

# THERMODYNAMICS REVIEW FOR PHYSICAL CHEMISTRY OF MACROMOLECULES IN SOLUTION

## TABLE OF CONTENTS

Known problems with this document:  
Figures not labeled, many style inconsistencies.

## GENERAL REVIEW

First Law

2<sup>nd</sup> Law:        Statistical Viewpoint & General Spontaneity Conditions

Automatic Spontaneity Functions

    Constant T & V

    Constant T & P

    General Remarks

## SOLUTION THERMODYNAMICS OF ORDINARY SMALL MOLECULES

Ideal Gas: paradigm for all other systems

Nonideal Gases

Partial Molar Quantities

    Intercepts Method

    3 basic relations

    Summary

Basic Mixing Thermodynamics

    Ideal Mixtures

    Real Mixtures

        Activity approach:

            Analogy to gases & meaning

            Of standard state

    Regular solutions/phase separation

    Lever rule

Equilibria

Colligative Properties

    General Effects of Entropically Reduced Chemical Potential

    Osmotic pressure: how to measure  $\mu$

## GENERAL REVIEW

1<sup>st</sup> law:

$$dU = dq + dw$$

Exact; path independent  $\swarrow$   $\nwarrow$  Inexact (small symbol)

Change in the total energy U is sum of heat and work. These effects combine to make dU independent of path.

2<sup>nd</sup> law:

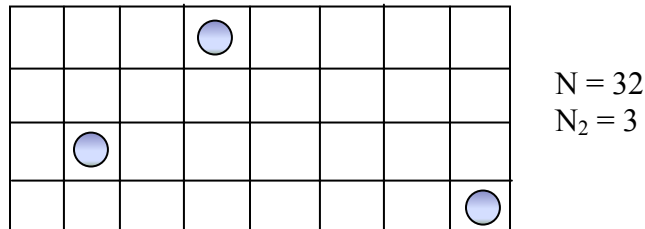
$$dS = \frac{dq^{rev}}{T} \geq \frac{dq}{T}$$

↑  
define

Measures the randomness or dispersion of energy U. There is a statistical approach and a true thermo approach to entropy. The latter is a big pain but very intellectually satisfying (take Chem 4596, if it is ever offered again).

STATISTICAL APPROACH: use this to calculate the IDEAL ENTROPY OF MIXING. (This is nicely done in Van Holde, Ch. 1. & many other books, too)

Let W = the number of ways to arrange  $N_2$  solute molecules and  $N_1$  solvent molecules is given by:



$$W = \frac{(N_1 + N_2)!}{N_1! N_2!} = \frac{N!}{N_1! N_2!}$$

Explanation:

- A) Put on the  $N_2$  solutes first, one at a time:  
N sites for first of  $N_2$  identical solutes

$$\rightarrow \frac{N}{N_2} \text{ distinguishable ways}$$

$$(N - 1) \text{ sites for next of } N_2 - 1 \text{ identical solutes}$$

$$\rightarrow \frac{N - 1}{N_2 - 1} \text{ distinguishable ways}$$

The numerator is the number of open sites remaining. The denominator is the number of solute molecules not yet placed; it accounts for our inability to distinguish identical solutes.

We multiply these together for all solutes to get

$$W = \frac{N!}{N_2!(N - N_2)!} \equiv \frac{N!}{N_2!N_1!}$$

- B) There is only one way to put on identical solvent molecules when all solutes have been placed. Note that the final result is independent of how we label the molecules or whether we put molecule 1 or molecule 2 on the lattice first.

For the more general case of multicomponent mixtures,

$$W = \frac{N!}{N_1! N_2! \dots N_n!} \quad ; \quad N = \sum_i N_i$$

Now, how should entropy  $S$  relate to  $W$ ?  $S$  is extensive; it should increase like  $N$ . So  $S$  is clearly not proportional to  $W$ .

Try the following:

$$S \stackrel{?}{=} k \ln W$$

$$\rightarrow S = k [\ln N! - \ln N_1! - \ln N_2! - \dots]$$

$$\text{But } \ln N! \xrightarrow{(N \text{ large})} \simeq N \ln N - N$$

$$\begin{aligned} -S &= k [N \ln N - N - (N_1 \ln N_1 - N_1) - (N_2 \ln N_2 - N_2) - \dots] \\ &= -k [N_1 \ln N_1 + N_2 \ln N_2 + \dots - N \ln N] \\ &= -k [N_1 (\ln N_1 - \ln N) + N_2 (\ln N_2 - \ln N) + \dots] \end{aligned}$$

$$S = -k [N_1 \ln x_1 + N_2 \ln x_2 + \dots]$$

$$\text{where } x_i = \frac{N_i}{N}$$

or...multiply and divide by  $N_a = \text{Avogadro's number}$

$$S = -nR \sum_i x_i \ln x_i$$

$n = \text{mole\#}; R = \text{gas constant}$

Since  $x_i < 1$ ,  $S$  is positive, as required. What is  $\Delta S_{\text{mix}}$ ? Prior to mixing you have  $W = 1$  (1 way to arrange solute & solvent if unmixed;  $S$  before mixing =  $k \ln 1 = 0$ ).

$$\rightarrow \Delta S_{\text{mix}} = -nR \sum_i x_i \ln x_i$$

Note:

- this is an approximation:  $S = 0$  only at absolute zero (0 K).
- simple  $n^1$  behavior of  $S$  ( $S = \text{extensive property}$ )
- bad thing about entropy is that it has the spontaneity condition entropy of universe must increase.
- means you must always consider everything.

### Automatic Spontaneity Functions

It turns out that for a spontaneous reaction:

$$dS^{\text{sys}} \geq \frac{dq^{\text{sys}}}{T^{\text{sys}}}$$

Despite the "sys" superscript, the latter term ( $dq^{\text{sys}}$ ) is actually related to the surroundings—i.e., the universe. Also,  $q$  is not a state function. However, under certain conditions  $q$  behaves like a state function and then we can invent more convenient state functions:

#### 1. Constant Temperature and Volume

Under these conditions,  $q$  behaves like  $U$ :

$$\text{if } dU = dq + dw$$

$$\text{And } dw = -pdV \text{ (only)}$$

$$\text{Then } dq = dU$$

$$\text{So } dS \geq dU/T = \text{spontaneity condition (T, V const; pV work only)}$$

or...  $dU - TdS \leq 0$

Define:  $A = U - TS$   
 $dA = dU - TdS - SdT$

Note that A = state function.

With this definition, the NEW SPONTANEITY CONDITION for const. T & V is:

$dA \leq 0$  (T, V constant; pdV only work)

2. Constant Pressure and Temperature

Heat may be replaced by enthalpy at constant T & p;

$dq \rightarrow dH$

proof:  $H = U + pV; dH = dq - pdV + pdV + Vdp$

$TdS \geq dq \rightarrow TdS \geq dH$

or...  $dH - TdS \leq 0$

Define  $G = H - TS$ ; Note  $G =$  State Function

$dG = dH - TdS - SdT \leq 0$

The NEW SPONTANEITY CONDITION is:

$dG \leq 0$  p, T const; no non—pV work

Remarks on A and G {Utility beyond just being spontaneity conditions, etc...}

$A \leftrightarrow$  Arbeit ("work", in German)

1. A measures the maximum work which a given process can do:

$dA = dw_{max}$ .

2. There is a tendency to say  $dA \leq 0$  because  $dU \leq 0$  and  $dS \geq 0$  inherently seem to lead to greater stability. This is not really accurate. The condition  $dA \leq 0$  really is just a restatement of the one true spontaneity condition ( $\Delta S^{univ} \geq 0$ ) for  $V =$  const.;  $T =$  const. And no non-pV work.

$G \leftrightarrow$  Gibbs ("genius" in any language)

1. G measures the maximum non-pV work. It is of interest to generation of electricity and other forms of non pV work (i.e., useful work).

$dG = dH - TdS - SdT$   
 $= dU + d(PV) - TdS - SdT$   
 $= dq + dw + pdV + Vdp - TdS - SdT$

if reversible:

$\rightarrow dq = TdS$

$\rightarrow w = w_{max}$

then  $dG = dw_{\max} + pdV + Vdp - SdT$   
 Now...  $dw_{\max} = -pdV + dw_{e,\max}$ ;  $dw_{e,\max} = \text{non } pV \text{ work}$

$$\rightarrow dG = dw_{e,\max} + Vdp - SdT$$

$$dG_{p,T \text{ constant}} = dw_{e,\max}$$

This result, which we used reversible conditions to derive, is not actually reliant on reversible reactions because  $dG = \text{state function}$ .

2. Same remark as for A:  $dG \leq 0$  is an expression (at const T,P) of  $\Delta S^{\text{univ}} \geq 0$ .

## SOLUTION THERMODYNAMICS OF ORDINARY SMALL MOLECULES

We already have seen one important quantity,  $\Delta S_{\text{mix}}$ , in our reintroduction to entropy by statistical approach. We need other elements, and we begin with the simplest possible system—ideal gases.

### Ideal Gas

We begin by considering a pure gas. In a lattice formalism, this is a "mixture" of "point particles" with vacuum. What is its free energy,  $G$ , at a given temperature?

$G$  will depend on the pressure:

$$G = H - TS = G(T,P)$$

$$dG = dH - d(TS)$$

$$= d(U + PV) - d(TS)$$

$$= dU + d(PV) - d(TS), \text{ but } dU = TdS - pdV$$

$$\text{so... } dG = Vdp - SdT$$

$$\text{For ideal gas } V = \frac{nRT}{P}$$

$$\text{then } dG = VdP - SdT$$

$$= nRT \left( \frac{dP}{P} \right) - SdT \quad ; \text{ now assume constant } T \text{ and integrate:}$$

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

In general, define:  $\mu_i = \text{chemical potential of species } i$

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_{j \neq i}}$$

For a pure gas =  $\frac{G}{n}$

$$\mu = \mu(P^\circ) + RT \ln \left( \frac{P}{P^\circ} \right) \quad \text{Pure Ideal Gas; Const.T}$$

How do we choose  $P^\circ$ ? We could have any choice we wanted, but usually  $P^\circ$  is taken as 1 atm, in which case we write  $\mu = \mu^\circ + RT \ln P$ .

### Nonideal Gases

Let there be some function,  $f$  = fugacity which satisfies:

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

even when the gas is not ideal

Note: 1) for ideal gas  $f = P$

2) fugacity is defined to make this equation true

3) The fugacity requires that  $\mu^\circ$  have a known role in order to be useful

### What is the standard state of a Real Gas?

let us write  $f = \gamma P$   
 $\gamma$  = dimensionless fugacity  
 $\gamma$  = a function of  $P$   
 $(\gamma = 1$  for an ideal gas)

Then:  $\mu = \mu^\circ + RT \ln \left( \frac{f}{P^\circ} \right); f = \gamma P$

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

Ideal Term  $\uparrow$        $\uparrow$  Nonideal Term

Now:  $\mu$  will =  $\mu^\circ$  when 2 conditions are met simultaneously:

1)  $P = P^\circ = 1$  atm (usually)

AND 2)  $\gamma = 1$

Now, most gases are not exactly ideal at  $P = 1$  atm ( $\gamma \neq 1$  at  $P = 1$  atm).

So, for a real gas, when will  $\mu = \mu^\circ$ ?

- Terse answer: Never!

- Detailed Answer:  $\mu$  will equal  $\mu^\circ$  when the real gas is placed in some *hypothetical* state where  $P = P^\circ$  and  $\gamma = 1$  simultaneously.
- Alternate Statement: The (*hypothetical*) standard state is the gas at 1 atm pressure and behaving ideally.
- One more time: Even if the gas is non—ideal at  $P^\circ$ , the standard state is still that of this gas behaving ideally at  $P^\circ$ .

We will soon return to the idea of a standard state for fluids. First, we need more experience with Partial Molar Quantities.

## PARTIAL MOLAR QUANTITIES

### Method of Intercepts

Use volume as most obvious example. Could also use G, A, H, U, S, etc.

Consider Binary Mixture case (mixture of a & b):

$$V_{\text{avg}} = \frac{V}{n} ; n = n_a + n_b$$

$$x_a = \frac{n_a}{n} ; x_b = \frac{n_b}{n}$$

Define:  $\bar{V}_b = \left( \frac{\partial V}{\partial n_b} \right)_{n_{a \neq b}, T, P}$  ; Note  $\bar{V}_b = \bar{V}_b(x_a, x_b)$

(i.e.,  $\bar{V}_b$  is a function of composition)

We imagine  $\bar{V}_b$  to be the amount by which an ocean of a,b mixture expands upon addition of one mole of b.  $n_a$  is unchanged and  $x_b$  is virtually unchanged.

But  $V = nV_{\text{avg}}$

$$\Rightarrow \bar{V}_b = \left( \frac{\partial}{\partial n_b} nV_{\text{avg}} \right)_{n_a, T, P}$$

$$\Rightarrow n \left( \frac{\partial V_{\text{avg}}}{\partial n_b} \right)_{n_a, T, P} + V_{\text{avg}} \left( \frac{\partial n}{\partial n_b} \right)_{n_a, T, P}$$

Use Chain rule:

$$\left( \frac{\partial V_{\text{avg}}}{\partial n_b} \right) = \left( \frac{\partial V_{\text{avg}}}{\partial x_b} \right) \left( \frac{\partial x_b}{\partial n_b} \right)$$



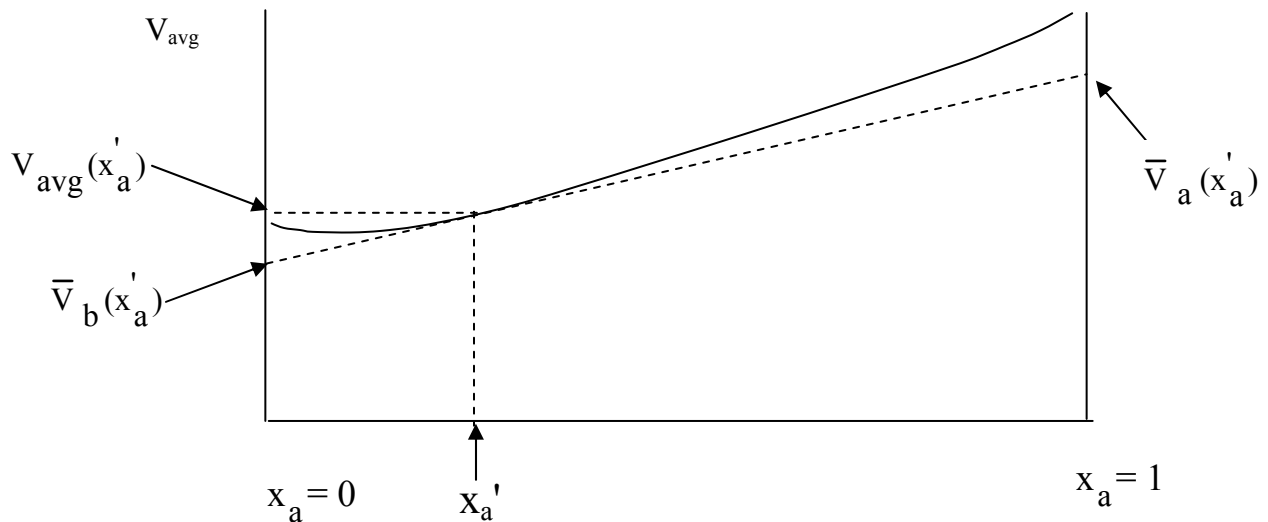
$$\frac{\partial}{\partial n_b} \left( \frac{n_b}{n_b + n_a} \right) = \frac{n_b + n_a - n_b}{(n_b + n_a)^2} = \frac{x_a}{n}$$

$$\Rightarrow \bar{V}_b = n \left( \frac{\partial V_{\text{avg}}}{\partial x_b} \right) \left( \frac{x_a}{n} \right) + V_{\text{avg}}$$

$$\Rightarrow V_{\text{avg}} = \bar{V}_b - x_a \left( \frac{\partial V_{\text{avg}}}{\partial x_b} \right)$$

$$\text{or... } V_{\text{avg}} = \bar{V}_b + x_a \left( \frac{\partial V_{\text{avg}}}{\partial x_a} \right)$$

These equations suggest an "intercept method" for determining The Partial Specific Volume:



$$\text{At } x'_a, V_{\text{avg}} = V_{\text{avg}}(x'_a) = \bar{V}_b + x'_a \left( \frac{\partial V_{\text{avg}}}{\partial x_a} \right)$$

A similar equation holds for component a:

$$V_{\text{avg}} = \bar{V}_a + x_b \left( \frac{\partial V_{\text{avg}}}{\partial x_b} \right)$$

This allows us to identify the point  $\bar{V}_a$  at right.

So, in order to determine  $\bar{V}_a$  and  $\bar{V}_b$  at a given composition, we determine  $V_{\text{avg}}$  over a range of compositions.

Note that  $\bar{V}_a(x'_a) \neq \bar{V}_a(x''_a)$  in general unless  $x'_a = x''_a$ .

I.E.  $\bar{V}_a$  and  $\bar{V}_b$  depend on  $x_a$  !!

**Important!** The intercepts equation/method works for any state function not just volume.

### 3 Basic Equations

Besides the intercepts relation, there are 3 more important relations:

- 1)  $dV = \bar{V}_1 dn_1 + \bar{V}_2 dn_2$
- 2)  $V = \bar{V}_1 n_1 + \bar{V}_2 n_2$  or....  $V_{avg} = \bar{V}_1 x_1 + \bar{V}_2 x_2 = V/n$
- 3)  $n_1 d\bar{V}_1 + n_2 d\bar{V}_2 = 0$

{Note: we switched from "a, b" to "1, 2" subscripts. Ordinarily, 1 = solvent and 2 = solute.}

These are, like intercept equations, MATHEMATICAL facts. We will prove them as such, again staying in the binary (component 1, component 2) limit to conserve space. There are analogous expressions for solutions with any number of components.

#### Prove eq. 1

The volume  $V$  depends on  $T, P, n_1, n_2$

$$V = V(T, P, n_1, n_2)$$

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

$$dV = \bar{V}_1 dn_1 + \bar{V}_2 dn_2 \quad \text{Eq. 1}$$

(T, P constant)

#### Prove eq. 2

This isn't as obvious as it looks, because  $\bar{V}_1$  and  $\bar{V}_2$  are, in general functions of  $x_1, x_2$ . But we can imagine "building" the solution by holding composition ( $x_1, x_2$ ) constant while integrating over  $n$ , the total # of molecules. We perform a volume-building integral

$$V = \int_0^V dV = \int_0^{n_1} \bar{V}_1 dn_1 + \int_0^{n_2} \bar{V}_2 dn_2$$

at constant composition  $x_1, x_2 (= 1 - x_1)$ . This is like adding little aliquots of a premixed solution and it means that  $\bar{V}_1$  and  $\bar{V}_2$  are constants so we immediately see that Eq. 2 is true. But,  $V$  is a state of function, so it wouldn't matter how we actually make the solution up. Thus, Eq. 2 is generally true.

Prove Eq. 3

Use eq. 1:  $\Rightarrow$

$$dV = \bar{V}_1 dn_1 + \bar{V}_2 dn_2$$

Now eq. 2 says:  $V = \bar{V}_1 n_1 + \bar{V}_2 n_2$

$\Rightarrow$

$$dV = \bar{V}_1 dn_1 + n_1 d\bar{V}_1 + \bar{V}_2 dn_2 + n_2 d\bar{V}_2$$

Comparing the 2 boxed eqns. shows that:

$$+ n_1 d\bar{V}_1 + n_2 d\bar{V}_2 = 0 \quad \text{Equation 3}$$

What this shows is:

Any change in  $\bar{V}_1$  is directly tied to a change in  $\bar{V}_2$ :

$$\frac{d\bar{V}_1}{d\bar{V}_2} = - \left( \frac{n_2}{n_1} \right)$$

NOTE: for more than 2 components, the relationship is not as simple.

### Summary

#### Four things to note

- 1) Equations 1, 2, 3 and the intercept equation are mathematically exact.
- 2) They work for any Thermodynamic state function, not just volume.
- 3) They aren't limited to binary mixtures. They can be extended to many components.
- 4) There is one very important example of the type 3 equation:

#### Gibbs - Duhem Equation:

$$\sum n_i d\mu_i = 0$$

{mnemonic device: Duhem  $\Leftrightarrow$   $d\mu$ }

Important Example of type 2 eq.

$$G = \sum_i n_i \mu_i \quad \text{where } \mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{n_j \neq i; P; T}$$

**One last thing on partial quantities:**

They are often defined as partial "specific" quantities where specific means to use weight in this substance. Usually use lower case letters for these:

e.g.

$$\bar{v}_2 = \left( \frac{\partial V}{\partial g_2} \right)_{g_1, T, P}$$

i.e. the change in volume for a given change in weight ( $g_2$ ) of species 2 at T,P constant and holding  $g_1$  constant.

Example:  $\bar{v}_2 \simeq \frac{0.73 \text{ ml}}{\text{gm}}$  for most proteins (at infinite dilution).

## MIXING THERMO

### 1) Ideal Mixtures

$$\Delta H_{\text{mix, ideal}} = 0$$

$$\Delta S_{\text{mix, ideal}} = -nR \sum_i x_i \ln x_i$$

$$\therefore \Delta G_{\text{mix, ideal}} = nRT \sum_i x_i \ln x_i$$

Note that  $\Delta G < 0$

$\Rightarrow$  Ideal mixtures always mix

$$\Delta V_{\text{mix}} = \left( \frac{\partial \Delta G}{\partial P} \right)_{n_a, n_b, T} \Rightarrow 0$$

The mixing in an ideal system is driven by entropy.

### 2) Real Mixtures

Activity in Real Mixtures is Like Fugacity in Real Gases:

$$\mu_i = \mu_i^0 + RT \ln a_i$$

$a_i$  = "activity" of  $i^{\text{th}}$  species is **defined** by this equation.

$a_i = \gamma_i x_i$  or  $\gamma_i (m_i/m_i^0)$  an alternate possibility often used for the solute species;  $m$  = molality = moles solute/kg solvent;  $m_i^0 = 1$  (usually).

Note the units (i.e. lack thereof) of both the activity and activity coefficients.

Let A  $\Rightarrow$  Solvent

B  $\Rightarrow$  Solute

Solvent

$$a_A = \gamma_A x_A; \gamma \Rightarrow 1 \text{ in ideal limit } \underline{\text{for solvent}}$$

$$\text{i.e. } \gamma \Rightarrow 1 \text{ as } x_A \Rightarrow 1$$

This is called the Raoult law limit because you can trace it back through the vapor phase (presumed in equilibrium with liquid solvent) and relate it by Raoult's law to the gas expression:  $\mu = \mu^{\circ} + RT \ln (P/p^{\circ})$ .

### Solute

$a_B = \gamma_B x_B$ ;  $\gamma \Rightarrow 1$  in ideal solute limit, which is  $x_B \rightarrow 0$ .

or

$a_B = \gamma_B (m_B/m_B^{\circ})$  i. e.  $\gamma \Rightarrow 1$  as  $x_B \Rightarrow 0$ .

This is called the Henry law limit even when the solute is not volatile.

### Meaning of Standard State

#### Solvent

$$\mu_A = \mu_A^{\circ} + RT \ln \gamma x_A$$

$$\text{as } x_A \Rightarrow 1, \gamma \Rightarrow 1 \text{ and: } \mu_A = \mu_A^{\circ} @ x_A = 1$$

The standard state of solvent is pure solvent. (If you were fussy you might wish to specify: pure solvent in equilibrium with its vapor. Not really required, but does emphasize the Raoult's law nomenclature.)

This is a realistic, achievable standard state.

### Solute

The situation for the solute is analogous to the standard state considerations of the nonideal gas. The system will be in its standard state when 2 conditions are met:

$$\begin{array}{l} 5) \quad \gamma_B = 1 \\ \text{AND} \quad 2) \quad m_B = m_B^{\circ} = \frac{1 \text{ mole}}{\text{kg solvent}} \text{ (usually)} \end{array}$$

Such a state may or may not really exist. A hypothetical standard state, where one is at unit molality and the nonidealities are nil:  $\gamma = 1$ . Note that the "activity" could be viewed as phenomenological because we haven't considered why  $\gamma \neq 1$  in any serious, microscopic way. We shall do so later.

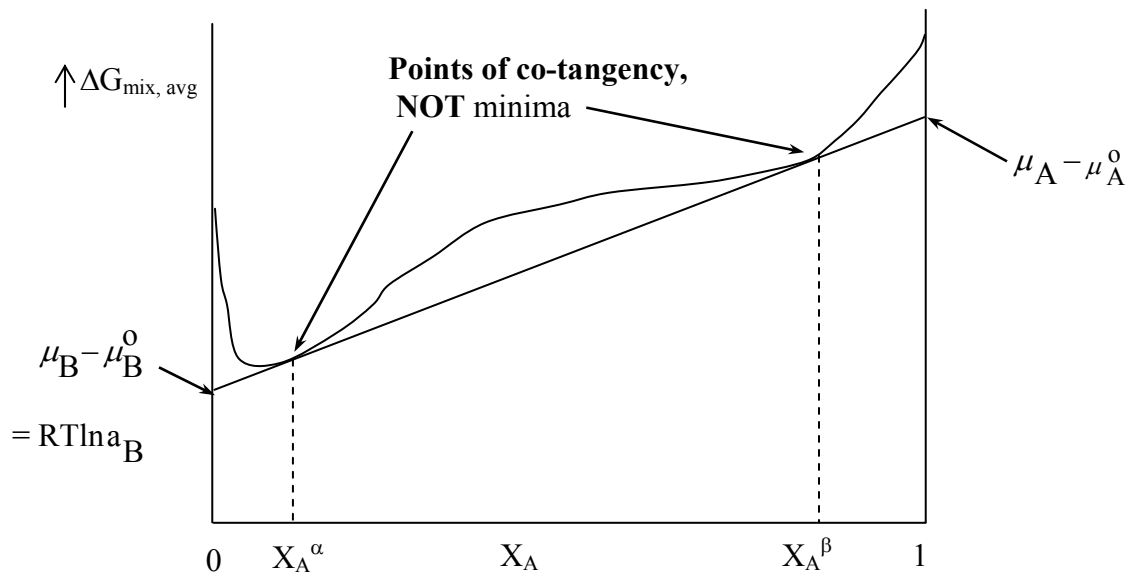
## Regular Solution/Phase Separation in Real Mixtures

$$\Delta H_{\text{mix}} \neq 0$$

$$\Delta S_{\text{mix}} = \text{ideal} = -nR [x_A \ln x_A + x_B \ln x_B]$$

$$\Delta G_{\text{mix}} = \Delta H - T \Delta S_{\text{mix, ideal}}$$

A system may separate into 2 phases (e.g. 2 liquid phases with different compositions) when it becomes possible for all the components in each of the 2 phases to have the same chemical potential.



In the  $\beta$  phase as drawn,  $x_A \simeq 0.85$

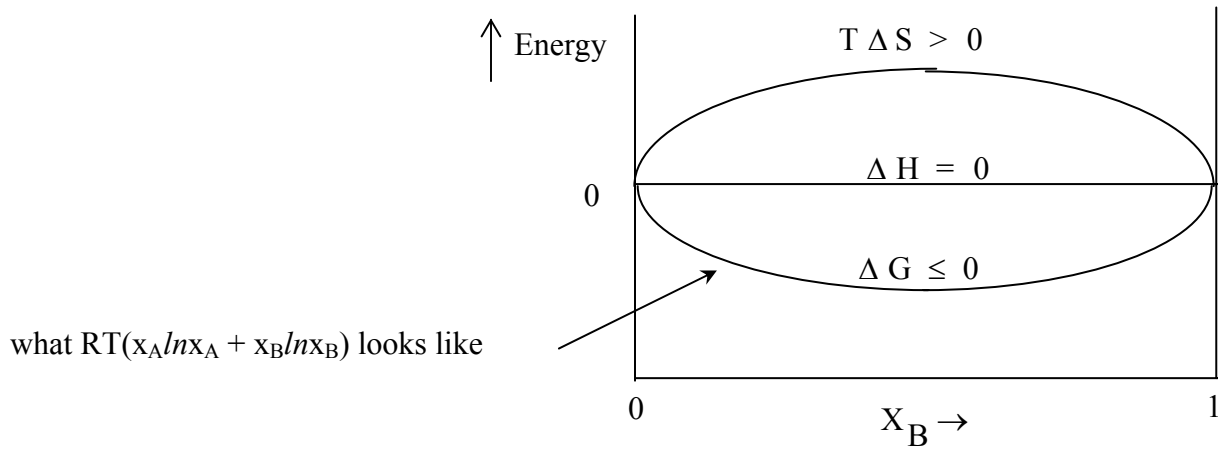
In the  $\alpha$  phase as drawn,  $x_A \simeq 0.10$

But  $\mu_A(x_A^\beta) = \mu_A(x_A^\alpha)$

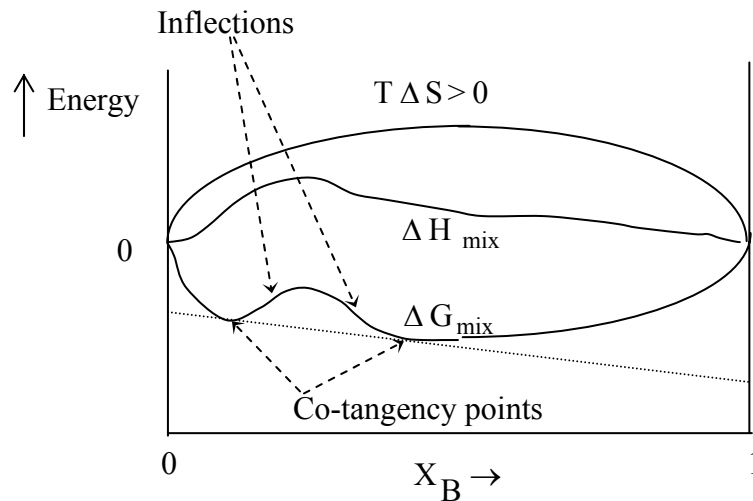
$$\mu_B(x_A^\beta) = \mu_B(x_A^\alpha)$$



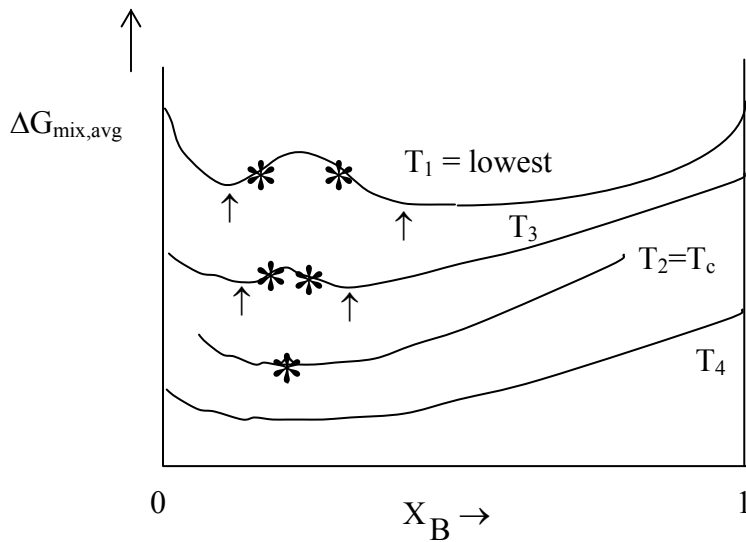
There is no way for an ideal solution to phase separate. That is because the free energy of mixing is:  $\Delta S_{\text{mix}} = -R[n_A \ln x_A + n_B \ln x_B]$ . This function has no wrinkles.



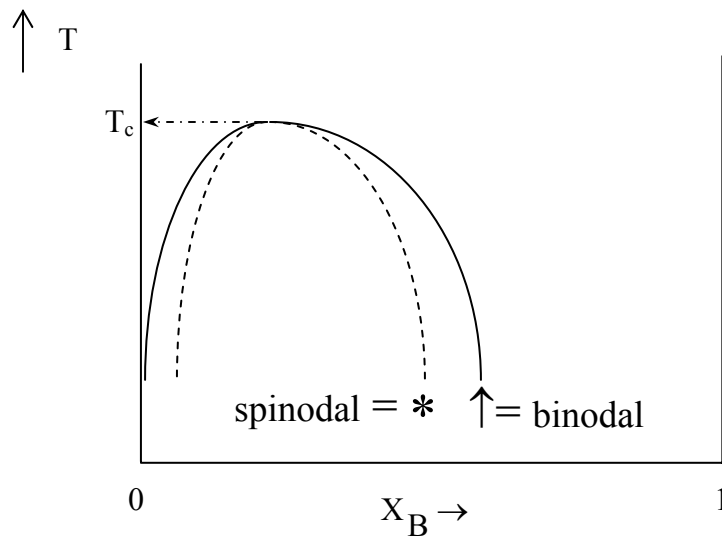
But the regular solution might or might not phase separate, depending on what wrinkles the  $\Delta H_{\text{mix}}$  function introduces. It is easy to imagine how this might happen (stoichiometric mixtures of solvent and solute that result in complexes with specific structures and heats of mixing). Even less specific interactions can produce the needed wrinkles. The requisite thing is a  $\Delta G_{\text{mix}}$  with a point of co-tangency. This requires two points of inflection, as shown.



Moreover, you have a  $\Delta G_{\text{mix,avg}}$  plot like the one shown for each temperature.



The necessary condition for phase separation is that two inflection points (\*) occur at some temperature. This ensures that 2 points of common tangency exist. At the critical temperature, only one inflection occurs. If we assemble the points of common tangency (↑) and the inflection points at various temperatures we produce a phase diagram:



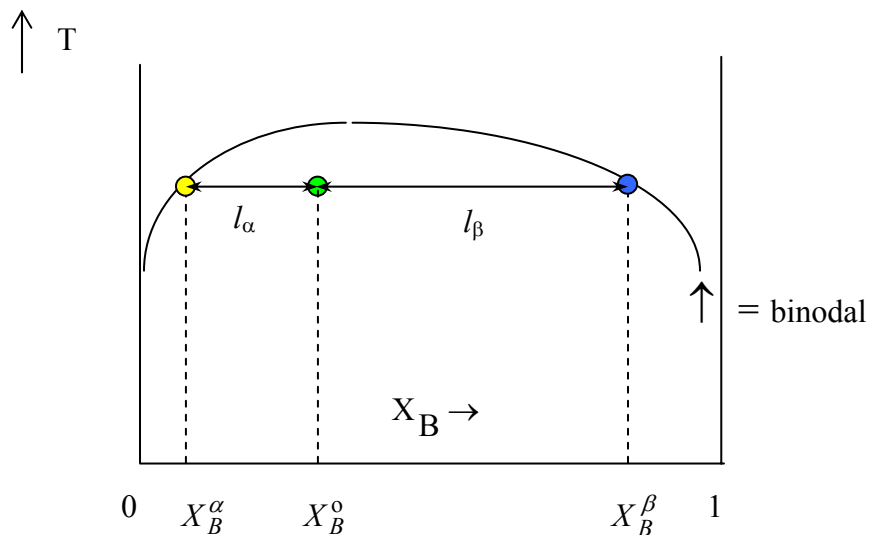
1) Above the solid curve  $\Rightarrow$  1 phase only

2) Anywhere under the solid line phase separation occurs. This is called the Binodal or "cloud point" curve. (Reason: phase separated systems are often turbid or cloudy: compare really shook up oil/vinegar to either fluid separately).

2. However, the solid curve says nothing about the rate at which phase separation occurs. In fact, between the solid & dashed curves, the system is actually metastable. It will take a while for phase separation to happen. How long? For polymers, the transition may be delayed essentially forever. Metastable polymer systems can act almost as if they are stable. Not always, but sometimes.
3. Under the dashed (or spinodal) curve  $\Rightarrow$  total instability. Under the spinodal curve, phase separation begins immediately. For small molecules, this often decomposes the solution into its components almost instantly (seconds). For polymers, it may take hours or longer.
4. The final result: if you ever do reach real equilibrium, the final result is always given by the binodal curve: two distinct phases. Imagine fully separated oil (with a tiny bit of water in it) and vinegar (with a tiny bit of oil in it). Polymers often get "trapped" or "frustrated" en route to that fully-separated state. This results in neat nanoscale morphologies and some interesting technical applications (such as filters).

### Lever Rule

The fact that a phase separation occurs says nothing about how much material goes into each phase. This, however, is known and it is called the lever rule:



If:  $x_B^0$  = overall (or bulk) composition of mixture

$$x_B^\alpha = x_B \text{ in } \alpha \text{ phase}$$

$$x_B^\beta = x_B \text{ in } \beta \text{ phase}$$

$$l_\alpha = |x_B^\alpha - x_B^0|$$

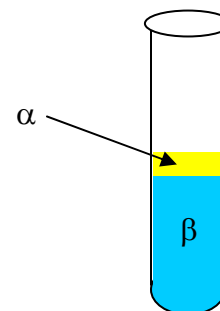
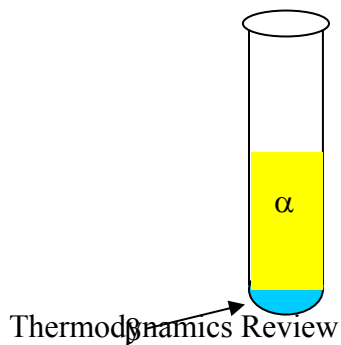
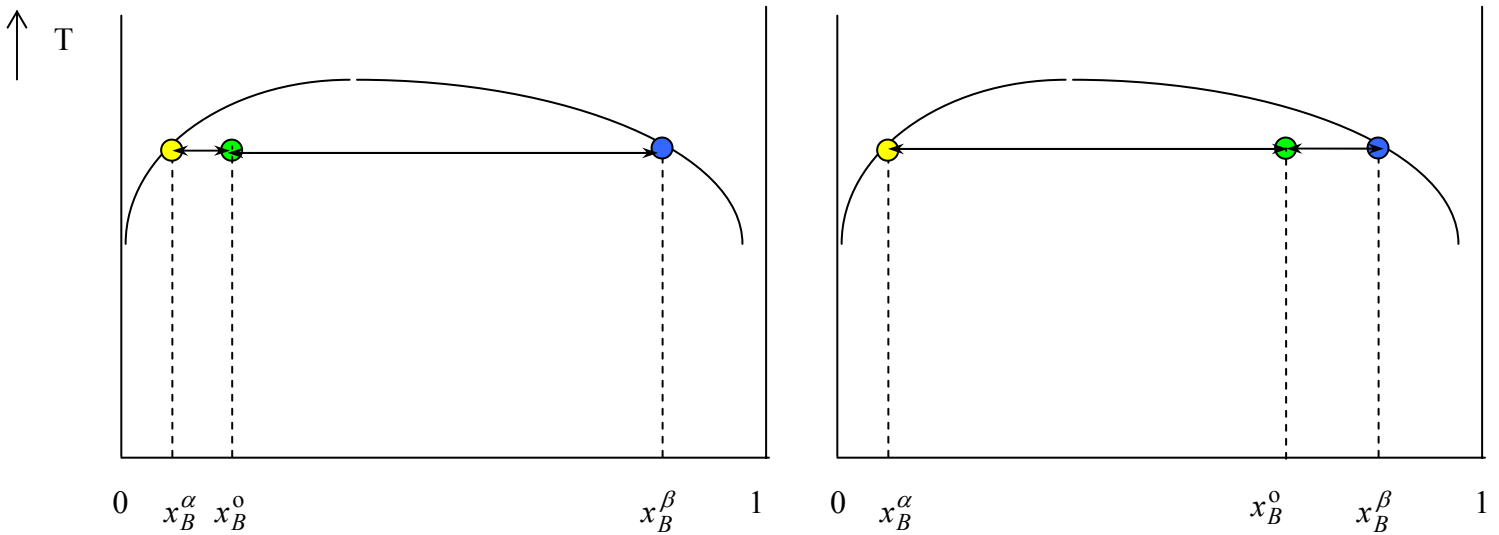
$$l_\beta = |x_B^\beta - x_B^0|$$

Then

$$n_\alpha l_\alpha = n_\beta l_\beta; n = \# \text{ moles}$$

What it means: near a phase boundary, almost all of the material (i.e. sample) will be in the nearby phase.

e.g. Suppose A is lighter than B



## EQUILIBRIUM

Recall that (I.E. from some previous class; see any PChem book)

$$\Delta G = \Delta G^\circ + RT \ln \frac{\Pi_{\text{prod}}}{\Pi_{\text{react}}}$$

where  $\Pi_{\text{prod}} = \prod_i a_i$ ; products

$\Pi_{\text{react}} = \prod_i a_i$ ; reactants

( $a_i$  = activity of  $i^{\text{th}}$  species)

e.g. for  $A + B \leftrightarrow 2C$

$$\Pi_{\text{prod}} = a_C^2$$

$$\Pi_{\text{react}} = a_A a_B$$

At equilibrium  $\Delta G = 0$

$$2) \Delta G^\circ = -RT \ln K_{\text{eq}}$$

$$\text{where } K_{\text{eq}} = \frac{\Pi_{\text{prod}}}{\Pi_{\text{react}}}$$

For now there are 2 things we want to say:

2)  $\Delta G^\circ$  can be measured this way by measuring  $K_{\text{eq}}$ .

3) It is the  $\Delta G$  for the standard state,  $\Delta G^\circ$ , that one obtain. I.E., in many cases it is  $\Delta G$  for hypothetical reaction conditions. This is the undesirable but unavoidable consequence of never having an absolute energy scale. Energy is always relative.

## COLLIGATIVE PROPERTIES

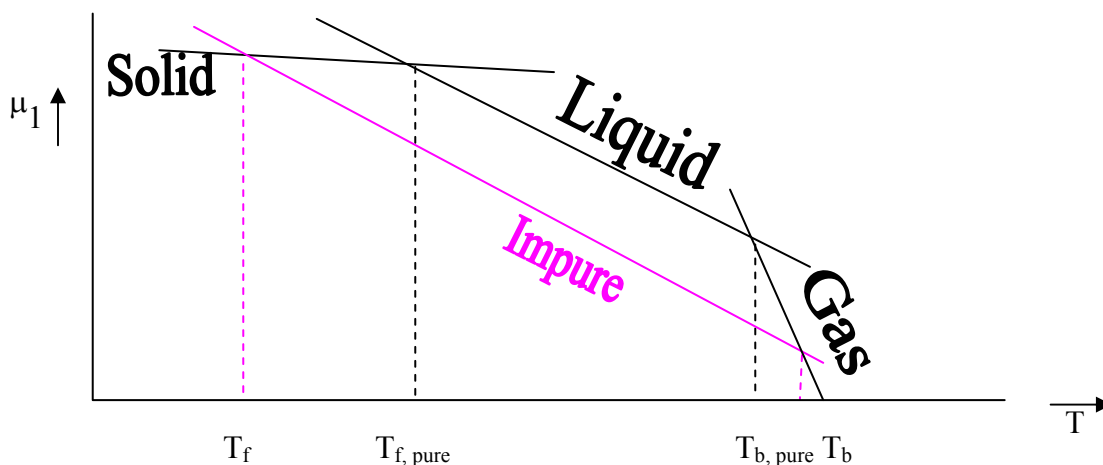
### General Effects of Entropically Reduced Chemical Potential

Vapor Pressure Lowering  
Freezing Point Depression  
Boiling Point Elevation  
Osmotic Pressure

All have reduced potential of solvent in common:

$$\mu_1 = \mu_1^\circ + RT \ln x_1$$

$\leq 0$   
this term is always negative, so chemical potential is reduced compared to pure solvent.



The reason the  $\mu$  vs.  $T$  diagram looks like this is:

$$dG = VdP - SdT$$

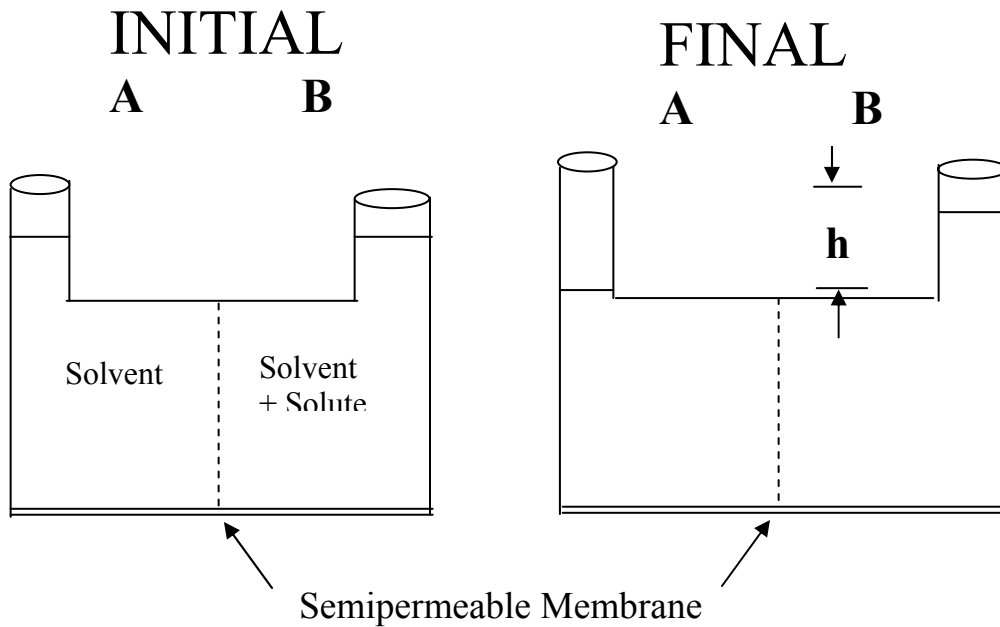
$$\Leftrightarrow -S = \left(\frac{\partial G}{\partial T}\right)_P \text{ or } \dots \left(\frac{\partial \mu}{\partial T}\right)_P = -\bar{S}$$

- 1) This says slope of  $\mu$  vs.  $T$  is always negative, because  $S$  is always positive.

- 2) Since  $S_{\text{gas}} > S_{\text{liq}} > S_{\text{solid}}$ , the magnitude of the slope increases in the order: solid; liquid; vapor.
- 3) As a natural consequence, we can see that a mixture (i.e., impure solvent) which has lower  $\mu_1 = \mu_1^\circ + RT \ln x_1$  will freeze at lower T and boil at higher T.

Qualitative reasoning why this makes sense:

- A liquid freezes because in so doing the entropy of the universe is increased. If a 2<sup>nd</sup> component is present, there is the extra entropy of mixing in the system, so the universe can wait.
  - A liquid boils because in doing, the entropy of the universe (and, in this case, the system itself) is increased. If a second component is present to lower, the potential of the solvent then one has to work harder to raise it to a point where the gas has more entropy—i.e., raise T.
- 4) Vapor pressure lowering: the liquid is made more stable; hence, there is less need to have material in the gaseous state to improve the universe's entropy picture.
  - 5) Osmotic Pressure



What happens?

The solvent goes to the B chamber because potential there is lower.

$$\mu_1^B = \mu_1^\circ + RT \ln x_1^B$$

$$\mu_1^A = \mu_1^\circ$$

Why doesn't the pressure continue indefinitely?

Because pressure builds up on the right side (Chamber B). This causes it to stop.

1  $\Rightarrow$  solvent

A  $\Rightarrow$  l.h.s. of chamber

2  $\Rightarrow$  solute

B  $\Rightarrow$  r.h.s. of chamber

At equilibrium

$$\mu_1^A = \mu_1^B$$

$$\mu_1^\circ = \mu_1^B + \int_{p=\text{ambient}}^{p+\pi} d\mu_1$$

{note:  $\mu_1^B = \mu_1^\circ - RT \ln x_1^B$ . But don't carry it into expression yet.}

But:  $d\mu_1 = \bar{V}_1 dP$  (at  $T = \text{constant}$ ) (From  $dG = VdP - SdT$ )

Also, most liquids are virtually incompressible and the composition changes as one goes from  $P$  to  $P + \pi$  are usually trivial, so  $\bar{V}_1 \simeq \text{constant} \simeq V_1^\circ$ . (Pure material indicated by no bar. Other notations possible. Richards:  $V_1^*$ ).

$$\therefore \mu_1^\circ = \mu_1^B + V_1^\circ \pi$$

or..... 
$$\pi = \frac{\mu_1^\circ - \mu_1^B}{V_1^\circ}$$

Extremely IMPORTANT! How to measure chemical potential.

Now use  $\mu_1^B = \mu_1^\circ + RT \ln x_1^B$

$$\Rightarrow \pi = \frac{-RT \ln x_1^B}{V_1^\circ}$$

But  $x_1^B \simeq 1 - x_2^B$  and let us drop the chamber superscript

Use  $\ln(1 - x_2^B) \simeq -x_2^B$



$$\Rightarrow \pi \simeq \frac{RT x_2}{V_1^\circ}$$

But  $x_2 = \frac{n_2}{n_2 + n_1} \xrightarrow[\text{limit}]{\text{dilute}} \simeq \frac{n_2}{n_1}$

$$5. \pi \simeq \frac{RT n_2}{n_1 V_1^\circ}$$

$$6. \pi = \frac{n_2 RT}{V}$$

Van't Hoft law: Like Ideal Gas law!

But  $n_2 = \frac{g_2}{M_2}$  where  $g_2$  is grams of solute

$$\Rightarrow \pi = \frac{g_2 RT}{M_2 V} = \frac{c R T}{M_2}$$

where  $c = \frac{g_2}{V}$  = concentration as wt./vol. (gram/ml for example)

This is ideal behavior because we started with  $\mu_1 = \mu_1^\circ + RT \ln x_1$

To handle nonidealities you could invoke the usual activity stuff. (See, for example, Tanford). However, another formalism is more commonly used instead. In this approach one forces a polynomial to  $\mu$ . From the Latin, this approach is called a virial expression.

$$4) = \mu^\circ - RT V_1^\circ c \left[ \frac{1}{M_2} + cA_2 + c^2A_3 + \dots \right]$$

{The virial coefficients are often given the symbol  $B_i$  instead or in some books

$A_2 = B$ ;  $A_3 = C$ ; etc....]

The virial coefficients are easily obtained experimentally, but also have theoretical importance: they contain the combined effects of finite solute size and mutual attraction. Note that the first virial coefficient is  $1/M_2$ , which we get by manipulations just like those performed for  $\pi$ :

$$\ln x_1 \cong -x_2 \cong \frac{-n_2}{n_1} = \frac{-V_1^\circ n_2}{V} = \frac{-cV_1^\circ}{M_2}$$

Since the expression

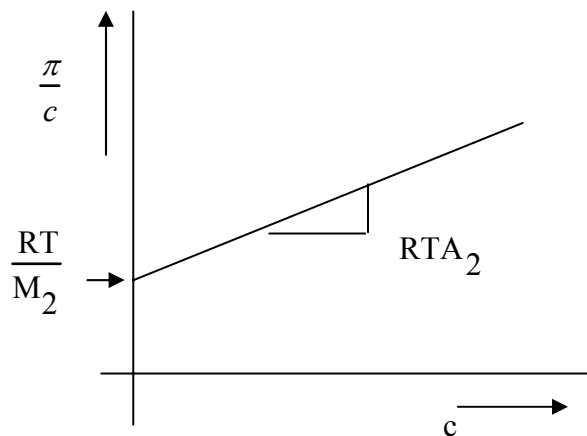
$$\pi = \frac{\mu_1^\circ - \mu}{V_1^\circ}$$

is general we can write immediately a virial expression for  $\pi$ :

$$\pi = cRT \left[ \frac{1}{M_2} + cA_2 + c^2A_3 + \dots \right]$$

### Osmotic Pressure Plots

$$\frac{\pi}{c} = RT \left[ \frac{1}{M_2} + A_2c + \dots \right]$$



Note 4 practical limitations of Osmometry:

- 3) Membrane must not pass macromolecule: means can't do very low molecular weights ( $\leq 10,000$ ).
- 4) Membrane must not be degraded by solvent.
- 5) As  $M_2$  goes up  $\pi$  goes down to levels which eventually become unmeasurable. As a practical limit, measurements are hard above  $\simeq 300,000$  but you occasionally see higher.
- 6) This experiment is a total pain in the neck.

Finally, it is easy to show that no other colligative method is as sensitive as membrane osmometry. (One variant, Vapor Pressure Osmometry, is nice for very low MW's  $\leq 20,000$ ).