Material and Energy Balances
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Lecture - 66
Energy Balances: A Review - Part 3

Welcome back to the review lectures for energy balances. We have looked at all the fundamentals associated with energy balances and in the last lecture, we actually performed a multiunit process where energy balances were performed for a phase change operation. Today we will start performing another energy balance calculation. Here we will actually be looking at a process where there is a reaction.

So we will be looking to perform a simple energy balance calculation for a system with a reaction. However, we will also see how it would be applicable for a closed system and we will look at different aspects associated with energy balances for a reactive process while we solve this example problem.

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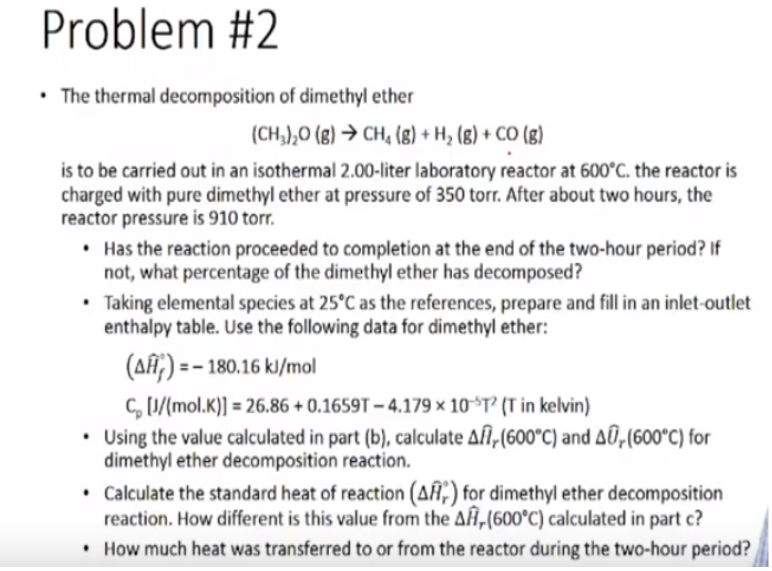

Problem #2

- The thermal decomposition of dimethyl ether

$$(CH_3)_2O\ (g) \rightarrow CH_4\ (g) + H_2\ (g) + CO\ (g)$$

is to be carried out in an isothermal 2.00-liter laboratory reactor at 600°C. the reactor is charged with pure dimethyl ether at pressure of 350 torr. After about two hours, the reactor pressure is 910 torr.

  - Has the reaction proceeded to completion at the end of the two-hour period? If not, what percentage of the dimethyl ether has decomposed?
  - Taking elemental species at 25°C as the references, prepare and fill in an inlet-outlet enthalpy table. Use the following data for dimethyl ether:

    $(\Delta\hat{H}_f^\circ) = -180.16$ kJ/mol

    C_p [J/(mol.K)] $= 26.86 + 0.1659T - 4.179 \times 10^{-5}T^2$ (T in kelvin)
  - Using the value calculated in part (b), calculate $\Delta\hat{H}_r(600°C)$ and $\Delta\hat{U}_r(600°C)$ for dimethyl ether decomposition reaction.
  - Calculate the standard heat of reaction $(\Delta\hat{H}_r^\circ)$ for dimethyl ether decomposition reaction. How different is this value from the $\Delta\hat{H}_r(600°C)$ calculated in part c?
  - How much heat was transferred to or from the reactor during the two-hour period?

So here is the problem. The thermal decomposition of dimethyl ether which is shown here is, dimethyl ether forms methane, hydrogen, and carbon monoxide, is to be carried out in an isothermal 2 liter laboratory reactor at 600 degree Celsius. The reactor is charged with pure dimethyl ether at a pressure of 350 torr. After about 2 hours, the reactor pressure is 910 torr. Has the reaction proceeded to completion at the end of the 2-hour period?

If not, what percentage of the dimethyl ether has actually decomposed? Taking elemental species at 25 degree Celsius as the reference state prepare and fill an inlet and outlet enthalpy table use the following data for dimethyl ether. Heat of formation for dimethyl ether is -180.16 kJ/mol. C p for dimethyl ether is in terms of kJ/mol K is given as 26.86 + 0.1659T - 4.179 times 10 power -5T square and temperature here is in Kelvin. So this is to be taken carefully.

So if you have the T value temperature value in Kelvin you should appropriately use the right units for the C p value. Using the value calculated in part B, you are asked to calculate delta H r cap at 600 degree Celsius and delta U r cap for dimethyl ether decomposition reaction. You are also asked to calculate the standard heat of reaction for dimethyl ether reaction and you are asked to calculate how different this value is from the heat of reaction at 600 degree Celsius that was calculated in the previous part. How much heat was transferred to or from the reactor during the 2-hour period?

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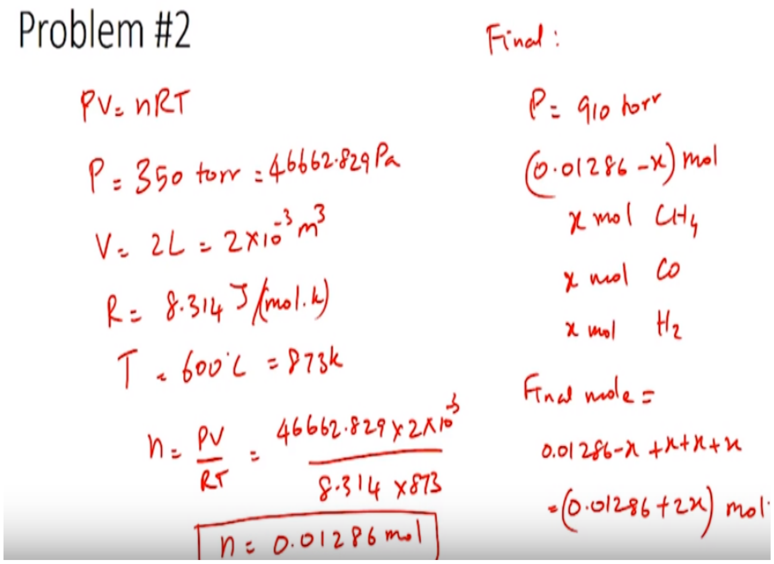

Problem #2

$PV = nRT$

$P = 350 \text{ torr} = 46662.829 \text{ Pa}$

$V = 2L = 2\times10^{-3} m^3$

$R = 8.314 \text{ J}/(\text{mol.k})$

$T = 600^\circ C = 873k$

$n = \frac{PV}{RT} = \frac{46662.829\times2\times10^{-3}}{8.314\times873}$

$\boxed{n = 0.01286 \text{ mol}}$

Final:

$P = 910 \text{ torr}$

$(0.01286 - x) \text{ mol}$

$x \text{ mol } CH_4$

$x \text{ mol } CO$

$x \text{ mol } H_2$

Final mole =

$0.01286 - x + x + x + x$

$= (0.01286 + 2x) \text{ mol}$

So now, let us look at this problem. So here in this problem, we actually have been given the initial and final pressure conditions for a closed system and we have been asked to calculate what would be the conversion in this process. So how would we do that? So assuming ideal gas behavior, we will be able to calculate the number of moles which is present initially and finally and from that we should be able to arrive at what would be the conversion which we are looking at. Let us try and do that.

Assuming ideal gas behavior we have PV = nRT as the ideal gas law. So pressure has been given as the initial condition as 350 torr. So this can be converted to SI units which is Pascal and you would get 46662.829 Pa. So 1 torr = 133.3 Pa. So using that roughly you will be able to get this value. And V which is volume is 2 L which can then be written as 2 times 10 power -3 meter cube. So I am converting everything to SI unit so that it will be easy to use the R value directly.

R is 8.314 J/mol K and you have temperature T which is 600 degree Celsius and in SI units it would be 873 K. So you can substitute these values to the equation ideal gas law and you will have n = PV/RT which = 46662.829 times 2 times 10 power -3 divided by 8.314 times 873 and you would end up with a value for n as 0.01286 moles. So that is the initial number of moles in the system.

So the final condition has been given as, the values we have done is for initial condition. So for final condition, we know that the pressure is 910 torr. So if we were to assume that x moles of dimethyl ether which was initially given is consumed so we have 0.1286 moles of dimethyl ether initially if we assume x moles of that actually was consumed, the final state would actually contain 0.01286 – x moles of dimethyl ether, right?

So this would be the number of moles of dimethyl ether. Looking at the stoichiometry, we know that for every mole of dimethyl ether consumed you would have 1 mole of methane, hydrogen and carbon monoxide produced. So if x moles of dimethyl ether is consumed, you will have x moles of methane, x moles of carbon monoxide and x moles of hydrogen present in the system after the reaction is completed.

So this would that the final number of moles, final moles would actually be = 0.01286 – x + x + x + x which is = 0.01286 + 2x number of moles. So this would be the number of moles in the final condition. So now, we need to calculate what x is for us to know what would be the conversion in this process.

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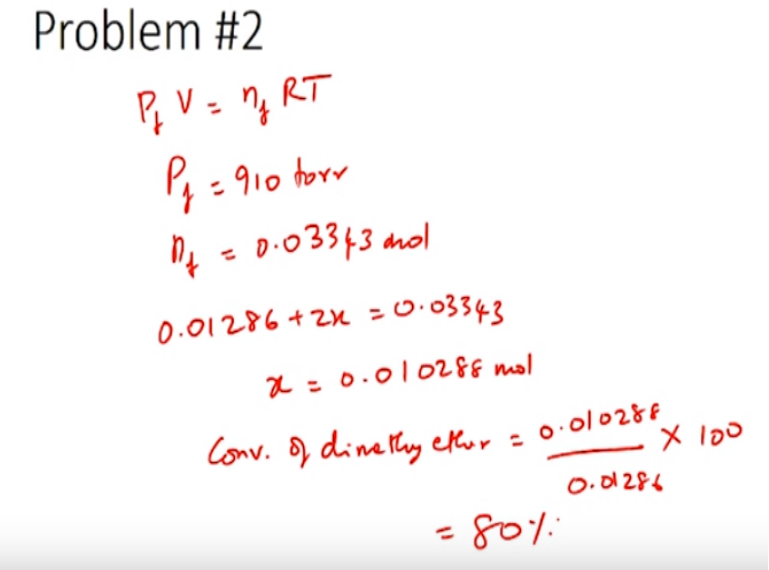

Problem #2

$P_f V = n_f RT$

$P_f = 910$ torr

$n_f = 0.03343$ mol

$0.01286 + 2x = 0.03343$

$x = 0.010288$ mol

Conv. of dimethyl ether $= \frac{0.010288}{0.01286} \times 100$

$= 80\%$

Using the ideal gas law, we would actually be able to identify the final number of moles and from there we can actually calculate what x is so that we can get the conversion for this process. So what we would have is P final V = n final RT. So here volume is constant because it is a constant volume vessel of 2 liter volume and temperature is also a constant because we have been told that it is an isothermal process.

So we can calculate n f from here and we know the final pressure P final is 910 torr. So we convert this to Pascal and from there we will be able to calculate the final number of moles which would be n final would be equal to 0.03343 moles. So from here we can calculate x. We know that n final was = 0.01286 + 2x based on stoichiometry. This = 0.03343. So x would be = 0.010288 moles.

So this x is the number of moles of dimethyl ether which has actually been consumed. So conversion of dimethyl ether would be equal to 0.010288/0.01286 which is the number of moles of dimethyl ether consumed divided by the number of moles of dimethyl ether fed times 100 which would be = 80%. So 80% of dimethyl ether which is fed is actually consumed in this process which means the reaction is actually not going to completion. Only 80% of the reactant is getting converted.

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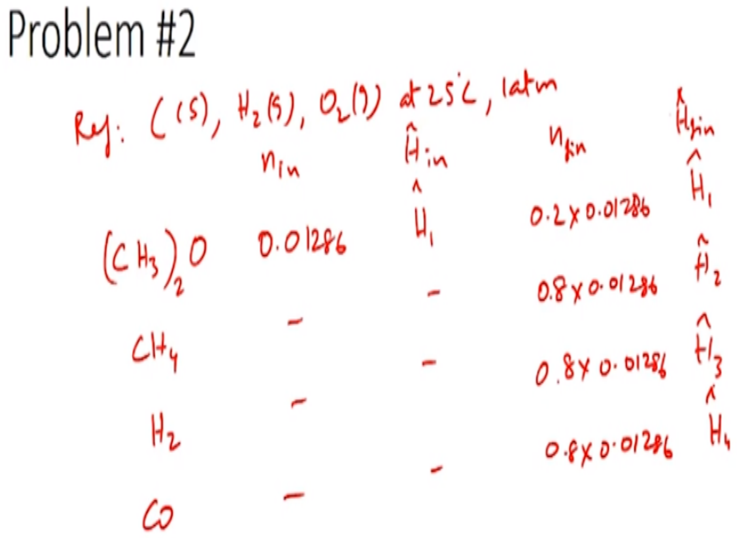

Problem #2

Ref: $C(s)$, $H_2(g)$, $O_2(g)$ at 25°C, 1atm

	n_{in}	$\hat{H}_{in}$	n_{fin}	$\hat{H}_{fin}$
$(CH_3)_2O$	0.01286	$\hat{H}_1$	0.2×0.01286	$\hat{H}_1$
CH_4	–	–	0.8×0.01286	$\hat{H}_2$
H_2	–	–	0.8×0.01286	$\hat{H}_3$
CO	–	–	0.8×0.01286	$\hat{H}_4$

In the second part of the problem, we have been asked to build the enthalpy table by assuming elements at 25 degree Celsius and 1 atmosphere as the reference state. So let us try to do that. So this would be the heat of formation technique for calculating energy balances if you were to perform that. So here we are only asked to build the table and complete the table. So let us do that.

So the reference state would be carbon solid, hydrogen gas, and oxygen gas all at 25 degree Celsius and 1 atmosphere. So this is the reference state. So assuming ideal gas behavior we will not have to worry about change in pressure. So we will only use the temperature effect on enthalpies. So the substances which we have are dimethyl ether, so CH3 2 O, then you have methane and hydrogen and carbon monoxide which are all present in the system.

So n initial and you have H cap initial, n final and H cap final. So we need to build this table and complete this table. So as far as the number of moles of dimethyl ether fed you have it as 0.01286. Number of moles of dimethyl ether which is remaining would be 0.2 times 0.01 286. So based on stoichiometry, the number of moles of methane fed would be equal to the number of moles of dimethyl ether consumed which would be 0.8 times 0.01286.

And this would also be the same would be the values for hydrogen and carbon monoxide as well. So it will be 0.8 times 0.01286, 0.8 times 0.01286. So you do not have any methane, hydrogen, or carbon monoxide in the initial condition. In the initial and final condition, we now need to identify which enthalpies will go to 0 and which enthalpies have to be accounted for. So let us say we have to identify H 1 cap for dimethyl ether.

So dimethyl ether initial condition is at a temperature of 600 degree Celsius and you are going to have the reference states as carbon, hydrogen, and oxygen at 25 degree Celsius and 1 atmosphere. So there is definitely a change in enthalpy here. So what about the dimethyl ether enthalpy for the final condition? So here the pressure is different.

However, the temperature is still the same because it is an isothermal process which means the enthalpy would still be the same because we are going to ignore the effect of pressure for an ideal gas and we are assuming gas we will ignore the effect on pressure. So you will be left with the same value of enthalpy for dimethyl ether for the initial and final condition. We need to calculate the enthalpies for methane, hydrogen, and oxygen for the final conditions as well. Now, let us go ahead and calculate these values H 1 cap, H 2 cap, H 3 cap, and H 4 cap.

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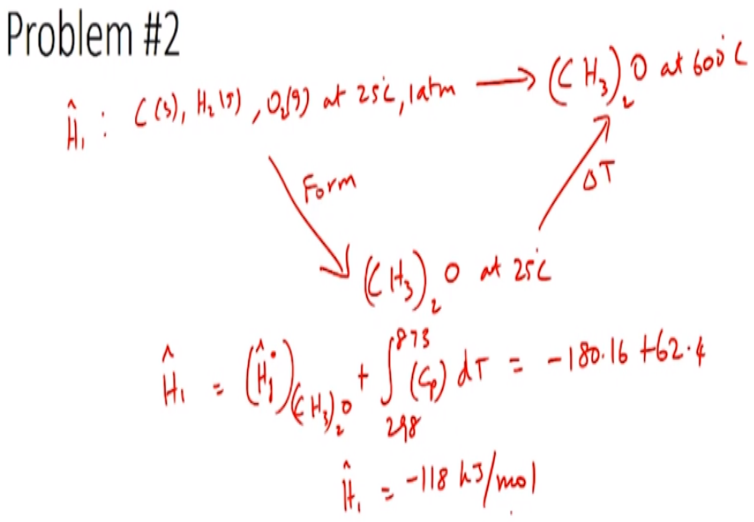

Problem #2

$$\begin{tikzcd}
\hat{H}_1 : C(s), H_2(g), O_2(g) \text{ at } 25^\circ C, 1\text{atm} \arrow[rr] \arrow[dr, "\text{Form}"] & & (CH_3)_2O \text{ at } 600^\circ C \\
& (CH_3)_2O \text{ at } 25^\circ C \arrow[ur, "\Delta T"'] &
\end{tikzcd}$$

$$\hat{H}_1 = (\hat{H}_f^\circ)_{(CH_3)_2O} + \int_{298}^{873} (C_p)\, dT = -180.16 + 62.4$$

$$\hat{H}_1 = -118 \text{ kJ/mol}$$

So what is H 1 cap? So H 1 cap is nothing but the process where you first have the reference state which is carbon solid, hydrogen gas, and oxygen gas at 25 degree Celsius and 1 atmosphere forming dimethyl ether at 600 degree Celsius which is the initial condition and let us look at this so you have to consider this as a single step process so which means we have to build a hypothetical path to identify the change in enthalpy because you have formation happening.

And we need to identify change in temperature as well. So this can be broken down into 2 steps. The first step would be the formation of dimethyl ether. So CH3 2 O at 25 degree Celsius and from here it can be heated to 600 degree Celsius. The first step is the formation reaction and the second step is the change in temperature. So this means H 1 cap would be equal to the standard heat of formation for dimethyl ether + integral 298 to 873 C p of dimethyl ether dT.

So I am using 298 and 873 because the C p value which has been given to us in the problem had stated that the temperature used in the C p value is in Kelvin. So I am using the temperature value in Kelvin. So if you were to substitute the values for heat of formation and the C p values, we would actually get -180.16 + 62.4 giving H 1 cap as -118 kJ/mol. So this is H 1 cap.

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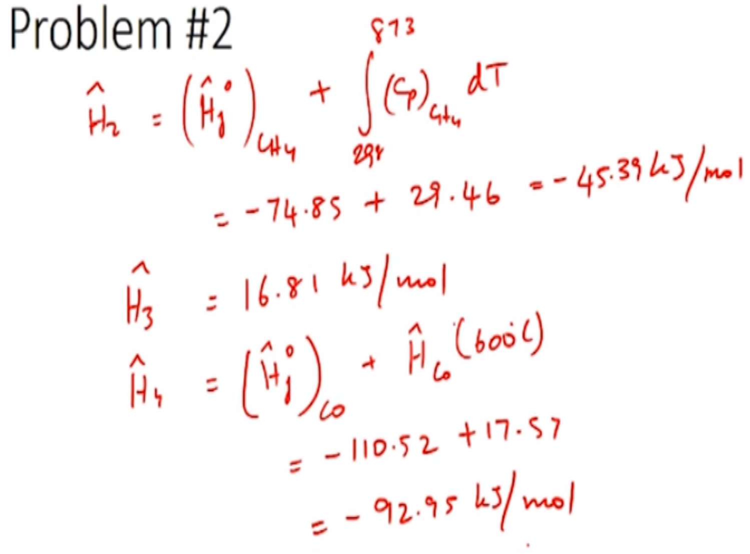

Problem #2

$$\hat{H}_2 = (\hat{H}_f^\circ)_{CH_4} + \int_{298}^{873} (C_p)_{CH_4}\, dT$$

$$= -74.85 + 29.46 = -45.39\ kJ/mol$$

$$\hat{H}_3 = 16.81\ kJ/mol$$

$$\hat{H}_4 = (\hat{H}_f^\circ)_{CO} + \hat{H}_{CO}(600^\circ C)$$

$$= -110.52 + 17.57$$

$$= -92.95\ kJ/mol$$

Now let us look at H 2 cap. So H 2 cap is basically again a similar thing where you have the first step which is the heat of formation, the formation of methane from carbon and hydrogen gases. Carbon solid and hydrogen gas. So now you have heat of formation, standard heat of formation as the first step. So heat of formation of methane + integral C p of methane dT and the temperature again would increase from 298 K to 873 K.

So using the C p value for methane from the tables and the heat of formation for methane, we can actually calculate this as -74.85 + 29.46 giving a value of -45.39 kJ/mol. So H 3 cap can actually be obtained directly from the tables which are available for combustion gases. So you have hydrogen gas which is present in the final condition at 600 degree Celsius. So taking that from the reference state you can actually calculate this and this value would be 16.81 kJ/mol.

And H 4 cap, here again you have carbon monoxide formation and then heating of carbon monoxide. So the first step would be the heat of formation of carbon monoxide and in the second step we do not have to do integral C p dT. We would be able to get the enthalpy value for carbon monoxide with reference to 25 degree Celsius from the combustion gases table. So you have H cap CO at 600 degree Celsius and this would be = -110.52 + 17.57 giving -92.95 kJ/mol. So now we have all the enthalpies and we can fill the enthalpy table.

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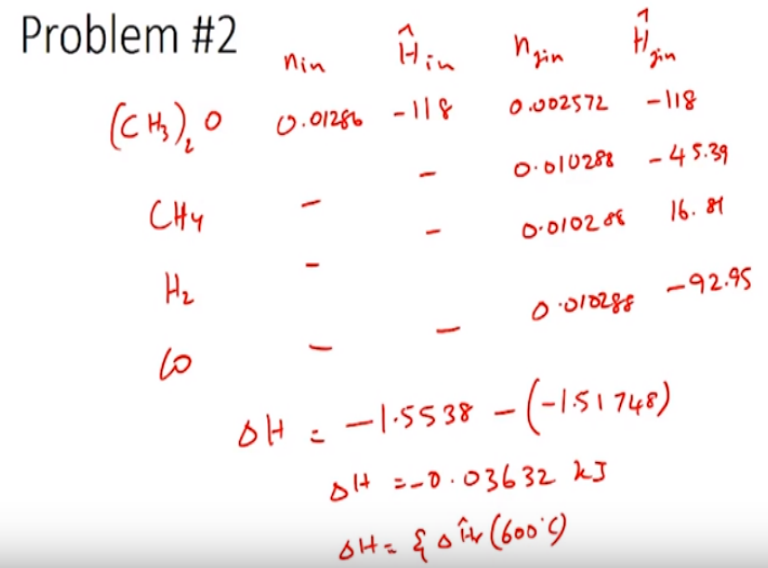

Problem #2

	n_{in}	$\hat{H}_{in}$	n_{fin}	$\hat{H}_{fin}$
$(CH_3)_2O$	0.01286	-118	0.002572	-118
CH_4	–	–	0.010288	-45.39
H_2	–	–	0.010288	16.81
CO	–	–	0.010288	-92.95

$$\Delta H = -1.5538 - (-1.51748)$$

$$\Delta H = -0.03632 \text{ kJ}$$

$$\Delta H = \xi \Delta \hat{H}_r (600°C)$$

Substituting the values we obtained into the enthalpy table, we would have dimethyl ether, methane, hydrogen, and carbon monoxide. We will have to fill in n initial, H cap initial, n final, and H cap final and from here we would have 0.01286 and zeroes here with 0.002572, 0.010288, 0.010288, 0.010288. So enthalpy would be -118, -118, -45.39, 16.81, -92.95, and with this the enthalpy table is complete.

So for the third part of the problem we have been asked to calculate the heat of reaction at 600 degree Celsius using this table. So how would we do that? So we can actually calculate delta H from this and if we have the extent of reaction, we have always been using extent of reaction times heat of reaction as the change in enthalpy for the process whereas now we will do the other way. We will actually calculate heat of reaction from that equation.

So we will calculate delta H from here. So delta H will actually be, from this table you can actually calculate the enthalpy of the final condition minus the enthalpy of the initial condition. The final condition enthalpy is -1.5538 and enthalpy of the initial condition would be – (-1.51748). So giving you a delta H of -0.03632 kJ and we need to now have the extent of reaction if we want to calculate the heat of reaction because delta H is also equal to psi delta H r at 600 degree Celsius. So now we need to know the value for psi which is the extent of reaction.

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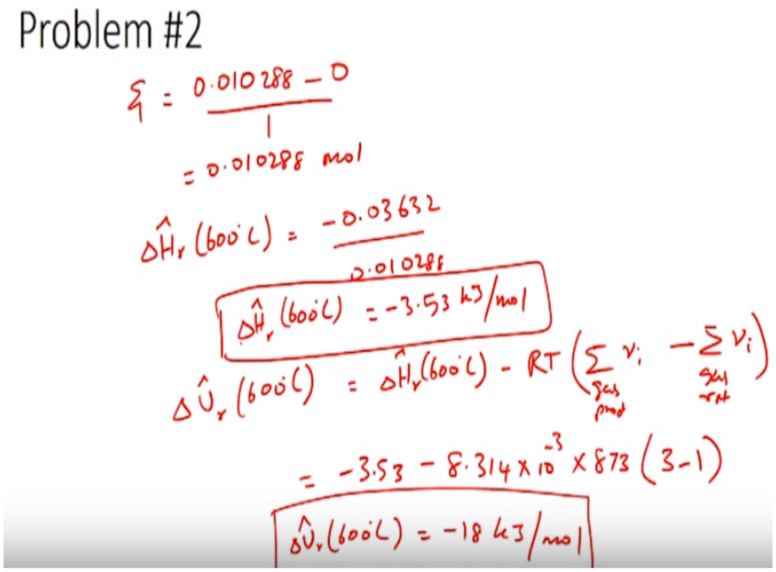

Problem #2

$$\xi = \frac{0.010288 - 0}{1}$$

$$= 0.010288 \text{ mol}$$

$$\Delta \hat{H}_r (600^\circ C) = \frac{-0.03632}{0.010288}$$

$$\boxed{\Delta \hat{H}_r (600^\circ C) = -3.53 \text{ kJ/mol}}$$

$$\Delta \hat{U}_r (600^\circ C) = \Delta \hat{H}_r (600^\circ C) - RT \left(\sum_{\text{gas prod}} \nu_i - \sum_{\text{gas rct}} \nu_i \right)$$

$$= -3.53 - 8.314 \times 10^{-3} \times 873 (3-1)$$

$$\boxed{\Delta \hat{U}_r (600^\circ C) = -18 \text{ kJ/mol}}$$

We can calculate the extent of reaction psi as follows using methane final and initial amounts we would actually have 0.010288 which is the final minus initial would be 0 divided by the stoichiometric coefficient of methane which would be 1 giving you the extent of reaction as 0.010288 moles. So from here we can calculate delta H r cap at 600 degree Celsius as -0.03632 which is the delta H we calculated divided by 0.010288 giving a value for delta H r cap at 600 degree Celsius as -3.53 kJ/mol.

So we have also been asked to calculate delta U r cap at 600 degree Celsius and this would be equal to delta H r cap at 600 degree Celsius minus RT times the summation of gaseous products stoichiometric coefficient minus the summation of the gaseous reactants stoichiometric coefficients. So this would be -3.53 kJ/mol – 8.314 which is the value for R times 10 power -3 because everything is in kilo joules, I am converting it into appropriate units.

And you would want to multiply it with the temperature which is 873 K times the gaseous products are actually 3 moles. So 1 + 1 + 1 – 1 which is the reactant. So this would give delta U r cap at 600 degree Celsius as -18 kJ/mol. So you have calculated delta H r cap and delta U r cap for 600 degree Celsius condition.

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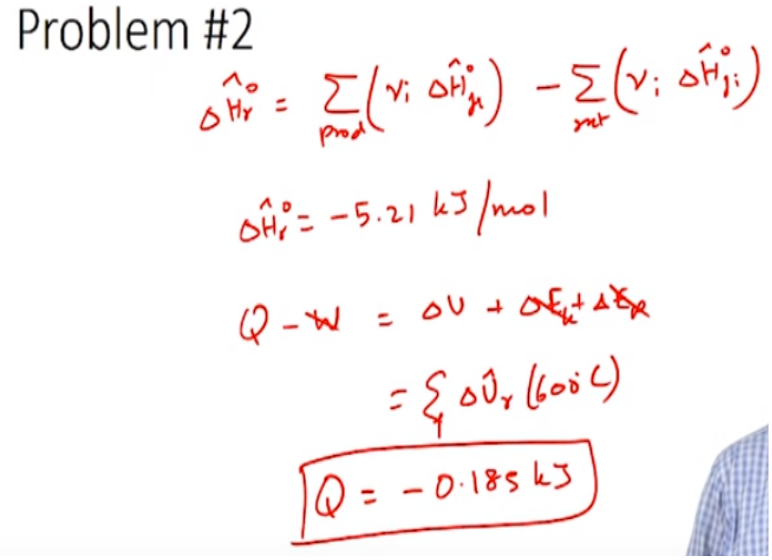

Problem #2

$$\Delta \hat{H}_r^\circ = \sum_{prod} \left(\nu_i \Delta \hat{H}^\circ_{f_i}\right) - \sum_{rxt} \left(\nu_i \Delta \hat{H}^\circ_{f_i}\right)$$

$$\Delta \hat{H}_r^\circ = -5.21 \text{ kJ/mol}$$

$$Q - W = \Delta U + \Delta E_k + \Delta E_p$$

$$= \xi \Delta \hat{U}_r (600^\circ C)$$

$$\boxed{Q = -0.185 \text{ kJ}}$$

So the next step is to identify the standard heat of reaction. So how would we find the standard heat of reaction? So that we can actually get using the heats of formation for the compounds which are present in the reaction. So using the heat of formation you would have the standard heat of reaction would be equal to sigma of products where stoichiometric coefficient times standard heat of formation for a compound minus sigma of reactants stoichiometric coefficient times standard heat of formation.

So you can get the values for the standard heat of formation from the tables and using the values from the tables and whatever data has been given, this value can be calculate as delta H r cap standard would be = -5.21 kJ/mol. So as you can see it is significantly different from the heat of reaction at 600 degree Celsius. At 600 degree Celsius, the heat of reaction was -3.53 kJ/mol whereas here it is -5.21 kJ/mol. Almost a difference of 50% compared to the 600 degree Celsius.

So now, the last part is to calculate the amount of heat that needs to be transferred to the reactor for the process to actually happen. So this is a close system so we would actually have to calculate only the, so here the only effect is the heat of reaction and because it is isothermal there is no effect on temperature so you will be able to use the internal energy of the reaction directly. So the equation actually is Q – W = delta U + delta E k + delta E p.

As usual, E k, E p and W go to 0. And you are left with only delta U and delta U would here would actually only be psi times delta U r at 600 degree Celsius. You have the heat of reaction, the internal energy of reaction at 600 degree Celsius which can be directly used. So doing that you would get Q = - 0.185 kJ. So with this we have solved this problem and we are at the end of how to perform energy balances for a close system.

And we have also looked at how simple pressure data could be converted to moles and so on and to calculate conversion and so on. So we actually performed, we have completed this problem and in the next lecture we will look at one more, which looks more like a case study which tries to apply all the concepts you have learnt from the material balances and energy balances and that will give us an overall review of all the fundamentals that we have learnt. Until then thank you.