Lecture 23

We now turn to considerations of **mixtures.** To keep our discussion reasonably simple, we will limit our discussion to non-reacting systems, and to non-ionic systems. In other words, we will consider at first only systems that interact weakly. (As opposed to daily.) Furthermore, we will begin our treatment, and in fact spend most of our time, on mixtures of two components, i.e., **binary mixtures**. Toward the end of the chapter we will expand our studies to mixtures of three components. However, even though most real mixtures contain more than two components, we will learn a great deal about the properties of mixtures in general by thinking carefully about two component systems. One reason that we will focus on binary mixtures is that if we label our components A and B, a binary mixture has the nice property that $X_A + X_B = 1$, where X is the mole fraction of the component. This equation will make it much easier to simplify some of our results.

In dealing with mixtures we will have to depend heavily on **partial molar quantities**. The basic rationale for introducing these partial molar quantities is that **because the components of a mixture will interact, the parameters that describe these components will be different for the mixture than for the pure substances**. In other words, vapor pressure, density, chemical potential and molar volume will tend to be different for ethanol than for ethanol in an aqueous solution.

We will illustrate this for the case of molar volumes. Suppose we have a sample of pure $H_2O(l)$ at 298K. We add one mole and the volume increases by 18 ml. We therefore say that the partial molar volume of pure $H_2O(l)$ at 298 K = 18 ml. Now suppose that we have a large sample of pure ethanol(l) at 298 K, and add one mole of $H_2O(l)$. In this case, the volume of the solution increases only by 14 ml. In order to describe this increase we say that the partial molar volume of H_2O in a large volume of EtOH at 298 K = 14 cm^3. CAN ANYONE SUGGEST WHY THE PARTIAL

MOLAR VOLUME OF WATER IN ETHANOL IS SO SMALL?

We define the **partial molar volume** as **the change in volume of a mixture when a mole of a substance is added**. The formal definition of the partial molar volume of the jth component in a mixture is

$$\overline{V}_j = (\frac{\partial V}{\partial n_j})_{p,T,n_i}$$

It is important to note that $\overline{V}_j$ is a function of p, T and the composition of the mixture. This latter is most clear if we look at a plot of the partial molar volume of water as a function of the mole fraction of water in a water-ethanol mixture. You can see from this graph that the partial molar volume of water in ethanol continually changes as the mole fraction changes.

The result of this is that we can write that for a two component system, V = V(p, T, n_A, n_B). This means that we can write the differential of V at constant T and p as

$$dV_{T,p} = (\frac{\partial V}{\partial n_A})_{n_B,T,p} dn_A + (\frac{\partial V}{\partial n_B})_{n_B,T,p} dn_B = \overline{V}_A dn_A + \overline{V}_B dn_B.$$

In other words for small changes in the mole number of the components of a mixture, the change in volume equals the partial molar volume times the change in mole number. We can also write

$$V = \overline{V}_A n_A + \overline{V}_B n_B.$$

However, great care must be taken in using both of these equations since the partial molar volume

is not a constant but changes as the composition changes.

Unlike molar volumes, partial molar volumes can be negative. As an illustration, if we take one mole of $MgSO_4$ and add it to one liter of water we find that the volume decreases by 1.4 ml. Thus the partial molar volume of $MgCl_2$ in pure H_2O is -1.4 cm^3, i.e., $\left(\dfrac{\partial V}{\partial n}\right)$ = -1.4 ml. This leads to an interesting and important distinction - partial molar volumes can be negative - molar volumes cannot be negative.

Partial molar quantities can be defined for all extensive variables and can generally be defined as $W_j \equiv (\dfrac{\partial W}{\partial n_j})$, where W is any extensive variable. The chemical potential is a partial molar quantity since it is defined as $\mu_j = (\dfrac{\partial G}{\partial n_j})$. As is the case for all partial molar quantities, the value of the chemical potential depends on the composition. In other words, the chemical potential of pure ethanol is different from that of ethanol in a 50:50 mixture of ethanol with cyclohexane and is different from that of ethanol in a 20:80 mixture of ethanol with cyclohexane. As we showed earlier we can use chemical potentials to relate changes in mole number to the change in the Gibbs free energy. For a change in mole number of components in a two component system,

$$dG_{T,p} = \mu_A dn_A + \mu_B dn_B$$

We also related the Gibbs function at a given temperature and pressure to the chemical potential by

$$G = \mu_1 n_1 + \mu_2 n_2 + ... + \mu_j n_j + ...$$

For a two component system,

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

If we take the differential of G for this two component system, we get

$$dG = \mu_A dn_A + n_A d\mu_A + \mu_B dn_B + n_B d\mu_B$$

Since G is a state function, this differential must equal the differential we wrote earlier for dG.

$$\mu_A dn_A + \mu_B dn_B = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B.$$

If we cancel out the common terms, we get

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

which is the form of the Gibbs-Duhem equation for a two component system, and at constant T and p. The general Gibbs-Duhem equation for a system at constant T and p is

$$\sum n_j d\mu_j = 0$$

This is a very interesting result. It tells us that the changes of chemical potentials of a mixture are coupled. If one changes the other must change to compensate for the first change.

EXAMPLE: Consider a two component system. The chemical potential of A changes by $d\mu_A$, What is the corresponding change in $d\mu_B$?

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

$$d\mu_B = -(n_A / n_B) d\mu_A$$

The most fundamental transformation of a two component system, and one that we must understand if we are going to understand more complicated processes, is **mixing**. How does mixing affect our most important thermodynamic state functions, H, G, and S?

Before we turn to a quantitative treatment, let's consider a simple system, a mixture of gases. Suppose we take a sample bulb containing one mole of H_2 at one atm on one side of a stopcock and one mole of N_2 at one atm on the other side of the stopcock. The temperature of both gases is the same.

IF WE OPEN THE STOPCOCK WHAT WILL HAPPEN? WHAT DO YOU CALL A PROCESS THAT OCCURS WITHOUT NEEDING WORK APPLIED? WHAT DO WE KNOW ABOUT THE FREE ENERGY OF A SPONTANEOUS PROCESS AT CONSTANT T AND P? Therefore we can conclude that $\Delta G < 0$ for the mixing of gases.

Let's consider what the driving force is for mixing in this example. It's not pressure, since the pressures were the same on both sides. It's not temperature, since that's the same for both sides. It's not energy, since both gases are very non-polar and therefore the energy change due to mixing will be negligible. On reflection, it becomes apparent that the only change that's occurred on mixing the two gasses is that the disorder increases, since nitrogen molecules that were surrounded initially solely by nitrogen molecules are now surrounded by a combination of nitrogen and hydrogen molecules, and vice-versa. In other words, the driving force for mixing is an increase in the entropy of the universe. It should be noted that energy does have a part in determining the extent to which two substances mix - but only because it affects the total entropy change by changing the entropy of the surroundings. Thus, in a case when the process of mixing is exothermic, both ΔS_{sys} and ΔS_{surr} are positive, and the mixing occurs readily. For a case like the mixing of oil and water, the unfavorable ΔH_{mix} results in a ΔS_{surr} that is so negative that the overall entropy change for the universe is negative as well. As a result oil and water mix only sparingly.

Let's demonstrate this quantitatively for a mixture of ideal gases by generalizing the

example we just considered. We begin with two containers containing different ideal gases both at temperature T and pressure p. The first contains a number of moles n_A in volume V_A, while the second contains a number of moles n_B in volume V_B at the same p and T. Remember now that we can express the free energy of a system in terms of the chemical potentials of its components with the equation

$$G = \sum_j \mu_j n_j$$

So for these two components before mixing, we can write

$$G_i = \mu_A n_A + \mu_B n_B.$$

The chemical potential of a system of ideal gases at a given pressure is related to the standard chemical potential by

$$\mu = \mu^0 + RT \ln \frac{p}{p^0}$$

So our equation for the initial free energy becomes

$$G_i = n_A (\mu_A^0 + RT \ln \frac{p}{p^0}) + n_B (\mu_B^0 + RT \ln \frac{p}{p^0}).$$

Now we bring our two containers together and remove the barrier between them so they can mix. The p and T stay the same, because the gases are ideal. However, even though the total pressure stays the same, the pressures that substances A and B exert are now different, since they are spread over the entire volume of the combined containers. Now the pressure of A is p_A, the partial pressure of A and the pressure of B is p_B, the partial pressure of B. The free energy of the mixture is given by

$$G_f = n_A (\mu_A^0 + RT \ln \frac{p_A}{p^0}) + n_B (\mu_B^0 + RT \ln \frac{p_B}{p^0}).$$

The difference in free energies before and after mixing, **ΔG_{mix}**, is given by

$$\Delta G_{mix} = G_f - G_i = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$

We can simplify this by noting that $n_A = X_A$ n, and $n_B = X_B$ n, where X_A and X_B are the mole

fractions of A and B respectively, and by noting that the partial pressures can also be expressed in

terms of mole fractions, using $p_J = X_j p_T$. Substituting these expressions yields

$$\Delta G_{mix} = X_A nRT \ln \frac{X_A p}{p} + X_B nRT \ln \frac{X_B p}{p} = nRT(X_A \ln X_A + X_B \ln X_B).$$

Since the mole fractions of a mixture are always less than one, both logarithms are negative, and

$\Delta G_{mix} < 0$. In general for a mixture of n substances,

$$\Delta G_{mix} = nRT \sum_{j=1}^{n} X_j \ln X_j$$

Let's look at an example. Suppose we have 10^{-2} mole C_2H_4, 10^{-2} mol H_2S and one mol Ar

at a temperature of 298K. What is the free energy of mixing assuming that all gases are ideal?

$$\Delta G_{mix} = nRT(X_{C_2H_4} \ln X_{C_2H_4} + X_{HI} \ln X_{HI} + X_{Ar} \ln X_{Ar})$$

$$= (1.02)(8.314)(298)(.01 \ln .01 + .01 \ln .01 + .98 \ln .98)$$

$$= -282 \text{ J.}$$

We can use our equation for ΔG_{mix} to calculate **ΔS_{mix} and ΔH_{mix}**. From our fundamental equations

we can write

$$dG = -SdT + Vdp + \mu_A dn_A + \mu_B dn_B.$$

Therefore S = $-(\frac{\partial G}{\partial T})_{p,n_A,n_B}$, and for an ideal gas,

$$\Delta S_{mix} = -(\frac{\partial \Delta G}{\partial T}) = -nR(X_A \ln X_A + X_B \ln X_B).$$

and for a n component system

$$\Delta S_{mix} = -nR\sum_{j=1}^{n} X_j \ln X_j$$

In our above example,

$$\Delta G_{mix} = nRT(X_{C_2H_4} \ln X_{C_2H_4} + X_{HI} \ln X_{HI} + X_{Ar} \ln X_{Ar}) = -282J$$

From our above result we see that

$$\Delta S_{mix} = \frac{-\Delta G_{mix}}{T} = 0.949JK^{-1}.$$

Finally we can calculate ΔH_{mix} by noting that $\Delta H = \Delta G + T\Delta S$. Substituting our equations

for ΔG_{mix} and ΔS_{mix}, we get

$$\Delta H_{mix} = nRT \ln (X_A \ln X_A + X_B \ln X_B) - nRT (X_A \ln X_A + X_B \ln X_B) = 0.$$

Can anyone explain why the enthalpy of mixing of an ideal gas is zero?

<u>Lecture 24</u>

What we've done so far is fine for gases, but most chemistry is done in condensed phases, so it is important to be able to extend these ideas to liquids. Our first step in doing this is to determine the **chemical potential of a liquid**. In doing this we want to start with something we know, and what we know is the form of the chemical potential of an ideal gas, $\mu_g = \mu^0 + RT \ln \dfrac{p}{p^0}$

. It would be nice if we could relate this to the chemical potential of a liquid. WHEN ARE THE CHEMICAL POTENTIALS OF A LIQUID AND A VAPOR EQUAL? [Along the coexistence line.] So for a pure substance when the liquid and vapor are at equilibrium,

$$\mu_A^*(\ell) = \mu_A^{*\,0} + RT \ln \frac{p^*}{p^0}$$

where we use the asterisk to indicate that we are dealing with a pure substance. WHAT DO WE CALL THE PRESSURE WHEN A LIQUID IS IN EQUILBRIUM WITH ITS VAPOR? If we use p_A* to indicate the vapor pressure of pure A, then

$$\mu_A^*(\ell) = \mu_A^{*\,0} + RT \ln \frac{p_A^*}{p^0}.$$

If instead of being a pure liquid, A is a component in a mixture, its vapor pressure will be different than when it is a pure substance. How does the vapor pressure of a substance in a solution differ from that of the pure liquid? The answer depends on the way the components of the solution interact. The simplest case is that of an **ideal solution**. An ideal solution is a solution of two or more substances where the intermolecular interaction between the substances (A-B) is the same as the average of the interactions between A-A and B-B. For an ideal solution of two volatile components, the vapor pressure of each component is given by **Raoult's Law**. If we use the vapor

pressure of A as an example, Raoult's law says that

$$p_A = X_A p_A^*$$

Because all ideal solutions follow Raoult's Law, we can alternately define an ideal solution as one that follows Raoult's Law.

We can find the chemical potential of A when it is in an ideal solution by using this result for the vapor pressure of an ideal solution in our formula for the chemical potential of a liquid. This yields

$$\mu_A(\ell) = \mu_A^0 + RT \ln \frac{X_A p_A^*}{p^0}.$$

If we take the difference between this equation and that for the chemical potential of the pure liquid, we get

$$\mu_A(\ell) - \mu_A^*(\ell) = RT(\ln \frac{X_A p_A^*}{p^0} - \ln \frac{p_A^*}{p^0})$$

or

$$\mu_A(\ell) = \mu_A^*(\ell) + RT \ln X_A.$$

What we've accomplished is to derive an equation relating the chemical potential of a pure liquid to the chemical potential of that liquid in any solution. While we've used the ideal gas law in deriving this equation, it is equally valid for real gases. However, it is only valid for ideal solutions.

When are solutions most likely to be ideal? I.e., **when can we use Raoult's law?** Raoult's law applies equally well for solutions where one of the solvents is volatile and the other is not, like sugar in water, or for solutions with two volatile components like hexane in octane. It is most valid when the two components are chemically similar, like two non-polar substances or two polar substances. In these situations, Raoult's law predicts that when we change the mole fraction of A,

p_A will change in a linear fashion with a slope equal to the vapor pressure of pure A.

For non-ideal solutions, p_A can be greater or lower than Raoult's law predicts.

For ideal solutions, Raoult's law holds for both the solute, which we define as the component with the smaller mole fraction, and the solvent, which we define as the component with the larger mole fraction. However, **real solutes at low concentrations do not follow Raoult's law**. For the solute Raoult's law predicts that $p_B = X_B \, p_B^*$. A real solution at low concentrations does have a vapor pressure proportional to X_B, but not with a slope equal to the vapor pressure of the pure liquid. The slope for the real solution can be larger or smaller than the vapor pressure of the pure liquid. The vapor pressure of a real solute in the limit of low concentration is given by **Henry's Law**,

$$p_B = X_B \, k_B,$$

where k_B, called the Henry's law constant, has units of pressure and is different than the vapor pressure of the pure substance.

Although Henry's law is valid for real solutions, it is only valid in the limit of low concentration of solute, and thus is an example of a **limiting law**. It is a type of ideal law, since it is only valid for a limited range of conditions, and therefore solutions that obey Henry's Law are known as **ideal dilute solutions**. To get a graphical feel for the relation between Henry's law and Raoult's Law, let's look at the variation of vapor pressures for an acetone-chloroform mixture.

First we have the prediction of Raoult's Law that the partial pressure of the chloroform varies linearly with mole fraction between 0 and the vapor pressure of pure chloroform. If we draw in the vapor pressure of the chloroform in the real solution, we see that **the slope of the vapor pressure of the real solution coincides with the Raoult's law vapor pressure only at high mole fractions of chloroform**.

Henry's law says that the variation of vapor pressure with mole fraction at low mole fractions will be linear with a slope different than $p^*_{CHCl_3}$. We can see that we can draw a fairly accurate straight line through the lower part of the CHCl$_3$ vapor pressure curve. Note that we can find the Henry's law constant k by extrapolating this straight line to X = 1. In short, what we see from our graph is:

1) Raoult's law approximates the vapor pressure of a liquid in a real solution, when that liquid is present in mole fractions close to one, i.e., it approximates the vapor pressure of real solvents.

2) Henry's law approximates the vapor pressure of a liquid for real solutions in which the liquid is present in a small mole fraction, i.e., it approximates the vapor pressure of real solutes.

3) The true vapor pressure of the liquid lies between the value given by Raoult's law and the Henry's law constant. In other words, $p_{RAOULT} \leq p \leq p_{HENRY}$ or $p_{RAOULT} \geq p \geq p_{HENRY}$. If the vapor pressure of a real solution is lower than that predicted by Raoult's law, it is called a negative deviation from ideality. If the vapor pressure of a real solution is higher than that predicted by Raoult's law, it is called a positive deviation from ideality.

When we began our treatment of solutions, we started by calculating the free energy of mixing of ideal gases. This was based on our definitions of the chemical potentials of ideal gases. Now that we've developed definitions for the chemical potentials both of pure liquids and liquids in solution, let's calculate the free energy of mixing of liquid solutions. For simplicity, we'll begin with the free energy of mixing of ideal solutions.

For two pure liquids, A and B, the Gibbs function before mixing is

$$G_i = n_A\,\mu_A{}^*(l) + n_B\,\mu_B{}^*(l)$$

On mixing the Gibbs Function becomes

$$G_f = n_A\,\mu_A(l) + n_B\,\mu_B(l)$$

$$= n_A\,(\mu_A{}^*(\,l) + RT\ln X_A) + n_B\,(\mu_B{}^*(\,l) + RT\ln X_B).$$

If as before, we define $\Delta G_{mix} = G_f - G_i$, we obtain

$$\Delta G_{mix} = RT(n_A\ln X_A + n_B\ln X_B)$$

$$= nRT\,(X_A\ln X_A + X_B\ln X_B).$$

This is the same result that we obtained for mixing two ideal gases. The other results are the same as well.

$$\Delta S_{mix} = nR\,(X_A\ln X_A + X_B\ln X_B)$$

$$\Delta H_{mix} = \Delta U_{mix} = 0$$

$$\Delta V_{mix} = 0$$

It is important to clearly understand that when we talk of a mixture of ideal gases and of an ideal solution, the definitions of ideality are different. When we talk of an ideal gas, we talk of a gas in which there are no interactions between particles. WHY CAN'T WE USE THIS DEFINITION FOR AN IDEAL SOLUTION? The definition we use of an ideal solution is, crudely, that the average interaction

between particles in the solution is the same as the average interactions in the liquids before the solution was made. In other words **for an ideal gas we say that there are no interactions, while for an ideal solution we say that there is no net change in interactions.** A real solution differs from an ideal solution in that the interactions in the solution are different from the average of those in the pure liquids.

How do we treat the chemical potential of real solutions? Remember that the chemical potential of a pure liquid is given by

$$\mu_A^*(\ell) = \mu_A^0 + RT \ln \frac{p_A^*}{p^0}$$

Here, p_A^* is the vapor pressure of the pure liquid. For that same substance in solution, the chemical potential would be given by

$$\mu_A(\ell) = \mu_A^0 + RT \ln \frac{p_A}{p^0}$$

In this equation p_A is the vapor pressure of the liquid in the solution. If as before, we take the difference between the chemical potential of the pure liquid and the chemical potential of the mixture, we get

$$\mu_A(\ell) = \mu_A^*(\ell) + RT \ln \frac{p_A}{p_A^*}$$

This equation is exact and applies to any solution, real or ideal. Since for an ideal solution, $p_A = X_A \, p_A^*$, our earlier result was

$$\mu_A(\ell) = \mu_A^*(\ell) + RT \ln X_A$$

In this equation, we effectively have a new standard state for the liquid, called $\mu_A^*(l)$, the pure liquid at a pressure of 1 bar.

 Lecture 25

If we wanted to determine an equation for the chemical potential of a real solute or solvent

by substituting an equation of state for p_A, the vapor pressure of A, as we did for the pressure of

gases, we would run into a couple of problems. First, an accurate equation of state for real

solutions would be a far worse equation than the virial equation. It would be very messy and

would have lots of terms. Second, no accurate equation of state is known for liquids, let alone real

solutions.

To avoid both the first problem and the second, we can modify our ideal solution result as

we did when we derived equations for the chemical potential of a real gas, by introducing a quantity

called the activity into our equation. Thus our equation for the chemical potential of a liquid in a

real solution becomes

$$\mu_A(\ell) = \mu_A^*(\ell) + RT \ln a_A,$$

where in this case, the activity a represents an effective mole fraction.

For volatile liquids, the activity can be determined experimentally. Remember that

$$\mu_A(\ell) = \mu_A^*(\ell) + RT \ln \frac{p_A}{p_A^*}$$

Since this equation is true for all solutions, comparison with the previous equation shows that

$$RT \ln a_A = RT \ln \frac{p_A}{p_A^*}$$

and that therefore

$$a_A = \frac{p_A}{p_A^*}$$

Therefore we conclude that to measure the activity of a volatile solute or solvent we measure the

vapor pressure in the solution and divide it by the vapor pressure of the pure liquid. We see from this that **the activity depends on p, T, and composition.** This means that for each substance, there will be a different activity for each composition of a solution.

When we defined the fugacity for real gases, we related it to the pressure by introducing the fugacity constant γ. Here again, we use a constant γ to relate the activity of a real solute or solvent to that of the ideal quantity, the mole fraction. The relation is

$$a_A = \gamma_A\, X_A.$$

Let's see what we can figure out about this activity coefficient. Remember that as the mole fraction of a solvent approaches one, that the vapor pressure of the solvent approaches the value predicted by Raoult's law, i.e., the ideal value. This would be expressed in the form of an equation as

$$\lim_{X_A \to 1} \frac{p_A}{p_A^*} = X_A$$

But $p_A/p_A^* = a_A$, and therefore

$$\lim_{X_A \to 1} a_A = X_A$$

Now since $a_A = \gamma_A\, X_A$, we will also have

$$\lim_{X_A \to 1} \gamma_A = 1$$

If we substitute the equation $a_A = \gamma_A\, X_A$, in our equation for the chemical potential of a real solvent or solute, we get

$$\mu_A(\ell) = \mu_A^*(\ell) + RT \ln X_A + RT \ln \gamma$$

We see that as was the case for the chemical potential of real gases, the chemical potential of real liquids is composed of an ideal term, $\mu_A^* + RT \ln X_A$, and a correction term which contains all the deviations from ideality, $RT \ln \gamma_A$.

At this point, we've obtained an equation for the chemical potential of real solvents, introducing a new definition of the activity that applies to volatile liquids. The results we've obtained for the activity have general applicability, since they are based on the measurement of vapor pressures at various compositions. However, as we discovered for real gases, these data are often cumbersome. For gases, we find that if the problem doesn't require the accuracy that the virial equation provides, we invariably turn to the ideal gas equation, because it is easier to use.

It would be nice if we find a simple useful approximate equation for solutions. If we turn back to our equation comparing the vapor pressure of real solutions with the various equations that describe them, we find that at mole fractions approaching 1 that Raoult's Law gives a good approximation to the vapor pressure of the real solvent. We therefore find that the appropriate chemical potential for the solvent is the chemical potential of the ideal solvent,

$$\mu_A(\ell) = \mu_A{}^*(\ell) + RT \ln X_A.$$

This equation should be simple enough for anyone's tastes, but again, because it applies only in the limit $X \to 1$, it is only valid for solvents.

What do we do for solutes? It turns out that examination of our graphs shows that in the limit of low concentration, the vapor pressure is fairly accurately given by Henry's Law. This tells us that we should be able to come up with a simple equation for the chemical potential of the solute, the low mole fraction component, based on Henry's law, $p_B = K_B X_B$.

The exact chemical potential of the solute B is given by

$$\mu_B = \mu_B^* + RT \ln \frac{p_B}{p_B^*}.$$

If we substitute the Henry's Law value for p_B in this equation we get

$$\mu_B = \mu_B^* + RT \ln \frac{K_B X_B}{p_B^*},$$

which yields in turn

$$\mu_B = \mu_B^* + RT \ln \frac{K_B}{p_B^*} + RT \ln X_B.$$

Because both the Henry's constant K_B and the vapor pressure of the pure solute, P_B^*, are characteristics of the pure solute, we can define a new standard state for solutes,

$$\mu_B^+ = \mu_B^* + RT \ln \frac{K_B}{p_B^*},$$

which yields a new equation for the chemical potential of the solute in the limit of low concentration,

$$\mu_B = \mu_B^+ + RT \ln X_B.$$

Remember now that although Henry's Law applies to real solutes, it does so only in the limit of low concentrations. If we move to concentrations high enough that Henry's law doesn't apply, we could turn to our previous result for real liquids, but it is a more common practice to use a specific solute activity a_B. The solute activity is based on our Henry's Law chemical potential, and is defined in the equation

$$\mu_B = \mu_B^+ + RT \ln a_B,$$

where $a_B = p_B/K_B$. Once again we introduce the activity coefficient γ_B, as in the defining equation, $a_B = \gamma_B X_B$. However, unlike the case of the activity coefficient for the solvent, $\gamma_B \to 1$ as X_B approaches 0. In other words, the ideal limit of a solvent is the pure solvent, but the ideal limit of a solute is in the limit of infinitely low concentration.

Why did we go through this relatively tedious process of defining all these new standard

states, and all these new equations for the chemical potential under various conditions? One reason is that our eventual goal is to apply these results to chemical equilibrium. When we treat chemical equilibria, we will initially do so for ideal gases, and then generalize to real gases, solutions and other real systems. By defining the chemical equilibria in terms of activities, all we need to do to modify our results for a new kind of system is to define the activity for that new phase. In defining these activities it is useful if they can be defined so that our equations for chemical potential have consistent forms. For example, if we insert our definition that $a_B = \gamma_B X_B$ into our equation for the chemical potential of the solute we get

$$\mu_B = \mu_B{}^+ + RT \ln X_B + RT \ln \gamma_B.$$

If we compare this with the chemical potential of the solvent,

$$\mu_A = \mu_A{}^* + RT \ln X_A + RT \ln \gamma_A,$$

we see that we have succeeded in obtaining consistent forms for the chemical potential at both low and high concentration. In order to do so we've had to define different standard states for the two cases. In the high concentration (solvent) case, the standard state is $\mu_A{}^*$, the chemical potential of the pure liquid. In the low concentration case, the standard state is given by

$$\mu_B^+ = \mu_B^* + RT \ln \frac{K_B}{p_B^*}.$$

It is useful to note that all we've been doing in defining each of these standard states is manipulating our original equation for the chemical potential of a liquid in a solution,

$\mu_A(\ell) = \mu_A^*(\ell) + RT \ln \dfrac{p_A}{p_A^*}.$ Each of our other equations for the chemical potential is a version of

this equation in terms of convenient constants. To see this lets take our equation for μ_B, $\mu_B = \mu_B{}^+$

+ RT ln a_B, and combine it with our definitions $a_B = \dfrac{p_B}{K_B}$, and $\mu_B^+ = \mu_B^* + RT \ln \dfrac{K_B}{p_b^*}$. A few steps

of simplification leave us with the chemical potential of B in a solution, $\mu_B(\ell) = \mu_B^* + RT \ln \dfrac{p_B}{p_B^*}$.

So we see that no matter what the form, the physical content of these equations is identical.

When we calculated the chemical potential of the solute and defined the solute activity, it was in terms of the mole fractions. For most solution chemistry, it is more convenient to calculate solute concentrations in terms of molality, where molality is defined as moles of solute/kg of solvent, i.e., $m = \dfrac{n_B}{kg(A)}$. To calculate chemical potentials and define activities in terms of molalities, we turn again to dilute solutions. In a dilute solution $n_B \ll n_A$, so the mole fraction of the solute,

$$X_B = \frac{n_B}{n_B + n_A} \approx \frac{n_B}{n_A}.$$

Since $m \, \alpha \, X_B$, or equivalently $km_B = X_B$, where k is a proportionality constant, we can rewrite our chemical potential for the solute at low dilution as

$$\mu_B = \mu_B^+ + RT \ln \frac{km_B}{m^0}$$

where m° = 1 mole/kg. m^0 serves two purposes in this equation. First, it defines a new standard state, m° = 1molal = 1 mol/kg. Second, it makes the quantity km_B/m^0 dimensionless. Our μ_B now becomes

$$\mu_B = \mu_B^+ + RT \ln k + RT \ln \frac{m_B}{m^0}.$$

If we define yet another standard chemical potential, $\mu_B^0 = \mu_B^+ + RT \ln k,$ we now get

$$\mu_B = \mu_B^0 + RT \ln \frac{m_B}{m^0}$$

Now if we incorporate deviations from ideality in this equation, we get

$$\mu_B = \mu_B^0 + RT \ln a_B,$$

where $a_B = \dfrac{\gamma_B m_B}{m^0}$ and as before $\gamma_B \to 1$ as $m_B \to 0$. This is true for any solute at any molality.

In addition to these standard states there is an additional important one, known as the "Biochemist's Standard State". This standard state is of particular interest to those studying biochemical problems in aqueous solution. Biochemical systems are so complex that it is often difficult to characterize the concentrations of each species in solution. For example, a solution containing H_3PO_4 may contain $H_2PO_4^-$, $HPO_4^=$ and PO_4^{-3} in amounts that are difficult to characterize because of the easy interconversion between the species. As a result, the Biochemist's standard state focuses on the easy to characterize pH. The pH of choice for this standard is pH 7 exactly, since this is close to physiological pH. This means that the standard activity of H^+ is defined as 10^{-7} M, and $a_{H^+} = 1$ at this concentration. The activity of all other species is defined as the total concentration of all species of that molecule at pH 7:

$$\text{Dilute solution: } a_B = \sum_i^{species} c_{i,B},$$

where the sum is over the concentration of all the species of molecule B. In this example above, this would be the sum of the concentrations in moles/l of H_3PO_4, $H_2PO_4^-$, HPO_4^{-2}, and PO_4^{-3}.

<u>Lecture 26</u>

Having derived expressions for the chemical activities of ideal and real solutes and solvents, it's time to use them. We'll look at three applications. The first is fractional distillation, a purification method based on the fact that the composition of a solution of two volatile liquids and the composition of the vapor above it will be different. The second and third examples, boiling point elevation and osmotic pressure, arise from the difference in chemical potentials of pure substances and substances in solution, and are in a class called colligative properties.

Let's consider fractional distillation first. As I just said, fractional distillation is a purification method that is based on a liquid solution and its vapor having different compositions. Consider an arbitrary solution of two volatile components, A and B. A has a vapor pressure in its pure form of p_A^*, and a mole fraction $X_A(l)$, while B has a vapor pressure in its pure form p_B^* and a mole fraction $X_B(l)$. For the sake of simplicity let's assume that the solutions are ideal. Then the partial pressure of A is given by $p_A = X_A\, p_A^*$, and the partial pressure of B is given by $p_B = X_B\, p_B^*$. Now remember that for a gas the mole fraction $X_i = \dfrac{p_i}{p_T}$. This means that the mole fraction of A in the vapor phase is given by

$$X_A(g) = \frac{p_A}{p_A + p_B} = \frac{X_A(\ell)p_A^*}{X_A(\ell)p_A^* + X_B(\ell)p_B^*}$$

A similar equation can be determined for $X_B(g)$. It should be clear from this that the composition of the vapor, given by $X_A(g)$ and $X_B(g)$, will be different from the composition of the liquid, given by $X_A(l)$ and $X_B(l)$. If we can remove the vapor to a separate container and then condense it, we will have a new liquid solution with a composition equal to that of the vapor. Examination of our equations shows that this new liquid solution will be enriched in the higher vapor pressure

component, and therefore the remainder of the original solution will be enriched in the lower vapor pressure component. It should also be apparent that a repetition of this procedure with the new solution will result in further enrichment, leading eventually to complete purification for ideal solutions.

This process is usually represented by the following diagram. The diagram is one

Hexane - Heptane Mixture
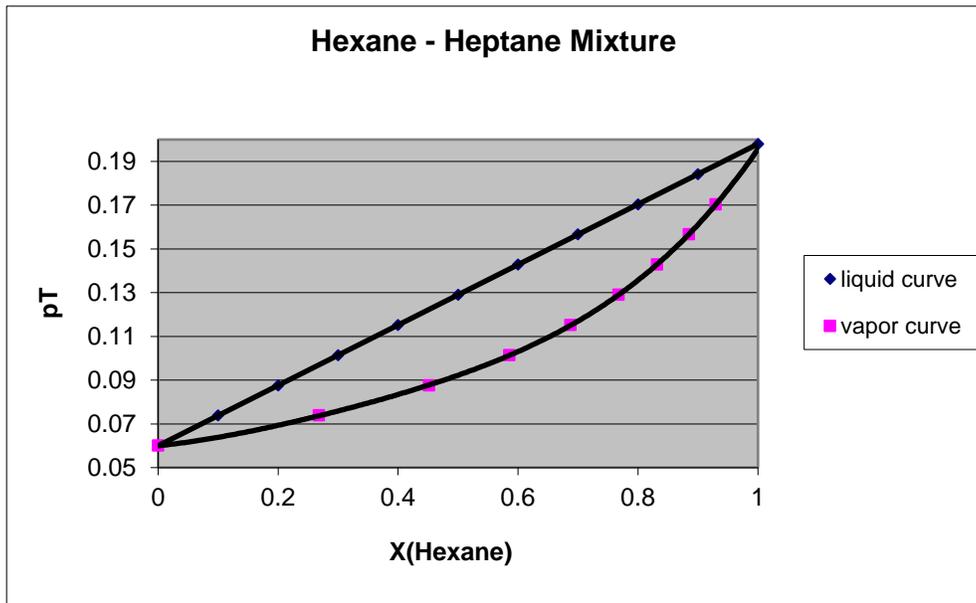
 of total pressure vs. mole fraction. It contains two curves. One curve, the upper one, gives total pressure as a function of the composition of the liquid. The lower curve gives total pressure as a function of composition of the vapor. Remember that the curves will be different because the composition of the liquid and the vapor are different.

We can represent the process we just discussed on this diagram as follows. First we find the mole fraction of one of our components on the x-axis. We now go to the liquid curve to find the vapor pressure of the solution with this composition. Having found the appropriate pressure, we now move horizontally at that pressure, until we intersect the vapor curve. Moving down from the vapor curve to the x-axis tells us the composition of the vapor.

We can illustrate the purification process for a mixture of heptane and hexane. The vapor pressure of pure hexane is $p_A* = 0.198$ atm and the vapor pressure of pure heptane is $p_B* = 0.0600$ atm. Suppose we begin with a mixture which is half hexane and half heptane by moles, i.e., $X_{Hep} = X_{Hex} = 0.5$. The vapor pressure of the hexane will be 0.5 x 0.198 atm = 0.099 atm, and the vapor pressure of the heptane is .5 x .0600 atm = .03 atm. Thus the mole fraction of the hexane in the vapor phase, $X_{Hex} = .099/(.03 + .099) = .77$. $X_{Hep} = 1. - .77 = .23$. Condensing this vapor would yield a liquid solution with this new composition. So you see that even a single distillation step can lead to substantial purification.

Remember that I said that for an ideal solution, successive distillations will eventually lead to complete purification. This will not necessarily be true for a real solution. For real solutions there are sometimes solutions whose vapor and liquid phases have exactly the same composition. Such a composition is called an azeotrope. Clearly if we have a solution with such a composition, distillation would not produce any purification. If we make a diagram for a real solution with an azeotrope, it looks like this.

Note that unlike the ideal case, both the liquid and vapor curves are curved. The azeotrope is the point on the diagram where the two curves meet. A very common azeotrope is that between ethanol and water, at a composition of 96% EtOH by volume. This is the highest degree of purification which can be achieved by simple distillation.

Our second application is to calculate the boiling point of a solution containing a non-volatile solute. We will assume that our solution is ideal. By looking at our equation for the chemical potential of the solvent, $\mu_A(l) = \mu_A^* + RT \ln X_A$, we can immediately see that the chemical potential of the solution will be lower than the chemical potential of the pure solvent. This effectively means that the vapor pressure of the solution will be lower and in order to raise it sufficiently high for the solution to boil we will have to raise the temperature beyond the temperature necessary to boil a pure liquid. So just by using qualitative reasoning we see that solutions will have higher boiling points than pure solvents.

To quantify this we note first that our situation can be drawn as follows.

In the liquid phase we have our solution, which is composed of a volatile solvent plus nonvolatile solute. Since the solute is nonvolatile, only the solvent evaporates, and the vapor phase contains pure solvent. Our equilibrium is therefore between a pure vapor and a liquid solution. WHAT IS THE CONDITION FOR EQUILIBRIUM? Therefore we can write

$$\mu_A^*(g) = \mu_A^*(\ell) + RT \ln X_A$$

Since we have a two component system, $X_A = 1 - X_B$. Substituting this in our equation yields,

$$\mu_A^*(g) = \mu_A^*(\ell) + RT \ln(1 - X_B)$$

which we can rewrite as

$$\ln(1 - X_B) = \frac{\mu_A^*(g) - \mu_A^*(\ell)}{RT} = \frac{\Delta \overline{G}_{vap}}{RT} = \frac{\Delta \overline{H}_{vap}}{RT} - \frac{\Delta \overline{S}_{vap}}{R}.$$

The whole point of this calculation is to determine the change in boiling point of a solution relative

to the pure solvent, so we need to introduce the boiling temperature of the pure solvent. We do this by taking the equation we've just obtained, setting $X_B = 0$ (pure solvent) and setting $T = T^*$, where T^* is the boiling temperature of the pure solvent. This gives us for the pure solvent,

$$\ln(1) = 0 = \frac{\Delta H_{vap}}{RT^*} - \frac{\Delta S_{vap}}{R}$$

We'll introduce the boiling temperature of the pure solvent by taking the difference between the equation for the solution and this one. Before we do this however, we note that the effect of solutes on boiling points is often small and as a result we can make the approximation that ΔH_{vap} and ΔS_{vap} are constant over this temperature range. Subtracting the equations therefore yields,

$$\ln(1 - X_B) = \frac{\Delta H_{vap}}{R}(\frac{1}{T} - \frac{1}{T^*})$$

Our next approximation is to assume that $X_B \ll 1$, in other words, that we have a dilute solution. Remember that earlier we said that if $X \ll 1$ that $\ln(1 + x) \approx x$. Thus $\ln(1 - X_B) \approx - X_B$. Our equation now becomes

$$-X_B = \frac{\Delta H_{vap}}{R}(\frac{1}{T} - \frac{1}{T^*})$$

Again if X_B is small, then T will be close to T^* and we can make the following approximation,

$$\frac{1}{T} - \frac{1}{T^*} = \frac{T^* - T}{T^*T} \approx \frac{-\Delta T}{T^{*2}}$$

Substituting this into our equation finally yields

This change in ΔT refers only to the mole fraction and not to the identity of the solute. In other words, ΔT refers only to X_B and not to the identity of B. Such properties are called **colligative properties**. It is important to note that the independence of the boiling point elevation on the

identity of the solute is only an approximation. Can you identify in which step we introduced the approximation that resulted in this independence?

Other examples of colligative properties are freezing point depression, and osmotic pressure. The calculation of freezing point depression is similar to that of boiling point elevation so let's look at a different property, osmotic pressure. **Osmosis** is the passage of a pure liquid into a solution separated from it by a **semi-permeable membrane**. Such a membrane is one that allows solvent to pass through, but not solutes. An important parameter that indicates the driving force for osmosis is the **osmotic pressure**, π. The osmotic pressure is defined as the pressure that must be applied to a solution in order for osmosis to stop. To see how this can come about, consider a solution and a pure solvent separated by a semipermeable membrane, with external pressure p exerted on both sides. Liquid flows through a semipermeable membrane when molecules of the liquid strike the pores of the membrane. The molecules will strike the pores more frequently for the pure liquid than for the solution, since part of the volume of the solution is made up of the solute molecules. Thus liquid will pass from the pure side to the solution side. As this happens the pressure on the solution side increases. When the pressure increases, the frequency of collisions with the membrane increases. When the pressure increases to the point where the frequency of solvent molecules colliding with both sides of the membrane is equal osmosis will stop.

As was the case with boiling points this can be treated quantitatively by using chemical potentials. The chemical potential on the pure liquid side is $\mu_A^*(p)$, while the chemical potential on the solution side is $\mu_A(p + \pi, X_A)$. Note that on the solution side both the pressure and the composition are different than on the pure liquid side. At equilibrium the two chemical potentials

are equal.

$$\mu_A^*(p) = \mu_A(p + \pi, X_A)$$

For an ideal solution this becomes

$$\mu_A^*(p) = \mu_A^*(p + \pi) + RT \ln X_A$$

In addition we know that the pressure dependence of μ is given by

$$\mu(p_2) = \mu(p_1) + \int_{p_1}^{p_2} \overline{V} dp.$$

Applying this result to our problem yields

$$\mu_A^*(p) = \mu_A^*(p) + RT \ln X_A + \int_p^{p+\pi} \overline{V} dp$$

We can see already what is going on in osmosis. We need the chemical potentials of the pure and liquid sides to be equal for equilibrium. The effect of having a solution is to lower the chemical potential relative to the pure liquid. The effect of increasing the pressure is to increase the chemical potential. Osmosis occurs until the pressure increases enough that the two opposing effects balance, and equilibrium is achieved.

Canceling the common terms in our equation yields the condition for equilibrium,

$$\int_p^{p+\pi} \overline{V} dp = -RT \ln X_A$$

For dilute solutions, $\ln X_A = \ln (1-X_B) \approx -X_B$. In addition if X_B is small we can conclude that $\overline{V}$ is approximately constant as well. Therefore we can write

$$\overline{V} \pi = RT \, X_B$$

Since our solution is dilute, $n_B \ll n_A$ and we can write $X_B \approx n_B/n_A$, which yields

$$\pi \overline{V} = RT \, n_B/n_A.$$

Finally we note that for a dilute solution, $n_A \overline{V} \approx V$. Substitution of this result yields the van't Hoff equation,

$$\pi V = n_B RT,$$

a wonderful equation which relates osmotic pressure, volume, temperature and mole number of the solute in a way analogous to the ideal gas law. ARE THERE ANY LIMITS TO THE APPLICABILITY OF THIS EQUATION?

Lecture 27

I'd like to go back to one-component systems for a while, and look again at our phase diagram. Remember that we have three regions, solid, liquid and vapor. Now suppose that we are within the vapor region and at equilibrium. We can change both the pressure and temperature independently and retain the equilibrium. If in contrast we are along one of the phase boundaries, we can change only one variable independently and maintain equilibrium. For example, if water and water vapor are at equilibrium at 373.15 K and 101 kPa, then if we change the temperature to 300 K, there will be only one pressure at which the two phases will be remain in equilibrium. Finally, if we are at the triple point, where all three phases are in equilibrium, then changing only one variable will remove the system from equilibrium. In other words, when there is only one phase we can vary both intensive variables independently. When two phases are in equilibrium, we can vary one intensive variable independently, and when three are in equilibrium we can't vary any. We call the number of variables we can vary independently the number of **degrees of freedom** of the system.

It is useful to be able to predict how many degrees of freedom a system will have. In part this is because in the practical task of making new materials, it can be crucial to know how to control phase transitions, and to know just how precisely the experimental conditions need to be controlled to retain the desired phase. This may be trivial for one component systems, but for systems involving several components, which include most chemical reaction mixtures and many of our advanced materials, the number of degrees of freedom may not be transparent.

Fortunately there is a simple rule that relates numbers of components, number of phases, and degrees of freedom, called the **Gibbs phase rule**. We will derive this rule in a moment, but first we need to clarify the idea of **number of components**. We define the **number of components**

in a system as the minimum number of independent species necessary to define the composition of all the phases present in the system. Note that we specifically mention independent species.

Let's do a simple example. Suppose that we have water at its triple point. Here we have ice, liquid water, and water vapor, but we have only one component, since water is the only species necessary to define all three phases. Similarly, if we have a mixture of Ar and Cl_2, we have two components, no matter how many phases are present.

Now let's turn to a more complex case, one in which there are chemical species in equilibrium. Here we need to look carefully at the independence of the species. Suppose now that we have $NH_4Cl(s)$ in an evacuated container, and it decomposes according to the equation

$$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g).$$

This system has only one component. This is because all three of the chemical species are interdependent. The gases are equimolar because they both came from the solid. Even if we had started with the two gases in equimolar quantities, we still would have only one component, since the number of components is the **minimum** number of independent species necessary to define the composition of all phases, and the presence of the solid is enough to define the composition of the gas and the solid.

Now here comes a subtlety. Let's consider the same system, but now let's start with 4 moles of $NH_3(g)$ and 1 mole of $HCl(g)$ and let them come to equilibrium with the solid. We now have two components, because the presence of the solid can no longer account for all species. To see this more clearly consider the limit in which all of the HCl has reacted. We are left with two components, the $NH_4Cl(s)$ and the $NH_3(g)$. Thus the solid cannot account for all species present.

Notice that the issue of independence only comes into play when there is an equilibrium between two or more of the chemical constituents of a system. The effect of these equilibria on the number of components is represented by the equation

$$c = s - r$$

where c is the number of independent components, s is the number of different chemical components, and r is the number of restrictive conditions.

Let's apply this equation to our two cases. In the case where we begin with $NH_4Cl(s)$, we have three chemical constituents, $NH_4Cl(s)$, $NH_3(g)$, and $HCl(g)$, so s = 3. We also have two restrictive conditions. One is the equilibrium,

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g).$$

The second is the condition that the two gases be present in equimolar quantities, which arises because both are formed from the solid,

$$p_{NH_3(g)} = p_{HCl(g)}$$

Therefore c = s - r = 3 - 2 = 1, and we have only one component.

Now if we consider the second case we have three chemical constituents as well, but now we have only one restrictive condition, the equilibrium, so c = s - r = 3 - 1 = 2 and we have two components.

We have been considering this issue so we could figure out how many degrees of freedom were present in a given chemical system. In other words, if we have a chemical system with multiple phases in equilibrium, is it possible to change any of our intensive variables and still maintain our equilibrium? We begin by considering a one component, two phase system. The Gibbs-Duhem equation tells us that for each phase

$$-S\,dT + V\,dp + n\,d\mu = 0,$$

so that when we fix T and P, μ is fixed as well. Therefore for any arbitrary place on the phase diagram, the state is defined by four variables, T_α, T_β, p_α, and p_β, where α and β are the two phases. Now let's require that the two phases be in equilibrium. By so doing we impose three restraints on the system. They are

1) $T_\alpha = T_\beta$ (Thermal Equilibrium)

2) $p_\alpha = p_\beta$ (Mechanical equilibrium)

3) $\mu_\alpha(T_\alpha, p_\alpha) = \mu_\beta(T_\beta, p_\beta)$ (phase equilibrium).

These three constraints are equations that relate the four variables so that only one variable is independent. This is similar to problems you work in algebra, where a system of three equations with four variables has only one independent variable. We conclude from this that **a one component system with two phases in equilibrium has only one degree of freedom**. In other words, if we have water and ice in equilibrium at 101 kPa and 273.15K, and raise the temperature to 278.15 K, then p_{eq} at 278.15 is fixed. If the system is under any other pressure at this temperature then there will be no equilibrium between the ice and the water. We can abbreviate this conclusion by saying that $f = 1$, $p = 2$, and $c = 1$, where f is the number of degrees of freedom, p is the number of phases and c is the number of components.

Now suppose we have a one component system with three phases in equilibrium. Now we have six variables that define the state, the temperature and pressure of each phase, T_s, p_s, T_l, p_l, T_g, p_g. In addition we have six equations that relate these variables.

$$T_s = T_l = T_g$$

$$P_s = P_l = P_g$$

$$\mu_s(T_s,p_s) = \mu_l(T_l,p_l) = \mu_g(T_g, p_g).$$

Since we have six variables with six equations, there are zero degrees of freedom. In other words, once we simultaneously solve the six equations, all values of T and p are fixed and there will be only one pair of T and p for which the three phases will be in equilibrium. In other words in this case, $f = 0$, $p = 3$ and $c = 1$.

We can **generalize these arguments to any number of phases and any number of components, but with the limitation that we consider only neutral mixtures**. Remember that our free energy is a function of T, P and the n_i. This is equivalent to the free energy being a function of T, p and the X_i. Since the X_i are not the same for each phase in a multiphase system, the free energy must be a function of T, p and the set of X_i's for each phase. The T, p, and X_i's define the number of variables that describe the system. How many variables is this and how many are independent?

Let the number of components be denoted by c and be numbered from 1 to c, and the number of phases by p, and be designated by Greek letters, α, β, γ, etc. Thus each phase is described by c mole fractions, and therefore the p phases are described by cp mole fractions. Adding in T and p yields $cp + 2$ variables describing the system.

To determine how many are independent, we need to define the equations that link these variables. First, in each phase, the total of the mole fractions must be one:

$$x_1^{\alpha} + x_2^{\alpha} + ... + x_c^{\alpha} = 1.$$

Since this is true for each of the p phases, this yields a set of p equations. Now we need to add the requirements for equilibrium. We have already included the requirement for thermal and mechanical equilibrium by choosing only one temperature and pressure to describe the whole

system. What is left is the material equilibrium. The way this is expressed for a multicomponent multiphase system is that the chemical potential for each phase must be the same for each component, i.e. for component α we have

$$\mu_1{}^{\alpha} = \mu_1{}^{\beta} = \mu_1{}^{\gamma} = ...$$

Since there are p equalities this equals p-1 equations. Since we have c components this means that we have p-1 equations for each of the c components. Therefore the material equilibrium requirement adds a total of c(p-1) equations.

We started out with cp + 2 variables, and now we can figure out our degrees of freedom.

$$f = cp + 2 - p - c(p-1)$$

$$= cp + 2 - p - cp + c = c + 2 - p \ .$$

This equation is known as the **Gibbs Phase Rule.**

So for our one component two phase example, we have c = 1, p = 2 and f = 1+2-2=1. In addition to telling us the number of variables we can vary and still maintain equilibrium, the Gibbs phase rule tells us the maximum number of phases that can simultaneously be in equilibrium. For example, in our one component system, if we let p = 4 we get f = 1 + 2 - 4 = -1, which is impossible, so as a result we find we can have a maximum of three phases in a one component system.