## Phase Diagrams: Conditions for Equilibrium (CfE)

- Write down the conditions for equilibrium for: a pure single phase system, a pure multi-phase system, and a multi-phase mixture
- Explain how energetic and entropic effects balance at equilibrium
- Use the Clapeyron equation and/or the Clausius-Clapeyron equation to relate T and P for pure species phase equilibrium
- Use the Antoine equation to relate T and P for pure species phase equilibrium
- Explain the relationship between the Clausius-Clapeyron equation and the Antoine equation
- Write exact differentials for extensive properties in terms of m+2 independent variables for mixtures of m species
- Define and explain the difference between the terms: pure species property, total solution property, and partial molar property
- Calculate total solution properties from partial molar properties
- Calculate partial molar properties
  - using graphical methods
  - using equations of state
  - using the Gibbs-Duhem equation
- Explain the origin of enthalpy, entropy, and volume changes due to mixing
- Calculate the enthalpy of solution from the enthalpy of mixing and vice versa
- Explain why the chemical potential is the relevant property for determining solution equilibrium

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CfE: Gibbs Free Energy (Balancing Energy and Entropy)

Gibbs Free Energy (Balancing Energy and Entropy)

We spoke at the beginning of the course about the fact that equilibrium requires:
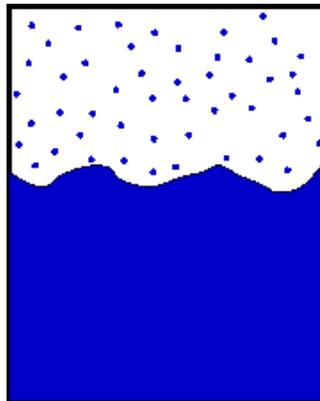
$T_v = T_L \rightarrow$ thermal equilibrium
$P_v = P_L \rightarrow$ mechanical equilibrium
What else?!

Our discussion of entropy suggests that our other condition(s) for equilibrium should be related to minimizing entropy; however, that is difficult to quantify because we need to examine the entire **universe** in order to do so.

Instead, let's start with the first law for the closed system above (where a pure-species vapor and liquid are in equilibrium):

$$dU = \delta Q + \delta W$$

$$dU = \delta Q - PdV$$

Since we must have mechanical equilibrium, we know that $P = P_v = P_L$ so that $dP = 0$. Because of this we can subtract VdP from this equation without changing anything, so

$$dU = \delta Q - PdV - VdP = \delta Q - d(PV)$$

Rearranging and using the definition of enthalpy:

$$dU + d(PV) = dH = \delta Q$$

Now invoking the second law, we know that a real process satisfies:

$$dS \geq \frac{\delta Q}{T}$$

Rearranging and using our result from above:

$$TdS \geq \delta Q = dH \text{ so that } TdS \geq dH$$

Rearranging:

$$dH - TdS \leq 0$$

Recalling the definition of the Gibbs free energy (G), we write

$$G \equiv H - TS$$

so that

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

Once again, equilibrium requires that $T = T_v = T_L$ so that $dT = 0$, and

$$dG = dH - TdS$$

Combining with earlier result, we find that a useful condition for equilibrium is that

$$dG \leq 0$$

NOTE:

*While one might be tempted to presume that equilibrium between vapor and liquid would not be possible, due to the fact that the entropy of a vapor is higher than that of a liquid (so why wouldn't it all become vapor?!), this is not true. The fact that it requires **energy from outside the system** to change the liquid into a vapor means that the increase in entropy of our system would be offset by a decrease in entropy of the surroundings.*

USEFUL:

*The Gibbs free energy simplifies equilibrium considerations because it allows us to **only consider the system** rather than the universe. It does this by explicitly accounting for entropy changes in the system and energy interactions with the surroundings.*

OUTCOME:

Explain how energetic and entropic effects balance at equilibrium.

Equilibrium: Two (pure) Phases

We have shown that the criteria for equilibrium is:

$$dG \leq 0$$

For a mixture of two phases we can write:

$$G = n_l g_l + n_v g_v$$

so that

$$dG = n_l dg_l + g_l dn_l + n_v dg_v + g_v dn_v$$

Since we are assuming thermal equilibrium (constant T) and mechanical equilibrium (constant P), the state postulate says that g is fixed so that $dg_l = dg_v = 0$, so

$$dG = g_l dn_l + g_v dn_v$$

At equilibrium the rate of change of material *from* one phase must be balanced by the rate of change of material *to* that phase, so that $dn_v = -dn_l$ and

$$dG = (g_l - g_v) dn_v \leq 0$$

Once we reach equilibrium the inequality takes on the value of zero, so

$$g_l = g_v$$

OUTCOME:

Write down the conditions for equilibrium for: a pure single phase system, a pure multi-phase system, and a multi-phase mixture

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Clapeyron Equation

Taking the criteria for phase equilibrium as out starting point:

$$g_l = g_v$$

We can write:

$$dg_l = dg_v$$

Using one of our fundamental property relations, for phase "k"

$$dg_k = v_k dP - s_k dT$$

so

$$v_l dP - s_v dT = v_l dP - s_l dT$$

$$\frac{dP}{dT} = \frac{s_l - s_v}{v_l - v_v}$$

Recalling that we could also write

$$g_k = h_k - T s_k$$

we have

$$h_l - T s_l = h_v - T s_v$$

$$s_l - s_v = \frac{h_l - h_v}{T}$$

combining we get

DEFINITION:

*The **Clapeyron equation** relates the phase equilibrium pressure (often called P_{sat}) to the temperature for any combination of phases:*

$$\frac{dP}{dT} = \frac{h_l - h_v}{T(v_l - v_v)}$$

OUTCOME:

Use the Clapeyron equation and/or the Clausius-Clapeyron equation to relate T and P for pure species phase equilibrium

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CfE: Clausius-Clapeyron Equation

Clausius-Clapeyron Equation

Starting from the Clapeyron Equation:

$$\frac{dP}{dT} = \frac{h_l - h_v}{T(v_l - v_v)}$$

We can note that, in general:

$$(v_l - v_v) \approx -v_v$$

Taking v_v from the ideal gas law ($v_v = \frac{RT}{P}$), and combining

$$\frac{dP}{dT} = \frac{h_l - h_v}{T(-v_v)} = \frac{-P(h_l - h_v)}{RT^2} = \frac{P(h_v - h_l)}{RT^2} = \frac{P\Delta h_v}{RT^2}$$

rearranging and integrating

$$\int \frac{dP}{P} = \int \frac{\Delta h_v}{R} \frac{dT}{T^2}$$

$$\ln P = \frac{-\Delta h_v}{R} \frac{1}{T} + Const$$

NOTE:

This suggests that a plot of saturation pressure, P_{sat} versus $\frac{1}{T}$ should yield a straight line. This is close to correct for most materials.

Perhaps a more useful way to use this equation is to know the saturation pressure at a particular temperature (say, the normal boiling point ... i.e., $P_{sat} = 1bar$):

$$\ln \frac{P_2}{P_1} = \frac{-\Delta h_v}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

DEFINITION:

*The **Clausius-Clapeyron equation** is a special case of the Clapeyron equation that assumes ideal gas behavior for the vapor and exploits the fact that the specific volume of a vapor is substantially larger than that of a liquid.*

OUTCOME:

Use the Clapeyron equation and/or the Clausius-Clapeyron equation to relate T and P for pure species phase equilibrium

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CfE: Antoine Equation

Antoine Equation

Since the Clausius-Clapeyron equation assumes ideal gas behavior for the vapor it is not strictly accurate for all fluids.

An empirical relation is often used that exploits the same general form of equation ...

DEFINITION:

*The **Antoine Equation** is an empirical relation for the saturation pressure as a function of temperature that is loosely based on the Clausius-Clapeyron relation.*

$$\ln P = A - \frac{B}{C+T}$$

NOTE:

The units on this equation make no sense, so we need to be careful with the constants A, B, and C.

OUTCOME:

Use the Antoine equation to relate T and P for pure species phase equilibrium

OUTCOME:

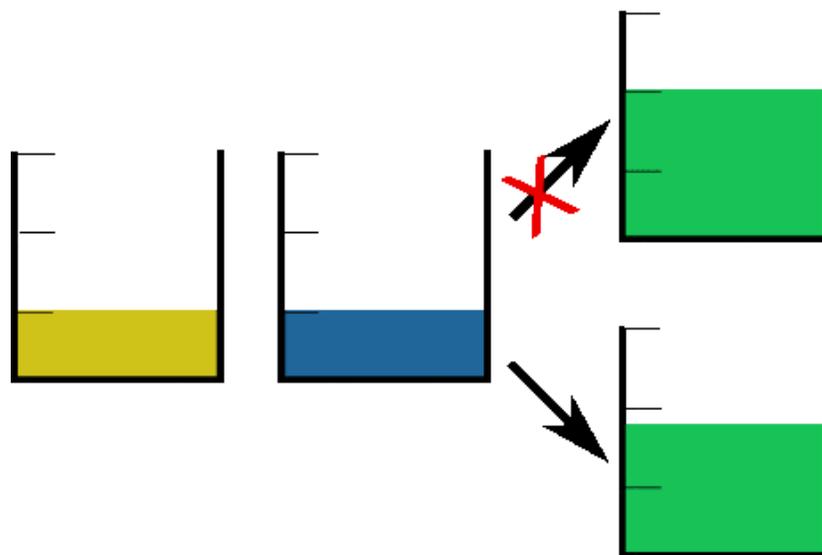*Explain the relationship between the Clausius-Clapeyron equation and the Antoine equation*

TEST:

Use the Antoine equation to prove that the normal boiling point of water (which is pretty non-ideal) is 100C.

CfE: Mixture Properties

Mixing: One Phase

We know from experience that:

In other words, since the interactions between molecules of A-A and B-B differs from the interaction between A-B, we get:

$$V = V_{mixture} \neq V_A + V_B$$

but we know that

$$n_{mixture} = n_A + n_B$$

Combining these, we can show that the *intensive* property v gives

$$v = v_{mixture} \neq x_A v_A + x_B v_B$$

NOTE:

*This is actually quite general. That is, typically the mixture properties (either extensive or intensive) are **not** simply the sum (or weighted average) of the individual pure component properties.*

Recall that, by the state postulate, we can write (note that we will now drop the subscript "mixture"):

$$v = F(P, T)$$

We know that this works for a single phase pure component (we have a common example, $Pv = RT$). We can also write

$$V = F(P, T, n)$$

which we also have experience with ($PV = nRT$). It turns out that for multiple components, the **Duhem relation** tells us that we can write

$$V = F(P, T, n_1, n_2, n_3, ..., n_m)$$

Therefore, following the same procedure that we used for fundamental property relations, we can write

$$dV = \left(\frac{\partial V}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial V}{\partial T}\right)_{P,n_i} dT + \sum_j \left(\frac{\partial V}{\partial n_j}\right)_{P,T,n_{i \neq j}} dn_j$$

OUTCOME:

Write exact differentials for extensive properties in terms of m+2 independent variables for mixtures of m species

since at equilibrium we have $dP = dT = 0$, we can reduce this to

$$dV = \sum_j \left(\frac{\partial V}{\partial n_j}\right)_{P,T,n_{i \neq j}} dn_j$$

DEFINITION:

*We define the **partial molar properties** as being*

$$\bar{V}_j = \left(\frac{\partial V}{\partial n_j}\right)_{P,T,n_{i \neq j}}$$

which we can think of as the contribution of species j to the mixture property.

We can rewrite our expression for dV then as

$$dV = \sum_j \bar{V}_j dn_j$$

Integrating this (and noting that the constant of integration is zero -- we will simply accept this for now):

$$V = \sum_j \bar{V}_j n_j$$

dividing by n_{tot} we can also write:

$$v = \sum_j \bar{V}_j x_j$$

Just to be sure that we have our nomenclature right ...

CfE: Relations for Partial Molar Properties

Partial Molar Property Relations

Recall that:

$$H \equiv U + PV$$

If we take the derivative of both sides with respect to the number of moles of species j:

$$\left(\frac{\partial H}{\partial n_j}\right)_{P,T,n_{i \neq j}} \equiv \left(\frac{\partial U}{\partial n_j}\right)_{P,T,n_{i \neq j}} + \left(\frac{\partial (PV)}{\partial n_j}\right)_{P,T,n_{i \neq j}}$$

since P is a constant

$$\left(\frac{\partial H}{\partial n_j}\right)_{P,T,n_{i \neq j}} \equiv \left(\frac{\partial U}{\partial n_j}\right)_{P,T,n_{i \neq j}} + P\left(\frac{\partial V}{\partial n_j}\right)_{P,T,n_{i \neq j}}$$

using the definition of partial molar properties, we note

$$\bar{H}_i \equiv \bar{U}_i + P\bar{V}_i$$

NOTE:

This procedure works for any of the derived property definitions (i.e., G or A also).

Using the Duhem relation, we know that we can write a total differential for G in terms of $T, P,$ and n_j as follows:

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \sum_j \left(\frac{\partial G}{\partial n_j}\right)_{P,T,n_{i \neq j}} dn_j$$

From analysis of pure substance systems, we already had written

$$dG = -SdT + VdP$$

so we can combine these to get (recognize that we have invoked the definition of the partial molar $\bar{G}_i$):

$$dG = -SdT + VdP + \sum_j \bar{G}_j dn_j$$

Recalling from our Maxwell relations, we showed that

$$-S = \left(\frac{\partial G}{\partial T}\right)_P$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T$$

Taking the derivative with respect to the number of moles of species j for these relations:

$$-\left(\frac{\partial S}{\partial n_j}\right) = \frac{\partial}{\partial n_j}\left(\frac{\partial G}{\partial T}\right)_P$$

$$\left(\frac{\partial V}{\partial n_j}\right) = \frac{\partial}{\partial n_j}\left(\frac{\partial G}{\partial P}\right)_T$$

Invoking the definition of the partial molar Gibbs free energy, and taking either the derivative with respect to T or P of that expression we get:

$$\left(\frac{\partial \bar{G}_i}{\partial T}\right)_P = \left(\frac{\partial}{\partial T}\left[\frac{\partial G}{\partial n_j}\right]\right)_P$$

$$\left(\frac{\partial \bar{G}_i}{\partial P}\right)_T = \left(\frac{\partial}{\partial P}\left[\frac{\partial G}{\partial n_j}\right]\right)_T$$

Noting that the right hand sides of the top equations in the last two groups are the same (as are the bottom two), we can write:

$$-\bar{S}_i = \left(\frac{\partial \bar{G}_i}{\partial T}\right)_P$$

$$\bar{V}_i = \left(\frac{\partial \bar{G}_i}{\partial P}\right)_T$$

NOTE:

The Maxwell relations (and all other fundamental property relations) can be re-written in terms of partial molar properties. This second expression in particular is of utility in calculations as it relates $\bar{G}_i$ to measurable properties.

Calculating Partial Molar Properties: Gibbs-Duhem Relation

Noting that the partial molar volumes, $\bar{V}_i$, may be summed to yield the total solution (extensive) volume:

$$V = \sum_i \bar{n}_i V_i$$

Taking the derivative of both sides:

$$dV = d\left[\sum_i \bar{n}_i V_i\right] = \sum_i (\bar{V}_i dn_i + n_i d\bar{V}_i)$$

recall that, from the definition of partial molar properties:

$$dV = \sum_i \bar{V}_i dn_i$$

so this can be eliminated from our equation to give the Gibbs-Duhem relation:

$$\sum_i n_i d\bar{V}_i = 0$$

DEFINITION:

*The **Gibbs-Duhem** equation relates the partial molar property values of one of the components in a mixture to that of the other species. This makes sense since the reason that we do not use the*

pure component specific volumes ($\bar{V}_i \neq v_i$) is specifically because the interaction a-a is different from a-b (but it should not be different from b-a!).

Using the Gibbs-Duhem relation for a binary mixture goes as follows:

$$d\bar{V}_a n_a + d\bar{V}_b n_b = 0$$

if we divide both sides by dx_a and $n_{tot} = (n_a + n_b)$,

$$x_a \frac{d\bar{V}_a}{dx_a} + x_b \frac{d\bar{V}_b}{x_a} = 0$$

if we note that $x_b = 1 - x_a$, we can rearrange and integrate to get

$$\bar{V}_b = \int d\bar{V}_b = -\int \left(\frac{x_a}{1-x_a}\right)\left(\frac{d\bar{V}_a}{dx_a}\right)dx_a$$

NOTE:

If we know an expression for $\bar{V}_a$ (or at least how the slope changes with x_a), we can evaluate this integral to get $\bar{V}_b$.

OUTCOME:

Calculate partial molar properties using the Gibbs-Duhem equation

TEST YOURSELF:

If the partial molar volume of component "a" in an a-b mixture is known to be given by:

$$\bar{V}_a = 50x_a + 150x_b + 30x_a x_b$$

determine $\bar{V}_b$ using the Gibbs-Duhem equation.

CfE: Calculating Partial Molar Properties: Equations of State

Calculating Partial Molar Properties: EOS

Another method of calculating partial molar properties is to use equations of state. If we have a mixture that is well described by a volume-explicit virial equation of state, so that:

$$z = \frac{Pv}{RT} = 1 + B_{mix}P$$

NOTE:

Here v is the "total solution property", so it represents the specific volume of the actual mixture of the fluids.

If we assume that we have a binary mixture of materials "1" and "2", we have discussed in the past that B_{mix} is related to binary interactions between molecules of types 1 and 2:

$$v = \frac{RT}{P} + y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}$$

We know that, in order to calculate a partial molar property, we need to start with an *extensive* property, so we multiply by $n_{tot} = n_1 + n_2$, so

$$V = n_{tot}v = (n_1 + n_2)\frac{RT}{P} + \frac{n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}}{(n_1 + n_2)}$$

Taking the derivative with respect to n_1 will give us $\bar{V}_1$ so

$$\bar{V}_1 = \left(\frac{\partial V}{\partial n_1}\right)_{P,T,n_2} = \frac{RT}{P} + \frac{2n_1 B_{11} + 2n_2 B_{12}}{(n_1 + n_2)^2} - \frac{n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}}{(n_1 + n_2)^2}$$

which we can simplify to

$$\bar{V}_1 = \frac{RT}{P} + 2y_1 B_{11} + 2y_2 B_{12} - B_{mix}$$

NOTE:

*We can then calculate $\bar{V}_2$ either following the same procedure of the **Gibbs-Duhem** equation.*

OUTCOME:

Calculate partial molar properties using equations of state (and mixing relations)

CfE: Calculating Partial Molar Properties: Graphical Methods

Calculating Partial Molar Properties: Graphical Methods

Start with the summation equation for partial molar properties:

$$v = \sum_j x_j \bar{V}_j$$

For a binary mixture this gives:

$$v = x_1 \bar{V}_1 + x_2 \bar{V}_2 = x_1 \bar{V}_1 + (1-x_1)\bar{V}_2$$

Taking the derivative with respect to x_1 of both sides:

$$\frac{dv}{dx_1} = \bar{V}_1 - \bar{V}_2$$

Multiplying both sides by x_1 and then adding and subtracting $x_2 \bar{V}_2$ gives:
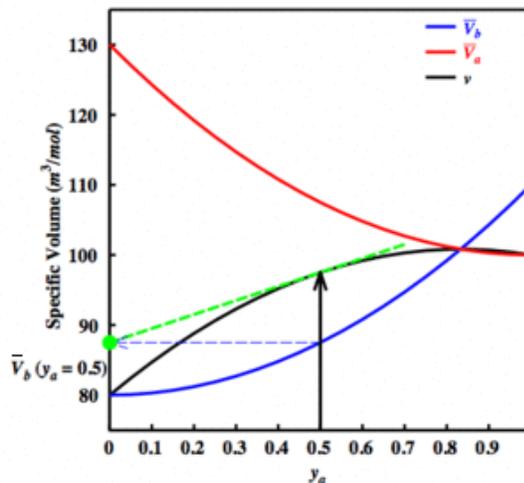
$$x_1 \frac{dv}{dx_1} = x_1 \bar{V}_1 - x_1 \bar{V}_2 + (x_2 \bar{V}_2 - x_2 \bar{V}_2) = (x_1 \bar{V}_1 + x_2 \bar{V}_2) - (x_1 \bar{V}_2 - x_2 \bar{V}_2) = v - \bar{V}_2$$

When we rearrange this, we note that v versus x_1 gives a straight line:

$$v = \bar{V}_2 + x_1 \frac{dv}{dx_1}$$

NOTE:

The slope of this line will be the local slope (often called the tangent line) of the v curve, and the intercept of the line will be $\bar{V}_2$.

PROCEDURE:

At the desired concentration (y_a value) go up to the v curve (black). Draw a tangent line. Follow the tangent line to the y-intercept to

get $\bar{V}_b$. *Note that you go to an "a" concentration to get a "b" partial molar quantity. Also, note that the $\bar{V}_a$ and $\bar{V}_b$ curves are shown for display purposes only, they are not typically known.*

NOTE:

Using this procedure at $y_a = 1$ will yield the "infinite dilution" value for $\bar{V}_b$ ($\bar{V}_b^\infty$, that is the value of $\bar{V}_b$ where $y_b = 0$).

OUTCOME:

Calculate partial molar properties using graphical methods.

CfE: Property Changes upon Mixing

Property Changes upon Mixing

As discussed previously, mixtures do not simply exhibit the weighted average properties of their component parts. We have spent the last several sets of notes showing exactly how to calculate the contribution of each of the components to the mixture. That is, we have recognized that:

$$V \neq \sum n_i v_i$$

Instead:

$$V = \sum n_i \bar{V}_i$$

so that, in general:

$$v_i \neq \bar{V}_i$$

Besides the methods previously discussed, a typical way to experimentally handle this fact is to define *property changes of mixing*, such as the ΔV_{mix}, as:

$$\Delta V_{mix} = V - \sum n_i v_i$$

That is, ΔV_{mix} specifically accounts for the difference between the naive assumption (that mixtures yield the weighted average) and reality. Another way to write this is

$$\Delta V_{mix} = \sum n_i (\bar{V}_i - v_i)$$

or graphically, the ΔV_{mix} (or Δv_{mix} if we speak in terms of intensive rather than extensive volume):
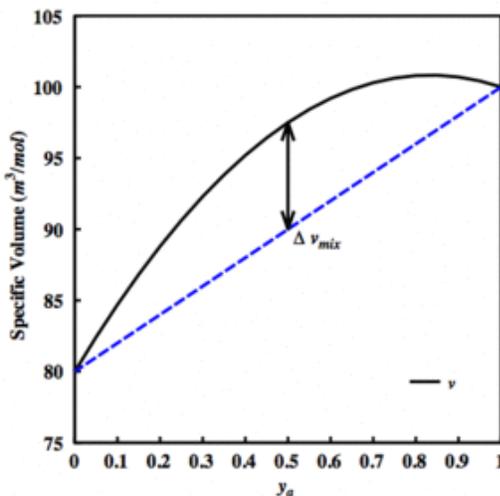
NOTE:

The value of ΔV_{mix} (or Δv_{mix}) goes to zero at the two endpoints (pure component solutions), and varies in magnitude as concentration varies.

When ΔV_{mix} is measured experimentally, it is typically tabulated for the mixture in question, so that it may be used to determine the total solution property by rearranging its definition:

$$V = \sum n_i v_i + \Delta V_{mix}$$

NOTE:

*One should note that the property changes are measured per unit mass/mole or **mixture/solution**. Also, a particularly useful property change that one can find tabulated is ΔH_{mix}.*

OUTCOME:

Explain the origin of enthalpy, entropy, and volume changes due to mixing.

CfE: ΔH_{mix} vs. ΔH_{sol}

ΔH_{mix} **vs.** ΔH_{sol}

Sometimes the tabulated values of property changes upon mixing and reported in terms of a change *per unit mass/mole solvent* rather than per solution.

DEFINITION:

The ΔH_{sol} or "delta H of solution" is measured as the enthalpy change when 1 mol of solute is mixed with a specified amount of solvent (rather than solution).

This definition leads to a simple relationship between ΔH_{mix} and ΔH_{sol}. That is:

$$\Delta H_{sol} = \frac{\Delta H_{mix}}{x_{solute}}$$

or:

$$\Delta H_{mix} = x_{solute} \Delta H_{sol}$$

where x_{solute} is the mole fraction of the solute (dissolved or minor component).

OUTCOME:

Calculate the enthalpy of solution from the enthalpy of mixing and vice versa.

NOTE:

Typically, one can find tabulated values of ΔH_{mix} and ΔV_{mix}, but not other properties. This is due to the fact that often the ΔS_{mix} is assumed to be given by the ideal gas result. That is $\Delta S_{mix} = -\sum_i R n_i \ln(y_i)$.

By combining the tabulated values with this result for ΔS_{mix}, one can calculate most other mixing values.

CfE: Phase Equilibrium for Mixtures

Phase Equilibrium for Mixtures

We have shown that, for pure components, equilibrium is given when:

$dG = 0$

or

$g_L = g_v$

For a mixture of multiple components (and at least two phases) we can start at the same place:

$dG = 0 = dG_L + dG_v = \left[-SdT + VdP + \sum \bar{G}_i dn_i \right]_L + \left[-SdT + VdP + \sum \bar{G}_i dn_i \right]_v$

Since we are again assuming mechanical and thermal equilibrium, we have

$T_L = T_v$ and $P_L = P_v$ so that

$dT_L = dT_v = 0$ and $dP_L = dP_v = 0$

this simplifies our dG expression to

$dG = 0 = \left[\sum \bar{G}_i dn_i \right]_L + \left[\sum \bar{G}_i dn_i \right]_v$

At the microscopic scale, the rate of change of material *from* one phase must be balanced by the rate of change of material *to* that phase *for each component*, so that $dn_{i_v} = -dn_{i_L}$ and

$dG = 0 = \sum \left[\bar{G}_{i_L} - \bar{G}_{i_v} \right] dn_{i_L}$

This is true when the partial molar Gibbs free energy of each component is equal across the phases. That is

$\bar{G}_{i_L} = \bar{G}_{i_v}$

DEFINITION:

*Differences in the partial molar Gibbs free energy create a potential for the material to change phase. Thus, thie quantity is often called the **chemical potential** or species, i, and denoted as μ_i.*

$\mu_i = \bar{G}_i$

so we can write our phase equilibrium condition (for mixtures) as

$\mu_{i_L} = \mu_{i_v}$

OUTCOME:

Explain why the chemical potential is the relevant property for determining solution equilibrium

CfE: Quick Quizzes

Here are the Equilibrium Quick Quizzes!