Chem 340 - Lecture Notes 10 – Fall 2013 – Ideal & real solutions (Ch.5)

Ideal solutions are analogous to mixed gases, and free energy proportional to # moles
Recall for gases: \( \Delta G_{\text{mix}} = nRT(x_A \ln x_A + x_B \ln x_B) \), \( \Delta S_{\text{mix}} = -nR(x_A \ln x_A + x_B \ln x_B) \), \( \Delta H_{\text{mix}} = 0 \)

Liquids have chemical potential like gases in equilibrium with their vapor pressure
\[ \mu^*_{\text{A}} = \mu^0_{\text{A}} + RT \ln P^*_{\text{A}} \]
where \( P^* \) is vapor pressure of pure liquid, * indicates liquid
If dissolve something in A, chem pot, \( \mu_{\text{A}} \), changes as does vapor pressure, \( P_{\text{A}} \), but
Vapor is in equilibrium with liquid, so
\[ \mu_{\text{A}} = \mu^0_{\text{A}} + RT \ln P_{\text{A}} \]

Raoult’s law: dilute sol’n, solvent v.p.: \( P_{\text{A}} = x_{\text{A}} P^*_{\text{A}} \)
experimentally observed partial pressure \( \sim x_{\text{A}} \)

Model:
rate evaporation = rate condensation \( \sim \)area
Pure liquid: \( R_{\text{ev}} = Ak_{\text{ev}} = A_k_{\text{CO}}P^*_{\text{sol}} = R_{\text{CO}} \rightarrow P^*_{\text{sol}} = k_{\text{ev}}/k_{\text{CO}} \)
Solution: \( R_{\text{ev}} = Ak_{\text{ev}}x_{\text{sol}} = A_k_{\text{CO}}P_{\text{sol}} = R_{\text{CO}} \rightarrow P_{\text{sol}} = x_{\text{sol}}k_{\text{ev}}/k_{\text{CO}} = x_{\text{sol}} P^*_{\text{sol}} \rightarrow \text{Raoult} \)

Real solutions (above right) solvent obeys Raoult law at low conc

Solute,B, does not, idea - different interaction, A-A vs A-B
Dash lines ideal, solid real, deviation increase/max at \( x = 0.5 \)
Henry’s law, \( P_B = x_B K_B \), -empirical correction for vapor press B

Free energy mix: Solutions before mix: \( G_{\text{B}} = n_A \mu^*_{\text{A}} + n_B \mu^*_{\text{B}} \)
after \( G_{\text{A}} = n_A (\mu^*_{\text{A}} + RT \ln x_{\text{A}}) + n_B (\mu^*_{\text{B}} + RT \ln x_{\text{B}}) \)
Ideal solutions: \( \Delta G^i_{\text{mix}} = nRT(x_A \ln x_A + x_B \ln x_B) \) like gases, \( n = n_A + n_B \)
Entropy: \( \Delta S^i_{\text{mix}} = -nR(x_A \ln x_A + x_B \ln x_B) \) from \( (\partial G/\partial T) = -S \)

Real solution have interactions, different for A-A, B-B and A-B,
which will vary and \( \Delta G^i_{\text{mix}} \) could become positive, in which case,
not miscible and separate phases form

Excess functions express difference in real and ideal solutions
\( S^E = \Delta S_{\text{mix}} - \Delta S^i_{\text{mix}} \), but \( H^E = \Delta H_{\text{mix}} \), because \( \Delta H^i_{\text{mix}} = 0 \)
(same for \( V^E = \Delta V_{\text{mix}} \) since \( \Delta V^i_{\text{mix}} = 0 \))
If regular solution \( H^E \neq 0 \) but \( S^E = 0 \), let \( H^E = n\xi RT x_A x_B \),
\( \xi \) = parameter for difference in interaction of A-B as compare to A-A & B-B
if \( \xi < 0 \) mixing exothermic, favor A-B, but if \( \xi > 0 \) mixing endothermic
then: \( \Delta G^i_{\text{mix}} = nRT(x_A \ln x_A + x_B \ln x_B + \xi x_A x_B) \) if \( \xi > 0 \), then separate into 2 phases, see \( \uparrow \)
Mole fraction of vapor and solution not the same since solution mole fraction drives the vapor pressure, but vapor fraction is the partial pressure of each. In diagram, solid part is phase, line is equilibrium. Cross hatch has no physical meaning. Can derive the difference, let \( y = f^{vap} \):

\[
y_1 = \frac{P_1}{P_t} = \frac{x_1 P_1^{*}/[P_1^{*} - P_2^{*}]}{x_1 P_1^{*}/[P_1^{*} - P_2^{*}]} \]

\[
x_1 = \frac{y_1 P_2^{*}/[(P_2^{*} - P_1^{*})y_1 + P_1^{*}]}{P_1 = P_1^{*}/[P_2^{*} - P_1^{*}] + P_1^{*}}
\]

\[
y_1 = (P_1^{*}P_1^{*}P_2^{*})/(P_1^{*} - P_2^{*}) \]

See in diagram, liquid to liquid-vapor boundary (x plot) is straight line, but vapor to vapor (y plot) is curve. Assume solvent more volatile than solute, then \( y_{solv} > x_{solv} \) for any \( x_s \).

Use reduced variable average composition, \( Z \):

\[
Z_A = n_A(\delta) + n_A(v)/(n_A(\delta) + n_A(v)) = n_A/n_T
\]

Diagram, below right, \( P \) vs. \( x_A \), see upper left (green) favor liquid, lower right (tan) favor vapor, pale area between is liquid-vapor equilibrium. Go down a vertical line, from liquid to liquid-vapor to vapor. At some pressure in pale region, can use tie line to calculate amount of each with lever rule:

\[
n_1(x)(Z_A - x_A) = n_1(y)(y_A - Z_A)
\]

**Example**

If one component in a solution obeys Raoult’s law over entire range of \( x \), \( \mu^{(sol)}_1 = \mu^{*}_1 + RT\ln x_1 \) show the other component also follows Raoult’s law.

Use Gibbs Duhem: \( n_1 d\mu_1 + n_2 d\mu_2 = 0 \), \( n_{1,2} = x_{1,2}n \)

Rearrange: \( d\mu_2 = -x_1 d\mu_1/x_2 = -x_1/x_2d(\mu^{*}_1 + RT\ln x_1) \)

\[
d\mu_2 = -RT(x_2/x_1)(dx_1/x_1) \quad \text{from } dx_1 = dx/x
\]

since: \( x_1 = 1 - x_2 \), \( dx_1 = -dx_2 \) and \( d\mu_2 = -RT(dx_2/x_2) \)

integrate: \( \mu_2 = -RT \ln x_2 + C \), limit \( x_2 \to 1 \) \( C \to \mu^{*}_2 \), \( \mu_2 = \mu^{*}_2 + RT\ln x_2 \)

**Colligative Properties**

Physical properties that only depend on the number of particles in solution, not character are called Colligative properties, include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure.

Saw this already in Raoult law. Consider solvent, assume solute has no vapor pressure and does not dissolve in solid solvent. Starting point is reduction of liquid chemical potential (since \( \ln x_A \) neg) caused by solute

\[
\mu_A = \mu^{*}_A + RT \ln x_A
\]

Diagram (right) blue line shift to red one.
In our diagram see liquid line goes down and intersections with vapor and solid (lines unchanged) shift $T_b$ higher and $T_m$ lower.

Note not an energy effect, true for ideal solution, its entropy, solute increases entropy of solvent, free energy decreases from $\Delta G = \Delta H - T \Delta S$ and slope increases $(\partial G/\partial T) = -S$

Effect of solute is lower vapor pressure $\rightarrow$ higher boiling pt
Similarly, more random inhibit crystalize, lower freezing pt.

**Boiling point elevation**, liquid and vapor in equilibrium: $\mu_{A(g)}^* = \mu_{A(l)}^* + RT \ln x_A = \mu_{A(sol)}^*$

Rearrange: $\ln x_A = (\mu_{A(g)}^* - \mu_{A(l)}^*)/RT = \Delta G_{vap}/RT$ relates to free energy of vaporization

$$d(ln x_A)/dT = \frac{-\Delta H_{vap}/RT^2}{d\Delta G_{vap}/dT}$$ move $dT$, get $G-H$, and integrate

$$\int d(ln x_A) = -\Delta H_{vap}/R \int d\Delta G_{vap}/T \rightarrow \ln x_A = (\Delta H_{vap}/R)(1/T - 1/T^*)\left(\frac{1}{T^*(1/T - 1)}\right) = \Delta T/T^* ~ \Delta T/T^2$$

so

$$\Delta T_b = K_b b$$ where $K_b = R M_{solv} T^*/\Delta H_{vap}$ $M_{solv} -$ molecular weight of solvent, and $b$ is molality (mol/Kg solvent) $\sim$ mol frac. $x_{solv} (m -$ molality common use)

Some correlation of $T_b$ and $K_b$ from Trouton’s rule $\Delta H_{vap}/T^* ~$ const so $\Delta T ~ T^*$

### TABLE 9.2 Freezing Point Depression and Boiling Point Elevation

<table>
<thead>
<tr>
<th>Substance</th>
<th>Standard Freezing Point (K)</th>
<th>$K_f$ (K kg mol$^{-1}$)</th>
<th>Standard Boiling Point (K)</th>
<th>$K_b$ (K kg mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>289.6</td>
<td>3.59</td>
<td>391.2</td>
<td>3.08</td>
</tr>
<tr>
<td>Benzene</td>
<td>278.6</td>
<td>5.12</td>
<td>353.3</td>
<td>2.53</td>
</tr>
<tr>
<td>Camphor</td>
<td>449</td>
<td>40.0</td>
<td>482.3</td>
<td>5.95</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>161</td>
<td>3.8</td>
<td>319.2</td>
<td>2.40</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>250.3</td>
<td>30.0</td>
<td>349.8</td>
<td>4.95</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>279.6</td>
<td>20.0</td>
<td>353.9</td>
<td>2.79</td>
</tr>
<tr>
<td>Ethanol</td>
<td>158.8</td>
<td>20.0</td>
<td>351.5</td>
<td>1.07</td>
</tr>
<tr>
<td>Phenol</td>
<td>314</td>
<td>7.27</td>
<td>455.0</td>
<td>3.04</td>
</tr>
<tr>
<td>Water</td>
<td>273.15</td>
<td>1.86</td>
<td>373.15</td>
<td>0.51</td>
</tr>
</tbody>
</table>


Freezing point depression, same derivation: $\mu_{A(s)}^* = \mu_{A(l)}^* + RT \ln x_A$

so

$$\Delta T_m = -K_f b$$ where $K_f = R M_{solv} T^*/\Delta H_{fus}$ (defined so $K_f$ is positive, like $K_b$)

**Example**: 4.5g dissolve in 125g CCl$_4$ $\Delta T_b = 0.65$K what is $\Delta T_m$?

$$\Delta T_m = -(K_f/K_b) \Delta T_b = \left(\frac{30}{4.95}\right)(-0.65 \text{ K}) = 3.9 \text{ K}$$

Conc: $b = \Delta T_m/K_f = (3.9 \text{ K})/30 \text{ K} = 0.13$ molal

$M_x = m_x/n$, $b = n/m_{solv} \rightarrow n = 0.13 \text{ mol/kg} \times 0.125 \text{ kg} = 0.0163 \text{ mol}$

$\rightarrow M_x = 4.5g/0.0163 \text{ mol} = 277 \text{ g/mol}$
Osmosis  common use: movement of a solvent through a barrier into solution and create a pressure, \( \Pi \), difference that balances chem pot

\[
\mu^*_{A(P)} = \mu^*_{A(x_AP+\Pi)} = \mu^*_{A(P+\Pi)} + RT \ln x_A
\]

\[
\mu^*_{A(P+\Pi)} = \mu^*_{A(P)} + \int_{P,P+\Pi} V_m dP
\]

So if \( V_m \sim \text{const} \), come out of integral

\[
\mu^*_{A(P)} = \mu^*_{A(P)} + (P+\Pi) V_m + RT \ln x_A - V_m \Pi - RT \ln(1-x_B)
\]

\[
V_m \Pi = RT x_B
\]

van’t Hoff equation: \( \Pi = RT(n_B/V) \)

experimentally can view added pressure \( \Pi \) as the height of the column above the solution in diagram to right

Osmosis is critical property of solvents in biology, keeps a balance between interior and exterior of cells and other biological systems, since cell wall is semi-permeable. Small molecules and water can pass through, but large molecules (e.g. DNA, proteins) generally cannot, so inside cell higher concentration of particles (colligative effect).

Imagine transfusion, need to input solution of similar osmotic properties (isotonic) to avoid having too dilute a solvent (hypotonic) go into cell raise pressure and cause rupture or too concentrated a solution (hypertonic) extract solvent and collapse cell

**Example.** Calculate osmotic pressure for a cell with total concentration of 0.5 mol/L if immersed in pure water at \( T=298 \) K. Cell wall is permeable to water, not the solutes.

\[
\Pi = n_{sol} RT/V = 0.5 \text{ mol/L} \times 8.206 \times 10^{-2} \text{ L-atm/molK} \times 298K = 12.2 \text{ atm}
\]

Clearly this is high, so adding pure water to cells will damage them

Fluctuating concentrations around cells will have a huge effect in terms of osmotic pressure. For animals differentiation and multilayer structures provide a barrier so we do not “pop”. For bacterial and plants the situation is different, their cell walls have more structure to withstand pressures. So hypotonic solution is OK for plants, the cells do not rupture and the structures thrive (rain). But for animals, isotonic conditions are best. If in hypertonic conditions (too much salt on the outside) the cells can die due to plasmolysis (shrink up) because some cellular functions demand a certain level of hydration.
Osmosis is used to determine molecular weights of macromolecules.

Use \( n_{\text{solute}} = \frac{m_2}{M_2} \) (mass divided by molecular weight)

\[
\Pi = \left(\frac{m_2}{M_2}\right)(RT/V) \rightarrow M_2 = \left(\frac{RT}{\Pi(V)}\right)m_2 = \left(\frac{RT}{\Pi}\right)C_2 \quad \text{where } C_2 = \frac{m_2}{M_2}
\]

**Example.** 1.5 g chymotrypsinogen dissolved in 100 ml water. Separating this from pure water with a membrane results in osmotic pressure supporting a column 150 mm height. What is the molecular weight, \( M_{ch} \), for chymotrypsinogen, assume \( T=298 \text{ K} \).

Convert height to pressure – trick convert water to Hg equivalent (13.6 g/cc), then to atm

\[
\Pi = 150 \text{ mm} / (13.6/1.00) = 11.0 \text{ mmHg} / (760 \text{ mmHg/atm}) = 0.0145 \text{ atm}
\]

\[
M_{ch} = \left(\frac{RT}{\Pi}\right)(m_2/V) = (0.082 \text{ L-atm/molKx298K}/0.0145 \text{ atm})(1.5g/0.1L) = 25 \text{ kD}
\]

Nice idea, but real solutions deviate from ideality, so extrapolate concentration to zero to get best value

\[
M_2 = \lim_{C_2 \to 0} \left(\frac{RT}{\Pi}\right)C_2
\]

**Example, Engel 8.10**

Multicomponents all affect \( \Pi \) in same way so cannot determine real molecular weight, but just the average

\[
\Pi_T = \left(\frac{C_T}{M_{av}}\right)RT
\]

The following table gives the osmotic pressure as a function of concentration for solutions of polyisobutylene dissolved in benzene. Using the data and Equation (8.44), determine the molecular weight of polyisobutylene. Assume \( T = 298 \text{ K} \).

<table>
<thead>
<tr>
<th>( C_2 ) (g mL(^{-1}))</th>
<th>0.0200</th>
<th>0.0150</th>
<th>0.0100</th>
<th>0.0050</th>
</tr>
</thead>
<tbody>
<tr>
<td>Osmotic Pressure (atm)</td>
<td>0.00208</td>
<td>0.00152</td>
<td>0.00099</td>
<td>0.00049</td>
</tr>
</tbody>
</table>

**Solution**

Calculate the ratios \( \frac{\pi}{C_2} \):

\[
\begin{array}{c|c|c|c|c}
C_2 (g mL\(^{-1}\)) & 0.0200 & 0.0150 & 0.0100 & 0.0050 \\
\pi/C_2 (atm mL g\(^{-1}\)) & 0.104 & 0.101 & 0.099 & 0.098 \\
\end{array}
\]

Now plot the data and extrapolate to \( C_2 = 0 \).

The plot extrapolates to \( \pi/C_2 = 0.097 \text{ atm mL g}^{-1} \) at \( C_2 = 0 \). Now, using Equation (8.44):

\[
M_2 = \lim_{C_2 \to 0} \frac{RT}{\pi/C_2} = \frac{0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{0.097 \text{ atm mL g}^{-1} \times 0.001 \text{ L mL}^{-1}} = 2.5 \times 10^5 \text{ g mol}^{-1}
\]

**Desalination**

Opposite process, apply pressure, push pure water out of sea water, \( \Pi=27\text{ bar} \), problem to find separation membrane separate ions from water and not get clogged (algae)
**Activity**

Real solutions deviate from Raoult's law, see example at right, so introduce activity to compensate and keep the same forms or relationships for determining chemical potential.

\[ \mu_A = \mu_A^* + RT \ln P_A/P_A^* \]

So \( a_A = x_A \) for ideal solution, fit Raoult's law

And similarly \( a_A \to x_A \) as \( x_A \to 1 \)

Can express with activity coefficient \( \gamma_A \), where \( a_A = \gamma_A x_A \) where \( \gamma_A \to 1 \) as \( x_A \to 1 \)

\[ \mu_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A \]

with the standard state being the pure solvent at 1 bar.

Solute, need to correct for Henry's law if ideal-dilute and then allow for deviation

\[ \mu_B = \mu_B^* + RT \ln P_B/P_B^* = \mu_B^* + RT \ln x_B + RT \ln K_B/P_B^* \] define new standard state

\[ \mu_B^* = \mu_B^* + RT \ln K_B/P_B^* \] makes the same form again \( \mu_B = \mu_B^* + RT \ln a_B \)

For real solute, use activity concept, \( a_B = P_B/K_B \to a_B = \gamma_B x_B \) but now \( \gamma_B \to 1 \) as \( x_B \to 0 \)

Important to see that this standard state for solutes, hypothetical vapor pressure \( K_B \), does not exist, but is not dependent on the solute having a measurable vapor pressure.

Can redefine activity in terms of different standard states, e.g. molality

\[ a_B = \gamma_B b_B/b^a \text{ now } \gamma_B \to 1 \text{ as } b_B \to 0 \]

(note: \( b_B \to x_B/M_A \) as \( x_B \to 0 \))

Biological standard state, want to refer to pH=7 conditions, not pH=0 \( \to b = 1 \) molal

\[ \mu(H^+) = \mu^*(H^+) + RT \ln a(H^+) = \mu^*(H^+) - RT \ln(10) x \text{ pH} \]

\[ \mu^*(H^+) = \mu^*(H^+) - 7RT \ln(10) \]

biological standard state for H+ about 40 kJ/mol less

Defining the reference or standard state is vital since this will affect the values of \( \mu_B^* \) and \( \mu_B^* \) which in turn will change the numerical values of the equilibrium constant, \( K_{eq} \)

If use molarity or molality as concentration, see that \( a_B \to b_B \) as \( b \to 0 \)

or \( a_B \to c_B \) as \( c_B \to 0 \) since in both cases an effective \( \gamma_B^{\text{molar}} \to 1 \) or \( \gamma_B^{\text{molar}} \to 1 \)

but the reference states are different, i.e. \( b^a = 1 \) molal or \( c^a = 1 \) molar, even though at these concentrations Henry's and Raoult's laws not obeyed

**Solution equilibrium**

At equilibrium know:

\[ \Sigma_i v_i \mu_i^{\text{solute}} = 0 = \Sigma_i v_i \mu_i^{\text{solute}} + RT \Sigma_i \ln(a_i^{\text{eq}})^{v_i} \]

\[ \Delta G_{\text{rxn}}^o = -RT \Sigma_i \ln(a_i^{\text{eq}})^{v_i} = -RT \ln K_{eq} = \Pi_i (a_i^{\text{eq}})^{v_i} = \Pi_i (\gamma_i^{\text{eq}})^{v_i} (c_i^{\text{eq}} / c^0)^{v_i} \]

This equilibrium formulation is now general, same form as \( K_P \) but applies to all solutions

To use these need to get \( \Delta G_{\text{rxn}}^o \) as before, but now depend on solvent for \( K \)

In concentration units

\[ K = \Pi_i (\gamma_i^{\text{eq}})^{v_i} (c_i^{\text{eq}} / c^0)^{v_i} \approx \Pi_i (c_i^{\text{eq}} / c^0)^{v_i} \text{ as } c \to 0 \]

Must know standard states to get \( K \) or \( \Delta G_{\text{rxn}}^o \), dilute neutrals \( \gamma_i \to 1 \), but charged not so