# Chemical Engineering Thermodynamics
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## Lecture - 22
## Ideal Solutions

Hello and welcome back we are talking about Solution Thermodynamics in the last two lectures, we will continue our discussion on solution thermodynamics solve two examples using the concepts we have learned so far in solution thermodynamics and then we move on to mixtures of ideal gases and how we calculate the properties in a mixture of ideal gases. But before we do that as usual let us quickly recap what we discussed so far in solution thermodynamics.

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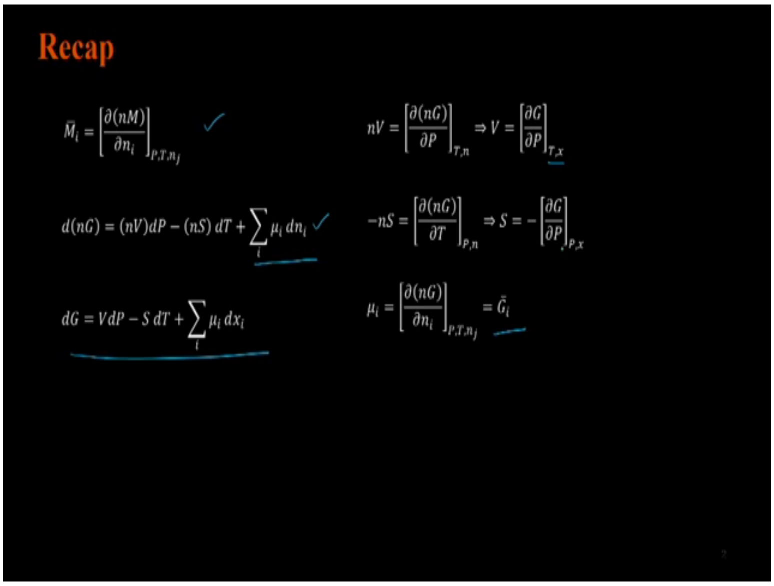

Recap

$$\bar{M}_i = \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_j} \checkmark \qquad nV = \left[\frac{\partial(nG)}{\partial P}\right]_{T,n} \Rightarrow V = \left[\frac{\partial G}{\partial P}\right]_{\underline{T,x}}$$

$$d(nG) = (nV)dP - (nS)\,dT + \underline{\sum_i \mu_i\,dn_i} \checkmark \qquad -nS = \left[\frac{\partial(nG)}{\partial T}\right]_{P,n} \Rightarrow S = -\left[\frac{\partial G}{\partial P}\right]_{P,x}$$

$$\underline{dG = V\,dP - S\,dT + \sum_i \mu_i\,dx_i} \qquad \mu_i = \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j} = \underline{\bar{G}_i}$$

First thing we have defined is what is known as a partial molar property which is the property of a substance at the same temperature and pressure or the derivative of the total property with respect to the number of moles of one of the species at the same temperature pressure and all the other moles held constant, this is a molar property so it is an intensive variable. And the fundamental property relation for an open system which allows for exchange of species or matter with the surroundings is given by the second equation in here.

So, in addition to the closed system equation and V dP minus and S dT for d n G we get on the last term which is sigma mu i dn i and if you recall we said mu i is the chemical potential which is same as the partial molar Gibbs free energy. This fundamental property relation also can be written for one mole of the system in which case we get the equation shown here at the end right dG is VdP minus S dT sigma mu i dx I, all of these are intensive variables in this equation.

And also we can using the fundamental property relation we can write the derivatives of various properties with respect to pressure and temperature in this for example, volume will be derivative of the Gibbs free energy with respect to pressure at constant temperature and mole fraction etcetera.

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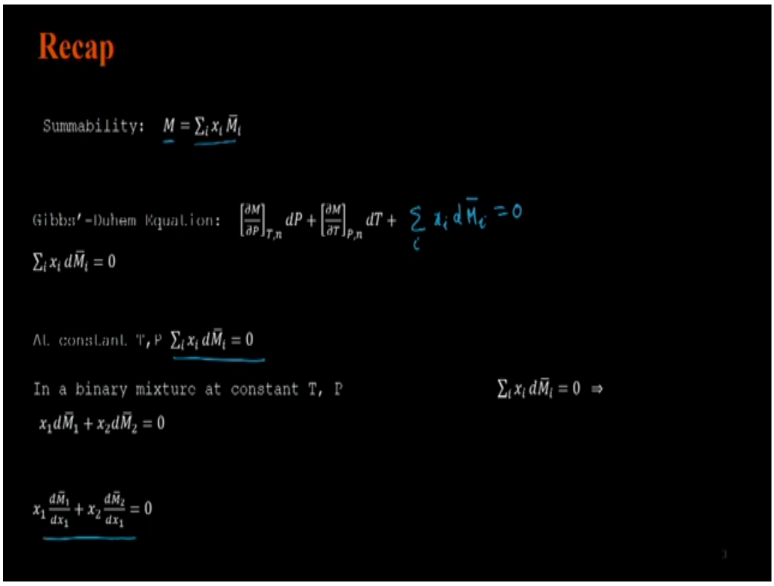

## Recap

Summability: $M = \sum_i x_i \bar{M}_i$

Gibbs'-Duhem Equation: $\left[\frac{\partial M}{\partial P}\right]_{T,n} dP + \left[\frac{\partial M}{\partial T}\right]_{P,n} dT + \sum_i x_i d\bar{M}_i = 0$

$\sum_i x_i d\bar{M}_i = 0$

At constant T, P $\sum_i x_i d\bar{M}_i = 0$

In a binary mixture at constant T, P

$\sum_i x_i d\bar{M}_i = 0 \Rightarrow$

$x_1 d\bar{M}_1 + x_2 d\bar{M}_2 = 0$

$x_1 \frac{d\bar{M}_1}{dx_1} + x_2 \frac{d\bar{M}_2}{dx_1} = 0$

.

Then we had what is called as the summability relation which gives the total property as weighted with mole fraction the partial molar properties weighed with the mole fraction and we add all of these quantities; we get the total property we call this as the summability relation this is true for any molar property M.

Then we had the Gibbs Duhem equation we could write this here to make it clear sigma x i; dM i bar will be equal to 0 and at constant temperature and pressure of course, gets DM equation reduces to this form which is more convenient to use it and it inter relates various partial molar properties or partial molar properties of one species with the rest right. For example, in a binary mixture than x 1 DM 1 bar by dx 1 plus x 2 DM 2 bar by dx 1 equals 0.

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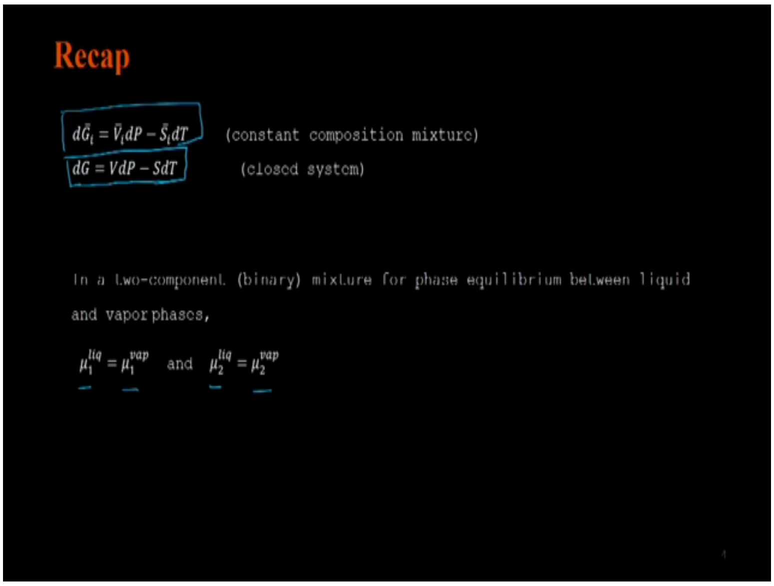

## Recap

$\boxed{d\bar{G}_i = \bar{V}_i dP - \bar{S}_i dT}$ (constant composition mixture)

$\boxed{dG = VdP - SdT}$ (closed system)

In a two-component (binary) mixture for phase equilibrium between liquid and vapor phases,

$\mu_1^{liq} = \mu_1^{vap}$ and $\mu_2^{liq} = \mu_2^{vap}$

Also we looked at the relation between the partial molar properties themselves, they are related to one another in almost analogous manner to the closed system equation. For example, dG is VdP minus SdT for a closed system and the partial molar properties dG i bar is V i bar dP minus S i bar dT this is in a constant composition mixture right.

And finally, we also talked about the phase equilibrium for example, in vapor liquid equilibrium in a binary mixture we said the chemical potential of the liquid phase for component one should be equal to the chemical potential of the vapor mixture in the vapor mixture for component one chemical potential of the component two in the liquid mixture should be equal to the chemical potential of component two in the vapor mixture and so on, we can extend this to a multi component multi phase system as well.

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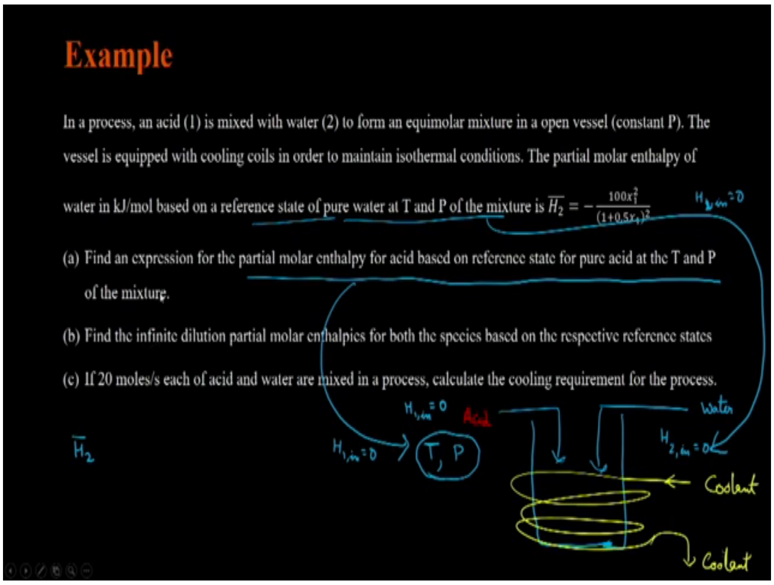

## Example

In a process, an acid (1) is mixed with water (2) to form an equimolar mixture in a open vessel (constant P). The vessel is equipped with cooling coils in order to maintain isothermal conditions. The partial molar enthalpy of water in kJ/mol based on a reference state of pure water at T and P of the mixture is $\overline{H_2} = -\frac{100x_1^2}{(1+0.5x_1)^2}$

(a) Find an expression for the partial molar enthalpy for acid based on reference state for pure acid at the T and P of the mixture.

(b) Find the infinite dilution partial molar enthalpies for both the species based on the respective reference states

(c) If 20 moles/s each of acid and water are mixed in a process, calculate the cooling requirement for the process.

So, now what we will do is try to use these ideas in a solving a few examples all right, the first one it says we have a process in which we mix acid subscript for acid is 1 with water to form an equal molar mixture in an open vessel. So, we have an open vessel it is at constant pressure let us say ambient pressure and then we are mixing acid and water. This vessel is equipped with cooling coils in order to maintain isothermal conditions so we flow coolant through these coils when we mix acid and water usually the temperature rises.

So, we want to take away heat from the vessel so it is equipped with cooling coils. Now the partial molar enthalpy for water in kilo Joules per mole based on a reference state of pure water rate temperature and pressure of the mixture will come back to this reference state in a minute is given as H 2 bar is some expression in terms of x 1 which is the mole fraction for the acid

Now, we are required to find them expression for partial molar enthalpy of pure acid, the infinite dilution partial molar enthalpies and then the heat requirement for the process if we mix 20 moles each of acid and water. Now let us see what is happening in this problem let us try to analyze what is happening in this problem. So, we have acid I have an open vessel in which I am putting acid and putting water right and this of course, has cooling coils let us give that a different color right.

So, we have cooling coils around this vessel so we are flowing water in or coolant into it and the coolant comes out alright. Now we are mixing acid with water let us say the temperature and pressure for this are T and P of the temperature and pressure for this process right. We are doing an isothermal operation at constant temperature T and the pressure being P. Now what we are given is the partial molar enthalpy for water so that is; obviously, H 2 bar with a reference state of pure water at temperature and pressure of the mixture.

Now, if you recall enthalpy is a state property and in most processes all we are interested in is calculating the change in enthalpy from one condition to another condition we really do not worry about the absolute value of enthalpy itself and for this change in condition I can always choose a convenient reference state as long as I use the same reference state throughout the calculation it does not matter what reference state I choose because the change will always be based as a difference between; difference between state one to state two and if and the reference state that appears in these calculations will cancel out.

So, it really does not matter what reference state I choose in this case the reference state for H 2 bar is based on pure water at T and P of the mixture. So, assume that the pure acid and pure water are also fed into this vessel at the same temperature and pressure of the mixture, then acid has some enthalpy, water has some enthalpy the pure water and pure acid and we are mixing them, the mixture has some other enthalpy if it is; obviously, different from that of the two pure species and then we have to take the heat away so that we maintain isothermal conditions

Now, so what we are saying? when I say that the reference state of pure water at the temperature and pressure of the mixture reference state is of pure water at the temperature and pressure of the mixture is that the water that is entering H 2 in is 0 right. This is what we are saying we can take that the enthalpy of the water entering in is 0 this is the reference state and whatever change happens after this reference state will be the value of the enthalpy so H 2 bar is based on this.

And similarly H 1 in now this reference state is for acid, this is for pure acid entering into it at the temperature and pressure of the mixture is 0 right, what we want to find is an expression for partial molar enthalpy of the acid based on the reference state for pure acid at temperature and pressure of the mixture this will translate to this; this will translate to this right. So, this will mean H 1 n is 0 and this will mean H 1 n is 0 right because for water and acid the reference states are the pure components at the temperature and pressure of the mixture I can take H 1 n and H 2 into P 0 ok.

Having said that now let us go back to the expression that is given to us.

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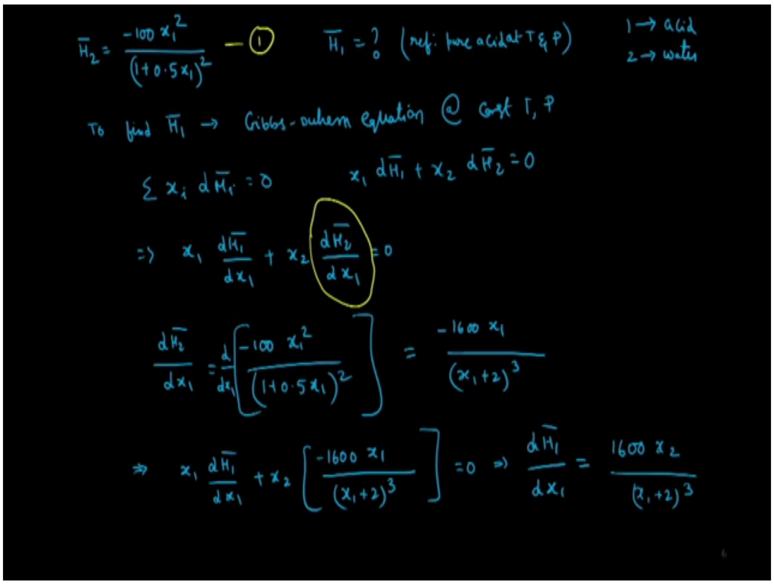

$\bar{H}_2 = \frac{-100 x_1^2}{(1+0.5x_1)^2}$ — ①  $\bar{H}_1 = ?$ (ref: pure acid at T & P)

1 → acid
2 → water

To find $\bar{H}_1$ → Gibbs-Duhem equation @ const T, P

$\sum x_i \, d\bar{M}_i = 0$  $x_1 \, d\bar{H}_1 + x_2 \, d\bar{H}_2 = 0$

$$\Rightarrow x_1 \frac{d\bar{H}_1}{dx_1} + x_2 \frac{d\bar{H}_2}{dx_1} = 0$$

$$\frac{d\bar{H}_2}{dx_1} = \frac{d}{dx_1}\left[\frac{-100 x_1^2}{(1+0.5x_1)^2}\right] = \frac{-1600 x_1}{(x_1+2)^3}$$

$$\Rightarrow x_1 \frac{d\bar{H}_1}{dx_1} + x_2\left[\frac{-1600 x_1}{(x_1+2)^3}\right] = 0 \Rightarrow \frac{d\bar{H}_1}{dx_1} = \frac{1600 x_2}{(x_1+2)^3}$$

We are given that the partial molar enthalpy expression for water H 2 bar is negative 100 x 1 squared x 1 being the mole fraction for acid 1 plus 0.5 x 1 whole squared, 1 represents acid and 2 represents water this is H 2 bar. Now we do not know H 1 bar and we want to calculate what H 1 bar is based on reference state of pure acid at T and P all right ok.

So, what we will do is to calculate H 1 bar we will use the Gibbs Duhem equation all right and we will apply gives you an equation at constant temperature and pressure at constant temperature and pressure recall that Gibbs Duhem equation say sigma x i dM i bar equal to 0 and for a binary system in terms of enthalpies this will be x 1 d H 1 bar plus x 2 d H 2 bar equals 0 the temperature and pressure are constant dH 1 dH 2 are changes in enthalpies or partial molar enthalpies which is only possible, if the composition changes.

So, we can write these derivatives as derivatives with respect to composition. So, this will be x 1 dH 1 bar by dx 1 plus x 2 dH 2 bar over dx 1 equals 0. So, I have an expression for H 2 let us give that a number, I can differentiate one and get dH 2 bar by dx 1. Once I have the dH 2 bar by dx 1 I can calculate dH 1 bar by dx 1 right so that is the idea. We will first find the derivative and then we will see if I can get H 1 bar from there dH 2 bar over dx 1 will be a negative 100 x 1 square by 1 plus 0.5 x 1 whole square and the derivative of this with respect to x 1 and I will leave it for you to simplify you should be able to do it fairly easily.

It turns out that this derivative is negative 1600 x 1 over x 1 plus 2 whole cube, this is the dH 2 bar by dx 1. So, what this means is x 1 dH 1 bar over dx 1 plus x 2 negative 1600 x 1 by x 1 plus 2 whole cube is 0 or dH 1 bar over dx 1 will equal 1600 x 2 over x 1 plus 2 molecule right, this is dH 1 bar by dx 1 and given H 2 bar I can find the derivative of H 1 bar with respect to x 1 using the Gibbs Duhem equation right, that is what we have right now.

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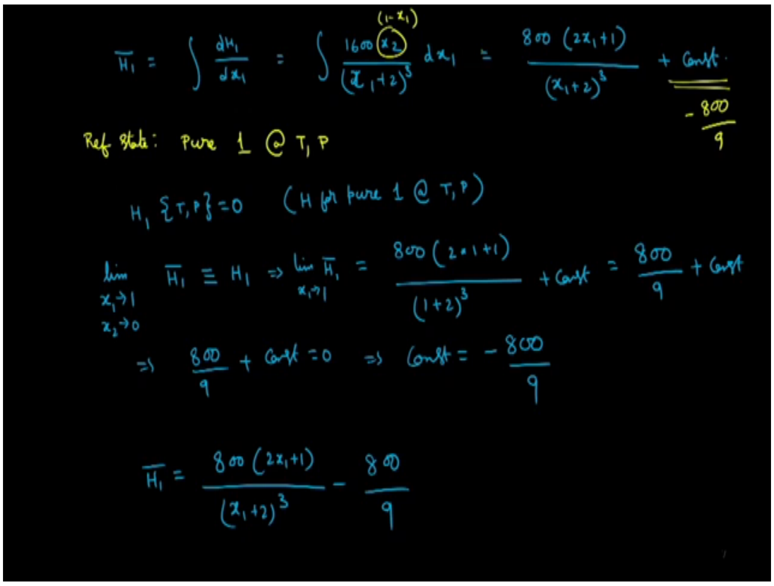

$$\bar{H}_1 = \int \frac{dH_1}{dx_1} = \int \frac{1600\,\overset{(1-x_1)}{x_2}}{(x_1+2)^3}\,dx_1 = \frac{800\,(2x_1+1)}{(x_1+2)^3} + \underline{\underline{\text{Const}}}$$

$$-\frac{800}{9}$$

Ref State: Pure 1 @ T, P

$$H_1\{T,P\} = 0 \quad (\text{H for pure 1 @ T, P})$$

$$\lim_{\substack{x_1 \to 1 \\ x_2 \to 0}} \bar{H}_1 \equiv H_1 \Rightarrow \lim_{x_1 \to 1} \bar{H}_1 = \frac{800\,(2 \cdot 1 + 1)}{(1+2)^3} + \text{Const} = \frac{800}{9} + \text{Const}$$

$$\Rightarrow \frac{800}{9} + \text{Const} = 0 \Rightarrow \text{Const} = -\frac{800}{9}$$

$$\bar{H}_1 = \frac{800\,(2x_1+1)}{(x_1+2)^3} - \frac{800}{9}$$

Now if I want H 1 bar then all I need to do is integrate that dH 1 bar over dx 1. So, that will be integral of that value which is 1600 x 2 by or x 1 plus 2 whole cube dx 1, what we will do is because we have to integrate it with respect to x 1 will replace this as 1 minus x 1 and then we can carry out the integration and what we will end up with after we integrate this particular expression is 800 2 x 1 plus 1 over x 1 plus 2 whole cube plus constant right, this is the expression we will have for H 1 bar ok.

Now there is a constant that appears in this expression because we are integrating it is a indefinite integral. So, this constant appears and if I have to find this constant I have to use the reference state conditions, we know that the reference state is pure species 1 at T, P right what this means is H 1 at T and P is 0 H for right because this is the reference state at this condition we can take this to be 0 H for pure species 1 at T and P is 0 right.

Now, limit of x 1 going to 1 which is pure component 1 which means x 2 goes to 0 H 1 bar will be exactly same as H 1 recall the property of partial molar property right at the pure component limit it will approach the pure component value. So, H 1 bar will be H 1 at this limit x 1 going to 1 right and in this particular case H 1 bar limit x 1 going to 1 H 1 bar is 800 2 times 1 plus 1 that is 3 over 1 plus 2 whole cube plus the constant; that means, this is 800 over 9 plus the constant.

But this is 0 800 plus because it is the reference state condition 800 plus constant is 0 or the constant value we have here is negative of 800 over 9. So, this value right there is negative 800 over 9 because at the reference condition it will if this H 1 bar has to be equal to H 1 which is 0. So, if this is negative 800 over 9, this is 800 over 9 they will cancel out and H 1 bar will be 0

So, we have the constant value using the reference state condition so I can finally, write the expression for H 1 bar based on reference state of pure acid at the temperature and pressure of the mixture would be 800 2 x 1 plus 1 over x 1 plus 1 whole cube minus 800 over 9, this is the expression for H 1 bar that completes part a of the problem right. Now for part b we want to find the infinite dilution partial molar enthalpies for both the species based on their respective reference states right.

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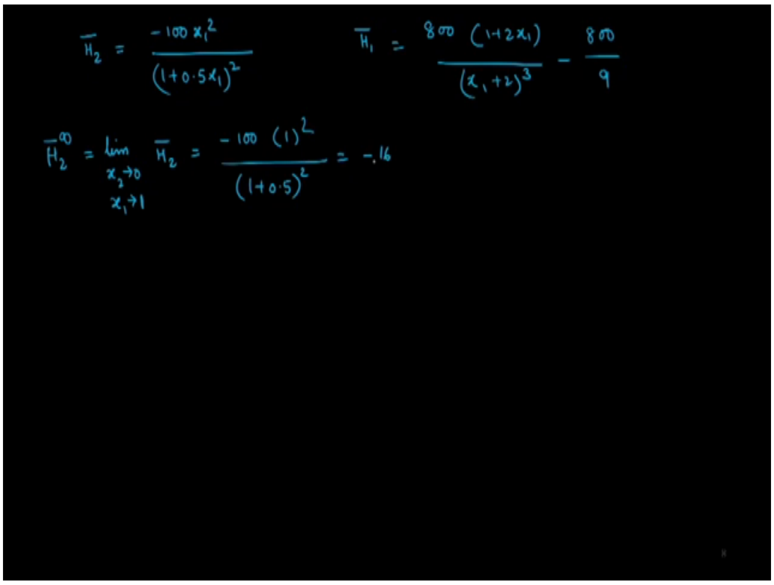

$$\bar{H}_2 = \frac{-100\, x_1^2}{(1+0.5x_1)^2} \qquad \bar{H}_1 = \frac{800\,(1+2x_1)}{(x_1+2)^3} - \frac{800}{9}$$

$$\bar{H}_2^{\infty} = \lim_{\substack{x_2 \to 0 \\ x_1 \to 1}} \bar{H}_2 = \frac{-100\,(1)^2}{(1+0.5)^2} = -.16$$

So, let us go back there let us re write the expressions for H 1 and H 2 H 1 we have is negative 100 x 1 squared over 1 plus 0.5 x 1; this is H 1 bar and H 2 bar is something we got just now it is 800 1 plus 1 x 1 over x 1 plus 2 cubed minus 800 by 9 of course, the constant value.

So, what I have done here is wrote the equations we just obtained H 2 bar is already given to us of course, and H 1 bar is what we have just obtained the partial molar enthalpy is for the two components. Now we are interested in finding the infinite dilution partial molar enthalpy is what we will do is apply suitable limits for sample limit of x 2 going to 0 H 2 bar will give us H 2 bar infinity and not an value when x 2 goes to 1 x 1 is going to 1 so this value will be negative 100 times 1 squared over 1 plus 0.5 squared and that turns out to be negative 16.

So, now for this step we are interested in finding the infinite dilution partial molar enthalpies. What I have done is read or the two equations we just got one of them H 2 bar is given to us of course, and H 1 bar is what we have obtained in the previous part and we are interested in finding the infinite dilution partial molar enthalpies.

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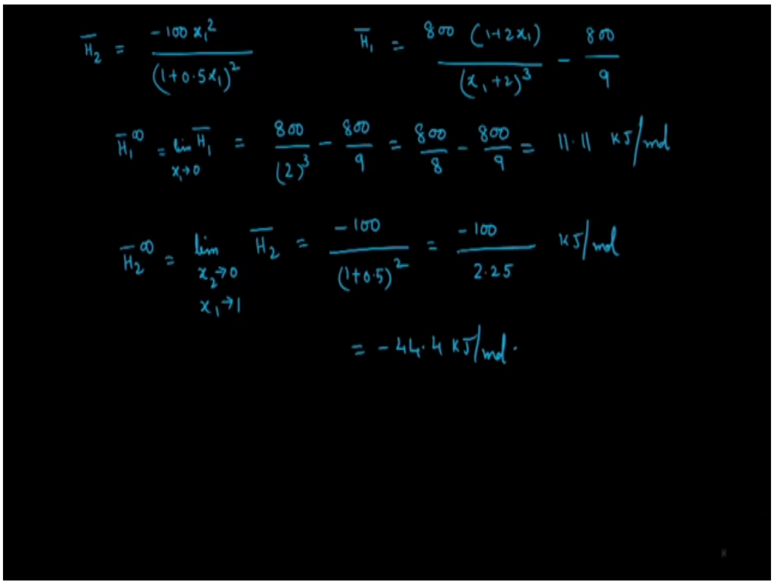

$$\bar{H}_2 = \frac{-100 x_1^2}{(1+0.5x_1)^2} \qquad \bar{H}_1 = \frac{800\,(1+2x_1)}{(x_1+2)^3} - \frac{800}{9}$$

$$\bar{H}_1^{\infty} = \lim_{x_1 \to 0} \bar{H}_1 = \frac{800}{(2)^3} - \frac{800}{9} = \frac{800}{8} - \frac{800}{9} = 11.11 \text{ KJ/mol}$$

$$\bar{H}_2^{\infty} = \lim_{\substack{x_2 \to 0 \\ x_1 \to 1}} \bar{H}_2 = \frac{-100}{(1+0.5)^2} = \frac{-100}{2.25} \text{ KJ/mol}$$

$$= -44.4 \text{ KJ/mol}.$$

So, for example, H 1 bar infinity will be equal to the limit of x 1 going to 0 right H 1 bar so that will be 800 over 8 right maybe I will just write it as 2 cubed minus 800 over 9.

So, that will be 800 over 8 minus 800 over 9 and that value turns out to be 11.11 kilo Joule per more. Similarly, if I am interested in finding H 2 bar infinity then it will be the limit of x 2 going to 0 or x 1 going to 1 H 2 bar and that will be negative 100 over 1 plus 0.5 whole squared all right. So, that will be negative 100 over x 1 is going to 1, 1.5, 2.25 right kilo Joules per mole so that will of course, be negative 44.4 kilo Joules per mole. Now for the final part of the problem what we are interested in is calculate the cooling requirement if we are mixing 20 moles each of acid and water right let us see if we can visualize the process right.

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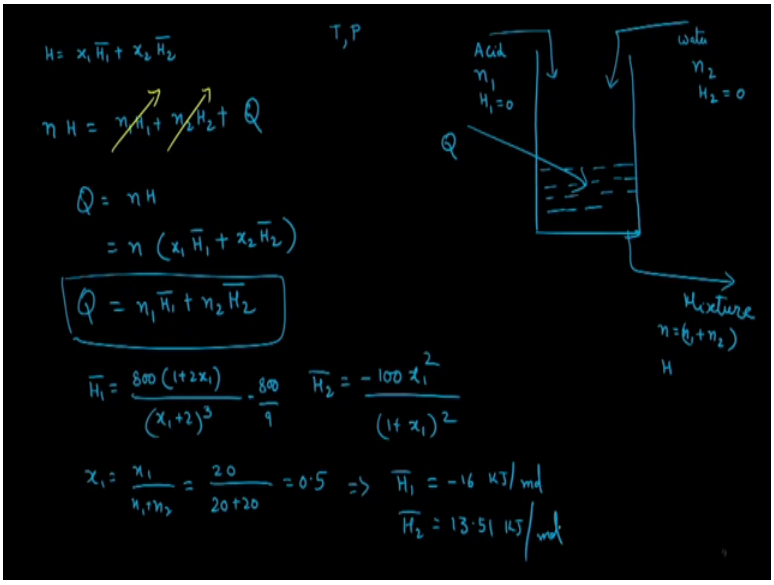

$H = x_1 \bar{H}_1 + x_2 \bar{H}_2$

$n H = \cancel{n_1 H_1} + \cancel{n_2 H_2} + Q$

$Q = n H$

$= n (x_1 \bar{H}_1 + x_2 \bar{H}_2)$

$\boxed{Q = n_1 \bar{H}_1 + n_2 \bar{H}_2}$

$\bar{H}_1 = \frac{800 (1 + 2x_1)}{(x_1 + 2)^3} - \frac{800}{9}$ $\quad \bar{H}_2 = \frac{-100 x_1^2}{(1 + x_1)^2}$

$x_1 = \frac{n_1}{n_1 + n_2} = \frac{20}{20 + 20} = 0.5 \Rightarrow \bar{H}_1 = -16 \text{ kJ/mol}$

$\bar{H}_2 = 13.51 \text{ kJ/mol}$

So, what we have is a vessel into this vessel there is two streams of acid and water coming in at some temperature and pressure we will not write the temperature and pressure separately, but for everything the temperature and pressure is constant T and P

Then I have a liquid mixture inside the vessel and there is a outlet mixture of acid plus water flowing out this is acid. So, in this temperature and pressure let us see I have n 1 moles of acid entering, n 2 moles of a water entering and the mixture will be n which is equal to n 1 plus n 2 moles of acid plus water leaving the vessel. Now there is a cooling arrangement so we are adding or removing some heat from the system cooling arrangement; obviously, we are removing it, but as per our convention Q is positive when we add it to the system.

So let us give that a Q added to the system if it is negative then it means we are removing the heat. And then let us also write the enthalpies because we will probably be doing an n th enthalpy balance let us say this is H 1 this is H 2 and this is H for the mixture. Now remember we are using reference states of pure acid and pure water for the partial molar enthalpies.

So based on that we can take H 1 to be 0 H 2 to be 0 because at the reference state conditions these two enthalpies are 0; now H obviously, will be x 1 H 1 bar plus x 2 H 2 bar will come back and try to use that in a minute. Now for this system if I can do an energy balance it turns out that the dH or n times H right that is the enthalpy leaving the system will be equal to n 1 H 1 plus n 2 H 2 plus Q and the two terms n 1 H 1 and n 2 H 2 are 0 because of the reference state conditions.

So, Q will be equal to n times H alright and for this particular process all I have to do then is use the expression for partial molar enthalpies or use the expression for H in terms of partial molar enthalpies right, this will be n times x 1 H 1 bar plus x 2 H 2 bar or n 1 H 1 bar plus n 2 H 2 this will be equal to Q, we already have expression for H 1 bar and H 2 bar I can use those expressions directly to calculate Q.

Now, we can use the expressions for H 1 bar and H 2 bar recall that H 1 bar is 800 1 plus 2 x 1 over x 1 plus 2 whole cube and H 2 bar is n minus 800 by 9 of course, the constant term and H 2 bar is negative 100 x 1 square over 1 plus x 1 whole square. So, once I have these expressions for H 1 bar and H 2 bar x 1 is n 1 by n 1 plus n 2 the flow rate is 20 moles per second so x 1 is going to be 20 over 20 plus 20 that is 0.5 this is an equal molar mixture.

So, I can calculate the H 1 bar and H 2 bar values at for an equi molar mixture it turns out that H 1 bar is negative 16 kilo Joules per mole and H 2 bar is 13.51 kilo Joules per mole. Once I have H 1 bar and H 2 bar I can go back and calculate Q.

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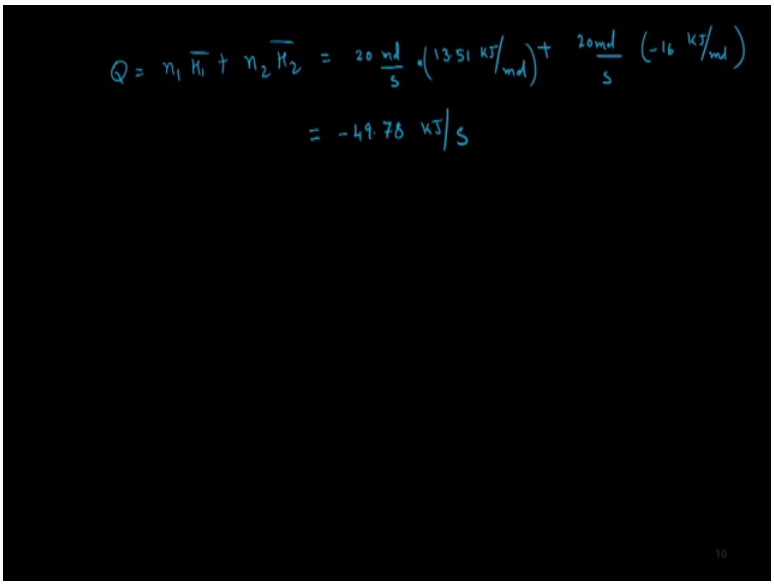

$$Q = n_1 \overline{H_1} + n_2 \overline{H_2} = 20 \frac{\text{mol}}{\text{s}} \cdot \left(13.51 \text{ kJ}/\text{mol}\right) + \frac{20 \text{mol}}{\text{s}} \left(-16 \text{ kJ}/\text{mol}\right)$$

$$= -49.78 \text{ kJ}/\text{s}$$

Q will be n 1 H 1 bar plus n 2 H 2 bar and in this case it turns out to be 20 moles per second times 13.5 kilo Joules per mole plus 20 moles per second times negative 16 kilo Joules per mole.

And once we simplify this expression what we end up is negative 49.78 kilo Joules per second. So, the cooling requirement for this process is negative 49.78 kilo Joules per second. So, what we have done in this exercise is use the information on one of the partial molar properties and if that information is given to us I can calculate the expression for other partial molar property as a function of composition

I can also calculate the heating and cooling requirements or enthalpy changes for this particular process.

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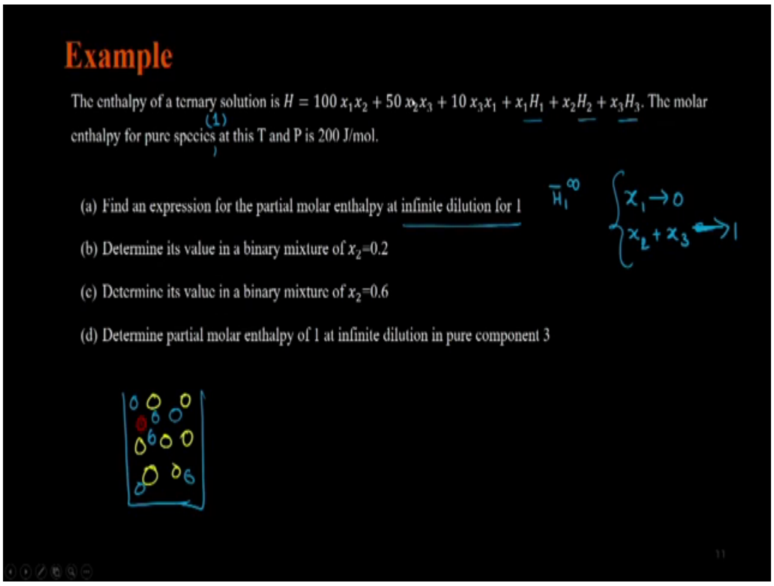

**Example**

The enthalpy of a ternary solution is $H = 100\,x_1x_2 + 50\,x_2x_3 + 10\,x_3x_1 + \underline{x_1H_1} + \underline{x_2H_2} + \underline{x_3H_3}$. The molar enthalpy for pure species (1) at this T and P is 200 J/mol.

(a) Find an expression for the partial molar enthalpy at infinite dilution for 1 $\bar{H}_1^{\infty}$ $\left\{\begin{array}{l} x_1 \to 0 \\ x_2 + x_3 \to 1 \end{array}\right.$

(b) Determine its value in a binary mixture of $x_2$=0.2

(c) Determine its value in a binary mixture of $x_2$=0.6

(d) Determine partial molar enthalpy of 1 at infinite dilution in pure component 3

Let us look at another example, this case I have a ternary solution and the expression for enthalpy of the ternary mixture is given to us now if I have a ternary solution there are 3 components 1 2 and 3. So, the expression for the enthalpy is dependent on all the three mole fractions of course, as well as the pure component enthalpy is x 1 H 1 H 2 and H 3. The molar enthalpy for pure species 1 of course, I should say at this temperature and pressure is 200 Joules per mole.

What we want to do is find an expression for partial molar enthalpy at infinite dilution for species 1 right. I am interested in calculating H 1 bar infinity or an expression for H 1 bar infinity right then we are also interested in determining what this value is for different mole fractions x 2 and finally, we are also interested in calculating H 1 bar infinity in pure component three. Now remember this is a ternary mixture.

So, if I have a ternary mixture i have three species that is 1 let us say and I have 2 in yellow and 3 in blue right this is infinite dilution of 1, but I can have 2 and 3 in varying compositions 2 can be 20 percent and 3 can be 80 percent or 2 can be 90 percent and 3 can be 10 percent. So, when I say infinite dilution of 1, the corresponding binary mixture of 2 and 3 can be in any proportion or in any composition so that is the scenario with a ternary mixture.

When we say a ternary mixture x 2 and x 3 can change, what is constant at infinite dilution is x 1 goes to 0 x 2 and x 3 can change such that x 2 plus x 3 will of course, approach 1. So, that x 1 plus x 2 plus x 3 is 1. So, this is what we mean by infinite dilution in a ternary mixture the ratio of the yellow circles to the blue circles can vary depending on the composition or the proportion of 2 and 3, but one is so diluted that we have a very small amount of 1 it x 1 goes to 0.

Irrespective of that fact if we have to calculate H 1 bar infinity the first thing we need to do is find an expression for H 1 let us see how we do that in the first place, what we are given is an expression for H ?

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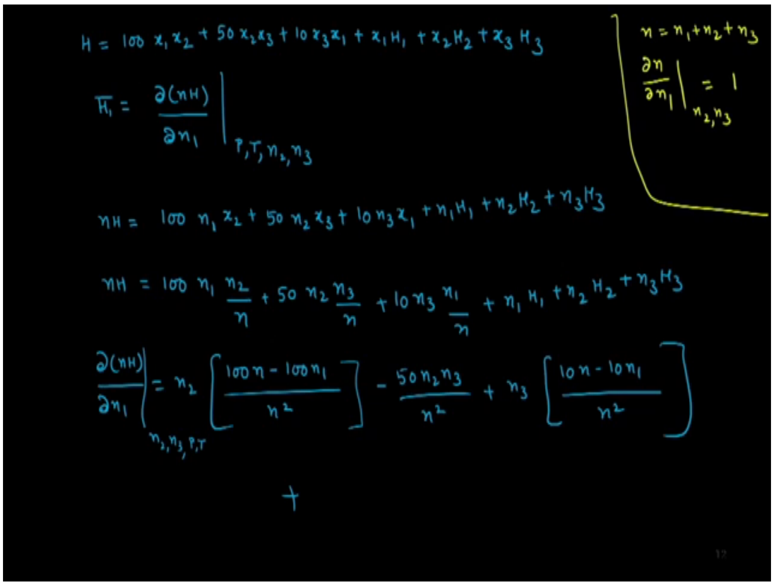

$$H = 100\,x_1x_2 + 50\,x_2x_3 + 10\,x_3x_1 + x_1H_1 + x_2H_2 + x_3H_3$$

$$\bar{H}_1 = \left.\frac{\partial(nH)}{\partial n_1}\right|_{P,T,n_2,n_3}$$

$$n = n_1 + n_2 + n_3$$

$$\left.\frac{\partial n}{\partial n_1}\right|_{n_2,n_3} = 1$$

$$nH = 100\,n_1x_2 + 50\,n_2x_3 + 10\,n_3x_1 + n_1H_1 + n_2H_2 + n_3H_3$$

$$nH = 100\,n_1\frac{n_2}{n} + 50\,n_2\frac{n_3}{n} + 10\,n_3\frac{n_1}{n} + n_1H_1 + n_2H_2 + n_3H_3$$

$$\left.\frac{\partial(nH)}{\partial n_1}\right|_{n_2,n_3,P,T} = n_2\left[\frac{100n - 100n_1}{n^2}\right] - \frac{50n_2n_3}{n^2} + n_3\left[\frac{10n - 10n_1}{n^2}\right]$$

H is given which is the total enthalpy of the solution is given to us and it is given as 10 x 1 x 2, 50 x 2 x 3, 10 x 3 x 1 right. So, it is 100 x 1 x 2 plus 50 x 2 x 3 plus 10 x 3 x 1 plus x 1 times H 1 plus x 2 times H 2 plus x 3 times H 3 this is the expression we have and from this expression we want to find H 1 bar.

The way we do that recall that H 1 bar is the derivative of the total enthalpy with respect to n 1 when we hold P T and all other ns in this case it is a ternary mixture. So, other than n 1 what we have is n 2 and n 3 constant. So, this is the expression for H 1 bar in a ternary mixture. So, I need n H first. So, what we do is take this expression for H and right n H; n H will be a 100 n 2 n times x 1 is n 1 and then I have x 2 plus 50 times n 2 x 3 plus 10 times n 3 x 1 plus n o1ne H 1 plus n 1 H 2 plus n 3 H 3 right.

We still have mole fractions left and we take the derivatives what we are taking the derivative is with respect to n 1 or n 2 or n thr3ee holding the others constant. So, we what we do is actually we convert all the mole fractions into n 1 n 2 s and n 3 s. So, what we are going to do is change this as 100 n 1 n 2 by n plus 50 n 2 n 3 over n plus 10 n 3 x 1 is n 1 over n plus the others can stay as they are they are already in terms of ns there is no x in these expressions this is expression for n H.

Now when we say n we mean the total moles of the mixture n is n 1 plus n 2 plus n 3. So, the derivative of n with respect to n 1, when we hold n 2 and n 3 constant right partial derivative of n with respect to n 1 when we hold n 2 and n 3 constant is simply going to be 1 right. The second and the third terms disappear so it will simply be 1 so we will keep that in mind.

Now, we will come back to this nH is this so if I take the partial derivative of n H with respect to n 1 if we look at the first term n 2 is constant and what I have is this 100 and 1 over n. So, the derivative of that is 100 n minus 100 n 1 over n square. This is the derivative of the first term with respect to n 1 when we hold n 2 and n 3 constant of course, P and T are constant anyway.

Similarly, I can write the derivative of the second term n 2 and n 3 both of them are constant so it will simply be negative 50 n 2 n 3 over n square. Derivative of n with respect to n 1 is 1 so derivative of 1 over n with respect to n 1 is going to be negative 1 over n squared plus again n 1 n 3 is constant. So, it will be n 3 10 n minus 10 and 1 over n squared plus all right maybe I should write this a little farther away.

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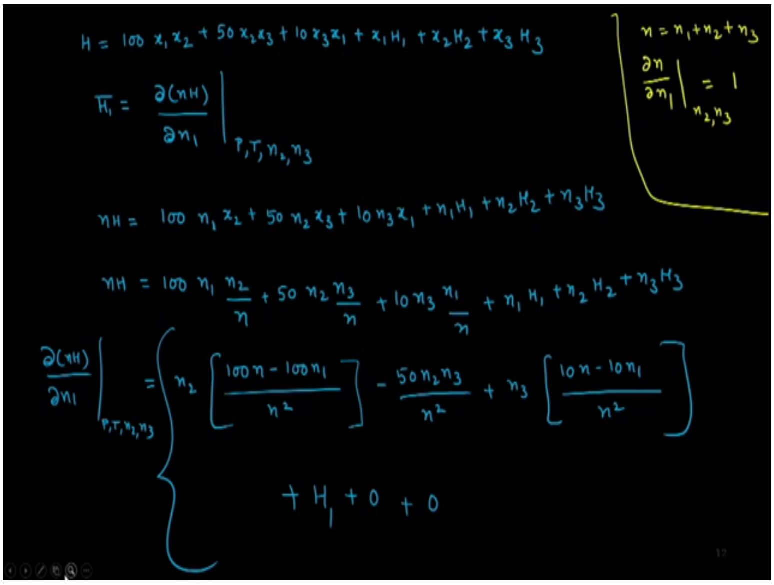

$$H = 100\,x_1x_2 + 50\,x_2x_3 + 10\,x_3x_1 + x_1H_1 + x_2H_2 + x_3H_3$$

$$n = n_1+n_2+n_3 \qquad \left.\frac{\partial n}{\partial n_1}\right|_{n_2,n_3} = 1$$

$$\bar{H}_1 = \left.\frac{\partial (nH)}{\partial n_1}\right|_{P,T,n_2,n_3}$$

$$nH = 100\,n_1x_2 + 50\,n_2x_3 + 10\,n_3x_1 + n_1H_1 + n_2H_2 + n_3H_3$$

$$nH = 100\,n_1\frac{n_2}{n} + 50\,n_2\frac{n_3}{n} + 10\,n_3\frac{n_1}{n} + n_1H_1 + n_2H_2 + n_3H_3$$

$$\left.\frac{\partial (nH)}{\partial n_1}\right|_{P,T,n_2,n_3} = \left\{ n_2\left[\frac{100n - 100n_1}{n^2}\right] - \frac{50n_2n_3}{n^2} + n_3\left[\frac{10n - 10n_1}{n^2}\right] + H_1 + 0 + 0 \right.$$

So, that it is clear this is the derivative of nH with respect to n 1 at P T n n 2 n 3, this is what we are writing plus derivative of n 1 times H 1 is with respect to n 1 is H 1 and plus 0 plus 0 n 2 and n 3 are constant H 2 H 3 of course, are constant so at constant temperature and pressure so those two terms two apart. Now we can simplify this right and when we do that notice that I have n n 1 and n 2 here, so n 2 over n will be x 2 n over n is 1 n 1 over n is x 1.

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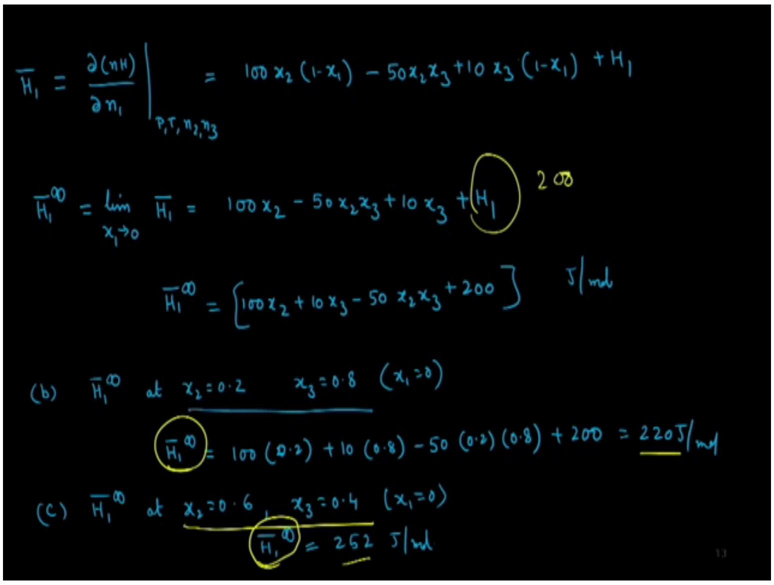

$$\bar{H}_1 = \left.\frac{\partial (nH)}{\partial n_1}\right|_{P,T,n_2,n_3} = 100\,x_2(1-x_1) - 50x_2x_3 + 10\,x_3(1-x_1) + H_1$$

$$\bar{H}_1^{\infty} = \lim_{x_1\to 0}\bar{H}_1 = 100\,x_2 - 50\,x_2x_3 + 10\,x_3 + \boxed{H_1}\ 200$$

$$\bar{H}_1^{\infty} = \left[100x_2 + 10x_3 - 50\,x_2x_3 + 200\right] \quad J/mol$$

(b) $\bar{H}_1^{\infty}$ at $\underline{x_2 = 0.2 \quad x_3 = 0.8}$ $(x_1 = 0)$

$$\boxed{\bar{H}_1^{\infty}} = 100\,(0.2) + 10\,(0.8) - 50\,(0.2)(0.8) + 200 = \underline{220}\,J/mol$$

(c) $\bar{H}_1^{\infty}$ at $\underline{x_2 = 0.6,\ x_3 = 0.4}$ $(x_1 = 0)$

$$\boxed{\bar{H}_1^{\infty}} = \underline{252}\ J/mol$$

So, what I am going to do is simplify this expression again noting that I can convert n 1's n 2's n 3's back into the mole fractions and when I do that derivative of n H over n 1 at P T n 2 and n 3 what I would get is 100 times x 2 1 minus x 1 minus 50 x 2 x 3 plus 10 x 3 1 minus x 1 plus H 1 and this is the derivative we call as partial molar enthalpy for 1.

Now, if you look at this expression we should know that everything that appears on the right hand side after simplification is independent of n 1 n 2 n 3 or n that should be the case because this is a partial molar property which is an intensive variable. So, the size of the system or the number of moles cannot appear on the right hand side once we simplify the number of moles will disappear and everything should be in terms of the mole fractions x 1 x 2 or x 3 this is the expression for H 1 bar right.

Now, if I am interested in partial molar enthalpy at infinite dilution limit of x 1 going to 0 H 1 bar will be what we call as H 1 bar infinity and at this condition when x 1 goes to 0, the first term is a 100 x 2 minus 50 x 2 x 3 plus 10 x 3 plus H 1 this is the expression for H 1 bar infinity. Now if you look at this it says that the molar enthalpy for pure species 1 at this temperature and pressure is 200 Joules per mole.

So, what this means is H 1 is 200 Joules per mole so what I have now then is an expression for H 1 bar infinity which reads a 100 x 2 plus 10 x 3 minus 50 x 2 x 3 plus 200 all of this in Joules per mole. Now for part b what we are interested in is finding H 1 bar infinity at x 2 equal to 0.1, when x 2 is 0.2 and we are talking about H 1 bar infinity x 3 will be 0.8 because x 1 is 0 and all the three should add up to 1, so if x 2 is 0.2 and x 1 is 0 then x 3 should be equal to 0.8.

So, I can substitute these in H 1 bar infinity or the expression for H 1 bar infinity it will be a 100 times 0.2 plus 10 times 0.8 negative 50 times 0.2 times 0.8 all right plus 200 right. So, if I simplify this it will be 220 Joules per mole. I can do a similar exercise for x 2 is 0.6 is what we are interested in this case x 3 will be 0.4 still x 1 is 0 because we are talking about H 1 bar infinity and H 1 bar infinity once we simplify everything turns out to be 250 Joules per mole.

Now here is the thing we said that the infinite dilution partial molar properties are constant, yes they are constant 220 Joules per mole it is independent of the mole fraction for x 1 or 1. But if you have a ternary mixture it will still depend on mole fraction of components 2 and 3, we have a different mixture when I have 20 percent 2 and 80 percent 3 as opposed to 60 percent 2 and 40 percent 3 these two are different species in both scenarios one is infinitely dilute, but the mixture that is making the rest of the mixture is different right, but the species that are in rest of the mixture is different and in such scenario we do expect that H 1 bar infinity is going to be different.

In one case it is 220 in the other case it is 252 Joules per mole, it will approach a constant value as long as the mixture we use is same, but if we have different mixtures then; obviously, we are comparing two different things. So, it can still change that is the scenario with a ternary mixture.

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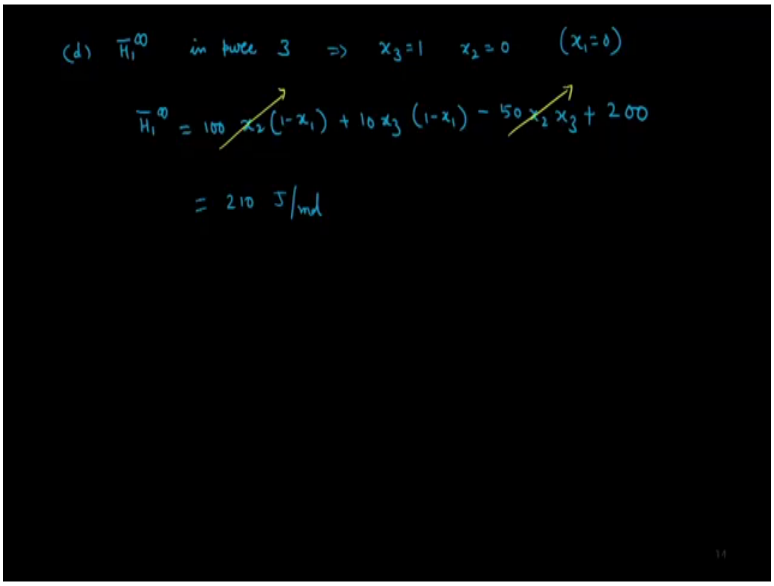

(d) $\bar{H}_1^{\infty}$ in pure 3 $\Rightarrow x_3 = 1 \quad x_2 = 0 \quad (x_1 = 0)$

$$\bar{H}_1^{\infty} = 100\,\cancel{x_2}(1-x_1) + 10\,x_3\,(1-x_1) - 50\,\cancel{x_2}\,x_3 + 200$$

$$= 210 \text{ J/mol}$$

And finally, what we are interested in is calculate H 1 bar infinity in pure species 3. In this case when we have pure 3, what this implies is x 3 is 1 which means x 2 is 0 and x 1 is 0 anyway because we are talking about H 1 bar infinity and if x 3 goes to 1 then x 2 will also go to 0 and we can still use the same equation we had H 1 bar infinity is 100 x 2 1 minus x 1 plus 10 x 3 1 minus x 1 minus 50 x 2 x 3 plus 200.

Now, I have x 2 to be 0 x 1 to be 0 x 3 is 1 x 2 is 0 so this term drops out x 2 zero,so this term also drops out x 1 is 0 we have 10 here and 200 there. So, this value would be 210 Joules per mole, this will be the value of H 1 bar infinity in pure species 3.

So, as the constituents of the solvent in the infinite dilution scenario change including pure it can be a pure component 3 as the constituents change then the value of H 1 bar infinity is going to change right. So, that completes our discussion on this particular problem what we have done in this exercise is calculated the total enthalpy H given the partial molar enthalpy that was in the previous scenario and in this particular example given the total enthalpy H, we calculated the partial molar enthalpies.

With that we will end today's lecture when we come back in the next lecture we will look at ideal gas mixtures. Remember all we have done so, far is prepared the groundwork for handling properties of mixtures, we said mixtures are going to behave differently and the total property of a mixture can be determined if we know the partial molar properties of the mixture, but we still do not know how to obtain the partial molar property of a mixture.

For example, in the previous case we looked at partial molar enthalpy in terms of x 1 x 2 and x 3. We do not know how we can obtain such relations or what would be a correct relation for a particular system. So, in the next lecture we will start our discussion with an ideal gas mixture and see how the partial molar properties in an ideal gas mixture vary as a function of composition and from that we will try to move on to other fluids other than ideal gases.

Thank you.