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Lecture - 47 Energy Balance on Nonreactive Processes with Processes Change

Welcome to today's lecture on performing energy balances on Nonreactive Phase Change Processes. In the previous few lectures we have looked at the fundamentals associated with phase change operations. We have also looked at how we can estimate the changes in enthalpy associated with phase change. So today we will perform some energy balance calculations using these fundamentals.

(Refer Slide Time: 00:41)

Phase Change Processes

- Internal energy/Enthalpy table should list the same chemical component in different phases separately
- Reference state should clearly indicate the phase along with temperature and pressure
- Specific enthalpy/specific internal energy should be calculated from the reference state to the state of the component in the table
 - Build hypothetical paths to use latent heat of phase change from tables



First thing we need to remember is for phase change operations the internal energy or the enthalpy table should list the same chemical components which are occurring in different phases separately. So when we build the enthalpy table during energy balance calculations we usually list out all the components that are present in the system. So here there are phase changes happening to explicitly account for that.

We need to ensure that the different phases are distinctly listed. For example, if you have methanol liquid and methanol vapor coming in then these should be listed as methanol liquid and methanol vapor although they are the same chemical component. The next thing we need to remember is the reference state should clearly indicate the phase along with the temperature and pressure.

So until now when phase change has not been happening it would not have mattered if we just listed only temperature and pressure. However here because there is phase change we should always list the reference state phase also. So even if the component is at the same temperature and pressure there could be change in phase and there would be change in enthalpy associated with change in phase.

So we need to explicitly list the phase of the reference state as well. When we calculate the specific enthalpy or specific internal energy we should be considering the change from the reference state to the state of the component in the table. So if we have a reference state which is liquid at T temperature and P pressure going to vapor at T temperature and P pressure then the process would be the vaporization from liquid to vapor at the temperature of T and P and pressure of P.

So this kind of thing has to be accounted for. We need to build hypothetical paths to use the latent heat of phase change which is available from tables. As I already mentioned there are tables where we can get these latent heats of phase change. So these enthalpy values can be obtained from different textbooks and handbooks and if they are not available only then you would be using the approximate estimation techniques which we had looked at like the Trouton's rule and Chen's equation and so on.

The first effort should be to identify if these latent heat of phase changes are available from some handbook or textbooks. If not, we can use approximate correlations to estimate the heat associated with the phase changes.

(Refer Slide Time: 03:10)

Example #1 Liquid glycerol flowing at a rate of 5000 L/h at 75 °C and 1 atm is cooled at constant pressure such that 60% of the glycerol solidifies. Given: MW = 92 g/mol, ρ = 1.26 kg/L, T_m = 18.2 °C, ΔĤ_m(T_m) = 18.3 kJ/mol, cp = 90.983+0.4335T J/mol.K • What is the outlet temperature? T_ = 18.2 C · Calculate the required cooling rate in kW. V = 5000 L/L m = Vg = 5000×126=6300kg/h $\dot{m} = V_{p}^{m} = \frac{6300}{92} = 68.5 \text{ kmol/h}$ $\dot{n} = \frac{\dot{m}}{MW} = \frac{6300}{92} = 68.5 \text{ kmol/h}$ $60.7 \text{ Gy widdpics} \Rightarrow Gy(s) = 0.6 \times 68.5 \pm 27.4 \text{ kmol/h}$ $Gy(1) = 0.4 \times 68.5 \pm 27.4 \text{ kmol/h}$

Here is an example problem where you will perform such energy balance calculations. So the data related to this particular component has been given here. So we would be able to use their data directly and perform the calculations. The examples read as liquid glycerol flowing at a rate of 5000 liters per hour at 75 degree Celsius and 1 atmosphere is cooled at constant pressure such that 60% of the glycerol solidifies.

You are given that molecular weight of glycerol is 92 grams per mol, density is 1.26 kilogram per liter, the melting point is 18.2 degree Celsius and the latent heat of fusion is 18.3 kilojoules per mol and Cp for glycerol is 90.983+ 0.4335 times T joules per mol Kelvin. So with all this information you have been asked to first identify what the outlet temperature would be and then identify the rate of cooling which is required in terms of kilowatt.

For the first part what would be the outlet temperature? Here we know that the outlet condition contains liquid so 40% of glycerol which comes in actually remains in the liquid phase while the other 60% has solidified. So this means at this particular temperature which is the outlet temperature the solid liquid is existing simultaneously. This would happen only when you have the mixture at melting point.

So because of this we can directly identify the temperature of the outlet stream as the melting point. So the outlet temperature would be=Tm which is=18.2 degree Celsius. So we do not need to perform any calculations to identify that. So now the next aspect is to calculate the required cooling rate in kilowatts. So we would have to perform some calculations to identify this.

Here we will perform the necessary energy balance calculations. So if we look at the data given we have information about the latent heat of fusion in terms of kilojoules per mol Cp has been given in terms of joules per mol Kelvin. So we need to identify these units and used them appropriately. So the flow rate has been given as volumetric flow rate which is 5000 liters per hour.

So this volumetric flow rate needs to be converted molar flow rate so that we can use the delta Hm cap and the Cp values directly. So for doing that this volume first needs to be converted to mass and then from there we can convert mass into mol. So we have the density so volumetric flow rate which is 5000 liters per hour can be converted to mass flow rate which would be volumetric flow rate times density which equals 5000 times 1.26 giving you 6300 kilograms per hour.

So this mass flow rate needs to be converted to molar flow rate using the molecular rate. So your mass flow rate/molecular weight would give you molar flow rate which is 6300/92 giving you a molar flow rate of 68.5 kilo mol per hour. So now that we have the molar flow rate we can use these to build the enthalpy table. So we have been told that 60% of glycerol solidifies.

So this implies glycerol solid in the outlet stream would be 0.6 times 68.5 which is =41.1 kilo mol per hour and the remaining would be the liquid which is glycerol liquid would be = 0.4 times 68.5 which is 27.4 kilo mol per hour. So we now have flow rates for the inlet glycerol liquid and the outlet glycerol liquid and solid. So with this we would be able to build the enthalpy table. So for building the enthalpy table we first need to identify the reference states.

As we are not going to be using any of the enthalpy tables which are readily available for performing the calculations associated with these energy balances. It is useful to assume either the inlet or the outlet conditions as the reference state. So we could either use glycerol liquid at 75 degree Celsius in one atmosphere which is the inlet condition as the reference state or we could choose glycerol liquid at 18.2 degree Celsius in 1 atmosphere which would be one of the outlet streams or glycerol solids at 18.2 degree Celsius in one atmosphere as the references states.

We could choose any one of these three. For these calculations I have used glycerol liquid at 75 degree Celsius in one atmosphere which is the inlet condition as the reference state.

(Refer Slide Time: 08:30)

Example #1
Ref state:
$$G_{4}(\ell, 75', 14tm)$$

 \dot{n}_{11} \dot{H}_{11} \dot{n}_{0ut} \hat{H}_{0ut}
 $G_{4}(J) = 68.5 = 27.4 + \hat{H}_{1}$
 $G_{4}(5) = -41.1 + \hat{H}_{2}$
 $\hat{H}_{1} = \int G_{p} dT = -b.32 + J/mol = -b.32 \times 10^{3} + J/kmol$
 $\dot{H}_{1} = \int G_{p} dT + (-D + \hat{H}_{m}) = -24.62 \times 10^{3} + J/kmol$
 $H_{1} = \int C_{p} dT + (-D + \hat{H}_{m}) = -24.62 \times 10^{3} + J/kmol$
 $\dot{H}_{1} = 27.4 \times -6.32 \times 10^{3} + 41.1 \times -24.62 \times 10^{3}$
 $\dot{H}_{2} = -1185.1 + J/L_{1}$

So let us write that down so reference state for this problem is glycerol liquids at 75 degree Celsius in 1 atmosphere. The components which are involved in this system are glycerol liquid and glycerol solid. So as I mentioned we have to list the different phases separately. So you would n in dot as the molar flow rate for the inlet H in cap n out dot and H cap out. So now for the inlet conditions we have only liquid glycerol coming in as 68.5 kilo mol.

And solid glycerol is not coming in through any stream and you have outlet streams where you have 27.4 kilo mol of glycerol of liquid leaving and 41.1 kilo mol of glycerol solid leaving. So now let us identify which of the enthalpy need to be calculated. Since the inlet conditions which is the liquid glycerol at 75 degree Celsius in one atmosphere has been used as the reference state.

We can have this as 0. Since we do not have any glycerol solid entering we do not have to worry about this enthalpy. However, we would have to calculate the enthalpies for both these conditions which are the outlet liquid and solid. Now the goal is to identify H1 cap and H2 cap so that we can use it for energy balance calculations. So first step is H1 cap which would be integral of Cp dT from 75 degree Celsius to 18.2 degree Celsius.

So here H1 cap is basically liquid glycerol at 75 degree Celsius in 1 atmosphere forming liquid glycerol at 18.2 degree Celsius in one atmosphere. So because of this the process is

only change in temperature phase and pressure are not changing so it is only integral Cp dT and we can calculate this as -6.32 kilo joules per mol. So since the values of molar flow rates are in kilo mol per hour we can convert this to kilo mol as well.

So you would have the value as -6.32 times 10 power 3 kilo joules per kilo mol. Now for the second enthalpy terms which is H2 cap we have 2 steps. Actually the process is liquid glycerol at 75 degree Celsius in 1 atmosphere forming solid glycerol at 18.2 degree Celsius in one atmosphere. So this would involve first the cooling of the liquid from 75 degree Celsius to 18.2 degree Celsius.

And then the solidification of the liquid glycerol at 18.2 degree Celsius to form the solid glycerol. So the first step is cooling which is 75 to 18.2 Cp dT so here only delta T happens no phase change or no change in pressure. So the next step is only phase change happening at 18.2 degree Celsius. So this would be dependent on the heat of fusion. Heat of fusion by definition is for solids to form liquids.

The change in enthalpy associated with phase change when solid actually melt to form liquid. So here we have the other way around where liquid is being solidified to form solids. So here is the freezing process which means the specific enthalpy change would be negative of heat of fusion. So this would be the total change in specific enthalpy for the process where liquid glycerol at 75 degree Celsius in 1 atmosphere is converted to solid glycerol at 18.2 degree Celsius in 1 atmosphere.

So using the values we have for Cp and delta H m cap we can calculate this to be -24.62 times 10 power 3 kilo joules per kilo mol. So please make sure the units are correct while you are performing the calculations. So now from here we can calculate delta H dot which should be basically n dot out times H cap out and the sigma of it. So we have 27.4 times – 6.32 times 10 power 3 + 41.1 times negative 24.62 times 10 power 3.

So here the inlet conditions do not have any specific enthalpy associated with them because it is the reference state. So there would not be anything to be subtracted from this. So the delta H dot value is calculated as -1185.1 kilo joules per hour. The question asks us to identify the required cooling rate which means we need to find Q dot. So for that we need to use this delta H dot in the general energy balance equation. So this being an open system.



The general energy balance equation would be Q dot-Ws dot equals delta H dot+ delta Ek dot+ Ep dot. So now no shaft work, no change in kinetic or potential energy which means Q dot equals delta H dot which we calculated as -1185.1 kilo joules per hour. We want to calculate Q dot in kilowatt which means Q dot equals -1185.1/3600 which is= -0.329 kilowatts.

So the rate of cooling that is required is 0.329 kilowatts. So because heat being removed we have negative sign associated with it. So this is one example problem to help us understand how to perform energy balance calculations. Let us look at one more problem. In the first problem we actually had a single component system where only one chemical component was present.

(Refer Slide Time: 14:58)

Example #2



Let us now look at second example problem which basically has 2 different chemical components present in the system. The problem statement is an equimolar liquid mixture of benzene and toluene at 10 degree Celsius is fed continuously to a vessel in which the mixture is heated to 50 degree Celsius. The liquid product is 40 mol% benzene and the vapor product is 68.4 mol% benzene. How much heat must be transferred to the mixture per mol of feed?

So now let us first convert this word problem into a flow sheet. So we have a system where an equimolar mixture of benzene and toluene is entering. So this means you have 0.5 mol of benzene per mol and 0.5 mol of toluene per mol which is entering. So from here you have 2 stream which are leaving one is a gas stream which is vapor phase stream and the other is liquid phase stream.

Let us call the number of mol in the vapor phase stream as nv mol and the mol in the liquid stream as nl mol. The composition for these 2 streams have been given as 68.4 mol% benzene in the vapor phase and 40 mol% benzene in the liquid phase which means the remaining 60 mol% is toluene in the liquid phase and the 31.6 mol% is toluene in the vapor phase. We have also been told to calculate the amount of heat which needs to be transferred per mol of the feed.

So this means we can use the basis of 1 mol of feed. So because of this you would have 1 mol of feed entering so we need to perform material balance calculations to identify what nv and nl are. So for any energy balance problem as I always say material balance is the first step.

(Refer Slide Time: 17:08)

Example #2



So here let us first perform the material balances. So the material balance here is reasonably simple. We have a 2 component system where there are 2 unknowns. So we can directly write the 2 equations and solve for them. So the first equation which we can write would be the total balance equation. So the total balance for this system would be 1 mol equals nv + nl. So this is the one equation nv+ nl= 1.

The second equation can be a component balance either for benzene and toluene. So I have written the balance for benzene which would be 0.5 mol of benzene entering=0.684 times nv+ 0.4 times nl. So now we have 2 equations and 2 unknowns. So we can solve these equations simultaneously to get nv= 0.352 mol and nl=0.648 mol. So these are the number of mol of the vapor and the liquid waste which are leaving the system.

So now that we have performed the material balance calculations we need to start looking at the energy balance part of the problem. So first thing we need to identify is whether the system is an open system or a closed system. Here we have flow rates which are coming in and leaving which means the system is an open system.

(Refer Slide Time: 18:40)



And our energy balance equation would become Q dot- Ws dot= delta H dot + delta Ek dot+ delta Ep dot. So as we have no change in kinetic and potential energies and there are no moving parts for associated with shaft work. You would have Q dot equals delta H dot. So we need to calculate delta H dot so that we can actually identify the rate at which heat needs to be supplied to the system. So now we need to build the enthalpy table.

For building the enthalpy table we need to have the reference states for benzene and toluene. So we will have to prepare the reference states for benzene, toluene and also account for the phases of these which means we would actually have 4 distinct components when we build the enthalpy table. We would have benzene liquid, benzene vapor, toluene liquid and toluene vapor and we need to make sure all are the listed separately while we build the table.

However, when we choose the reference state we will choose 1 reference state for each chemical component separately. So we will have 1 reference state for benzene and 1 reference state for toluene. So let us identify the reference states. Benzene and toluene we do not have any tables from which we can actually look up enthalpy data. So we can use either the inlet or the outlet conditions as the reference state.

So here I have used the inlet condition as the reference state. So benzene which is coming in as liquid at 10 degree Celsius in one atmosphere would be the reference state and toluene which is coming in as liquid at 10 degree Celsius in 1 atmosphere would be the reference state for toluene. Now that we have identified the reference state we can build the enthalpy table.

So the enthalpy table would have all the substances which would be benzene liquid, benzene vapor, toluene liquid and toluene vapor. So here you also have the flow rates which you have to write down n dot in enthalpy in would be H cap in n dot out for the outlet flow rates and H cap out for the specific enthalpies of the outlet streams. So in the inlet streams we have only benzene liquid and toluene liquid entering the system which means benzene vapor and toluene vapor do not have to be accounted for further inlet stream.

So from the mass balances which we performed at the basis we had we can identify the molar flow rates or the number of mol of benzene liquid and vapor and also the toluene liquid and vapor in the inlet and outlet streams. So we know 0.5 mol of benzene liquid and 0.5 mol of benzene and toluene liquids are actually entering into the system. So in the exit stream we need to calculate the number of mol of benzene liquid and benzene vapor.

Using the mol fraction of benzene liquid and benzene vapor provided and also the number of mol of the vapor phase and liquid phase which are entering. So we will do that. Let us first take the liquid phase. So the liquid phase exit stream which is here has 0.4 mol of benzene per mol so we have 0.4 times nl which is calculated to be 0.648 and similarly toluene would be 0.6 times 0.648.

And benzene vapor would be leaving through the vapor stream which is 0.684 the mol fraction of benzene in the vapor phase times nv which is 0.352. Similarly, the number of mol of toluene vapor would be 0.316 times 0.352. So we can calculate these values which would give us the number of mol of individual components which are entering and leaving the system.

So we now have to identify which enthalpy values have to be calculated and which go to 0 because we have used the inlet condition as the reference state so the specific enthalpy values for the inlet stream would be 0. So these terms go to 0 however we would have to calculate all these term H 1 cap H 2 cap H 3 cap and H 4 cap. So H1 cap and H3 cap we do not have any phase change happening we are only having change in temperature.

So we will first calculate these 2 because these are reasonably simple.

(Refer Slide Time: 23:19)



So we will calculate H1 cap as integral Cp dT where temperature changes from 10 degree Celsius to 50 degree Celsius. So H1 cap is for benzene liquid so we would use the Cp of benzene liquid for this calculation and for H3 cap we would have to use the Cp of toluene liquid for the calculation it would still be the integral of 10 to 50 Cp of toluene liquid dT. So we need to identify the Cp of benzene and toluene which can be obtained from any handbook or textbook.

Now for calculating H2 cap and H4 cap the reference state is liquid benzene at 10 degree Celsius and liquid toluene at 10 degree Celsius. From there it is going to vapor benzene at 50 degree Celsius and vapor toluene at 50 degree Celsius. So this means there is a phase change happening. So for this phase change to be accounted for we need to know the heat of vaporization for benzene and toluene.

However, this information would be available only at the standard boiling point for benzene and toluene at 1 atmosphere. So we first need to identify the boiling point for benzene and toluene. Let us first perform he calculation for benzene and the similar thing can be applied for toluene as well. So for benzene we first need to identify the boiling point. So boiling point of benzene when we look up a table as it can be identified as 80.1 degree Celsius.

The standard heat of vaporization of benzene at this particular temperature can be obtained from text books and handbooks. So this value would be given or represented as delta H cap v of benzene at 80.1 degree Celsius. So let us say this is available. So now our process actually does not reach 80 degree Celsius based on what is given here. However, we have the data for

enthalpy change for vaporization only at 80.1 degree Celsius.

So we will have to build a hypothetical path where benzene at reference state which is liquid at 10 degree Celsius is heated to liquid at 80.1 degree Celsius and that 80.1 degree Celsius it converts from liquid to vapor and the vapor benzene at 80.1 degree Celsius should be cooled back to 50 degree Celsius so this would be the hypothetical path.

(Refer Slide Time: 27:50)



So the hypothetical path which we would be looking to have is liquid 10 degree Celsius goes to liquid 80.1 degree Celsius and from here it goes to vapor at 50 degree vapor. So this would have 3 different enthalpy which have to be calculated. Let us call them H cap a, H cap b and H cap c. H cap b will be= standard heat of vaporization which is delta H cap v. So this would be delta H cap v.

So we can directly use the standard heat of vaporization for this step. For the other 2 steps we would have to perform integral Cp dT. So our H2 cap would be= integral 10 degree Celsius to 80.1 degree Celsius Cp of benzene liquid dT+ for the second step it is delta H cap v at 80.1 degree Celsius+ the third step which would be integral of Cp of benzene vapor dT with the limits of 80.1 degree Celsius to 50 degree Celsius.

By performing this calculation, we can calculate H2 cap to be fill to the enthalpy table. Similar to this we can build a hypothetical path for toluene as well. For this we need to know the boiling point of toluene. Using the boiling point of toluene, we can build the hypothetical path where toluene liquid is 10 degree Celsius which is the reference state gets heated to toluene liquid at the boiling point which is 110.62 degree Celsius.

And then it changes phase to become toluene vapor at the boiling point that is 110.62 degree Celsius and from there is it is cool back down to 50 degree Celsius. So the hypothetical path would be liquid 10 degree Celsius goes to liquid 110.62 degree Celsius and from here it goes to vapor at 110.62 degree Celsius and from here it finally is cooled to get your final condition which is vapor at 50 degree Celsius.

So now you have again 3 different enthalpy that have to be calculated let us call them Hx cap Hy cap and Hz cap. So this Hy cap would be= standard heat of vaporization for toluene. So that value can be used directly. So the total change in enthalpy for this particular step which is H4 cap would be= Hx cap+ Hy cap +Hz cap. So Hx cap here you have only change in temperature.

So it will be integral of Cp of toluene liquid dT from 10 degree Celsius to 110.62 degree Celsius+ delta h cap v at the standard boiling point of 110.62 degree Celsius+ integral of CP of toluene vapor dT where it is cooled from 110.62 to 50 degree Celsius. So this will give you the value for H4 cap. Using these calculations, we can get all the 4 enthalpy values. So I am not going to give you the Cp values and the standard heat of vaporization for toluene, benzene, liquid and vapors and so on.

I would want you to go and look up some tables either take your textbook and identify the appendix where you can find this information or pick up a handbook and find out what these values are and try to apply them to this equation and calculate the values. I will however give you the actual values which can be obtained for H1, H2, H3 and H4 cap and I will complete the problem using those values.

Once we perform all calculations the enthalpy table can be completed. (Refer Slide Time: 30:06)



And the enthalpy table would look like this. We would have benzene liquid, benzene vapor, toluene liquid and toluene vapor. You have inlet flow rates H cap in and outlet flow rates H cap outs. So when you fill the table it will be 0.5 you do not have anything coming in here and these values should be 0 because of the reference states. And you have 0.259 mol of benzene liquid leaving the system.

And 0.24 1 mol of benzene vapor leaving the system. Toluene liquid is leaving the system as 0.389 mol and toluene vapor is 0.111 mol leaving the system. H1 cap, H2 cap and H3 cap and H4 cap that have been calculated would be H1 cap is 5.332 all these are in kilo joules per mol and these values are in mol.

And we have toluene liquid which is leaving would have specific enthalpy of 6.340 benzene vapor which is H2 cap which we calculate it would be 37.52 kilo joules per mol and for toluene vapor it would be 42.93 kilo joules per mol. Once this table is complete we can calculate the delta H dot value so which would be here it would simply be n dot out times H cap out sigma.

So you do not have any inlet enthalpy because we have identified them to be 0. So this value can be calculated as 17.7 kilo joules. So you have Q=17.7 kilo joules. So the heat that needs to be supplied for this process is happen is 17.7 kilojoules with the basis of 1 mol of equimolar benzene, toluene mixture entering into the system. With that we have looked at some basic example that have given us an understanding of how to perform energy balance calculation.

We will perform more calculations along these lines to familiarize ourselves in the future classes as well until then thank you and good bye.