Material and Energy Balances
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Lecture - 63
Energy Balances on Reactive Processes - Part 6

Let us now continue with the third example problem.

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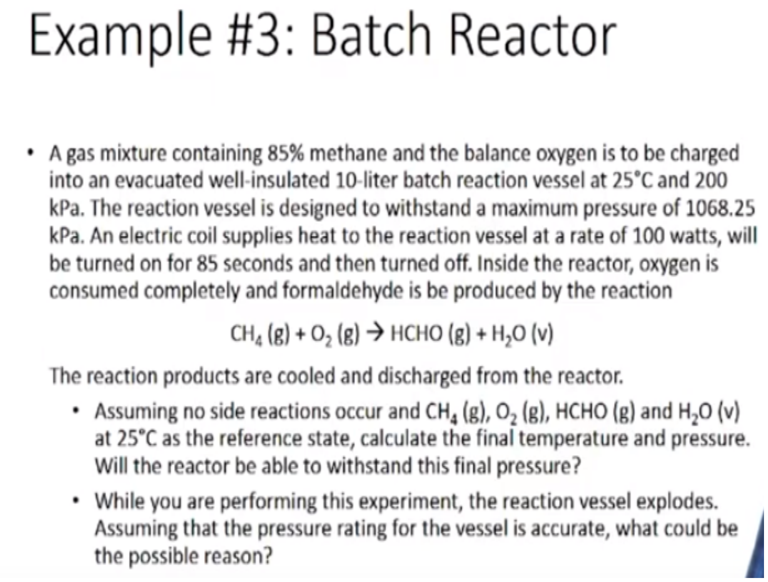

Example #3: Batch Reactor

- A gas mixture containing 85% methane and the balance oxygen is to be charged into an evacuated well-insulated 10-liter batch reaction vessel at 25°C and 200 kPa. The reaction vessel is designed to withstand a maximum pressure of 1068.25 kPa. An electric coil supplies heat to the reaction vessel at a rate of 100 watts, will be turned on for 85 seconds and then turned off. Inside the reactor, oxygen is consumed completely and formaldehyde is be produced by the reaction

$$CH_4\,(g) + O_2\,(g) \rightarrow HCHO\,(g) + H_2O\,(v)$$

The reaction products are cooled and discharged from the reactor.

  - Assuming no side reactions occur and CH_4 (g), O_2 (g), HCHO (g) and H_2O (v) at 25°C as the reference state, calculate the final temperature and pressure. Will the reactor be able to withstand this final pressure?
  - While you are performing this experiment, the reaction vessel explodes. Assuming that the pressure rating for the vessel is accurate, what could be the possible reason?

So here we will actually be looking at a batch reactor. Until now we have been looking at open systems. So we have always been calculating change in enthalpy, specific enthalpy, building enthalpy tables and so on. However, here we will actually be looking at a closed system. So we will be looking at internal energy changes and we will look at how to calculate these internal energy changes, how to build internal energy tables and so on.

So let us look at the problem statement. The problem statement reads, a gas mixture containing 85% methane and the balance oxygen is to be charged into an evacuated well-insulated 10-liter batch reaction vessel at 25 degree Celsius and 200 kPa. The reaction vessel is designed to withstand a maximum pressure of 1068.25 kPa. An electric coil supplies heat to the reaction vessel at a rate of 1000 watts and it will be turned on for 85 seconds and then turned off.

Inside the reactor oxygen is consumed completely and formaldehyde is to be produced by the reaction where methane reacts with oxygen to form formaldehyde and water. The reaction products are cooled and discharged from the reactor assuming no side reactions occur. Methane gas, oxygen gas and formaldehyde gas and water vapor at 25 degree Celsius as the reference state calculate the final temperature and pressure.

Will the reactor be able to withstand this final pressure? While you are performing this experiment, the reaction vessel explodes. Assuming that the pressure rating of the vessel is accurate, what could be the possible reason? So here you have two parts. The first part you are actually asked to calculate the temperature and pressure. So we had already looked at a problem where we had to calculate the outlet temperature.

So we are familiar with how to do this. So we would just be using internal energy instead of enthalpy here. So we will be looking to calculate the outlet temperature. We already have the value for Q. So Q is given at the rate of 100 watts for 85 seconds. So we can actually calculate the total amount of heat which is supplied and identifying the change in internal energy we will be able to write the appropriate energy balance equation and solve it for getting the final temperature.

So from the final temperature we can also calculate the final pressure and compare it against the pressure rating which has been given and identify whether the reactor can actually withstand. In the second part of the problem we have been asked to identify, if the reaction vessel does explode, what could be the reason and you will try to hypothesize a potential cause for something like that. So let us look at how to solve this problem.

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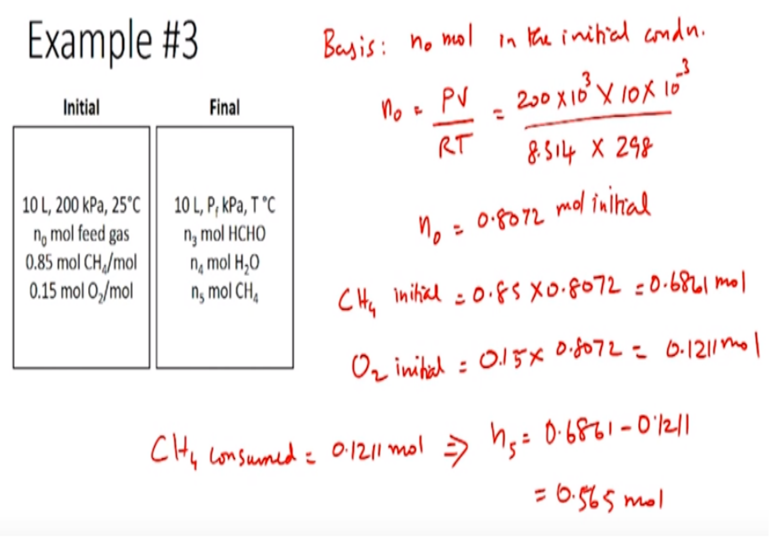

Example #3

Initial	Final
10 L, 200 kPa, 25°C n_0 mol feed gas 0.85 mol CH_4/mol 0.15 mol O_2/mol	10 L, P_f kPa, T °C n_3 mol HCHO n_4 mol H_2O n_5 mol CH_4

Basis: n_0 mol in the initial condn.

$$n_0 = \frac{PV}{RT} = \frac{200 \times 10^3 \times 10 \times 10^{-3}}{8.314 \times 298}$$

$n_0 = 0.8072$ mol initial

CH_4 initial $= 0.85 \times 0.8072 = 0.6861$ mol

O_2 initial $= 0.15 \times 0.8072 = 0.1211$ mol

CH_4 consumed $= 0.1211$ mol $\Rightarrow n_5 = 0.6861 - 0.1211$

$= 0.565$ mol

Here is the example problem in terms of the flow sheet. You have an initial and final condition. It is a closed system which is 10 L, 200 kPa and 25 degree Celsius in the initial condition. It contains n naught moles of feed gas and you know the composition of this feed gas. Initial condition is 0.85 moles of methane and 0.15 moles of oxygen per mole of the mixture.

So you have the final condition which would be 10 L because it is a constant volume reaction vessel and your pressure you do not know, the final pressure can be given as P at kilo Pascal and the temperature is marked as T degree Celsius. So you also have n 3, n 4, and n 5 moles of formaldehyde, water and methane which are in the final condition. Now let us see how we can perform the calculations to identify the amount of heat that can be supplied to the system.

So first we need to identify the basis. Here we do not know the conditions. We do not know the number of moles in the initial and the final conditions and that we need to perform using, identify using material balances. So for that we need a basis. So what would be the basis? We cannot randomly assume a basis. We need to identify the number of moles which are present in the initial condition. We have been given the temperature and pressure and the volume.

So if we were to assume ideal gas behavior you would be able to calculate the number of moles which are present in the initial condition. So that is what we are going to do. So the basis would actually be n naught moles in the initial condition. So taking that into account, let us calculate n naught. So n naught would be equal to PV/RT. So P is the pressure. We have it as 200 kPa. So we will call it 200 times 10 power 3 P and your volume is 10 L.

So it would be 10 times 10 power -3 meter cube divided by R in terms of SI units would be 8.314 times temperature in Kelvin would be 298 K. So using this we can calculate n naught as 0.8072 moles in the initial condition, okay? So this would be 0.8072 mol. We now need to identify n 3, n 4 and n 5 in the final condition. So for that we would have to perform simple material balance calculations.

So now to identify the number of moles in the final condition which is n 3, n 4 and n 5, we need to know how much of methane is consumed. Since we know that all of oxygen is consumed, we can use the stoichiometry to identify how many moles of methane would have been consumed. So first thing we need to identify is the number of moles of methane in the initial condition, number of moles of oxygen in the initial condition.

We know that 0.8072 moles are present as a feed gas mixture. So methane initial would be equal to 0.85 times 0.8072 which is 0.6861 moles. Oxygen in the initial condition would be equal to 0.15 times 0.8072 which is 0.1211 moles. So now we need to identify how much methane is consumed so we know all of oxygen is consumed. So 0.1211 moles of oxygen was consumed.

According to stoichiometry, for every mole of oxygen consumed, 1 mole of methane should also be consumed. So methane consumed would be equal to 0.1211 moles. So this implies methane in the final condition which is n 5 would be equal to initial methane minus methane consumed which is 0.6861 – 0.1211 giving you a value of 0.565 moles. So this is the number of moles of methane present in the final condition.

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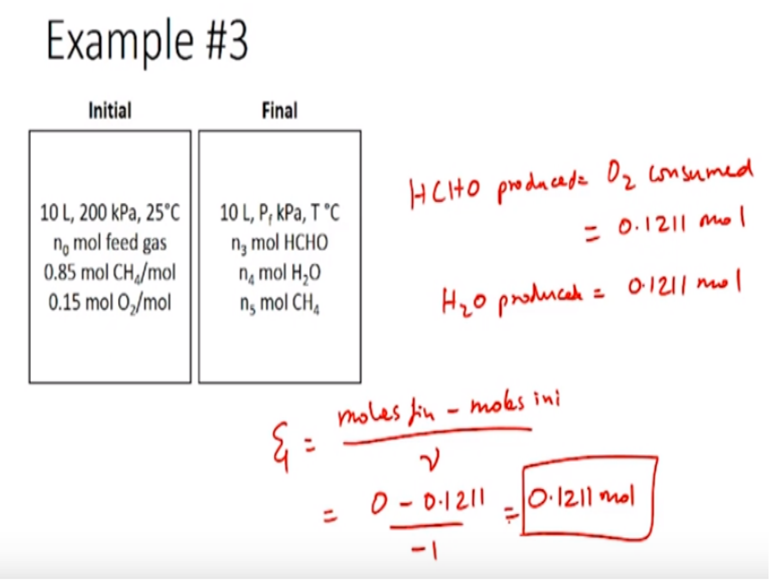

Example #3

Initial	Final
10 L, 200 kPa, 25°C n_0 mol feed gas 0.85 mol CH_4/mol 0.15 mol O_2/mol	10 L, P_f kPa, T °C n_3 mol HCHO n_4 mol H_2O n_5 mol CH_4

HCHO produced = O_2 consumed
= 0.1211 mol

H_2O produced = 0.1211 mol

$$\xi = \frac{\text{moles fin} - \text{moles ini}}{\nu} = \frac{0 - 0.1211}{-1} = \boxed{0.1211 \text{ mol}}$$

So we also need to identify the number of moles of formaldehyde and water which is present. Based on the stoichiometry for every mole of oxygen consumed 1 mole of formaldehyde and 1 mole of water is produced. So you can calculate formaldehyde produced would be equal to oxygen consumed and this would be 0.1211 moles. Similarly, water produced would also be equal to 0.1211 moles.

So now that we have the number of moles of each of the component in the final condition we can also calculate the extent of reaction. So the extent of reaction would be, so this extent of reaction would be required when we perform the energy balances, right? We have been told to use the heat of reaction method. So we need to know the extent of reaction. We will calculate the extent of reaction as moles final – moles initial/stoichiometric coefficient.

So if we were to use oxygen, you would have 0 – 0.1211/-1 giving you 0.1211 moles. So that is the extent of reaction. So this can be used while we perform the energy balance calculations.

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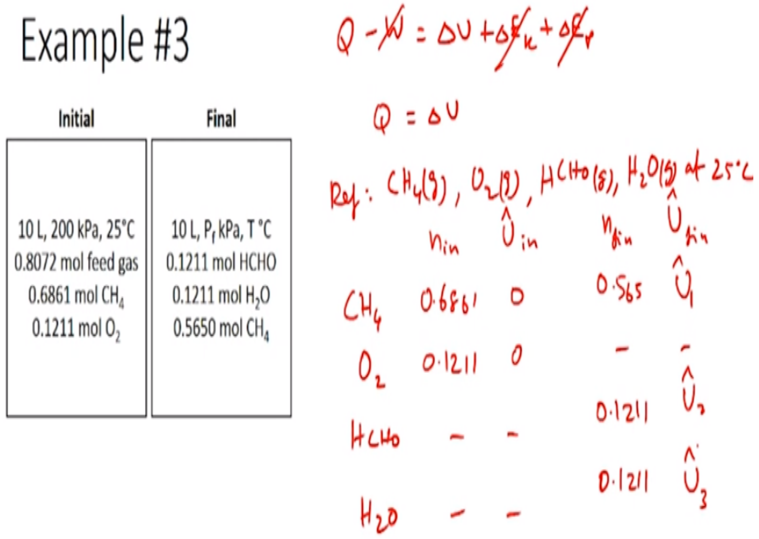

Example #3

Initial	Final
10 L, 200 kPa, 25°C 0.8072 mol feed gas 0.6861 mol CH_4 0.1211 mol O_2	10 L, P_f kPa, T °C 0.1211 mol HCHO 0.1211 mol H_2O 0.5650 mol CH_4

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

$$Q = \Delta U$$

Ref: $CH_4(g)$, $O_2(g)$, $HCHO(g)$, $H_2O(g)$ at 25°C

	n_{in}	$\hat{U}_{in}$	n_{fin}	$\hat{U}_{fin}$
CH_4	0.6861	0	0.565	$\hat{U}_1$
O_2	0.1211	0	–	–
HCHO	–	–	0.1211	$\hat{U}_2$
H_2O	–	–	0.1211	$\hat{U}_3$

Now that we have performed all the required material balances, we can start with the energy balance calculations. Here it is a closed system unlike all the systems which we have been looking at till now. For a closed system the equation would be Q – W = delta U + delta E k + delta E p. So here there is no change in kinetic and potential energy and there are no moving parts so you have work also = 0.

So you will end up with Q = delta U and once you have this equation we have to calculate delta U. So for that we have been told to use the reference states of methane gas, oxygen gas, formaldehyde gas and water gas at 25 degree Celsius. So let us take the reference states as given in the problem. Methane gas, oxygen gas, formaldehyde gas and water gas all at 25 degree Celsius. Using this reference state let us build the internal energy table.

So the table would look like this. You would have methane, oxygen, formaldehyde and water. You would have n initial and U cap initial, n final and U cap final. So initial moles are 0.6861 and 0.1211 and you do not have any formaldehyde and water. In the final condition you have 0.565 moles of methane and there is no oxygen. You have 0.1211 moles of formaldehyde and water.

So the initial condition is oxygen and methane at 25 degree Celsius which is the same as the reference state. So the internal energy for these two would be 0 and for the final condition, the temperature we have kept it as T. So we will have to use some internal energy values for this. We will call this as U 1 cap, U 2 cap and U 3 cap. So we need to calculate U 1, U 2 and U 3 to identify the temperature which we can reach and we will have to perform these calculations using C v instead of C p.

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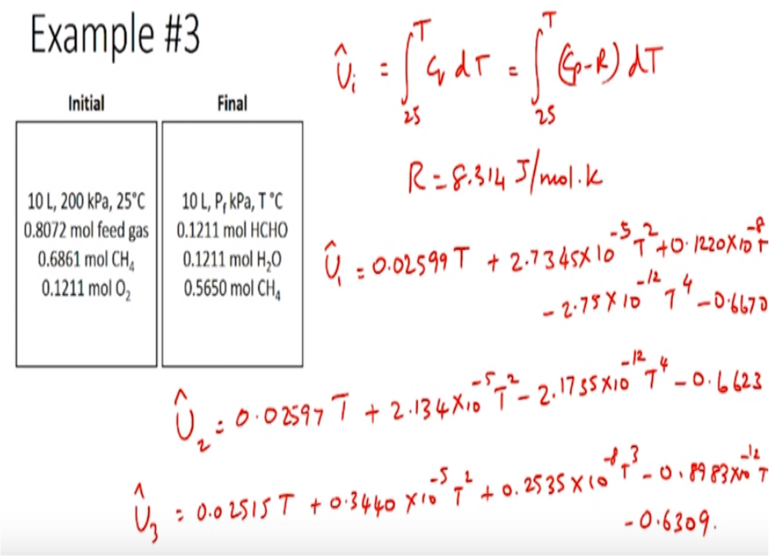

Example #3

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10 L, 200 kPa, 25°C 0.8072 mol feed gas 0.6861 mol CH_4 0.1211 mol O_2	10 L, P_f kPa, T °C 0.1211 mol HCHO 0.1211 mol H_2O 0.5650 mol CH_4

$$\hat{U}_i = \int_{25}^{T} C_v\, dT = \int_{25}^{T} (C_p - R)\, dT$$

$$R = 8.314\ J/mol.K$$

$$\hat{U}_1 = 0.02599\,T + 2.7345\times10^{-5}\,T^2 + 0.1220\times10^{-8}\,T - 2.75\times10^{-12}\,T^4 - 0.6670$$

$$\hat{U}_2 = 0.02597\,T + 2.134\times10^{-5}\,T^2 - 2.1735\times10^{-12}\,T^4 - 0.6623$$

$$\hat{U}_3 = 0.02515\,T + 0.3440\times10^{-5}\,T^2 + 0.2535\times10^{-8}\,T^3 - 0.8983\times10^{-12}\,T - 0.6309.$$

So we know that U 1 cap would be equal to integral 25 to T C v dT. So we have always been using C p. So we will use C v here. So if it is solid or a liquid, C p will be roughly equal to C v. However, here everything is a gas. For a gaseous system you would have C p = C v + R. So you will calculate C v as integral 25 to T C p – R dt. So C p value is readily available from your tables and from textbooks and reference books.

R would be 8.314 J/mol K. So you will use the R value as 8.314 J/mol K and you can actually substitute this value here to calculate the value for C v. You will be able to perform calculations to get U 1 cap, U 2 cap and U 3 cap. So using the C p values and the R value, we will get U 1 cap as 0.02599 T + 2.7345 times 10 power -5 T square + 0.1220 times 10 power -8 T cube – 2.75 times 10 power -12 T power 4 – 0.6670. This should again be in kilo joules per mole.

Similarly, you can get a U 2 cap. Similarly, you can get U 2 cap as 0.02597 T + 2.134 times 10 power -5 T square – 2.1735 times 10 power -12 T power 4 – 0.6623 again kilo joules per mole. So your final U 3 cap would be 0.02515 T + 0.3440 times 10 power -5 T square + 0.2535 times

10 power -8 T cube – 0.8983 times 10 power -12 T power 4 – 0.6309 kJ/mol. So again you will be able to get the C p values from the textbook or from other reference books. So you can substitute that to get C v value and you will be able to calculate the internal energy changes as I have shown here.

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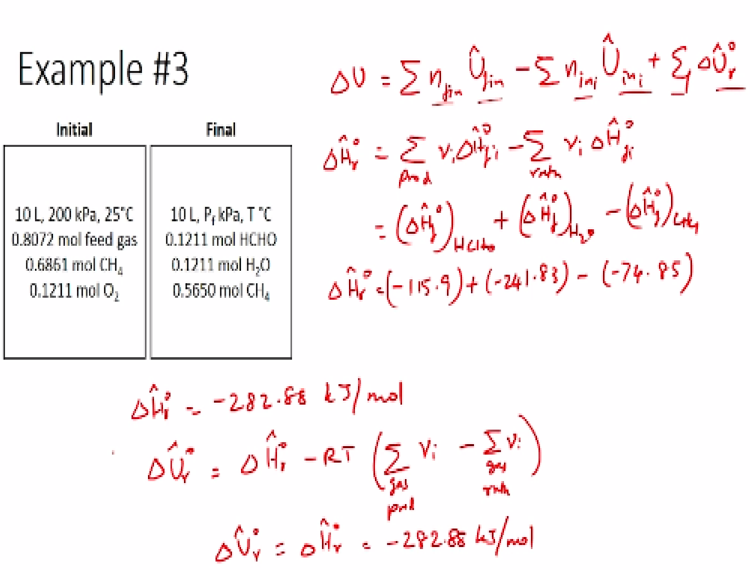

Example #3

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$$\Delta U = \sum n_{fin}\hat{U}_{fin} - \sum n_{ini}\hat{U}_{ini} + \xi\Delta\hat{U}_r^\circ$$

$$\Delta\hat{H}_r^\circ = \sum_{prod}\nu_i\Delta\hat{H}_{fi}^\circ - \sum_{rxn}\nu_i\Delta\hat{H}_{fi}^\circ$$

$$= \left(\Delta\hat{H}_f^\circ\right)_{HCHO} + \left(\Delta\hat{H}_f^\circ\right)_{H_2O} - \left(\Delta\hat{H}_f^\circ\right)_{CH_4}$$

$$\Delta\hat{H}_r^\circ = (-115.9) + (-241.83) - (-74.85)$$

$$\Delta\hat{H}_r^\circ = -282.88 \text{ kJ/mol}$$

$$\Delta\hat{U}_r^\circ = \Delta\hat{H}_r^\circ - RT\left(\sum_{\substack{gas\\prod}}\nu_i - \sum_{\substack{gas\\rxn}}\nu_i\right)$$

$$\Delta\hat{U}_r^\circ = \Delta\hat{H}_r^\circ = -282.88 \text{ kJ/mol}$$

To calculate the change in internal energy delta U, we need the internal energy of the reaction as well. So delta U would actually be equal to sigma of n final times U cap final – sigma of n initial times U cap initial + the psi which is extent of reaction times delta U r which would be the internal energy of reaction. So here we already identified the internal energy of the final and the initial conditions using the polynomials we have.

We also have a delta U r, we also have the psi value. We need to calculate the internal energy of reaction. So for calculating the internal energy of the reaction, we first need to know the standard heat of the reaction. So the standard heat of reaction can be calculated using the heat of formation of all the compounds.

So this would be heat of formation summation of the products where you have stoichiometric coefficient times heat of formation minus for the reactants you would have the stoichiometric coefficients times the heat of formation for the reactants. So now taking that into account, we have formaldehyde and water as the products and we have methane and oxygen as the reactants. So obviously oxygen would not have any heat of formation because it is an element.

So you would end up with, all of them have stoichiometric coefficients of 1. So the equation then becomes heat of formation, standard heat of formation of formaldehyde + standard heat of formation of water – standard heat of formation of the reactant which is methane. So doing this we can actually calculate the heat of reaction. So getting the values for these from the table, it would be -115.9 + (- 241.83) – (-74.85) and you would get a value for the standard heat of reaction as delta H r as -282.88 kJ/mol.

Now we need to calculate the specific internal energy change associated with the reaction. So which would be internal energy of the reaction delta U r dot. So we know that we can calculate this from the heat of reaction using this correlation. Heat of reaction – RT times sigma of gaseous products or the stoichiometric coefficients – the summation of this stoichiometric coefficients of gaseous reactants. So this is the equation.

So here we have all the components, reactants and products as gaseous components. The stoichiometric coefficients for all of them are 1. So you would end up with actually 1 + 1 – 1 – 1. So this term actually goes to 0 and you end up with standard heat of reaction to be equal to the internal energy of the reaction. So numerically they are the same. It should be 282.88 kJ/mol. So now we have all the terms.

We have the n final U cap finals, n initial, U cap initial, psi and your heat of reaction sorry internal energy of reaction. Now that we have all these values we can plug it into the equation for the heat balance which is Q.

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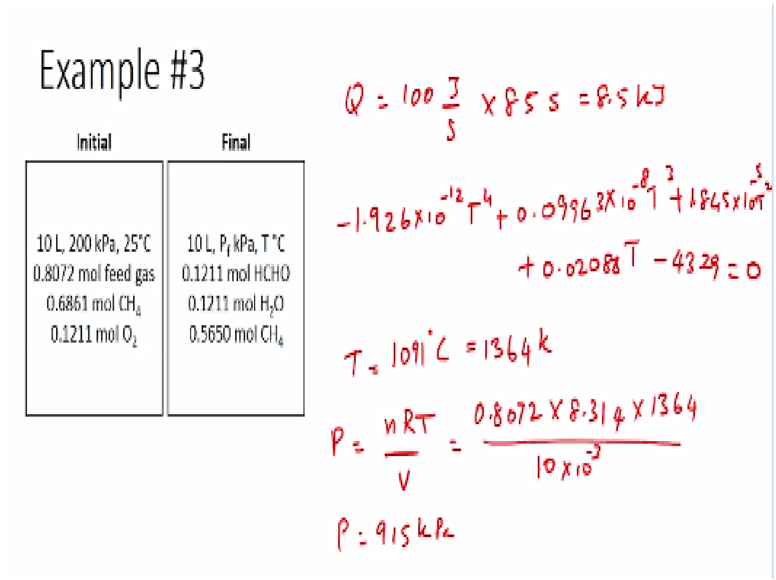

Example #3

Initial	Final
10 L, 200 kPa, 25°C 0.8072 mol feed gas 0.6861 mol CH_4 0.1211 mol O_2	10 L, P_f kPa, T °C 0.1211 mol HCHO 0.1211 mol H_2O 0.5650 mol CH_4

$$Q = 100\frac{J}{s} \times 85\,s = 8.5\,kJ$$

$$-1.926\times10^{-12}T^4 + 0.09963\times10^{-8}T^3 + 1.845\times10^{-5}T^2 + 0.02088T - 43.29 = 0$$

$$T = 1091^\circ C = 1364\,k$$

$$P = \frac{nRT}{V} = \frac{0.8072 \times 8.314 \times 1364}{10\times10^{-3}}$$

$$P = 915\,kPa$$

So in the problem statement, we have been told that heat is supplied by an electric coil at a rate of 100 watts for 85 seconds and then it is stopped. So the amount of heat which is supplied would be Q = 100 J/s times 85 s. So this would give us in terms of joules which is 8500 J or 8.5 kJ. So the total amount of heat supplied would be 8.5 kJ. So we have all the terms. So we have a polynomial representing the change in internal energies.

So substituting all that into the general energy balance equation we would end up with a polynomial which would be -1.926 times 10 power -12 T power 4 + 0.09963 times 10 power -8 T cube + 1.845 times 10 power -5 T square + 0.02088 times T – 43.29 kJ/mol as the equation = 0. So Q has also been accounted for in this equation and by solving this polynomial we will be able to get a temperature of 1091 degree Celsius and this reaches a pressure of P = nRT/v.

So this would basically be the number of moles in the final condition so which would add up to 0.8072 and so you have 0.8072 moles in the final condition. R is 8.314 and you have temperature as 1364 K. So we have 1091 degree Celsius which is = 1364 K. So this divided by volume which is 10 L which is 10 times 10 power -3 meter cube. So you are left with a pressure of 915 kPa. So this is below the threshold given for the problem.

So the vessel should be able to handle this pressure. However, in the second part of the problem we have been told that vessel explodes even though exactly that amount of heat is actually supplied. So this is a problem. So we need to identify why that is the case. So that is because you could actually have side reactions. The side reaction which you would observe would be for combustion reaction.

So methane when it is reacting with oxygen can actually have a combustion reaction and obviously the heat of reaction for a combustion reaction would be significantly higher than the formaldehyde formation reaction which we are looking at here. So because of that you would have had a much higher temperature which would have resulted in a very high pressure resulting in an explosion. So that is what the problem alludes to.

So with this we have actually completed the example problem and in the next few lectures we will have a review of all the aspects covering the energy balance concepts that we have learnt over the past few weeks. Thank you.