Intro to Solutions

We are now going to use our knowledge of thermodynamics to examine solutions…

Consider a solution of two components: 1 and 2

The Gibbs energy is a function of T, P, and the two mole numbers…

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1} dn_2$$

At constant T and P… (1)

We can show by Euler's theorem: $G = \mu_1 n_1 + \mu_2 n_2$

Differentiate: $dG = \mu_1 dn_1 + \mu_2 dn_2 + n_1 d\mu_1 + n_2 d\mu_2$ (2)

(1) - (2)

Divide by $n_1 + n_2$:

Gibbs-Duhem Equation
(constant T and P)

Short Mathematics Review

Equations will we use today:

$$G = G^\circ + nRT \ln\left(\frac{P}{P^\circ}\right)$$

Eq 22.59

- ° = standard (1 bar)

Eq 24.13

$$G = n_A \mu_A + n_B \mu_B$$

Eq 24.6

$$n_A d\mu_A + n_B d\mu_B = 0$$

-OR-

$$x_A d\mu_A + x_B d\mu_B = 0$$

Eq 24.10 or 24.11

Gibbs-Duhem Equation

-Divide everything by n (total number of moles)

Chemical Potential of Liquids

We need to know how the Gibbs energy of a liquid varies with composition in order to discuss properties of liquid mixtures (like solutions).

Vapor Pressure = P_A^*

For vapor phase:

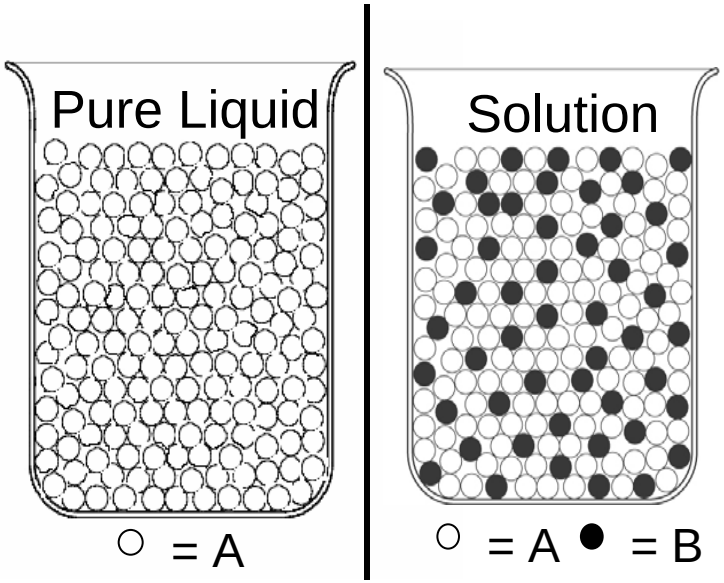
$$\mu_A^* = \mu_A^\circ + RT \ln\left(\frac{P_A^*}{P^\circ}\right)$$

At equilibrium…

$$\mu_A^*(g) = \mu_A^*(l)$$

For liquid phase:

$$\mu_A^* = \mu_A^\circ + RT \ln\left(\frac{P_A^*}{P^\circ}\right)$$



<u>Partial</u> Pressure = P_A

For vapor phase:

$$\mu_A = \mu_A^\circ + RT \ln\left(\frac{P_A}{P^\circ}\right)$$

At equilibrium…

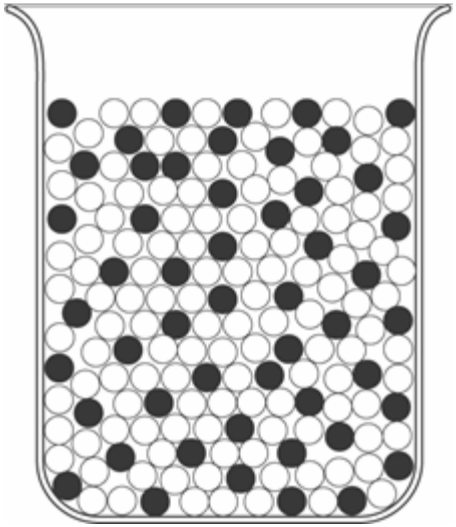
$$\mu_A(g) = \mu_A(l)$$

For solution:

$$\mu_A = \mu_A^\circ + RT \ln\left(\frac{P_A}{P^\circ}\right)$$

Combine these expressions…

Ideal Solutions



- Two types of molecules are randomly distributed
- Typically, molecules are similar in size and shape
- Intermolecular forces in pure liquids & mixture are similar
- Examples: benzene & toluene, hexane and heptane

(more precise thermodynamic definition coming)

In ideal solutions, the partial vapor pressure of component A is simply given by ***Raoult's Law***:

$$P_A = x_A P_A^*$$

mole fraction of A in solution

vapor pressure of pure A

Total VP of an ideal solution

$$\mu_A = \mu_A^* + RT \ln \frac{P_A}{P_A^*}$$

$$P_A = x_A P_A^*$$

$$\mu_A = \mu_A^* + RT \ln x_A$$

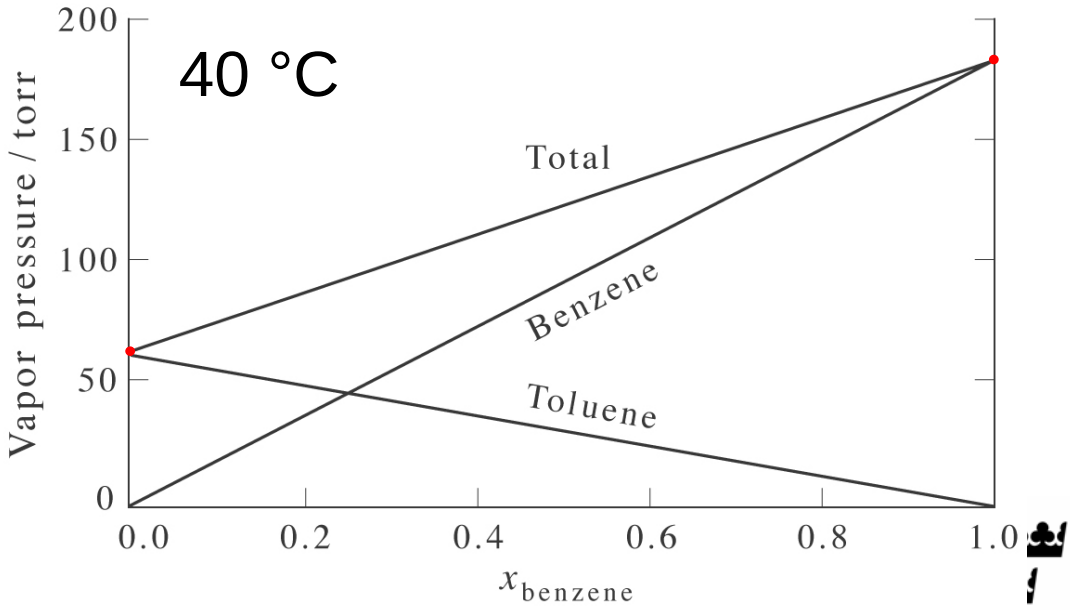
This serves to define an ideal solution if true for all values of x_A

The total vapor pressure of an ideal solution:

$$P_{total} = P_A + P_B$$

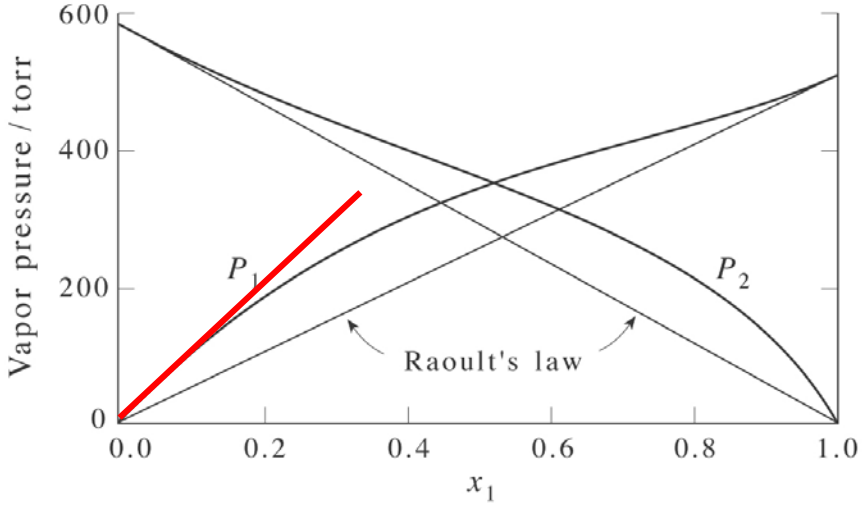
$$P_{total} = x_A P_A^* + x_B P_B^*$$

$$P_{total} = P_A^* + x_B (P_B^* - P_A^*)$$

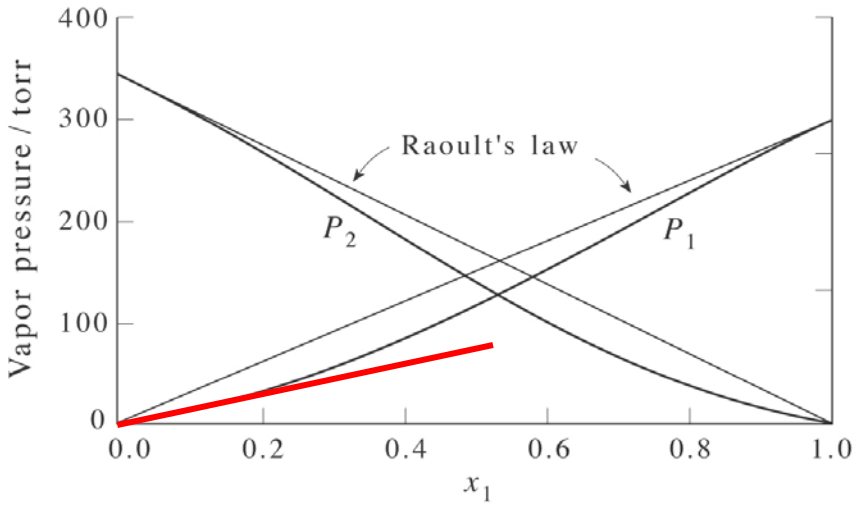


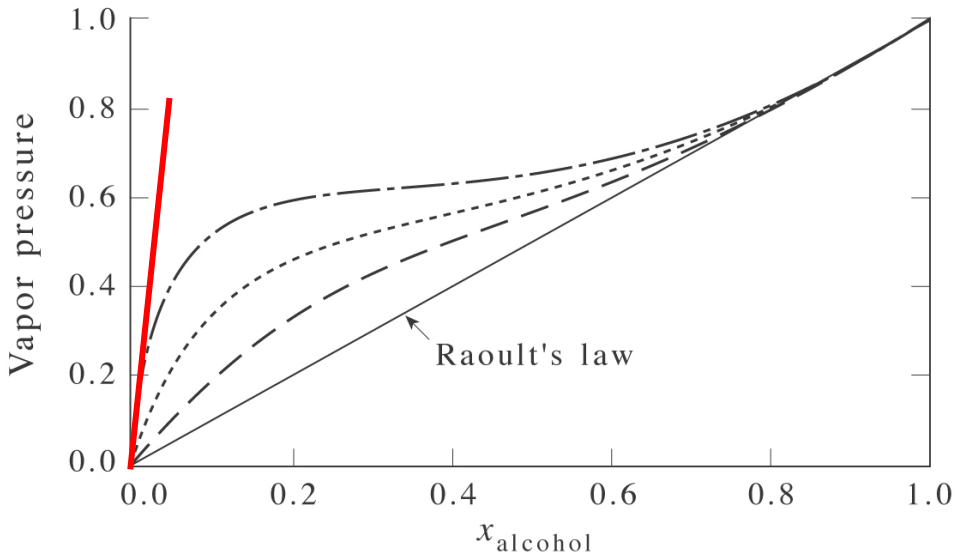
Deviations from Raoult's Law

CS_2 and dimethoxymethane: **Positive** deviation from ideal (Raoult's Law) behavior.



trichloromethane/acetone: **Negative** deviation from ideal (Raoult's Law) behavior.



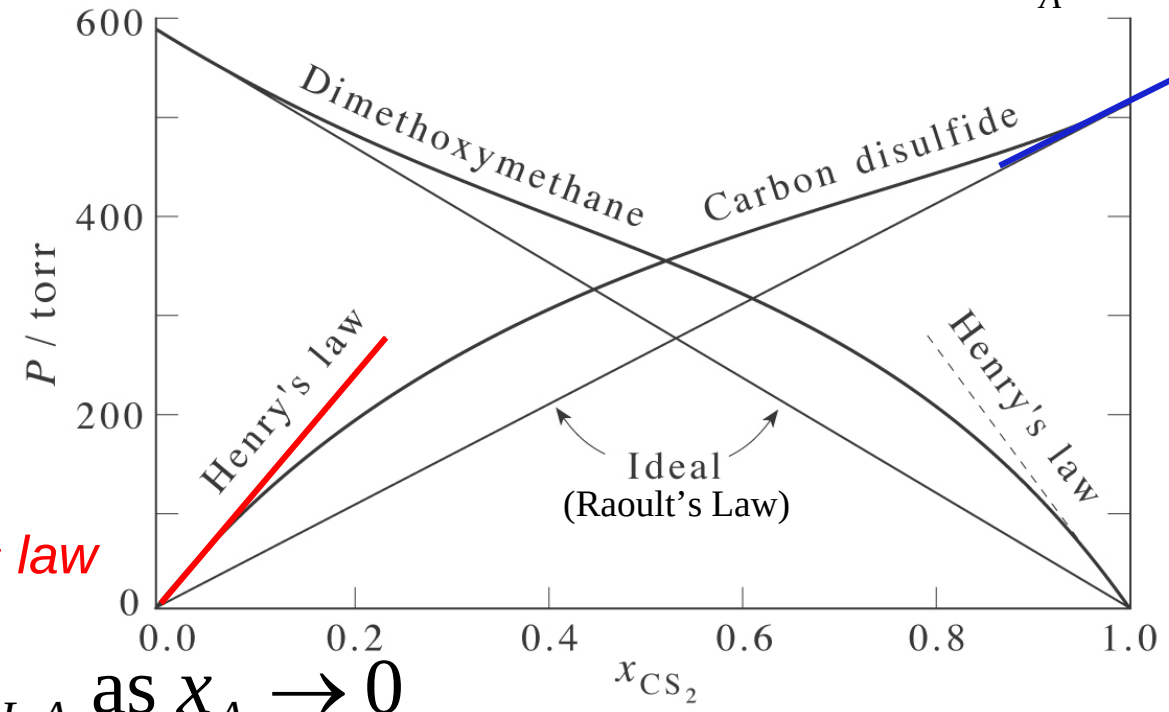


Methanol, ethanol, propanol mixed with water. Which one is which? (All show positive deviations from ideal behavior)

Raoult and Henry

$$P_A \to x_A P_A^* \text{ as } x_A \to 1$$

Raoult's law



Henry's law

$$P_A \to x_A k_{H,A} \text{ as } x_A \to 0$$

Henry's behavior:

Henry's law constant: $k_{H,A} \neq P_A^*$

- The *Henry's law constant* reflects the intermolecular interactions between the two components.
- Solutions following both Raoult's and Henry's Laws are called **ideal-dilute** solutions.

ΔG_{mix}, ΔS_{mix}, and ΔH_{mix} for ideal solution

$$\Delta G_{mix} = G^{sol} - G_1^* - G_2^*$$

$$G^{sol} = n_A\left(\mu_A^\circ + RT\ln(x_A)\right) + n_B\left(\mu_B^\circ + RT\ln(x_B)\right) \quad \& \quad G_i^* = n_i\mu_i^*$$

$$\Delta_{mix}G^{id} = n_A RT\ln(x_A) + n_B RT\ln(x_B)$$

$$\Delta_{mix}G^{id} < 0$$ Make sense?

$$\Delta_{mix}S^{id} = -\left(\frac{\partial \Delta_{mix}G^{id}}{\partial T}\right)_{P,n_1,n_2} =$$

$$\Delta_{mix}H^{id} = \Delta_{mix}G^{id} + T\Delta_{mix}S^{id} =$$

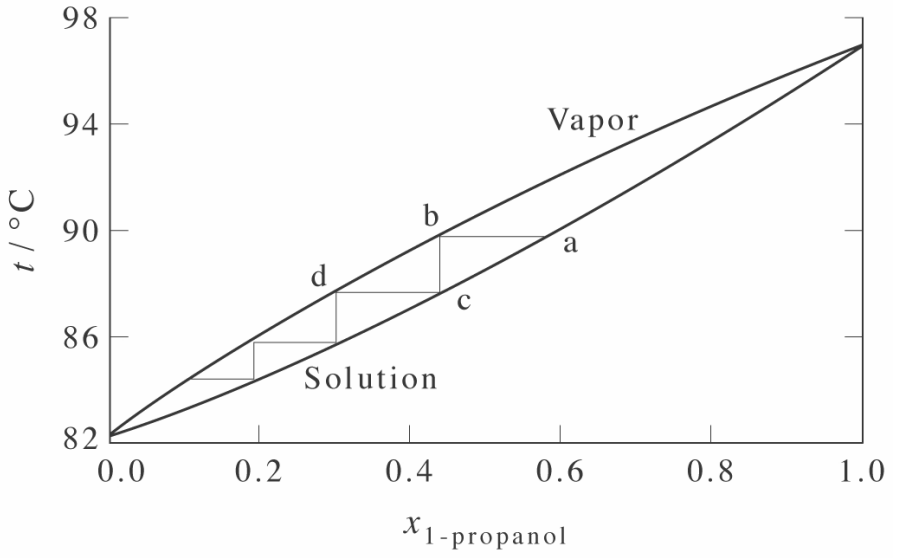
“The Bends”

- If a deep sea or scuba diver rises to the ocean surface too quickly, he or she can have great pain (mostly at the joints) and may double over in pain… they have “the bends”.

- In terms of what we’ve discussed today, brainstorm some causes of “the bends”.

Temperature-Composition Diagrams

1-propanol and 2-propanol at ambient pressure (i.e., 760 torr)

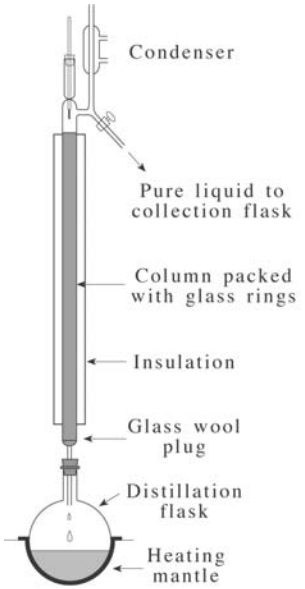


Point a: On solution line …

$$760 = x_1 P_1^* + x_2 P_2^*$$

$$x_1 = \frac{P_2^* - 760}{P_2^* - P_1^*}$$

How does this relate to fractional distillation?



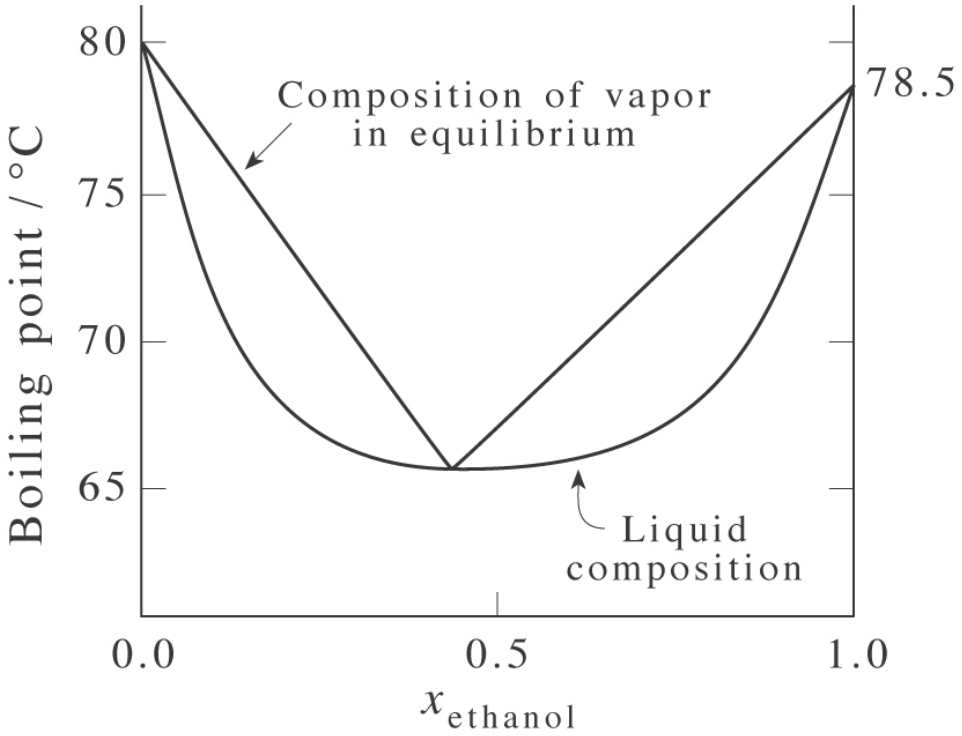
Point b: On vapor line …

$$y_1 = \frac{P_1}{760} = \frac{x_1 P_1^*}{760}$$

Dalton's Law

Distillation and Azeotropes

One example of non-ideal solutions: **Benzene and Ethanol at 1 atm**



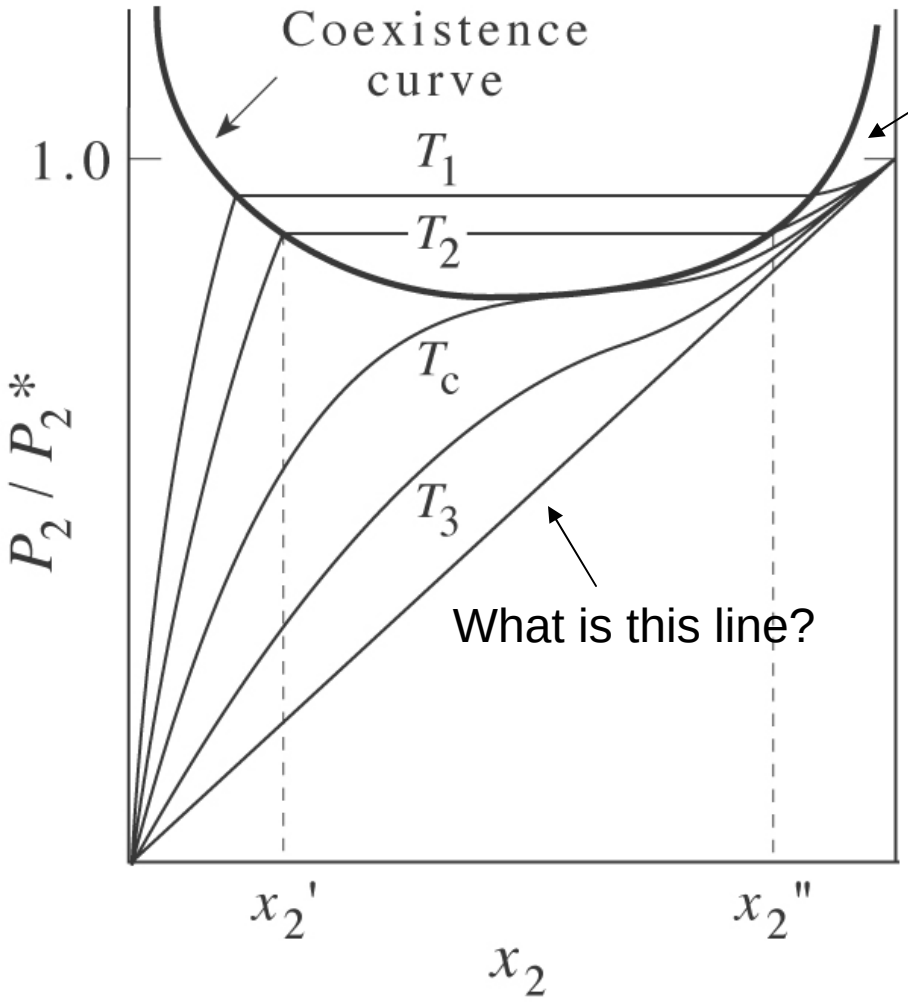
Azeotrope: A mixture for which there is no change in composition upon boiling.

Can you separate these compounds by distillation?

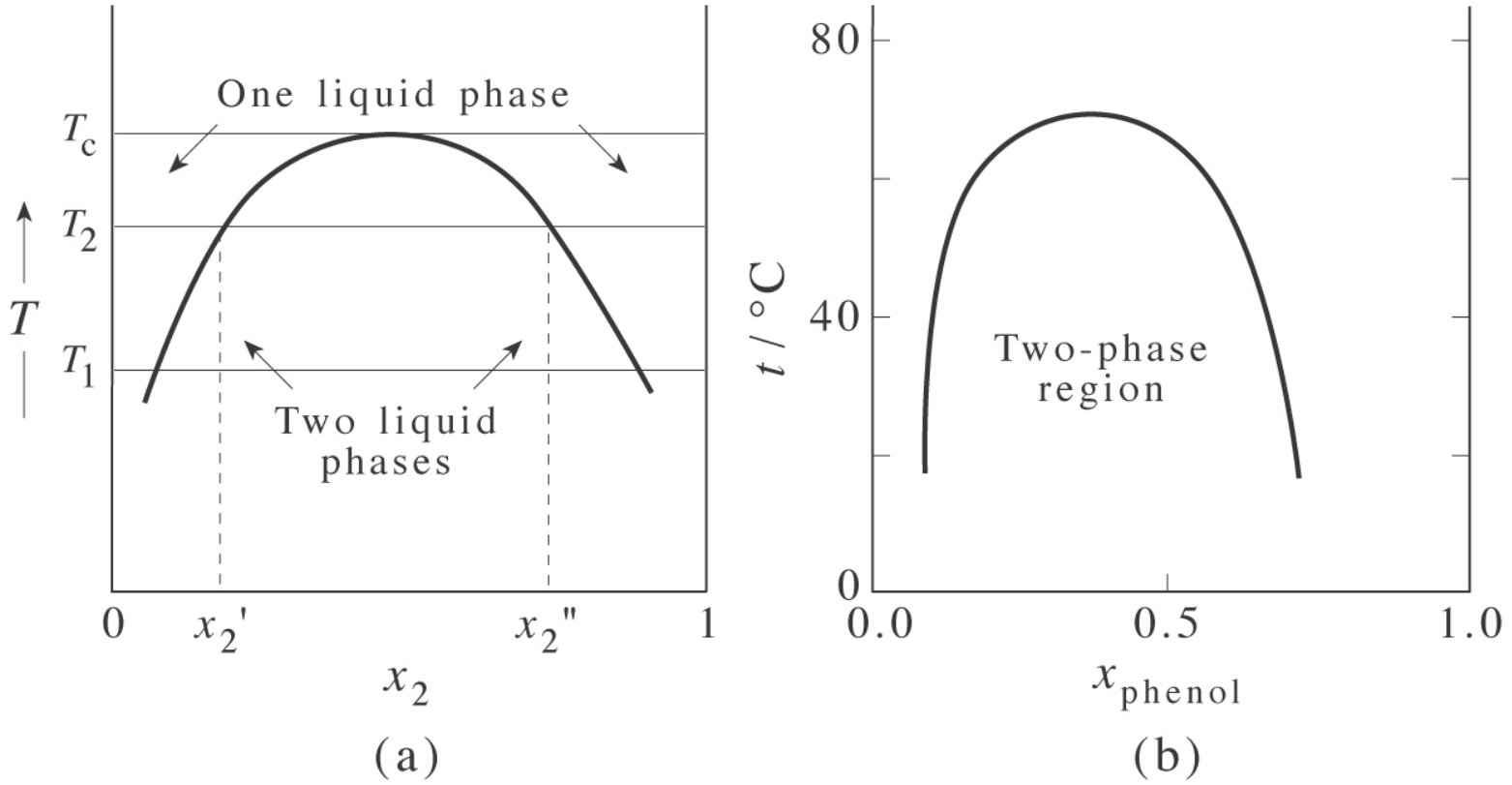
Really non-ideal: immiscible mixtures

$T_3 > T_C > T_2 > T_1$

Deviations greater with increasing T



Temp-composition diagrams for immiscibles

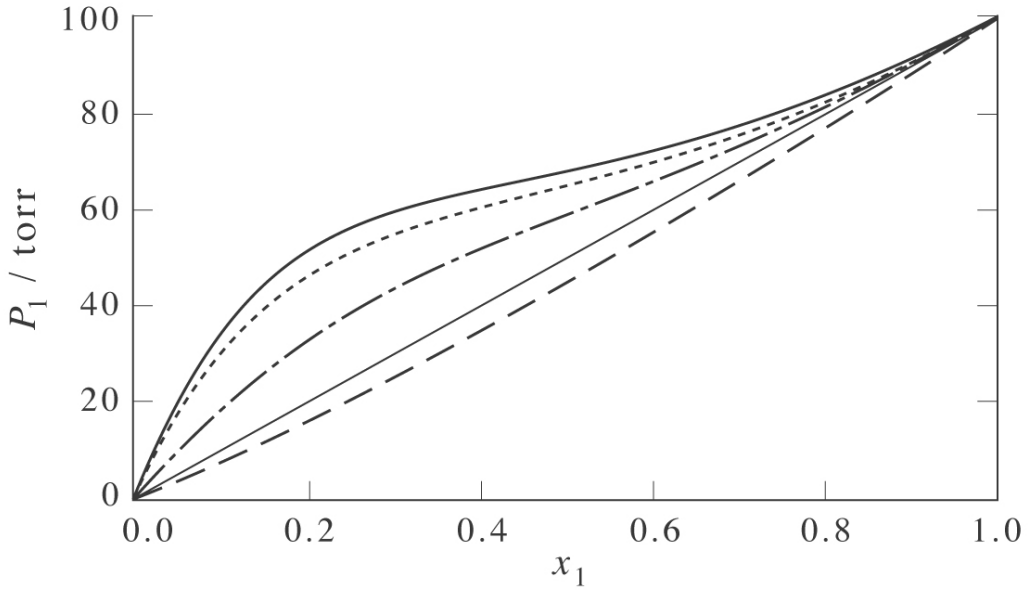


Other thoughts on non-ideal solutions

Vapor Pressures can often be represented empirically… for example:

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3} \qquad 0 \le x_1 \le 1$$

$$P_2 = x_2 P_2^* e^{\gamma x_1^2 + \delta x_1^3} \qquad 0 \le x_2 \le 1$$



Activity

For ideal solutions: $\mu_j^{sol} = \mu_j^*(l) + RT \ln x_j$

For non-ideal solutions: $\mu_j^{sol} = \mu_j^*(l) + RT \ln a_j$ ← Activity

Activity defined as: $a_j = \frac{P_j}{P_j^*}$ $a_1 \rightarrow$ as $x_1 \rightarrow 1$

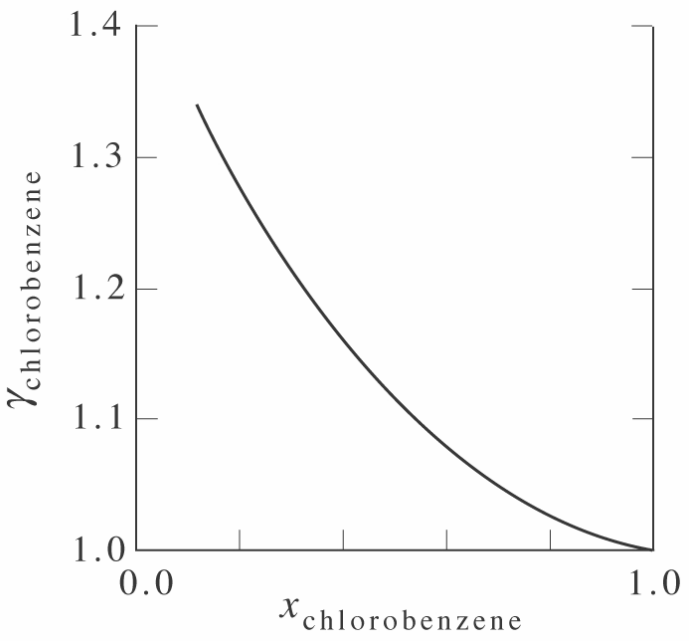
With definitions for vapor pressure of non-ideal solutions on Sol-15, what is a?

Activity coefficient (a measure of deviation from ideality): $\gamma_j = \frac{a_j}{x_j}$

Typical non-ideal solution

Chlorobenzene + 1-nitropropane at 75 °C, $P_1^* = 119$ torr

x_1	0.119	0.289	0.460	0.691	1.00
P_1/torr	19.0	41.9	62.4	86.4	119
a_1					
γ_1					



Activities must be calculated wrt standard states

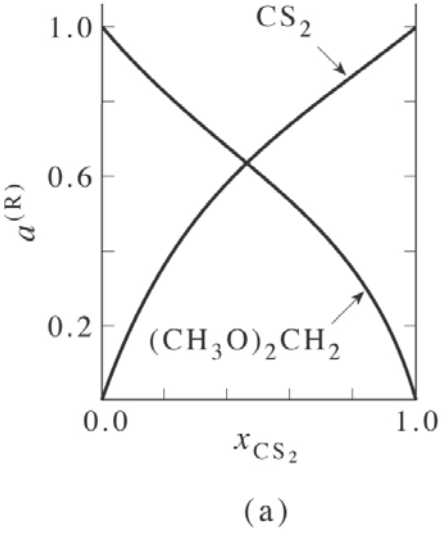
Activity using Raoult's law as standard state…

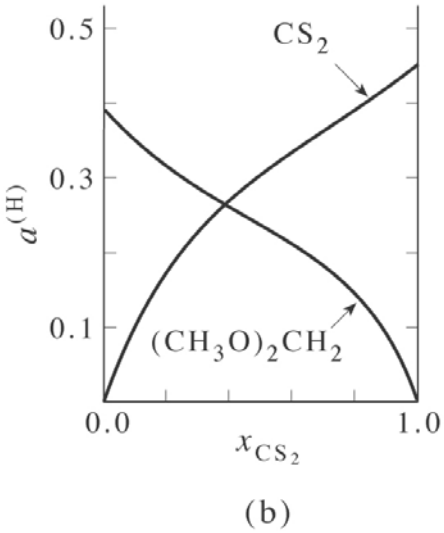
$$\mu_j^{sol} = \mu_j^*(l) + RT \ln a_j \qquad a_j = \frac{P_j}{P_j^*} \qquad a_j \to 1 \text{ as } x_j \to 1$$

Activity using Henry's law as standard state…

$$\mu_j^{sol} = \mu_j^*(l) + RT \ln \frac{k_{H,j}}{P_j^*} + RT \ln a_j \qquad a_j = \frac{P_j}{k_{H,j}} \qquad a_j \to x_j \text{ as } x_j \to 0$$

Using Rauolt's Law





Using Henry's Law

Gibbs Energy and Activity Coefficients

Ideal Solutions…

$$\Delta_{mix}\overline{G}^{id} / RT = x_A \ln(x_A) + x_B \ln(x_B)$$

Non-ideal Solutions…

$$\Delta\overline{G}_{mix} / RT = x_1 \ln x_1 + x_2 \ln x_2 + x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

(Derivations on pg 994)

Activity etc with other concentration scales

Table 25.1

A summary of the equations for the activities used for the various concentration scales for dilute solutions.

Solvent—Raoult's law standard state		
$a_1 = \frac{P_1}{P_1^*}$	$a_1 \to x_1$ as $x_1 \to 1$	
$\gamma_1 = \frac{a_1}{x_1}$	$P_1 \to P_1^* x_1$ as $x_1 \to 1$	(Raoult's law)
Solute—Henry's law standard state		
Mole fraction scale		
$a_{2x} = \frac{P_2}{k_{H,x}}$	$a_{2x} \to x_2$ as $x_2 \to 0$	
$\gamma_{2x} = \frac{a_{2x}}{x_2}$	$P_2 \to k_{H,x} x_2$ as $x_2 \to 0$	(Henry's law)
Molality scale		
$a_{2m} = \frac{P_2}{k_{H,m}}$	$a_{2m} \to m$ as $m \to 0$	
$\gamma_{2m} = \frac{a_{2m}}{m}$	$P_2 \to k_{H,m} m$ as $m \to 0$	(Henry's law)
Molarity scale		
$a_{2c} = \frac{P_2}{k_{H,c}}$	$a_{2c} \to c$ as $c \to 0$	
$\gamma_{2c} = \frac{a_{2c}}{c}$	$P_2 \to k_{H,c} c$ as $c \to 0$	(Henry's law)

You need to know how to convert between mole fraction, molality and molarity!

Recall colligative properties?!

$$\Delta P = P_1^* - P_1 = x_2 P_1^*$$

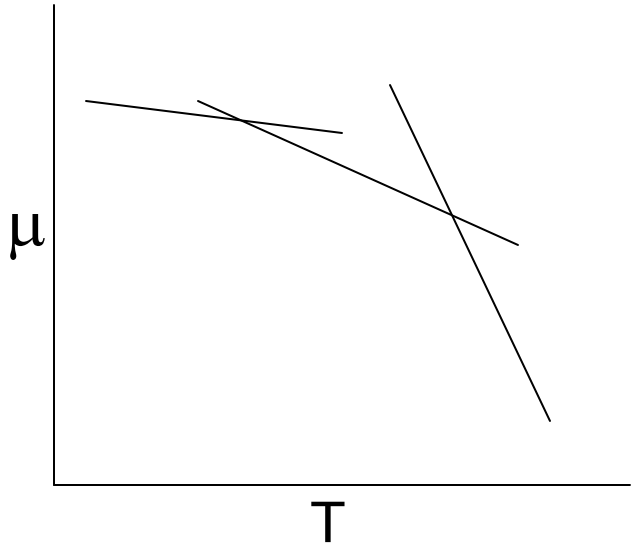
$$\Delta T_b = K_b m_2$$

$$\Delta T_f = K_f m_2$$

$$\Pi = cRT$$

Boiling point elevation

Label gas, liquid and solid lines
Label melting and boiling pt



At equilibrium…

$$\mu_1(g) = \mu_1(l) = \mu_1^*(l) + RT \ln a_1$$

or

$$\Delta\mu_1 = \mu_1(g) - \mu_1^*(l) = RT \ln a_1$$

Use Gibbs-Helmholtz equation (see A&G-18) and chemical potential def:

$$\frac{d(\Delta G/T)}{dT} = -\frac{\Delta H}{T^2} \qquad \Delta\mu_1 = \Delta_{vap}\overline{G}$$

Boiling pt elevation con't

Why these integrands?

$$\int d\ln a_1 = \int_1^{a_1} \frac{1}{a_1} da_1 = -\int_{T_{vap}^*}^{T_{vap}} \frac{\Delta_{vap}\overline{H}}{RT^2} dT$$

$$\ln a_1 = \frac{\Delta_{vap}\overline{H}}{R}\left(\frac{1}{T_{vap}} - \frac{1}{T_{vap}^*}\right) \qquad \ln a_1 = -\frac{\Delta_{vap}\overline{H}}{R}\left(\frac{\Delta T}{T_{vap}T_{vap}^*}\right) \approx$$

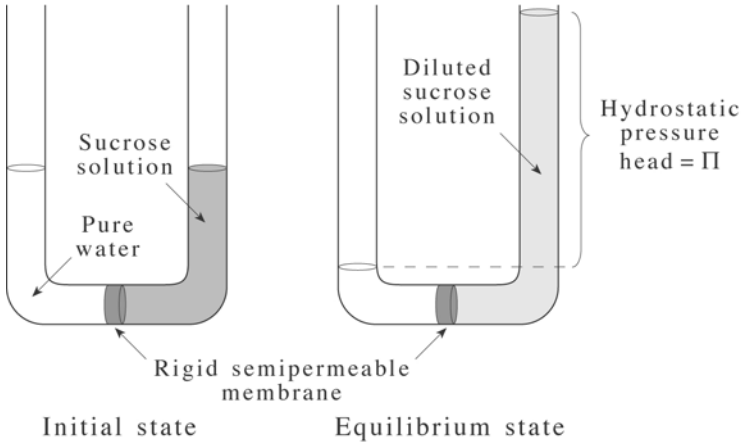
$$\Delta T = \frac{R\left(T_{vap}^*\right)^2}{\Delta_{vap}\overline{H}} x_2 \xrightarrow{x_2 = M_1 m_2} \Delta T = \frac{R\left(T_{vap}^*\right)^2 M_1}{\Delta_{vap}\overline{H}} m_2$$

Let… $K_b = \dfrac{R\left(T_{vap}^*\right)^2 M_1}{\Delta_{vap}\overline{H}}$

$\Delta T =$

<u>Assumptions on this page</u>

Osmotic Pressure



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

$$\mu_1^*(T,P+\Pi) - \mu_1^*(T,P) = \int_P^{P+\Pi}\left(\frac{\partial \mu_1^*}{\partial P}\right)_T dP = \int_P^{P+\Pi} \overline{V}_1^* dP = \Pi \overline{V}_1^*$$

$$\mu_1^*(T,P+\Pi) - \mu_1^*(T,P) + RT\ln a_1 = 0 \longrightarrow$$

Assume the solution is dilute… $\ln a_1 \sim x_2$ and $x_2 \sim n_2/n_1$

$$\Pi = \frac{RTx_2}{V_1^*} \longrightarrow \longrightarrow$$

Osmotic Pressure and Molecular Weight

It is found that 2.20 g of polymer dissolved in enough water to make 300 mL of solution has an osmotic pressure of 7.45 torr at 20 °C. Determine the molecular mass of the polymer.

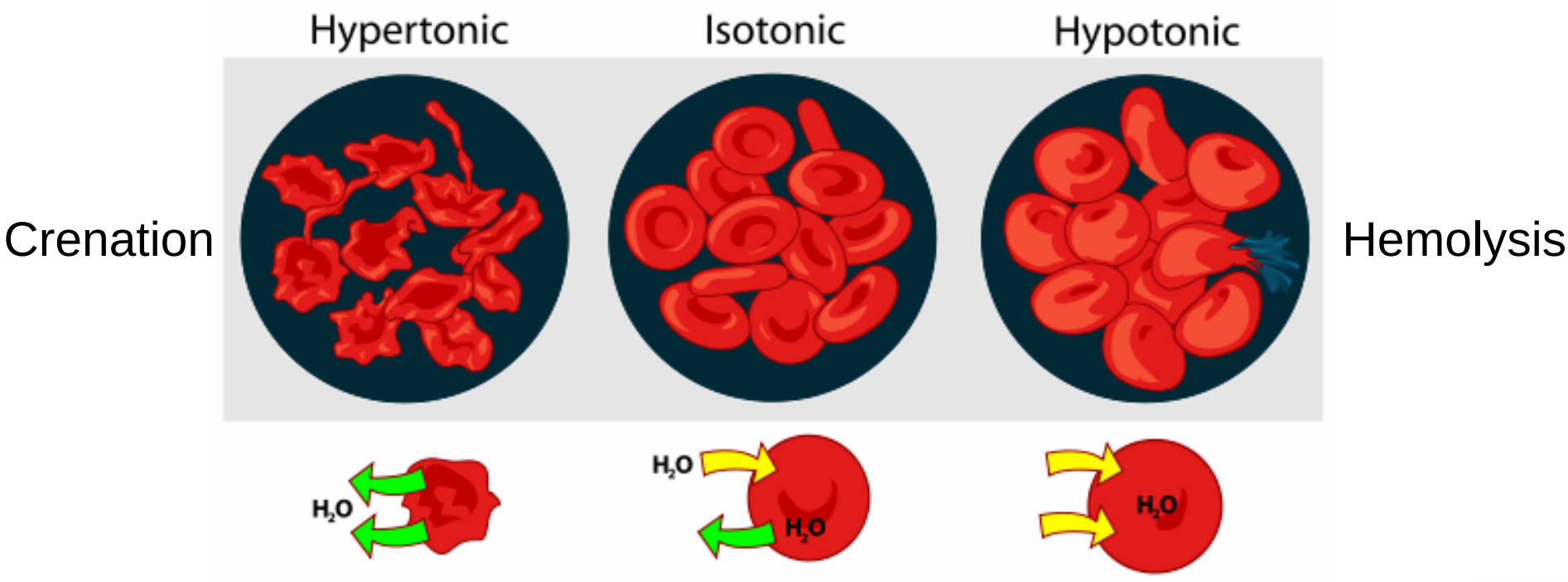
Why do we use osmotic pressure to find molecular weight and not one of the other colligative properties?

Osmotic Pressure and Cells

Sol-25

In the figure, red blood cells are placed into saline solutions.

1. In which case (hypertonic, isotonic, or hypotonic) does the concentration of the saline solution match that of the blood cells?
2. In which case is the saline solution more concentrated than the blood cells?



Electrolyte Solutions

Electrolyte solutions deviate from ideal behavior more strongly and at lower concentrations than nonelectrolyte solutions. (Why?)

Activities/activity coefficients are essential when working with electrolytes!

Examples of electrolytes… NaCl, $MgSO_4$, $MgCl_2$, Na_2SO_4

$$C_{\nu+}A_{\nu-}(s) \xrightarrow{H_2O(l)} \nu_{a+}C^{z+}(aq) + \nu_{-}A^{z-}(aq)$$

From this reaction…

$\mu_2 = \nu_+\mu_+ + \nu_-\mu_-$ or $\mu_2 = \nu_+(\mu_+^\circ + RT\ln a_+) + \nu_-(\mu_+^\circ + RT\ln a_-)$

Also know… $\mu_2 = \mu_2^\circ + RT\ln a_2$

Therefore… $a_2 = a_+^{\nu_+}a_-^{\nu_-}$ or

Ionic Activity, Molality, & Activity Coefficients

We can define single-ion activity coefficients…

$$a_+ = m_+\gamma_+ \qquad a_- = m_-\gamma_-$$

Mean ionic activity becomes…

$$m_\pm^{\nu} \qquad \gamma_\pm^{\nu}$$

Mean ionic molality

Mean ionic activity coefficient

Write out the mean ionic activity for $CaCl_2$…

Table 25.3: Activity and electrolytes

The relations between the activity of a strong electrolyte, its molality, and its mean ionic activity coefficient for various types of strong electrolytes.

Type	
1–1	
KCl(aq)	$a_2 = a_+ a_- = a_\pm^2 = m_\pm^2 \gamma_\pm^2 = (m_+)(m_-)\gamma_\pm^2 = m^2 \gamma_\pm^2$
1–2	
$CaCl_2$(aq)	$a_2 = a_+ a_-^2 = a_\pm^3 = m_\pm^3 \gamma_\pm^3 = (m_+)(m_-)^2 \gamma_\pm^3 = (m)(2m)^2 \gamma_\pm^3 = 4m^3 \gamma_\pm^3$
1–3	
$LaCl_3$(aq)	$a_2 = a_+ a_-^3 = a_\pm^4 = m_\pm^4 \gamma_\pm^4 = (m_+)(m_-)^4 \gamma_\pm^4 = (m)(3m)^3 \gamma_\pm^4 = 27m^4 \gamma_\pm^4$
2–1	
Na_2SO_4(aq)	$a_2 = a_+^2 a_- = a_\pm^3 = (m_+)^2 (m_-) \gamma_\pm^3 = (2m)^2 (m) \gamma_\pm^3 = 4m^3 \gamma_\pm^3$
2–2	
$ZnSO_4$(aq)	$a_2 = a_+ a_- = a_\pm^2 = m_\pm^2 \gamma_\pm^2 = (m_+)(m_-)\gamma_\pm^2 = m^2 \gamma_\pm^2$
3–1	
$Na_3Fe(CN)_6$(aq)	$a_2 = a_+^3 a_- = a_\pm^4 = m_\pm^4 \gamma_\pm^4 = (m_+)^3 (m_-) \gamma_\pm^4 = (3m)^3 (m) \gamma_\pm^4 = 27m^4 \gamma_\pm^4$

Colligative Properties of Electrolytes

For a strong electrolyte…

$$x_2 \approx \nu m M_1$$

ν = total # of dissociated ions
m = molality
M_1 = molar mass (in kg/mol)

If you use this definition in derivation of colligative properties …

Debye-Hückel Theory

Debye-Hückel Theory: Assumes ions are point ions (no radii) with purely Coulombic interactions and activity coefficients depend only on the ion charges and the solvent properties.

$$\ln \gamma_{\pm} = -\left|z_+ z_-\right| A I_c^{1/2}$$

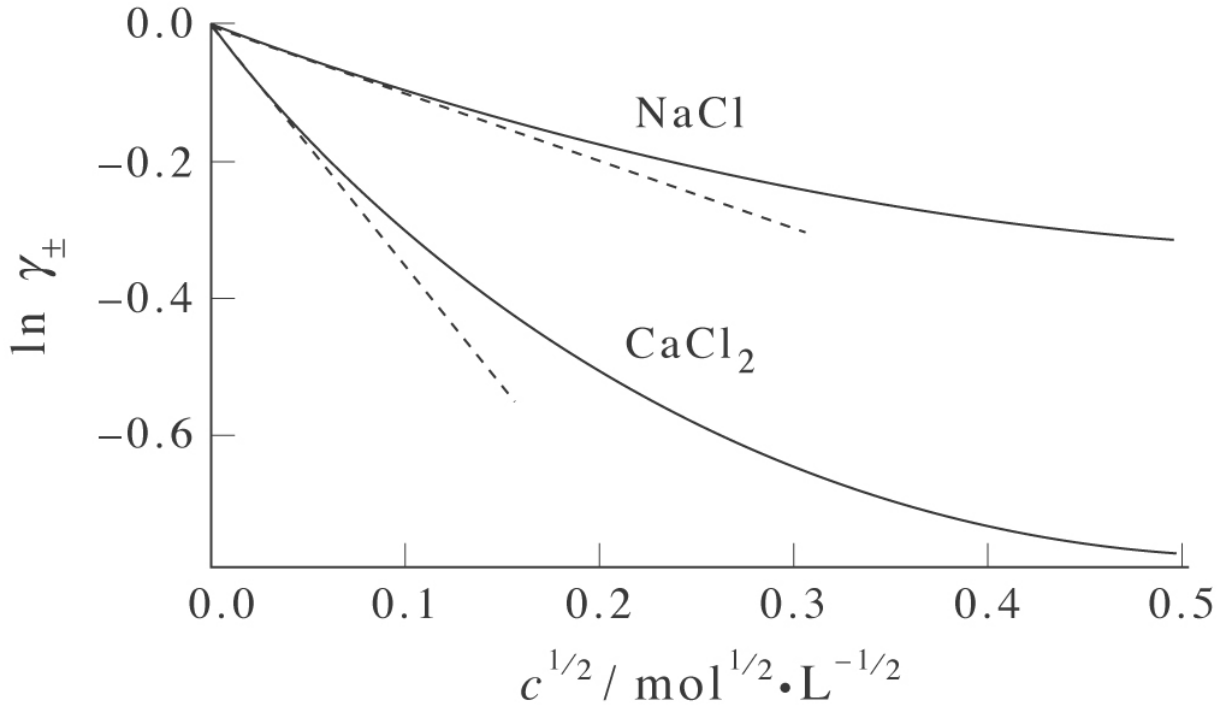
$$A = \left(2\pi N_A\right)^{1/2} \left(\frac{e}{4\pi\varepsilon_0 \varepsilon_r k_B T} \right)^{3/2}$$

$$I_c = \frac{1}{2}\sum_{j=1}^{s} z_j^2 c_j$$

Ionic Strength

For Aqueous Solutions…

Validity of Debye-Hückel Theory



Extended Debye-Hückel:

$$\ln \gamma_{\pm} = \frac{-A|z_+ z_-|I_c^{1/2}}{1 + BI_c^{1/2}}$$

Why are activities so important anyway?!

The activity can be thought of as “the real concentration”… anywhere concentrations are used, activities *should* be used instead.

$$a_1 = [1]\gamma_1 = \{1\}$$

Some examples: