Material and Energy Balances

Prof. Vignesh Muthuvijayan
Department of Biotechnology
Indian Institute of Technology - Madras

Lecture – 43
Energy Balances on Single-Phase Nonreactive Processes

Welcome to today's lecture on energy balances on single phase nonreactive processes. In the previous lecture we looked at the introduction for processes which were nonreactive and did not have any phase change. Today, we will talk about such systems where we can perform energy balances to calculate the amount of heat that needs to be supplied or to understand how we can measure the temperature of the exit stream or the inner stream.

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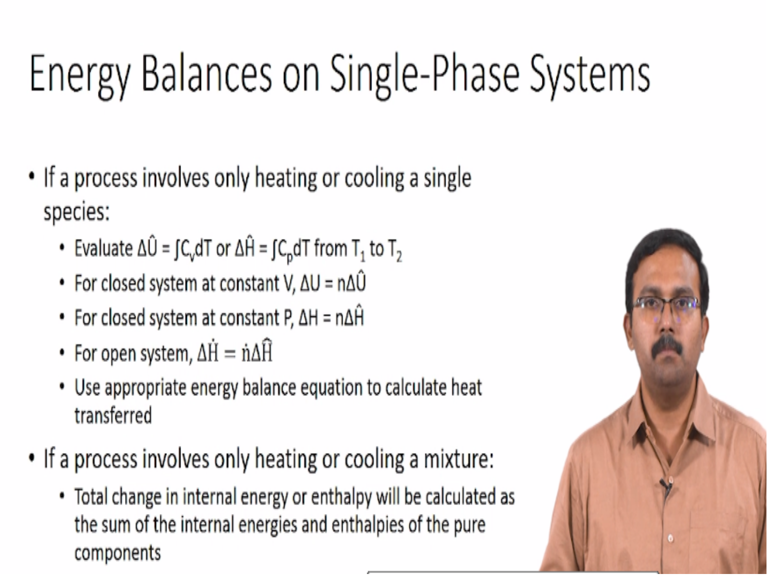

Energy Balances on Single-Phase Systems

- If a process involves only heating or cooling a single species:
  - Evaluate $\Delta\hat{U} = \int C_v dT$ or $\Delta\hat{H} = \int C_p dT$ from T_1 to T_2
  - For closed system at constant V, $\Delta U = n\Delta\hat{U}$
  - For closed system at constant P, $\Delta H = n\Delta\hat{H}$
  - For open system, $\Delta\dot{H} = \dot{n}\Delta\hat{H}$
  - Use appropriate energy balance equation to calculate heat transferred
- If a process involves only heating or cooling a mixture:
  - Total change in internal energy or enthalpy will be calculated as the sum of the internal energies and enthalpies of the pure components

For single-phase system you would have only heating or cooling of the components which are present in the system. So if you have a single species, then you can directly evaluate change in specific internal energy as integral CvdT and change in specific enthalpy as integral cpdT with temperature changing from initial temperature to final temperature or inlet temperature to outlet temperature.

For close systems, at constant volume you would be using delta U and for close system at constant pressure you would be using delta H for performing energy balances. For open systems you would always use delta H dot. So using the appropriate energy balance equation depending on whether the system is open system or close system you would be able to perform all the required calculations.

So obviously calculating kinetic energy, potential energy would be done based on the formula which we already know and shaft work would have to be accounted for if there are moving parts. If we have more than 1 component which is being heated or cooled, then the total change in internal energy or enthalpy will have to be calculated as the sum of the internal energies or the enthalpies of the pure components.

So here we are assuming that mixing does not cause any change in enthalpy. As I had already mentioned this type of an assumption is valid for ideal gases and for liquids which are similar. Having all these fundamentals in mind let us perform a few example problems which will help us familiarize ourselves with the concepts associated with this aspect of energy balances.

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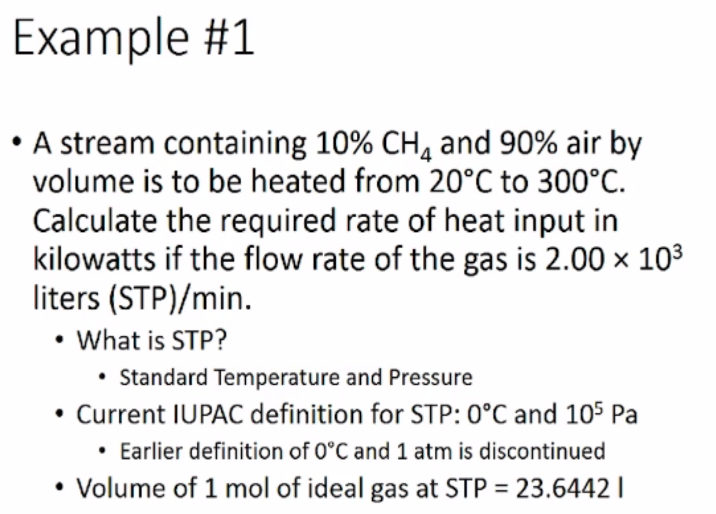

Example #1

- A stream containing 10% CH_4 and 90% air by volume is to be heated from 20°C to 300°C. Calculate the required rate of heat input in kilowatts if the flow rate of the gas is 2.00×10^3 liters (STP)/min.
  - What is STP?
    - Standard Temperature and Pressure
  - Current IUPAC definition for STP: 0°C and 10^5 Pa
    - Earlier definition of 0°C and 1 atm is discontinued
  - Volume of 1 mol of ideal gas at STP = 23.6442 l

Here is the first example problem. A stream containing 10% methane and 90% air by volume is to be heated from 20 degree Celsius to 300 degree Celsius. Calculate the required rate of heat input in kilowatts if the flow rate of the gas is 2 * 10 power 3 liters STP per minute. Now first thing you need to know is what is STP? STP stands for standard temperature and pressure. According to the latest definition by the IUPAC, STP is 0 degree Celsius and 10 power 5 Pascal.

The earlier definition which used to be used was 0 degree Celsius in 1 atmosphere so this has now been discontinued and we have to use 0 degree Celsius and 10 power 5 Pascal for STP. Now that we know this we can actually calculate the number of moles per liter or the volume occupied by 1 mole of a gas according to STP. So volume occupied by 1 mole of an ideal gas under STP conditions would be 23.6442 liters.

With all that said we should also understand why this problem gives the flow rate as liters STP. So here we have to calculate the number of moles which is coming in. So this can be done at STP. Although the inlet condition of gas itself is not STP this has been given in terms of STP because what it represents is if this gas were to be present under STP conditions, standard, temperature, and pressure, then it would have a volume of 2000 liters.

So the number of moles can be calculated from here. So this is just a way of representing molar flow rates instead of using the inlet conditions which is 20 degree Celsius we would have to use STP conditions to calculate the number of moles of the mixed gas which is entering into the system. With that fundamental covered let us continue with solving the energy balance. So this is the system we have 2000 liters of the mixer coming at 20 degree Celsius with 10% methane and 90% air.

So this 2000 liters is the volume if the gas would have been present at STP and you would have n. dot moles leaving at 300 degree Celsius with the same composition. Now we need to identify what this n dot would be. Here there are no reactions happening so whatever is the mixture which is coming in would be leaving.

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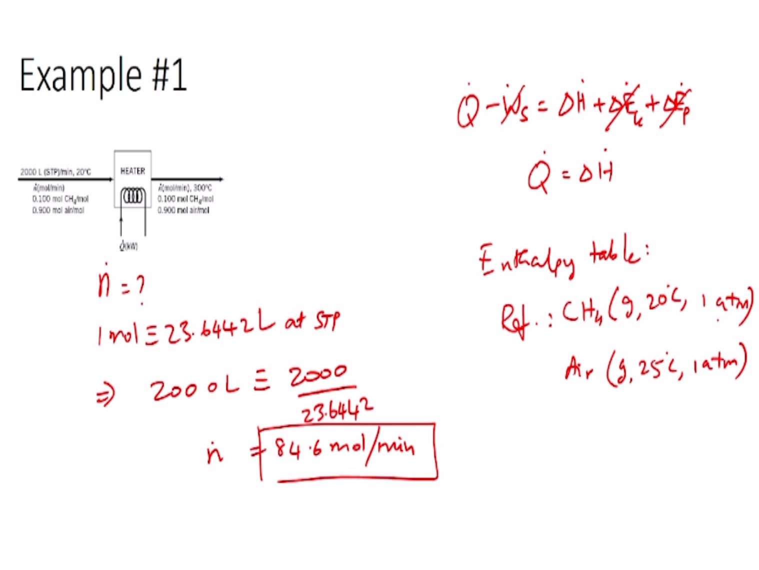

Example #1

$\dot{n} = ?$

$1 \text{ mol} \equiv 23.6442 \text{ L at STP}$

$\Rightarrow 2000 \text{ L} \equiv \frac{2000}{23.6442}$

$\dot{n} = \boxed{84.6 \text{ mol/min}}$

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

$\dot{Q} = \Delta\dot{H}$

Enthalpy table:

Ref.: CH_4 (g, 20°C, 1 atm)

Air (g, 25°C, 1 atm)

So first step is for us to identify what n dot is. So in this case we already identified that 1 mole occupies 23.6442 liters at STP. So this implies 2000 liters will contain 2000/23.6442 moles which would be the number of moles would be 84.6 moles per minute. So this is your n dot. Now that we have the number of moles coming in and leaving the system we can perform all the other energy balance calculations.

So here there are no material balance calculations required so the first step of performing material balance is not required. So the next step in any energy balance problem is to identify what type of a system is it? So here it is an open system because we have a flow rate so implies that our equation would be q dot - ws dot = delta H dot + delta Ek dot + delta Ep dot. Here there are no moving parts so the shaft wire could be 0.

The kinetic and potential energy changes would also be 0 because there is no change in velocity or change in position which has been given to us. So the equation gets simplified to Q dot = delta H dot. We have been asked to calculate Q dot so calculating H dot delta H dot will give us Q dot. So for calculating delta H dot we would have to build the table. So the enthalpy table has to be build. So enthalpy table would be built using reference states.

So we need to identify appropriate reference states. So here we have 2 components methane and air, so identify appropriate reference states is crucial for performing calculations in a simpler fashion. As I had already mentioned combustion gases, such as air, oxygen, carbon dioxide, carbon monoxide, these which are involved in combustion reactions commonly have a table where you can get enthalpy data from.

So using the reference state from the table would be appropriate for air. So the table which is there in your text book Felder Rousseau table B8. So if you have to use the table B8 we have to use the appropriate reference state from the table which is gas at 25 degree Celsius and 1 atmosphere and methane does not have any such table so we would have to use either the inlet or the outlet condition as the reference state.

So in our case we can use the inlet condition which is 20 degree Celsius as the reference state so which would be gas at 12 degree Celsius and 1 atmosphere. This would be the reference state for methane. Now that we have the reference state for methane and air we can go ahead and build the enthalpy table.

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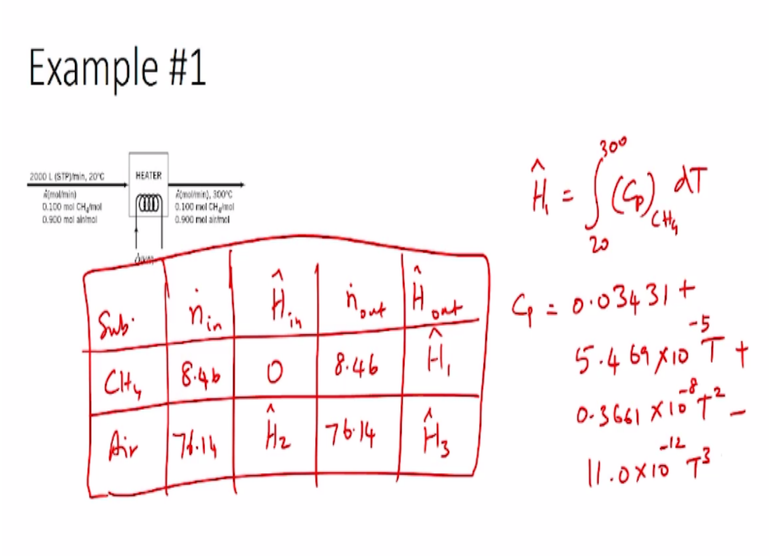

Example #1

Sub.	$\dot{n}_{in}$	$\hat{H}_{in}$	$\dot{n}_{out}$	$\hat{H}_{out}$
CH_4	8.46	0	8.46	$\hat{H}_1$
Air	76.14	$\hat{H}_2$	76.14	$\hat{H}_3$

$$\hat{H}_1 = \int_{20}^{300} (C_p)_{CH_4} \, dT$$

$$C_p = 0.03431 + 5.469 \times 10^{-5} T + 0.3661 \times 10^{-8} T^2 - 11.0 \times 10^{-12} T^3$$

So we have substances which are methane and air and the enthalpy table would have n dot n H cap n, n dot out, and H cap out. So now that we have this table let us start filling out all the information. We know that 10% of the mixture entering is methane. So this is the mole fraction so the value given is by volume which would mean that it is also proportional to the mole fracture. So because of this we can calculate the number of moles of methane coming in as 10%

of the total number of moles which is entering so this value would be 8.46 moles and air would be 76.14 moles.

So the outlet condition would also be the same with 8.46 moles of methane and 76.14 moles of air leaving the system. So our reference state for methane was the inlet condition which means the enthalpy of the inlet methane would be 0. So our reference state for air was different from the inlet and the outlet conditions so both these values would need to be calculated however we have a table so we can directly look it up a table.

So the outlet condition for methane has to still be calculated so we have to calculate 3 enthalpies out of which 2 can actually be looked up from tables. So, now first step is to calculate H1 cap. So H1 cap which is the change in enthalpy for a process where the methane goes from reference state to the final outlet condition which is from 20 degree Celsius to 300 degree Celsius. So integral 20 to 300 Cp of methane gas dT.

So we need to look at what Cp value for methane gas would be for this temperature range. So using the hand book or text book we can get Cp value for methane as 0.03431 + 5.469 * 10 power – 5 * T + 0.3661 * 10 power - 8 * T square - 11.0 * 10 power - 12 * T cube. So this is the Cp value. So integrating this from 20 to 300 degree Celsius we would be able to get the change in enthalpy which is H1 cap.

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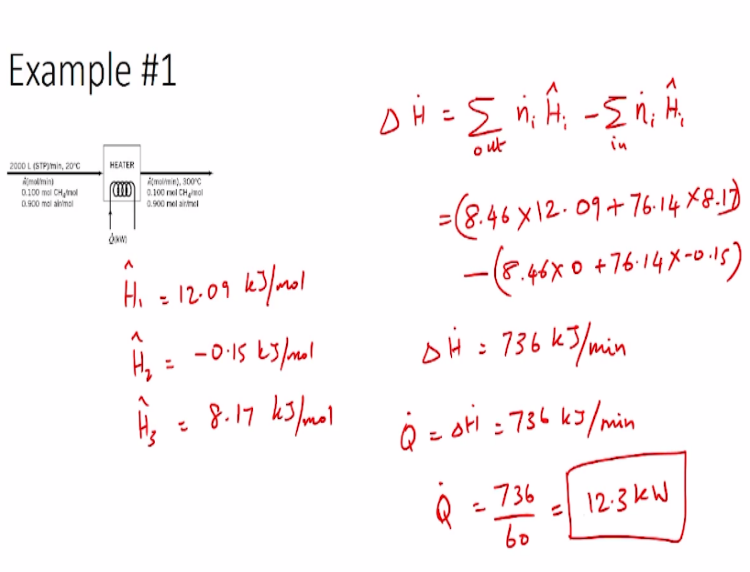

Example #1

$$\Delta \dot{H} = \sum_{out} \dot{n}_i \hat{H}_i - \sum_{in} \dot{n}_i \hat{H}_i$$

$$= (8.46 \times 12.09 + 76.14 \times 8.17)$$

$$- (8.46 \times 0 + 76.14 \times -0.15)$$

$$\hat{H}_1 = 12.09 \text{ kJ/mol}$$

$$\hat{H}_2 = -0.15 \text{ kJ/mol}$$

$$\hat{H}_3 = 8.17 \text{ kJ/mol}$$

$$\Delta \dot{H} = 736 \text{ kJ/min}$$

$$\dot{Q} = \Delta \dot{H} = 736 \text{ kJ/min}$$

$$\dot{Q} = \frac{736}{60} = \boxed{12.3 \text{ kW}}$$

So, doing that we get H1 cap as 12.09 kilo Joules per mole. From table B8 which is the table in Felder Rousseau for combustion gases the enthalpy data can be obtained so H2 cap would be = - 0.15 kilo Joules per mole and H3 cap would be = 8.17 kilo Joules per mole. In case, the direct value for that particular temperature is not available we could still perform a simple interpolation to get the values.

So now we have the values for H1 cap, H2 cap, and H3 cap. So the delta H dot value = sigma of outlet ni dot H i cap - sigma of inlet ni dot Hi cap has to be calculated. So the outlet is 8.46 mole of methane leaving with an enthalpy change of 12.09 + 76.14 moles of air * 8.17 – (8.46 * 0 - 76.14 * - 0.15). So, this term whichever is there within the brackets is the outlet enthalpy and this is the bracket, the second component is the inlet enthalpy.

So the total change in enthalpy delta H dot = 736 kilo Joules per minute. So substituting this back into the energy balance equation you would get Q dot = delta H dot = 736 kilo Joules per minute. The problem asks us to calculate the amount of heat that needs to be transferred in terms of kilowatts so Q dot would be = 736/60 which is 12.3 kilowatts. So the final answer which you are looking forward is 12.3 kilowatts. So this is 1 example problem where we have calculated the amount of heat that needs to be supplied for heating a mixture from 20 degree Celsius to 300 degree Celsius.

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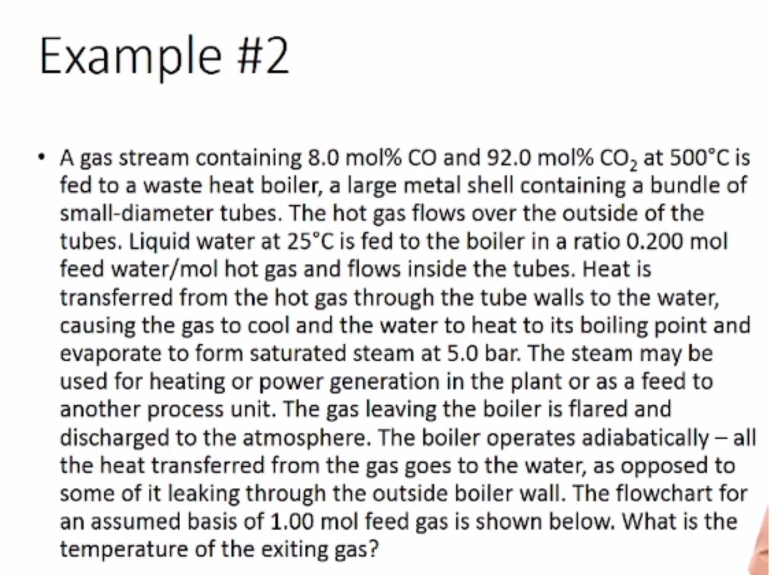

Example #2

- A gas stream containing 8.0 mol% CO and 92.0 mol% CO_2 at 500°C is fed to a waste heat boiler, a large metal shell containing a bundle of small-diameter tubes. The hot gas flows over the outside of the tubes. Liquid water at 25°C is fed to the boiler in a ratio 0.200 mol feed water/mol hot gas and flows inside the tubes. Heat is transferred from the hot gas through the tube walls to the water, causing the gas to cool and the water to heat to its boiling point and evaporate to form saturated steam at 5.0 bar. The steam may be used for heating or power generation in the plant or as a feed to another process unit. The gas leaving the boiler is flared and discharged to the atmosphere. The boiler operates adiabatically – all the heat transferred from the gas goes to the water, as opposed to some of it leaking through the outside boiler wall. The flowchart for an assumed basis of 1.00 mol feed gas is shown below. What is the temperature of the exiting gas?

So this is the second example problem. Here we are expected to calculate temperature instead of the heat which needs to be supplied. Let us see how we would approach such a problem. A gas stream containing 8 mol% carbon monoxide and 92 mol% carbon dioxide at 500 degree Celsius is fed to a waste heat boiler. A large metal shell containing a bundle of small diameter tubes. The hot gas flows over the outside of the tubes.

Liquid water at 25 degree Celsius is fed to the boiler in a ratio of 0.2 moles of feed water per mole of hot gas and flows inside the tubes. Heat is transferred from the hot gas through the tube walls to the water, causing the gas to cool and water to heat to its boiling point and then evaporate to form saturated steam at 5 bar. The steam may be used for heating or power generation in the plant or as a feed to another process unit.

The gas leaving the boiler is flared and discharged to the atmosphere. The boiler operates adiabatically all the heat transferred from the gas goes to the water, as opposed to some of it leaking through the outside of the wall. The flowchart for an assumed basis of 1 mol of feed gas is shown below. What is the temperature of the exiting gas? So this is the flow chart which we have. So you have 1 mol of carbon monoxide carbon dioxide mixed gas entering 0.2 moles of water liquid entering.

So which means 0.2 moles of water vapour would be leaving and you have 1 mole of carbon dioxide, carbon monoxide mixture leaving to be flared. So this is the system. So what you see here is the gas will flow only in the region which is white and water will flow only in the region which is gray. So these small tubes which are present will carry the water and heat from this gas which is present in the region which is white will get transferred to the water which is flowing in the tubes that are shaded gray.

So because there is so much heat being transferred water actually heats up, boils, and evaporates. So as I have promised today's lecture will only focus on no phase change processes. However here we do how a phase change, but we do not have to worry about how to account for phase change simply because we can use steam tables directly. So here water being heated and changing phase does not affect our calculations as we will be using steam tables.

However, if we were to have a phase change for any other component then we have to know how to account for the enthalpy associated with phase change which would not be the sensible heat which is supplied. It would not help in the increasing temperature. It is the latent heat which would help in changing the phase. We will discuss that in the subsequent lectures, but today we will use this problem just to understand how to perform energy balance calculations.

So the phase change is negated because we are using steam tables. As always the first step for any energy balance problem is to perform material balances. However here there are no material balances required because the carbon dioxide, carbon monoxide mixture which is coming in does not come in contact with water and water leaves separately, carbon monoxide, carbon dioxide mixture leaves separately and all the information about the compositions are also known so we can ignore any material balance calculations that might have to be performed.

So the next step is to identify what type of a system is this.

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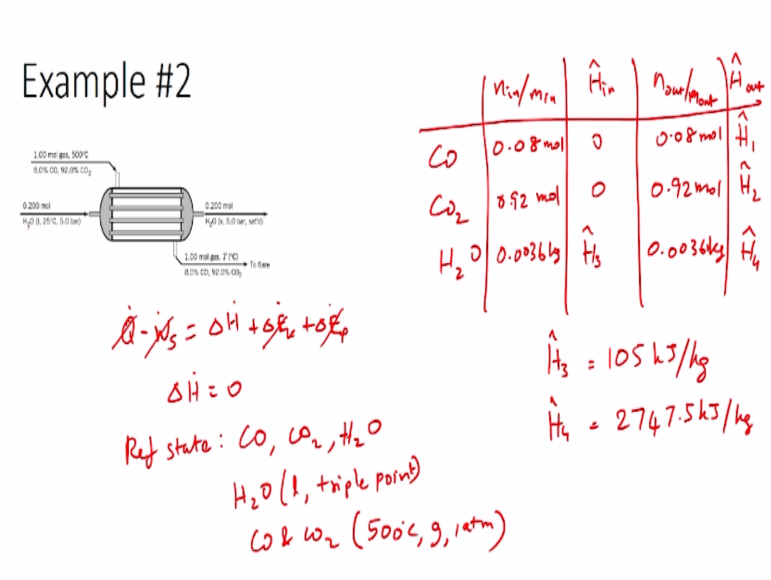

Example #2

	$\dot{n}_{in}/m_{in}$	$\hat{H}_{in}$	n_{out}/m_{out}	$\hat{H}_{out}$
CO	0.08 mol	0	0.08 mol	$\hat{H}_1$
CO_2	0.92 mol	0	0.92 mol	$\hat{H}_2$
H_2O	0.0036 kg	$\hat{H}_3$	0.0036 kg	$\hat{H}_4$

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

$$\Delta\dot{H} = 0$$

Ref state: CO, CO_2, H_2O

H_2O (l, triple point)

CO & CO_2 (500°C, g, 1 atm)

$\hat{H}_3 = 105$ kJ/kg

$\hat{H}_4 = 2747.5$ kJ/kg

So this would be an open system which means the general energy balance equation would be Q dot - Ws dot = delta H dot + delta Ek dot + delta Ep dot. So here there are no moving parts. So shaft work will be 0. You do not have any change in velocity or position so you can ignore kinetic and potential energies changes. In addition to all this it has also been given that the process operates adiabatically which means Q dot will also go to 0.

So you end up with a trivial equation which is delta H dot = 0. So this is useful because we actually are not trying to calculate heat transfer here. We are trying to calculate the temperature. So for this if you have this equation we would actually be writing the delta H dot in terms of temperature because we can actually get Cp values in terms of temperature and actually perform integrations.

So which would give us a polynomial of temperature which we can solve to get the value for temperature. So let us try to do that. Before that we first need to identify a reference state. So what would be the reference state for this problem? So here we have carbon monoxide, carbon dioxide and water are components which will be using. As I already mentioned water we will be using the steam tables.

So we need to use the appropriate reference state which is given in the steam tables. So I have used the Felder Rousseau steam table so we will be using water liquid at triple point as the reference state for water. What about carbon dioxide and carbon monoxide. Here we do not want to use tables because you ultimately have to find out the temperature of the carbon dioxide carbon monoxide mixture which is leaving the system.

So we would have to use 1 of the inlet or the outlet as the reference state. As we have to calculate the outlet temperature using the inlet temperature and pressure as the reference state would be the most appropriate thing to do. So for carbon monoxide and carbon dioxide the reference state used would be 500 degree Celsius gas and 1 atmosphere. Now that we have identified the reference state the next step is to draw the enthalpy table.

So the enthalpy table for carbon monoxide, carbon dioxide, and water vapour can be written. So you would have nin/min. So I am also writing min because the value for enthalpy given in the steam tables would be in terms of kilo Joules per kilogram however the enthalpy we calculate using integral CpdT would be in terms of kilo Joules per mole. So depending on what units for enthalpy would be you would have to write either the number of moles or the mass of the inlet and outlet streams and you would have H cap in and you have n out or m out and you would also have H cap out.

So this is the table you have to work with. So we have 0.08 moles of carbon monoxide and 0.92 moles of carbon dioxide entering the system. We also know that 0.2 moles of water is entering because we want to have the enthalpy values in kilo Joules per kilogram we will have to write this in terms of kilograms which would be 0.0036 kilograms. So using the molecular weight we can get this mass.

So the outlet streams would also have the same moles and masses because there are no reactions happening. So you have this 0.92 moles and 0.0036 kilograms. So we have used the inlet condition for carbon dioxide and carbon monoxide as the reference state which means these enthalpy values will be 0 and this enthalpy value for water has to be obtained from the steam tables. We have to calculate the values for the outlet streams H1 cap and H2 cap.

So these would be the terms were you would have the temperature term coming in so this would be H3 cap and H4 cap. So H3 cap and H4 cap we can look up steam tables. So we have information about the inlet and outlet conditions. So the inlet conditions say water at 5 bar, liquid 25 degree Celsius and outlet condition is water vapour at 5 bar unsaturated. So H3 cap would be = 105 kilo Joules per kilogram from the steam tables.

So here what I have done is I have ignored the effect of pressure because V cap values are actually very small and changes in pressure here is very small so from 1 atmosphere to about 5 bar is not too big after change impression. So we can actually ignore the V cap delta p effect on enthalpy so for that reason I have actually got an approximate value of 105 kilo Joules per kilogram from the steam tables and I will be using this for my calculations.

H4 cap can again been looked at steam tables and this value = 2747.5 kilo Joules per kilogram. This is the enthalpy of saturated steam at 5 bar. So now that we have H3 cap and H4 cap we can write polynomial expressions for H1 cap and H2 cap which can then be substituted into the equation which is delta H dot = 0 to calculate the value for temperature.

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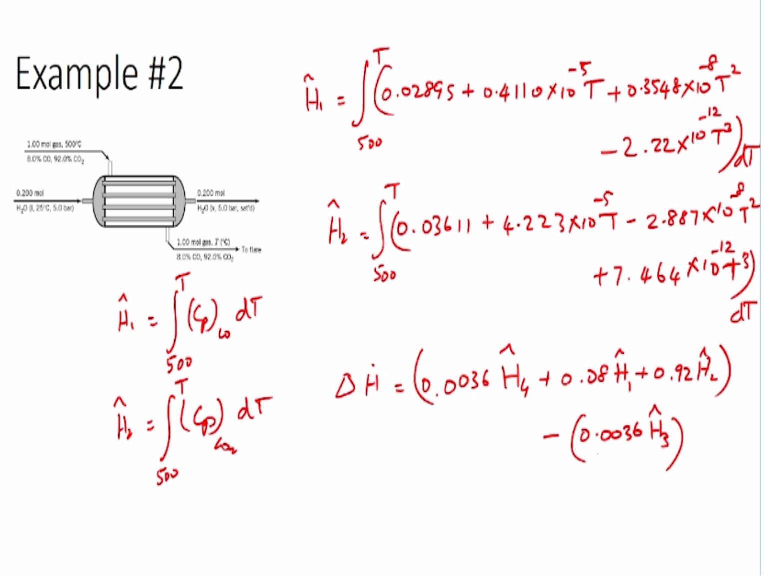

Example #2

$$\hat{H}_1 = \int_{500}^{T} (C_p)_{co}\, dT$$

$$\hat{H}_2 = \int_{500}^{T} (C_p)_{co_2}\, dT$$

$$\hat{H}_1 = \int_{500}^{T} \left(0.02895 + 0.4110\times10^{-5}T + 0.3548\times10^{-8}T^2 - 2.22\times10^{-12}T^3\right) dT$$

$$\hat{H}_2 = \int_{500}^{T} \left(0.03611 + 4.223\times10^{-5}T - 2.887\times10^{-8}T^2 + 7.464\times10^{-12}T^3\right) dT$$

$$\Delta\dot{H} = \left(0.0036\,\hat{H}_4 + 0.08\,\hat{H}_1 + 0.92\,\hat{H}_2\right) - \left(0.0036\,\hat{H}_3\right)$$

H1 cap = integral of 500 degree Celsius to temperature T Cp of carbon monoxide dT and H2 cap = integral 500 degree Celsius to temperature T Cp of Co2 dT. So here we need to know the Cp values for carbon monoxide and carbon dioxide from any text book or hand book we can get this value. So our H1 cap would be = integral 500 to T 0.02895 + 0.4110 * 10 power - 5 * T + 0.3548 * 10 power - 8 * T square - 2.22 * 10 power - 12 * T cube * dT.

Integrating this we can get a polynomial which would have the fourth order of temperature. So then we have H2 cap which should be integral 500 to T 0.03611 + 4.223 * 10 power - 5 * T - 2.887 * 10 power - 8 * T square + 7.464 * 10 power - 12 * T cube dT. So this gives us H1 cap and H2 cap. Again both of these will be fourth order polynomials of temperature. So now we can calculate delta H dot as 0.0036 * H4 cap + 0.08 * H1 cap + 0.92 * H2 cap - 0.0036 * H3 cap.

So this is the first term which in the brackets is the enthalpy of the outlet streams and the second term after the - is the enthalpy of the inlet streams.

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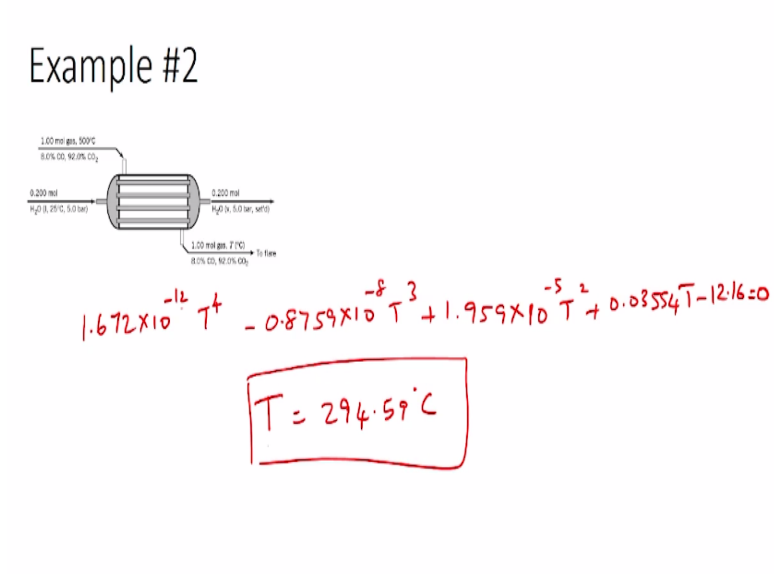

Example #2

$1.672\times10^{-12}T^4 - 0.8759\times10^{-8}T^3 + 1.959\times10^{-5}T^2 + 0.03554T - 12.16 = 0$

$\boxed{T = 294.59^\circ C}$

So with this equation we would actually end up with the fourth order polynomial of temperature which would be 1.672 * 10 power - 12 * T power 4 - 0.8759 * 10 power - 8 * T cube + 1.959 * 10 power - 5 * T square + 0.03554 * T - 12.16 = 0. So this is the fourth order polynomial that needs to be solved to get the value for temperature. Fourth order polynomials can be solved using some computational tool. You can do it numerically.

So if you find it hard you can also assume that the terms which are in the higher order to power which is T power 4 and T power 3 can be ignored because the coefficients for these are in the order of 10 power - 12 and 10 power - 12. So ignoring that you would not create too much of an error so which would be still be tolerable so you could explicitly state that you are ignoring the higher powers of temperature if you have to perform these calculations manually.

As long as you have the computing power to calculate the temperature then I would recommend using the entire polynomial to get the accurate value. If you were to use excel or polymath or one of those software to solve for this fourth order polynomial you would get the value for temperature as 294.59 degree Celsius. So this is the temperature of the exit stream for carbon dioxide carbon monoxide mixture.

Now today we have actually looked at 2 separate problems which are uniquely different, one where we try to calculate the amount of heat supplied and the other where we actually looked at identifying the temperature of the exit stream. So both these can be approached from the same energy balance procedures and you are able to arrive at the final answers.

Hopefully you have understood the principles behind this and in the subsequent lectures we will perform more calculations and more example problems to help us fully familiarize ourselves with these concepts. Until then thank you and good bye.