Thermodynamics of Fluid Phase Equilibria

Dr. Jayant K Singh
Department of Chemical Engineering
Indian Institute of Technology, Kanpur

Lecture – 22
Ideal Gas Mixture -part 2

Welcome back. Now, we are going to look at the change in the property upon mixing components.

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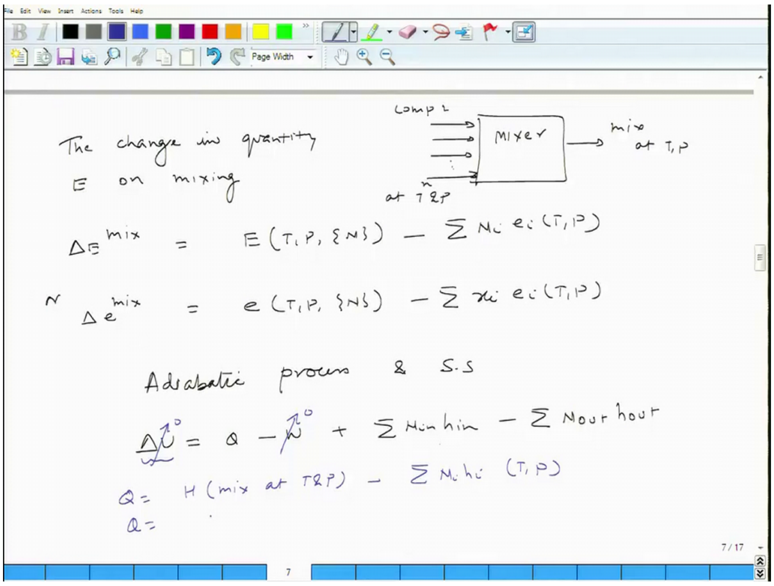

The change in quantity E on mixing

$$\Delta E^{mix} = E(T,P,\{N\}) - \sum N_i e_i(T,P)$$

$$N \quad \Delta e^{mix} = e(T,P,\{N\}) - \sum x_i e_i(T,P)$$

Adiabatic process & S.S

$$\cancel{\Delta U}^{0} = Q - \cancel{W}^{0} + \sum N_{in} h_{in} - \sum N_{out} h_{out}$$

$$Q = H(\text{mix at } T\&P) - \sum N_i h_i (T,P)$$

$$Q =$$

So, let us consider a mixer where various different components are getting mixed at temperature and pressure and what you get is basically a mixed fluid at temperature and pressure. And the question which you are asking is the change in quantity or a property E on mixing ok. So, you are asking like what is a typical change in E. E could be entropy, E could be enthalpy Gibbs free energy and so forth.

Let me first define this which is basically the delta e mix which is nothing, but the change upon mixing. So, this would be E which is a property of the mixture at T P and with all composition minus summation of N i number of moles an individual component molar property at temperature T P ok. So, this is basically by definition. I can divide by total number of moles and also can write in small e mix.

Now, in this case I am not making very strong statement by changing y is to x ok. So, it is just a composition at this point. Usually x is you represent to the composition then liquid phase and y represent composition in the gas phase that is by compare convention. But at this point is just a composition in the mixture ok. Now, let us consider an adiabatic process and steady state ok. Now, if you consider adiabatic process you can write down your first law in a continuous mode or flow system Q minus W plus summation N in H in minus summation H out N out H out ok.

Now, for being adiabatic of course, and is of course, we are saying that there is no work associated with it and what you see here is the temperatures are constant here. So, this is the component which is of the system which is let us say in this within this mixture ok. Now, being a steady state the changes are going to be 0 because all the properties are going to remain constant and hence the change is 0. So, this must be 0 of the system within the mixture right. There is no work associated the boundary work no other work is associated. So, we are going to make this to be 0.

Now, we are going to say either well Q is nothing but essentially the enthalpy of the mixed fluid at T P minus summation N in H in T P ok. So, this is basically for pure component as H in means it is like of a pure component. I can actually write this more in the language which we have been using here h i, ok. So, Q is basically has to be 0 that is what we are saying. Q is nothing but whatever the changes we are occurring since is adiabatic. Q need to be 0 ok, so this is a generic expression.

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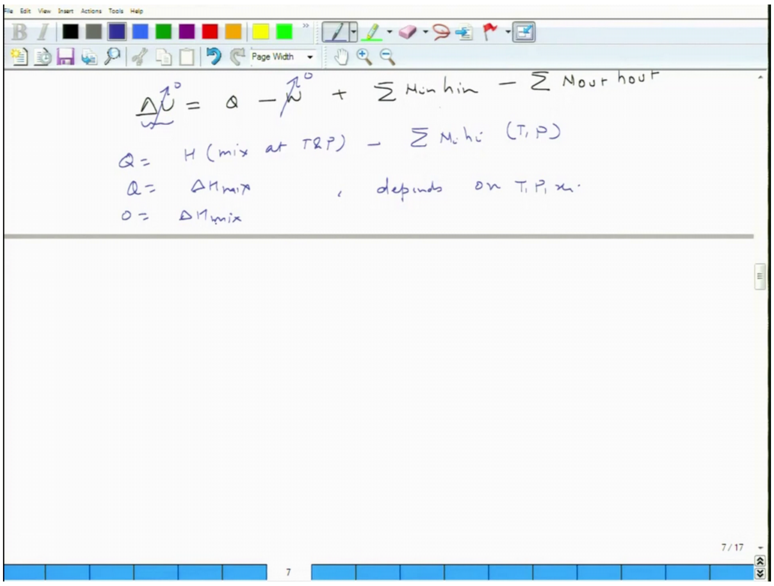

$$\cancel{\Delta U}^{0} = Q - \cancel{W}^{0} + \sum N_{in} h_{in} - \sum N_{out} h_{out}$$

$$Q = H(\text{mix at } T \& P) - \sum N_i h_i \ (T, P)$$

$$Q = \Delta H_{mix} \quad , \text{ depends on } T, P, x_i.$$

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

So, this would be nothing, but your delta H actually mix right considering by definition. Now, if Q is positive it means exothermic if Q is negative it means endothermic right. Now, if it is adiabatic it has to 0 it has to be 0. Now, in order to maintain it since there is no way to extract the heat out of the system if it is an exothermic the temperature will change of the system ok.

So, but then it depends on what is a typical delta H mix. So, it depends on whatever the temperature whatever the change is occurring depends on T P x i, ok. So, for adiabatic of course, this must be 0 right ok. So, what is the typical temperature of the system will vary and how this may vary with the composition. It will also vary with the system which we are considering ok.

So, let us try to understand it a little bit with an example. So, I will just go through an example for the same system which is an adiabatic and ask questions related to the temperature, but before that let me just give you what is a typical delta H mix for a binary system. So, it is not like monotonously, it is quite complex and it depends on as I said temperature pressure and composition ok. So, this is an example of a binary system, binary liquid mixture ok, which means basically we can write like this for water and ethanol ok.

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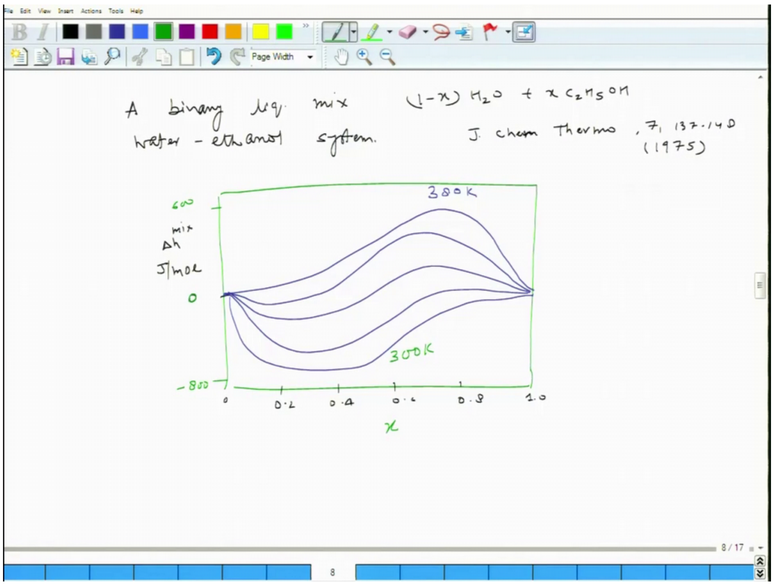

A binary liq. mix $(1-x)\,H_2O + x\,C_2H_5OH$

water - ethanol system. J. chem Thermo, 7, 137-140 (1975)

So, this is a water ethanol system. And the data are taken from a paper a journal paper which is a journal of chemical thermodynamics volume 7 page 137 to 148 1975. It is very old though, but nevertheless it gives any idea what we intend to learn from here.

So, let me as draw again it is not on perfect scale, but it will give us the idea. So, this is x which is a composition in this binary mixture ok. So, this is 1 0, so 0.2 0.4, 0.6, 0.8 this is somewhere its 0 and what I am plotting is basically delta small h mixture. So, basically the change in the property changes in enthalpy per mole ok. So, this is the unit is Joules per mole ok. Now, I am going to draw these values with changes in the temperature.

So, this is a typical value for 380 Kelvin this is how it looks. This is close to 800 here, minus 800 and this is close to 600 here plus 600 this is 0 and the temperature here is 300 Kelvin. So, as you see it is quite non-monotonous, it is quite a varying and now, if you have been given such a data to make use of it to calculate certain changes in the temperature in the system how you are going to do that.

So, let me just use this data to and then pose a simple question to you and the question is the following.

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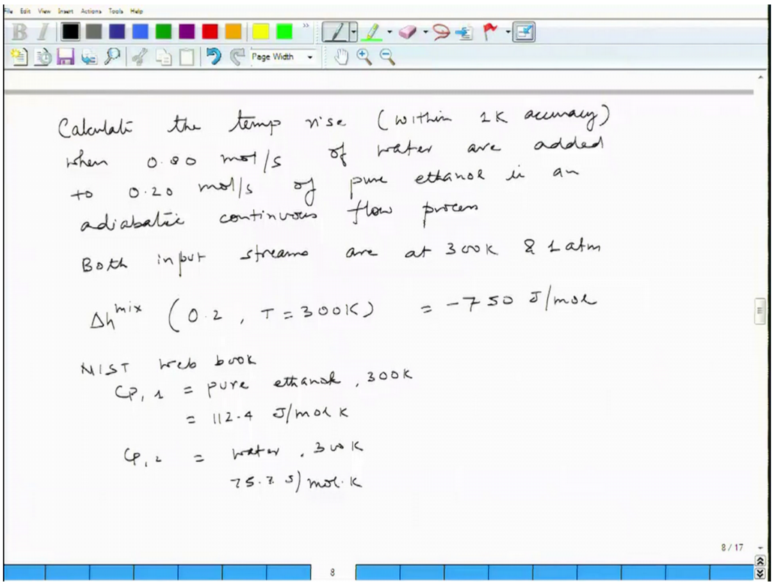

Calculate the temp rise (within 1K accuracy) when 0.80 mol/s of water are added to 0.20 mol/s of pure ethanol in an adiabatic continuous flow process

Both input streams are at 300K & 1 atm

Δh^{mix} (0.2 , T = 300K) = −750 J/mol

NIST web book

$C_{P,1}$ = pure ethanol , 300K
= 112.4 J/mol K

$C_{P,2}$ = water , 300K
75.3 J/mol·K

That we need to; calculate the temperature rise within 1 Kelvin accuracy when 0.8 moles per second of water are added to 0.2 moles of pure ethanol ok. And the condition is that its adiabatic continuous flow process ok. Now, both the input streams are at 300 Kelvin and 1 atmosphere ok. So, you have been asked to this particular question. Now, the data's are given here though it is not on scale, but I have these numbers with me.

So, what information we have is delta H mix at 0.2 mole fraction and temperature 300 Kelvin is minus 750 so, this basically x of ethanol ok. So, this would be your x ethanol somewhere at 300 it is around 750 Joules per mole ok, 750 Joule per mole.

What does that mean? It means being is negative changes in enthalpy it means the heat is being generated ok. So, which means considering that the process is adiabatic the temperature is going to rise ok, there is no way you can extract the heat out of the system the temperature is going to right. So, we need to find out the temperature ok. So, how are you going to solve this problem? So, you are only given delta h mix ok.

So, other thing which I can provide is basically C p also. So, I can give you the information of C p. So, from NIST neural science, are NIST web book which you can type it on internet and you can get this information its free of cost. C p for one which 1 is your ethanol and 2 is your water for pure ethanol at 300 Kelvin C p 1 is 112.4 Joules per mole Kelvin and C p 2 is for pure water is 300 Kelvin 75.3 Joules per mole Kelvin ok. So, this information is given to you. Now, how you are going to calculate your temperature?

So, when you said the first part actually what you meant that. So, let me just describe the idea this is and this is what you have done is perfectly fine. So, the idea to solve this is we have to make use of the fact that enthalpy is a state function earth is independent and it is independent of path. So, what we are going to do is that we will consider that component 1 at T P and component 2 at T P is taken from temperature to the final temperature and here we are going to mix it ok.

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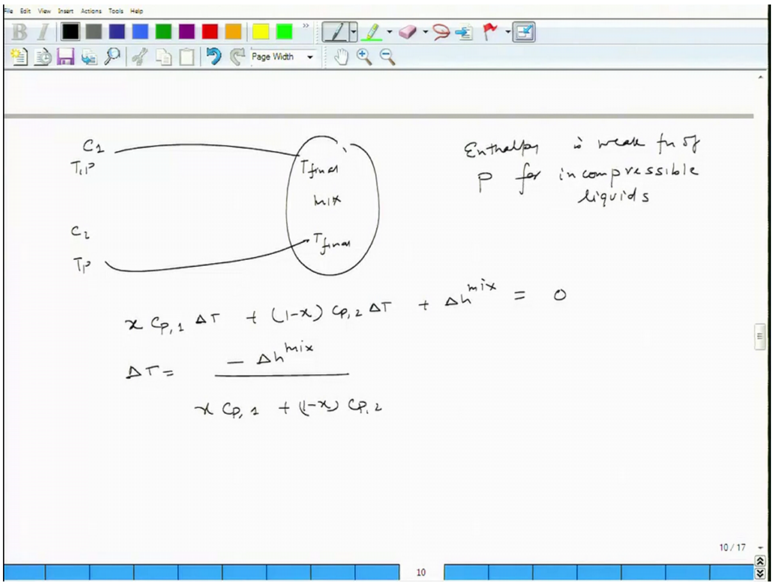

Enthalpy is weak fn of P for incompressible liquids

$$x\, C_{p,1}\, \Delta T + (1-x)\, C_{p,2}\, \Delta T + \Delta h^{mix} = 0$$

$$\Delta T = \frac{-\Delta h^{mix}}{x\, C_{p,1} + (1-x)\, C_{p,2}}$$

So, and then enthalpy the other important thing which we are going to assume by taking this approximation or from where we going to write the enthalpy change as C p delta T is the fact that enthalpy is a, enthalpy is a weak function of pressure for incompressible fluid ok.

So, with this, so what we are doing is basically we are taking component 1 to T finals which we do not know and similarly component 2 taking to T final and then we are going to mix it ok. So, with this we have got we have this composition of ethanol x multiplied by C p 1 delta T plus 1 minus x or C p 2 delta T ok, this plus whatever the change in the enthalpy due to the mixing this must be 0 ok. Why because Q is 0 this comes directly from our previous exercise. Now, with this we are going to write this expression as minus of delta h mix plus x C p 1 plus 1 minus x C p 2 ok. Now, the key issue is what would be our guest value ok.

So, what we have been given is this information via we can we can look at this graph and we can start from 300 does not mean that small changes are there they may be this outcome I know output stream is also a 300. So, at 300 for 0.2 composition because composition is fixed ok, because its 0.2 ethanol is there, minus 750 is our delta H mix. So, when you put that delta h mix for 300 Kelvin we get as 7 Kelvin ok. Now, which essentially means T final is 307, ok.

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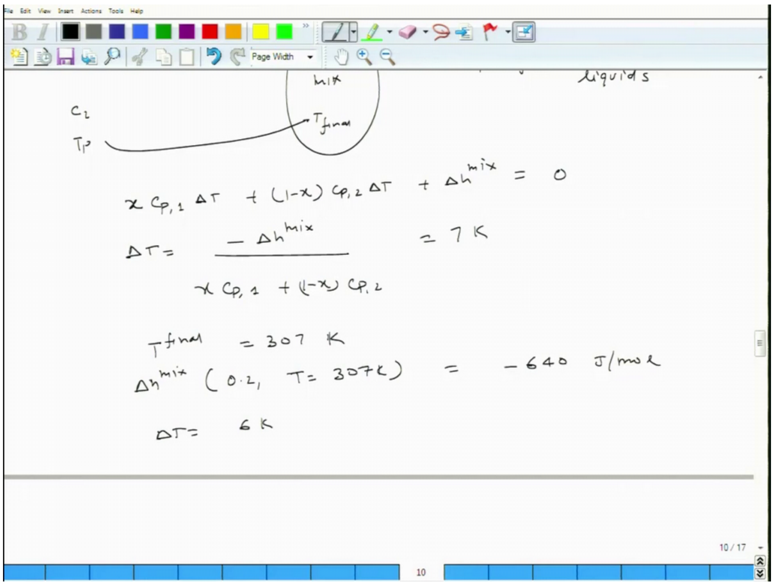

$$x\, C_{p,1}\, \Delta T + (1-x)\, C_{p,2}\, \Delta T + \Delta h^{mix} = 0$$

$$\Delta T = \frac{-\Delta h^{mix}}{x\, C_{p,1} + (1-x)\, C_{p,2}} = 7\ K$$

$$T^{final} = 307\ K$$

$$\Delta h^{mix}(0.2,\ T = 307K) = -640\ J/mol$$

$$\Delta T = 6\ K$$

So, T finally, is 307. So, this is our first iteration ok. Now, we again go back and find out our delta h mix at 0.2, T is equal to 307 Kelvin. We look at the graph it turns out to be 640 Joules per mole we plug in back this and this equation we got delta T is 6 Kelvin. So, the change from the first iteration to a second iteration is 1 Kelvin, and thus since the question was that within 1 Kelvin accuracy we wanted to find out the temperature rise we can stop here because we have got value which is 6 Kelvin ok. So, we got the change in the delta T temperature at 306 Kelvin ok.

So, this is how we make use of these expressions in order to solve problems using the experimental data as well as the first clause as well as the basic definition. So, this is only at 300 Kelvin. So, what we assuming is basically also that C p is a weak function of temperature that within small variation it is not changing it is almost constant ok.

So, we can stop here. Now, in the next lecture we will take another example I try to exploit further understanding of partial molar properties ok.