANOTHER IN THE SAME WAY

\[ P_{\text{real}} = \frac{n}{V} RT \text{ in limit } \frac{n}{V} \to 0 \]

and

\[ P = \frac{n}{V} RT \text{ for all } \frac{n}{V} \text{ iff } \]

there are no interactions between the molecules
"Derivation" of Raoult's law

- Consider the pure liquid (solvent) case, and the molecular-level situation corresponding to liquid-vapor equilibrium:

\[
\text{rate of evaporation} = R_{\text{evap}} = k_{\text{evap}} \frac{A}{\text{area}}
\]

\[
\text{rate of condensation} = R_{\text{cond}} = k_{\text{cond}} \frac{\text{A}}{\text{cond}} = k_{\text{cond}} P^*_s A
\]

Here \( P^*_s \) is the equilibrium vapor pressure of pure solvent

\((\text{NOTE: } k_{\text{evap}} \text{ and } k_{\text{cond}} \text{ have different dimensions)}\)

At equilibrium, \( R_{\text{evap}} = R_{\text{cond}}, \) i.e.,

\[
k_{\text{evap}} A = k_{\text{cond}} P^*_s A \implies P^*_s = \frac{k_{\text{evap}}}{k_{\text{cond}}}
\]

- Now consider an ideal solution of solute in solvent, i.e., one for which \( R_{\text{evap}} = k_{\text{evap}} A \to k_{\text{evap}} X_s A \) for solvent molecules

Also, \( R_{\text{cond}} \to k_{\text{cond}} P_s A \), where \( P_s \) is the partial pressure of solvent above the solution

At equilibrium, \( R_{\text{evap}} = R_{\text{cond}}, \) i.e.,
\[
K_{\text{evap}} \times S \overset{A}{=} K_{\text{cond}} \frac{P_s}{A}
\]

or
\[
P_s = S K_{\text{evap}} = S P_s^* \quad (\text{Raoult's law})
\]

- What are \( T \)-dependences of \( K_{\text{cond}} \) and \( K_{\text{evap}} \)? (Answer to this question:
  \( T \)-dependence of \( P_i^* = P_{\text{vap},i} \))

  - Note that \( K_{\text{cond}} \propto \overline{U} \), and that
  \[
  \overline{U} \propto \sqrt{T}
  \]
  
  - \[
  \begin{bmatrix}
  \overline{U} = (RT)^x (MW)^y \\
  M^o L^x T^{-x-1} = (ML^2 T^{-2})^x M^y
  \end{bmatrix}
  \]
  \[
  \Rightarrow 0 = x + y, \quad \text{or} \quad x = -y
  \]
  \[
  \begin{cases}
  1 = 2x, \quad \text{or} \quad x = \frac{1}{2}, \quad y = -\frac{1}{2} \\
  -1 = -2x
  \end{cases}
  \]

  - \[
  \therefore \overline{U} \propto \sqrt{\frac{RT}{M}} \propto \sqrt{T}
  \]

- Similarly, \( K_{\text{evap}} \propto \overline{U} \frac{F(\frac{1}{2} MW \overline{U}^2)}{\Delta H_{\text{vap}}} \)

  - Fraction of molecules in liquid that have enough kinetic energy to "escape."

- \[
\int_0^\infty \text{d}E f(E) = 1
\]

- \[
\begin{array}{cccc}
E = \frac{1}{2} m \overline{U}^2 & \text{f}(E) & \text{F} = \int_0^\infty \text{d}E f(E) \\
0 & \text{f}(E) & \Delta H_{\text{vap}} & \frac{1}{2} m \overline{U}^2 = E
\end{array}
\]

- \[
\overline{E} \approx RT \quad \Delta H_{\text{vap}} \gg RT
\]
• We can show (for $\Delta H_{vap} \gg RT$) that
  $$F(E > \Delta H_{vap}) \approx e^{-\frac{\Delta H_{vap}}{RT}},$$
  and hence
  $$\rho_{vap} \propto \sqrt{T} e^{-\frac{\Delta H_{vap}}{RT}}.$$

• Equating $\rho_{vap}$ and $\rho_{cond}$ for case of pure liquid gives
  $$P_{vap}(T) = P^* = \frac{k_{vap}}{k_{cond}} \propto \sqrt{T} e^{-\frac{\Delta H_{vap}}{RT}}$$
  and hence
  $$\frac{P_{vap}(T_2)}{P_{vap}(T_1)} = e^{-\frac{\Delta H_{vap}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)}$$
  or
  $$\ln \frac{P_2}{P_1} = -\frac{\Delta H_m}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right).$$

NOTE: This is identical to the Clausius-Clapeyron Eq. that we derived at the end of LECTURE #27 -- See, also, Eq. 8.20 (2nd edition) & 8.17 (1st edition).

• Here we've derived it from a microscopic molecular picture, whereas earlier we used thermodynamic arguments exclusively.
  More explicitly we started with
\[ d\mu = -S_m \, dT + V_m \, dP \]

and

\[ d\mu_\alpha = d\mu_\beta \text{ along coexistence curve} \]

and hence

\[ \frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T \Delta V_m} \]

along coexistence curve

For liquid-vapor coexistence, we have

\[ \Delta V_m \approx V_{gas, m} = \frac{RT}{P}, \text{ and hence} \]

\[ \frac{dP}{dT} = \frac{\Delta H_{vap}}{RT^2} P, \]

\[ \Delta H_{vap} \text{ depends only weakly on } T \]

\[ \int_{P_1}^{P_2} \frac{dP}{P} \approx \frac{\Delta H_{vap}}{R} \int_{T_1}^{T_2} \frac{dT}{T} \int d(-\frac{1}{T}) \]

\[ \ln \frac{P_2}{P_1} = -\frac{\Delta H_{vap}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]