Material and Energy Balances
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Lecture - 49
Energy Balances on Nonreactive Processes with Phase Change: Tutorials - 2

Welcome to today's lecture on energy balances on nonreactive processes with phase change. So in the last lecture we performed some tutorial problems, today we will be continuing with those tutorial problems. As promised today we will be solving a system where which is a closed system. Until now the problems which we looked at have all been open systems and we have been using enthalpy.

So today we will actually look at a closed system where we will be using internal energy for performing energy balancing. Just to refresh your memory, so why do we use internal energy for closed systems and why do we use enthalpy for open systems.

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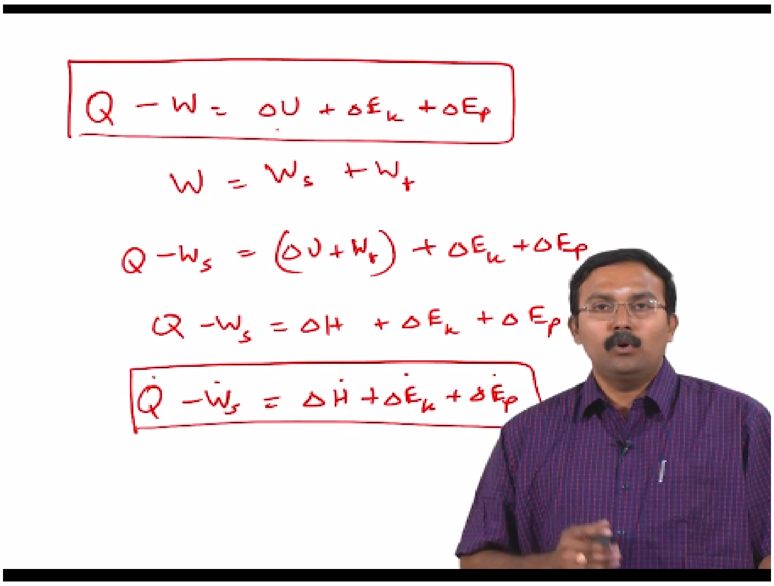

$$\boxed{Q - W = \Delta U + \Delta E_k + \Delta E_p}$$

$$W = W_s + W_f$$

$$Q - W_s = (\Delta U + W_f) + \Delta E_k + \Delta E_p$$

$$Q - W_s = \Delta H + \Delta E_k + \Delta E_p$$

$$\boxed{\dot{Q} - \dot{W}_s = \Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p}$$

If you remember the general energy balance equation, we start off with based on the first law of thermodynamics for a closed system is Q-W = delta U + delta Ek + delta Ep. So this work term which is W can have 2 different components, one is the shaft work and the other is the flow work and this shaft work is due to moving of a shaft which could be rotating something and flow work is the work associated with moving the system boundary which is the PDV work.

So the flow work is important in an open system because material is flowing in and out and therefore the flow work accounts for this equation and the equation becomes Q – Ws = delta U + Wf + delta Ek + delta Ep. As flow work can be written as PDV. So delta U + P delta v would become delta H giving you enthalpy and this would be the equation for an open system.

In an open system because there are flow rates and rates are used instead of masses or moles we would write these as Q dot – Ws dot = delta H dot + delta Ek dot + delta Ep dot. So for an open system we have been using this equation as the general energy balance equation for this reason we always calculate specific enthalpy and then the total change in enthalpy. However, today we will be looking at a closed system, so we will be using this equation.

So where you use specific internal energy instead of specific enthalpy and then finally calculate change in internal energy to understand how much heat is required. So this is applicable for closed systems at constant volume. If there are closed systems with constant pressure what you would have is a change in volume. When there is a change in volume the work term W would have either a shaft work and also it will have a work associated with moving the system boundary.

So this moving the system boundary would be the PDV work and to account for this PDV work we again have to convert the internal energy to enthalpy. So that is why when we have a closed system with constant volume we use internal energy and for a closed system with constant pressure we used enthalpy. For an open system we would always use enthalpy for energy balance calculations.

Now that we have quickly refreshed the fundamentals let us look at the tutorial problem for today.

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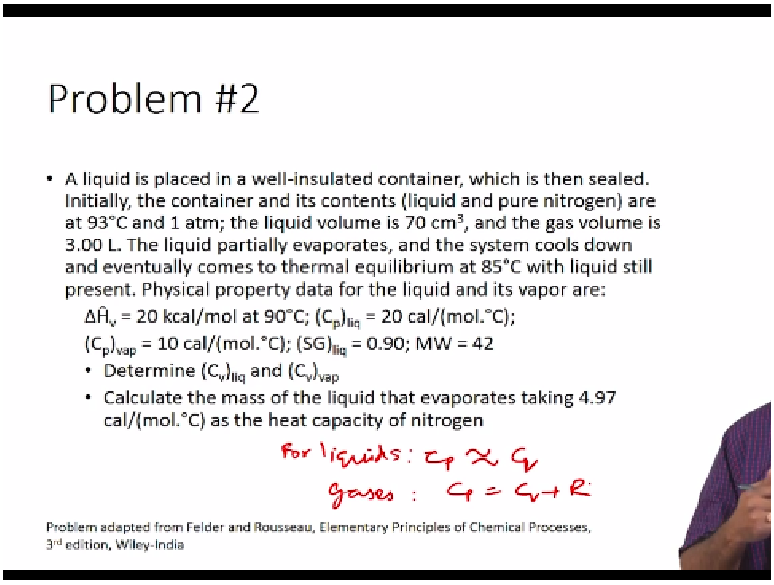

Problem #2

- A liquid is placed in a well-insulated container, which is then sealed. Initially, the container and its contents (liquid and pure nitrogen) are at 93°C and 1 atm; the liquid volume is 70 cm^3, and the gas volume is 3.00 L. The liquid partially evaporates, and the system cools down and eventually comes to thermal equilibrium at 85°C with liquid still present. Physical property data for the liquid and its vapor are:
  $\Delta\hat{H}_v$ = 20 kcal/mol at 90°C; $(C_p)_{liq}$ = 20 cal/(mol.°C); $(C_p)_{vap}$ = 10 cal/(mol.°C); $(SG)_{liq}$ = 0.90; MW = 42
  - Determine $(C_v)_{liq}$ and $(C_v)_{vap}$
  - Calculate the mass of the liquid that evaporates taking 4.97 cal/(mol.°C) as the heat capacity of nitrogen

For liquids: $C_p \approx C_v$

gases: $C_p = C_v + R$

Problem adapted from Felder and Rousseau, Elementary Principles of Chemical Processes, 3rd edition, Wiley-India

A liquid is placed in a well-insulated container which is then sealed. Initially the container and it is contents which is liquid and pure nitrogen are at 93 degree Celsius and 1 atmosphere, the liquid volume is 70 centimeter cube and the gas volume is 3 liters. The liquid partially evaporates and the system cools down and eventually comes to thermal equilibrium at 85 degree Celsius with liquid still present.

Physical property data for the liquid and it is vapour are given here. You are asked to estimate the Cv values for the liquid and the vapour and you are also asked to calculate the mass of the liquid that evaporates by assuming 4.97 calories per mole degree Celsius as the heat capacity of nitrogen. So for this problem we do not know what the liquid is, we have just been told it is a liquid.

So we will just call it as liquid A, so this liquid A is present along with nitrogen in a closed system. So it clearly states that it is placed in a well-insulated container and sealed. So this is before the process starts. So at the start of the process you have the liquid and nitrogen charge into a closed system. This is at 93 degree Celsius and 1 atmosphere pressure and after this basically some of this liquid evaporates and there is an equilibrium which is reached.

After some of the liquid evaporates you would have a gas phase which would have a mixture of nitrogen and the vapour component of this liquid A and the volume of the liquid would have come down. So now we need to perform required energy balance calculations and mineral balance calculations to identify whatever has been asked for which is finally the mass of the liquid that evaporates from the liquid which has been charged.

So before we start doing this we have also been asked to calculate the Cv terms. Why do we need Cv. As I already said for this problem being a closed system we will be looking at calculating change in internal energy. Change in internal energy can be calculated for temperature change processes as integral CvdT. So we need to know the Cv values, here in the problem we have been given the Cp values.

So we have to calculate the Cv values from the Cp values in one of the earlier lectures we have actually discussed how Cp and Cv can be correlated. For liquid Cp = Cv and this is an approximate equal and this is a good approximation to use and for ideal gases it is Cp = Cv + R. So these are the 2 correlations which we have been told. So using this we can calculate the Cv of the liquid and the vapour phase of component A.

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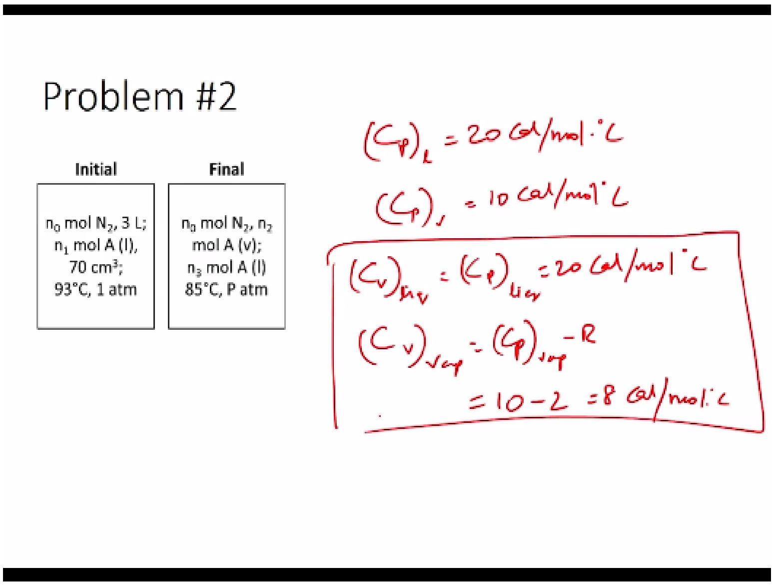

Problem #2

Initial	Final
n_0 mol N_2, 3 L; n_1 mol A (l), 70 cm^3; 93°C, 1 atm	n_0 mol N_2, n_2 mol A (v); n_3 mol A (l) 85°C, P atm

$(C_p)_L = 20$ cal/mol·°C

$(C_p)_v = 10$ cal/mol°C

$(C_v)_{liq} = (C_p)_{liq} = 20$ cal/mol°C

$(C_v)_{vap} = (C_p)_{vap} - R$

$= 10 - 2 = 8$ cal/mol°C

So Cp of liquid is given as 20 calories per mole degree Celsius and Cp of vapour phase is given as 10 calories per mole degree Celsius. Using this we can calculate Cv of the liquid component A as equal to Cp of the liquid component which is 20 calories per mole degree Celsius. Cv of the vapour phase would be equal to Cp of the vapour phase – R. So here R would be used in terms of calories per mole degree Celsius.

So which means it would be roughly 2 calories per mole degree Celsius. Using that we would have 10 - 2 = 8 calories per mole degree Celsius. So this would be the Cv value for vapour. So with this we have the Cv for the liquid and the vapour which is the first part of the problem. For the second part of the problem we have to do the required material balance calculations. So first thing we know is there are n0 moles of nitrogen and n1 moles of component A present in the initial condition.

So out of this n1 moles for some of the liquid A evaporate, so let us assume n2 moles of A has evaporated and mixed with n0 moles of nitrogen in the gas phase and you have liquid component of A as n3 moles. So we need to calculate what n0, n1 and n2 are to identify how much has actually been evaporated.

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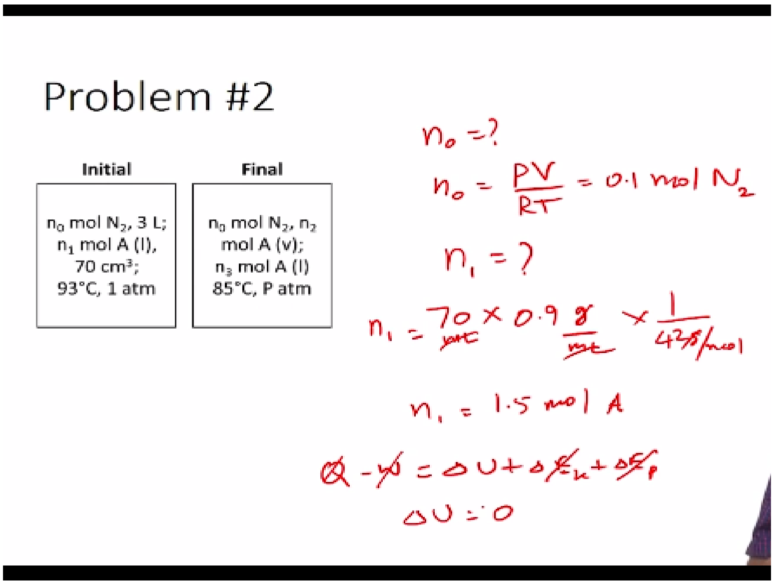

Problem #2

Initial	Final
n_0 mol N_2, 3 L; n_1 mol A (l), 70 cm³; 93°C, 1 atm	n_0 mol N_2, n_2 mol A (v); n_3 mol A (l) 85°C, P atm

$n_0 = ?$

$$n_0 = \frac{PV}{RT} = 0.1 \text{ mol } N_2$$

$n_1 = ?$

$$n_1 = \underset{\cancel{cm^3}}{70} \times 0.9 \frac{g}{\cancel{cm^3}} \times \frac{1}{42 g/mol}$$

$$n_1 = 1.5 \text{ mol } A$$

$$\cancel{Q} - \cancel{W} = \Delta U + \Delta \cancel{E_k} + \Delta \cancel{E_p}$$

$$\Delta U = 0$$

First to calculate n0 moles we have to use the ideal gas law. Assuming ideal gas behaviour for nitrogen we can calculate n0 as PV/RT. So we have been told that the condition, the temperature conditions is 93 degree Celsius, so which means the temperature T would be 93 + 273 Kelvin and you have volume as 3 liters and R would be 8.314 and P pressure is 1 atmosphere.

Applying all this we will be calculate n0 as 0.1 moles of nitrogen. So this would be the number of moles of nitrogen which is present in the initial condition and also in the final condition, so both are n0 moles. We now have to calculate the number of moles of component A which is present in the liquid form in the initial condition which is n1 moles. So to calculate n1 moles we have the volume and we have also been given the density of component A.

So using that we can convert it into mass and we have the molecular weight of the component A, so from because of that we can calculate the number of moles of component A. So let us first calculate the mass as volume times density 0.9 grams per mL. So this is 70 mL and we have the molecular weight is 42 grams per mole so we would have this dividing it by molecular weight we would be able to calculate the total number of moles.

So mL gets cancelled, grams get cancelled and we end up with number of moles. So n1 = 1.5 moles of A. So the total number of moles of component A present in the liquid component would be 1.5 moles at the initial condition. Some of this gets evaporated to form vapour phase in the final condition. To find out how much has evaporated we would not be able to use any material balances because the material balances would all be trivial.

So instead we could perform energy balances to calculate the amount of component A which has evaporated. So how would we go about doing that? First thing would be to identify whether this is an open system or a closed system, as I have been telling from the beginning of this lecture so we are looking at a closed system. So we will be using internal energy in the energy balance equation.

So the energy balance equation becomes Q-W = delta U + delta Ek + delta Ep. So here there are no moving parts. So W would go to 0, you have Ek and Ep going to 0 because there are no change in kinetic and potential energies. So you will be left with Q = delta U. In addition to the general cancellations which we have done the problem also states that the system is well insulated which means there is no heat being transferred from the system to the surrounds or vice versa.

This would imply Q is also equal to 0. So the equation then becomes delta U = 0. Now by building a specific internal energy table we will be able to calculate the number of moles of component A in the liquid and the vapour phase in the final condition. Let us go ahead and do that. To build this internal energy table we first need to identify the reference states. We can either use the initial condition or the final condition as the reference states. So here for the calculations I have used the final conditions as the reference state.

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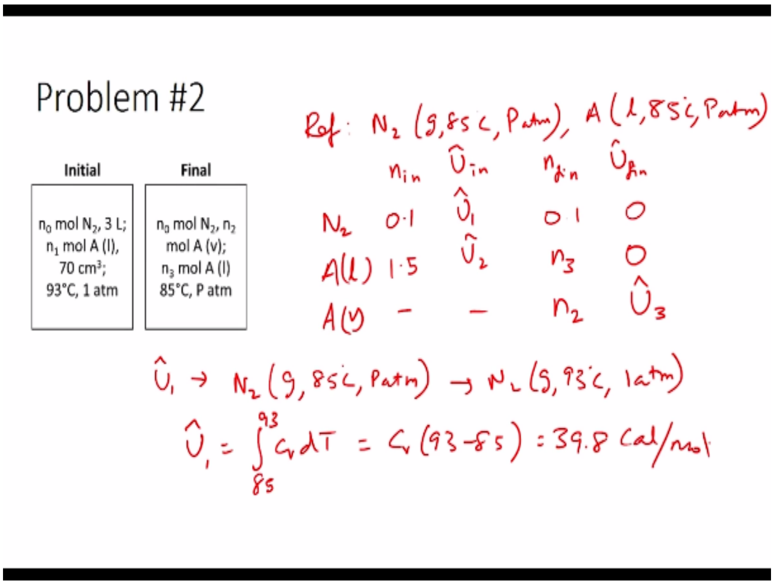

Problem #2

Initial	Final
n_0 mol N_2, 3 L; n_1 mol A (l), 70 cm^3; 93°C, 1 atm	n_0 mol N_2, n_2 mol A (v); n_3 mol A (l) 85°C, P atm

Ref: N_2 (g, 85 c, Patm), A (l, 85 c, Patm)

	n_{in}	$\hat{U}_{in}$	n_{fin}	$\hat{U}_{fin}$
N_2	0.1	$\hat{U}_1$	0.1	0
A(l)	1.5	$\hat{U}_2$	n_3	0
A(v)	–	–	n_2	$\hat{U}_3$

$$\hat{U}_1 \rightarrow N_2(g, 85c, Patm) \rightarrow N_2(g, 93c, 1atm)$$

$$\hat{U}_1 = \int_{85}^{93} C_v\,dT = C_v(93-85) = 39.8\ Cal/mol$$

So the reference states used are nitrogen gas 85 degree Celsius and pressure P atmospheres and you also have component A, I am assuming the liquid phase of the final condition which is liquid phase 85 degree Celsius P atmosphere as the reference state. So here I am taking P atmospheres which is the final condition as the reference state. We have the final condition as pressure as P atmospheres. So pressure P atmospheres to the initial condition pressure 1 atmosphere indicates that there is a change in pressure.

However, because we are going to assume ideal gas behaviour and we have a liquid as the other component we can ignore change in internal energy due to change in such small pressures. So because of this we will assume that pressure has no effect on our calculations and we will only look at change in temperature and change in phase. So using that assumption let us build the internal energy table.

So the components would be nitrogen, component A as liquid phase and component A as vapour phase. As I had already mentioned we should always list out components of different phases separately while we are writing these enthalpy or internal energy tables for phase change operations. In this table you have n initial and U cap initial. So instead of enthalpy we are using internal energy and you have n final and U cap final.

So which would be the specific internal energy for the final condition. So we have 0.1 moles of nitrogen in the initial and the final system and we have 1.5 moles of component A present in the liquid form in the initial system. We have n3 moles of liquid component A in the final system and N2 moles of vapour component A in the final system. We do not have any vapour component A in the initial system.

Now that we have this we have to identify which specific internal energies have to be calculated. So for the final condition which is gas 85 degree Celsius and pressure of P atmospheres the nitrogen would have 0 internal energy compared to the reference state. Similarly, A which is liquid 85 degree Celsius in P atmospheres would also have 0 in specific internal energy change from the reference state.

However, the final condition for A vapour would have an internal energy that needs to be calculated and similarly you would have internal energies for these 2 terms that have to be calculated. So we are calling them U1 cap, U2 cap and U3 cap. So we need to account for U1 cap, U2 cap and U3 cap. So U1 cap is basically change in temperature for nitrogen gas from 93 degree Celsius to 85 degree Celsius.

So it is nitrogen, so this is U1 cap. So U1 cap is basically nitrogen gas at 85 degree Celsius and P atmospheres going to nitrogen gas 93 degree Celsius and 1 atmosphere. So assuming that pressure has no effect you would end up with only change in temperature so this means U1 cap would be equal to integral CvdT with the limits of 85 degree Celsius to 93 degree Celsius and this can be calculated for nitrogen and we would be able to get this value as Cv times 93 – 85 which is equal to 39.8 calories per mole.

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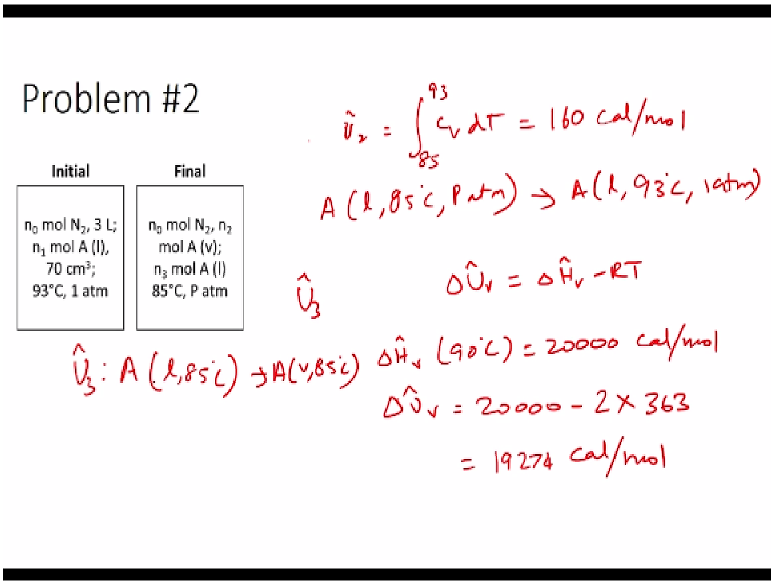

Problem #2

Initial	Final
n_0 mol N_2, 3 L; n_1 mol A (l), 70 cm^3; 93°C, 1 atm	n_0 mol N_2, n_2 mol A (v); n_3 mol A (l) 85°C, P atm

$$\hat{U}_2 = \int_{85}^{93} C_v\, dT = 160\ \text{cal/mol}$$

$$A(l, 85^\circ C, P\,atm) \rightarrow A(l, 93^\circ C, 1\,atm)$$

$$\hat{U}_3$$

$$\Delta\hat{U}_v = \Delta\hat{H}_v - RT$$

$$\hat{U}_3 : A(l, 85^\circ C) \rightarrow A(v, 85^\circ C)$$

$$\Delta\hat{H}_v\,(90^\circ C) = 20000\ \text{cal/mol}$$

$$\Delta\hat{U}_v = 20000 - 2 \times 363$$

$$= 19274\ \text{cal/mol}$$

So similarly we can calculate U2 cap as integral CvdT. So again here it is only a process where component A which is in liquid phase 85 degree Celsius and P atmosphere which is the reference state goes to A as liquid at 93 degree Celsius and 1 atmosphere. Again ignoring the effect of pressure the process is only change in temperature, so going from 85 to 93. So we already calculated the CV for the liquid component A using that we would be able to use and calculate the change in internal energy U2 cap for this process.

So this would be 160 calories per mole. Now the third component which is U3 cap is where you have the phase change also. So what information do we have. In the problem we have been given delta H cap v, which is the enthalpy change associated with vaporisation. Here we need to calculate the internal energy change associated with vaporisation. If you remember we have looked at this and we have identified this as delta H cap v would be equal to delta U cap – Rt.

If you look at the problem the problem gives you delta H cap v which is the enthalpy change associated with vaporization; however, in this calculations we are using internal energy. So we need to find out what would be the internal energy change associated with the vaporization process. So we have already looked at what the difference would be how we can actually calculate delta U cap V from delta H cap V in the introduction lectures.

So how would we do that, the correlation between delta U cap v and delta H cap v would be similar to the correlation you have for delta H cap and delta U cap. So you would have the PDVP delta V term and assuming ideal gas behaviour we would be able to convert it into RT term. So this would mean that your delta U cap v would be equal to delta H cap V – Rt. So you can calculate delta U cap v as delta H cap v – RT where T would be the temperature at which the phase change happens.

In this problem we have been given delta H cap v at 90 degree Celsius = 20,000 calories per mole and we can use this and calculate delta U cap v and perform calculations. So your delta U cap v would be equal to this 20,000 – R in terms of calories would be 2 times temperature which would be 90 degree Celsius or 363 Kelvin. So this value would be 19,274 calories per mole.

To calculate change in internal energy U cap 3 we would have to assume the process where component A basically goes from the reference state which is liquid 85 degree Celsius to A which is vapour at 85 degree Celsius. So for this we would have to build a hypothetical path. We have only phase change happening; however, we do not know the change in internal energy or enthalpy for the phase change at 85 degree Celsius.

We know that only for 90 degree Celsius. So we need to build a hypothetical path where the phase change happens at 90 degree Celsius.

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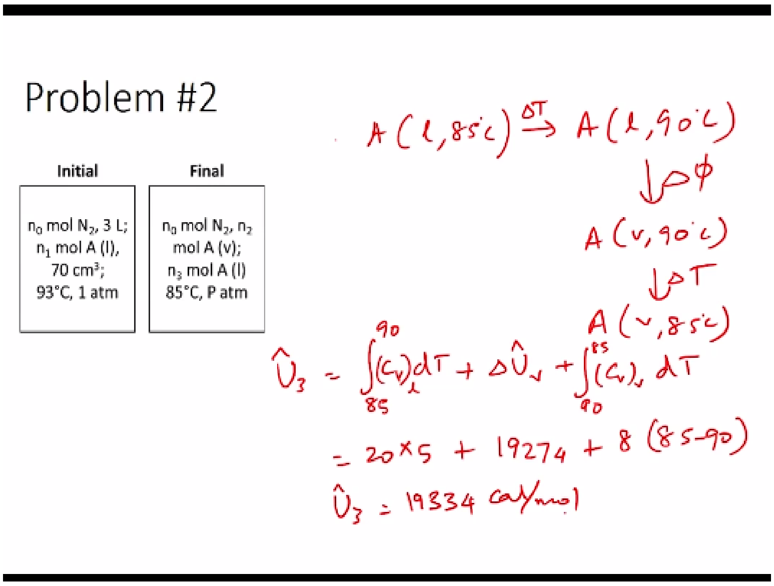

Problem #2

Initial	Final
n_0 mol N_2, 3 L; n_1 mol A (l), 70 cm³; 93°C, 1 atm	n_0 mol N_2, n_2 mol A (v); n_3 mol A (l) 85°C, P atm

$$A(l, 85°C) \xrightarrow{\Delta T} A(l, 90°C)$$

$$\downarrow \Delta\phi$$

$$A(v, 90°C)$$

$$\downarrow \Delta T$$

$$A(v, 85°C)$$

$$\hat{U}_3 = \int_{85}^{90} (C_v)_l \, dT + \Delta\hat{U}_v + \int_{90}^{85} (C_v)_v \, dT$$

$$= 20 \times 5 + 19274 + 8\,(85-90)$$

$$\hat{U}_3 = 19334 \text{ cal/mol}$$

So that would mean the process would be A which is liquid at 85 degree Celsius goes to A as liquid at 90 degree Celsius from here it goes to A as vapour at 90 degree Celsius and from here it goes to A as vapour at 85 degree Celsius. Again I am ignoring the effect of pressure for doing these calculations. So we have 3 different internal energy changes one with delta T, other with change in phase and the last one with again change in temperature.

So here we will be using the Cv for liquid for initial calculation and Cv for the vapour for the second calculations. So your U3 cap would be equal to integral CvdT from 85 to 90 where here you are using the Cv of liquid + delta U cap v where the phase change from liquid to vapour is happening + integral 90 to 85 Cv of vapour dT. So Cv of liquid was identified to be 20 calories per mole degree Celsius times 5.

So 20 times 5 + the change in internal energy was 19,274 + here you would have Cv as 8 times 85 – 90 which is -5. So this U3 cap would be equal to 19,334 calories per mole. These values can be plugged back into the specific internal energy table which we prepared and we can calculate the total change in internal energy and fit it back into the general energy balance equation which states delta U = 0.

So using that we would have a correlation which would have 1 unknown which would be the number of moles of vapour component of A in the final condition. So n2 would be the only this which we need to calculate from here.

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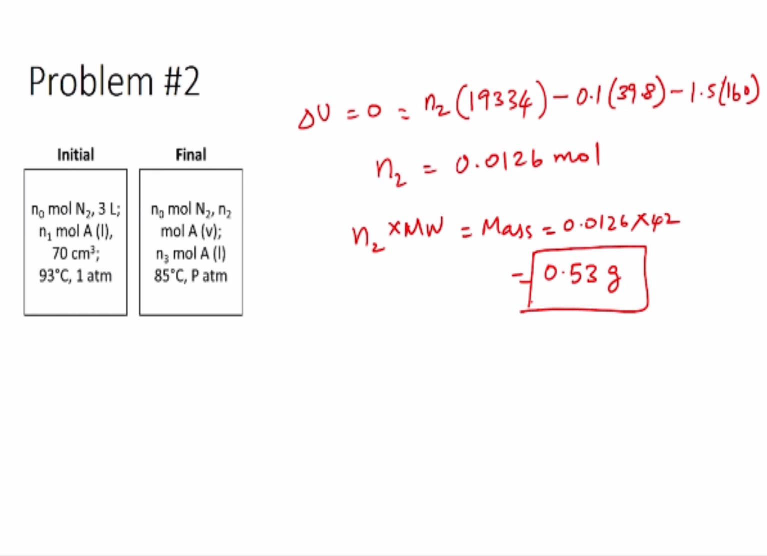

Problem #2

Initial	Final
n_0 mol N_2, 3 L; n_1 mol A (l), 70 cm^3; 93°C, 1 atm	n_0 mol N_2, n_2 mol A (v); n_3 mol A (l) 85°C, P atm

$$\Delta U = 0 = n_2(19334) - 0.1(39.8) - 1.5(160)$$

$$n_2 = 0.0126 \text{ mol}$$

$$n_2 \times MW = Mass = 0.0126 \times 42$$

$$= \boxed{0.53 \text{ g}}$$

So what we would do is the equation delta U = 0 which would be equal to final minus initial. So final would be n2 times 19,334 – initial which is 0.1 times 39.8 – 1.5 times 160 and this would give us an equation for n2 and from here we can calculate n2 as 0.0126 moles. So this means 0.0126 moles of the initial liquid component A has evaporated and this would be the amount which has entered into the gas phase in the final state.

So which this we have performed the required energy and material balance calculations to find out all the components that have been asked for. So this number of moles can also be converted to mass because we have been asked to calculate the mass of liquid which has been evaporated. So n2 times the molecular weight would give you the mass which is equal to 0.0126 * 42 giving you a value of 0.53 grams. So 0.53 grams has actually evaporated.

So which this we come to the conclusion of this tutorial session. So in the next lecture we will look at something called psychrometric charts. So just like how we use steam tables there are charts which can be used for 2 component systems and psychrometric charts are basically humidity charts where you have 2 components and the information related to specific enthalpy and other things like humidity so on can actually be obtained from these charts. We will look at how to use these psychrometric charts in the next lecture. Thank you.