Engineering Thermodynamics
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Department of Chemical Engineering
Module 8
Lecture No 58
Examples on reaction thermodynamics & property relations

Welcome to the final tutorial of this course, today we will solve few problems based on reaction thermodynamics and thermodynamics property relations, so let us start it.

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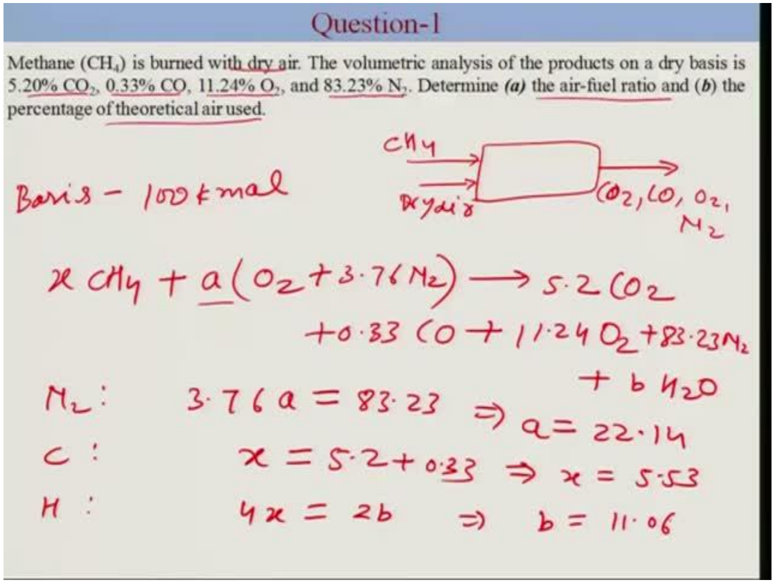

Question-1

Methane (CH_4) is burned with dry air. The volumetric analysis of the products on a dry basis is 5.20% CO_2, 0.33% CO, 11.24% O_2, and 83.23% N_2. Determine ***(a)*** the air-fuel ratio and (***b***) the percentage of theoretical air used.

Basis - 100 kmol

$$x\,CH_4 + \underline{a}(O_2 + 3.76N_2) \longrightarrow 5.2\,CO_2 + 0.33\,CO + 11.24\,O_2 + 83.23\,N_2 + b\,H_2O$$

N_2 : $3.76a = 83.23 \Rightarrow a = 22.14$

C : $x = 5.2 + 0.\underline{33} \Rightarrow x = 5.53$

H : $4x = 2b \Rightarrow b = 11.06$

Methane is burned with dry air, the volumetric analysis of product on a dry bases is 5.2 percent of CO2 is coming out point 33 percent of CO is coming out for 11.24 oxygen and 83.23 percent nitrogen. We have to determine the air fuel ratio and the percentage of theoretical air used, so what is happening here, methane is being burned with air and this air is dry ok. Now the product strength contains CO2 CO oxygen and nitrogen. So first we have to determine the air fuel ratio. We take a bases of 100 kilo mole of dry product bases is 100 kilo mole, so on this bases we can directly take the composition of CO2 COO2 and nitrogen in the product strength.

Before writing combustion equation first we assume that X kilo mole of methane is being burnt ok because it is not given in the question, so X kilo mole of methane is being burned with A A kilo mole of air, since 1 kilo mole of air contains 1 kilo mole of oxygen plus 3.76 kilo mole of nitrogen and the product strength will have 5.2 kilo mole of CO2 and point 33 kilo mole of carbon mono oxide plus 11.24 kilo mole of oxygen plus 83.23 kilo mole of nitrogen and oxygen and hydrogen will react and form water, so certain kilo mole of water will produce in the product strength.

From the mass balance we can obtain the unknown variables ok, so after making mass balance for nitrogen we get 3.76 A equal to 83.23, so from here we get A equal to 22.14. Similarly mass balance for carbon we get X equal to 5.2 plus point 33, so that gives X equal to 5.53 ok? And similarly for hydrogen 4X equal to 2V. That means V equal to 11.06 using X equal to 5.53 ok.

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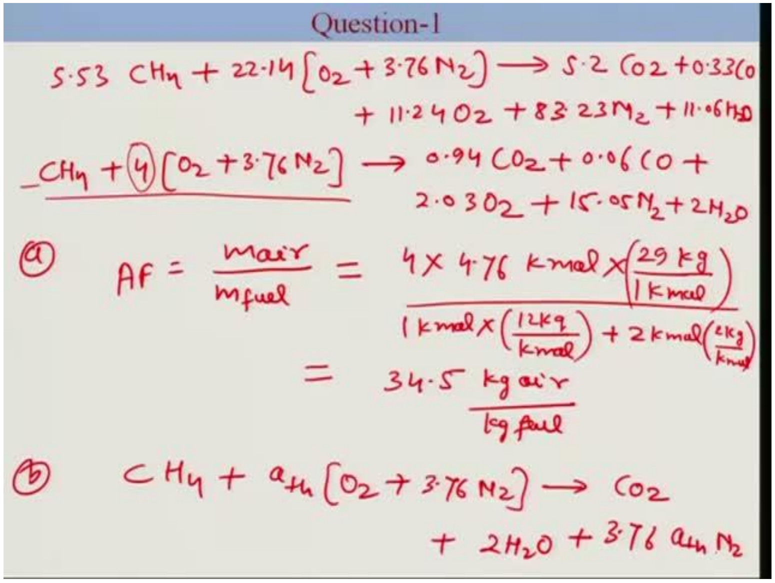

Question-1

$$5.53\ CH_4 + 22.14\,[O_2 + 3.76 N_2] \longrightarrow 5.2\ CO_2 + 0.33\ CO + 11.24\ O_2 + 83.23\ N_2 + 11.06\ H_2O$$

$$\underline{CH_4 + \textcircled{4}\,[O_2 + 3.76 N_2]} \longrightarrow 0.94\ CO_2 + 0.06\ CO + 2.03\ O_2 + 15.05\ N_2 + 2H_2O$$

ⓐ

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{4 \times 4.76\ kmol \times \left(\frac{29\ kg}{1\ kmol}\right)}{1\ kmol \times \left(\frac{12\ kg}{kmol}\right) + 2\ kmol\left(\frac{2\ kg}{kmol}\right)}$$

$$= 34.5\ \frac{kg\ air}{kg\ fuel}$$

ⓑ

$$CH_4 + a_{th}\,[O_2 + 3.76 N_2] \longrightarrow CO_2 + 2H_2O + 3.76\, a_{th}\, N_2$$

Now after substituting all these values in the combustion equation we get 5.53 CH4 plus 22.14 kilo mole of air that is 3.76 nitrogen and then product strength contain 5.2 kilo mole CO2, 0.33 carbon mono oxide and plus 11.24 oxygen that is 33.23 nitrogen and 11.06 water ok. So now for 1 kilo mole of fuel combustion equation can be written as CH4 plus O2 plus 3.76 and 2 gives 0.94 CO2 plus 0.06 of carbon mono oxide plus 2.03 of oxygen plus 15.05 nitrogen plus 2H2O ok.

Since we have been asked to calculate air fuel ratio ok, so in the first part we have to calculate air fuel ratio which is equal to mass of air divided by mass of fuel ok, so what is the mass of air? Stoichiometric coefficient of this reaction if you see, so stoichiometric coefficient is 4 for air multiplied by total kilo mole of air, so which is 4.76 kilo moles and since 1 kilo mole of air contain 29 kg ok divided by mass of the fuel that is mass of carbon plus mass of the hydrogen, so mass of carbon since here stoichiometric coefficient is 1, so 1 kilo mole times 12 kg per kilo mole 2 kilo mole tens 2 kg upon kilo mole ok.

So from here we get air fuel ratio equal to 34.5 kg of air divided by kg of fuel ok. Now in the second part we have to determine theoretical air so for that we need to know the theoretical amount of air and that can be obtained from theoretical combustion equation ok? So in the second part if you write combustion equation for theoretical air, that means complete combustion will take place 3.76 nitrogen, since complete combustion will take place, so product stream will contain CO2 H2 and nitrogen ok? So CO2 plus 2H2 plus 3.76 A theoretical into nitrogen ok.

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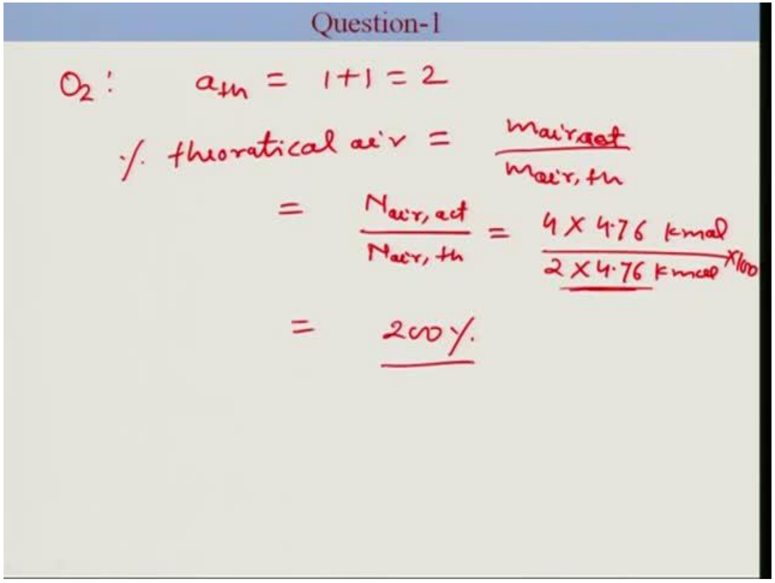

Question-1

$O_2: \quad a_{th} = 1+1 = 2$

$$\%\ \text{theoretical air} = \frac{m_{air,act}}{m_{air,th}}$$

$$= \frac{N_{air,act}}{N_{air,th}} = \underline{\frac{4 \times 4.76\ \text{kmol}}{2 \times 4.76\ \text{kmol}}} \times 100$$

$$= \underline{200\%}$$

From the mass balance of oxygen we get A theoretical equal to 1 plus 1 which is equal to 2 ok. Now the percentage theoretical air is equal to mass of air is equal to actual mass of air divided by theoretical mass of air ok. This is equal to actual moles of air divided by theoretical moles that we have used in the complete combustion. So 4 into, now we know actual moles of air which are 4 into 4.76 kilo mole divided by 2 times 4 into 76 kilo mole ok, this comes from theoretical combustion ok into 100. Now to get a percentage so this gives 200 percent of theoretical air.

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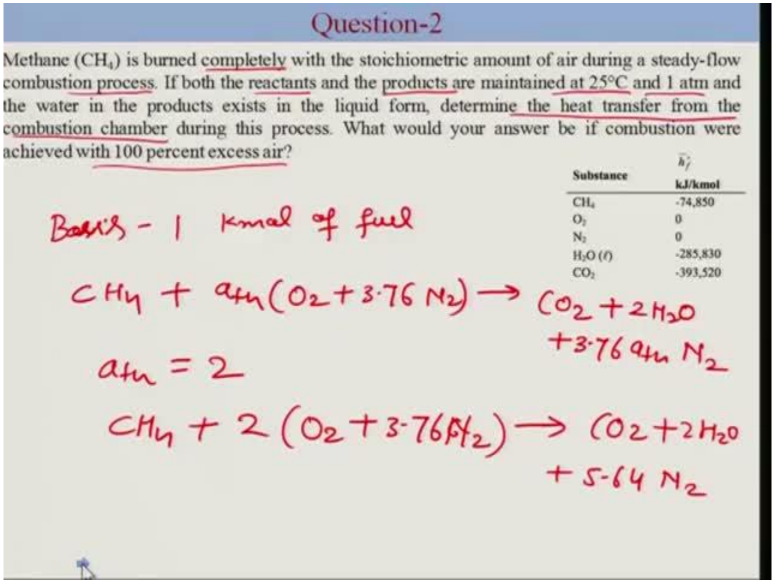

Question-2

Methane (CH_4) is burned completely with the stoichiometric amount of air during a steady-flow combustion process. If both the reactants and the products are maintained at 25°C and 1 atm and the water in the products exists in the liquid form, determine the heat transfer from the combustion chamber during this process. What would your answer be if combustion were achieved with 100 percent excess air?

Substance	$\bar{h}_f^{\circ}$ kJ/kmol
CH_4	-74,850
O_2	0
N_2	0
H_2O (ℓ)	-285,830
CO_2	-393,520

Basis - 1 kmol of fuel

$$CH_4 + a_{th}(O_2 + 3.76\,N_2) \rightarrow CO_2 + 2H_2O + 3.76\,a_{th}\,N_2$$

$$a_{th} = 2$$

$$CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 5.64\,N_2$$

Now moving to the next question, methane is burned completely with the stoichiometric amount of air during a steady flow combustion process. If both the reactants and products are maintained at 25 degree centigrade and 1 time and the water in the products exists in the liquid form determine the heat transfer from the combustion chamber during this process and what would your answer be if combustion were achieved with 100 percent excess air ok. Since fuel is burnt completely, so the product will contain only H2O, CO2 and nitrogen ok.

So considering 1 kilo mole of fuel ok, if you write combustion equation then it will be like CH4 plus A theoretical air will give CO2 plus water plus 3.76 A theoretical N2 ok. From mass balance A theoretical equal to 2 ok? After substituting we get CH4 plus 2 times O2 plus 3.76 nitrogen gives CO2 plus 2 H2O plus 5.64 kilo mole of nitrogen ok. But we have to determine amount of heat coming out of the combustion chamber.

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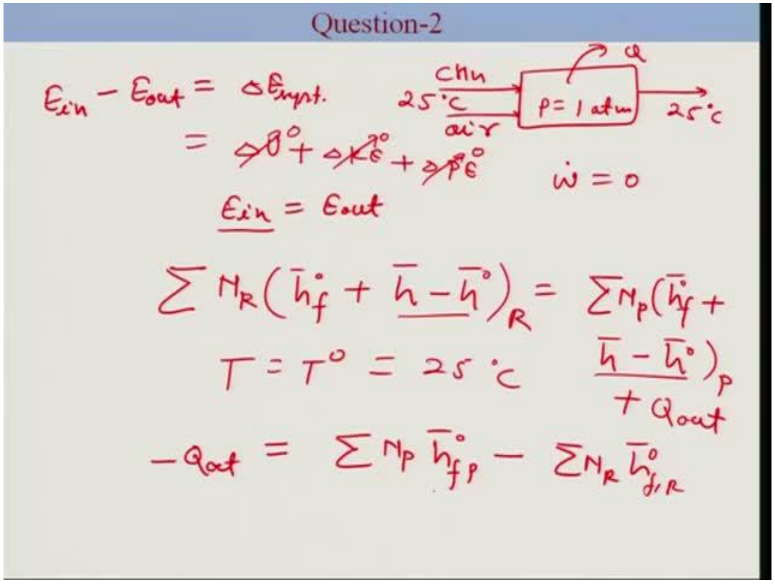


Question-2

$$E_{in} - E_{out} = \Delta E_{syst.}$$

$$= \cancel{\Delta U}^{0} + \cancel{\Delta KE}^{0} + \cancel{\Delta PE}^{0}$$

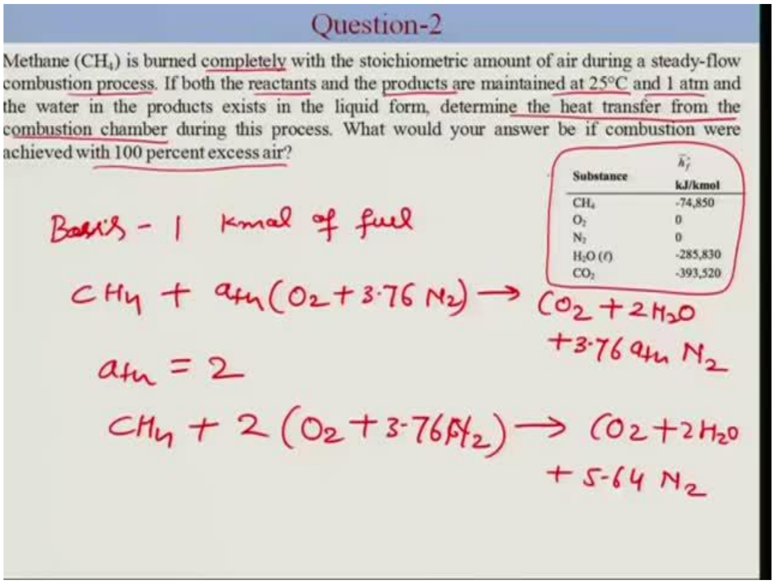
$$\dot{W} = 0$$

$$\underline{E_{in}} = E_{out}$$

$$\sum N_R\left(\bar{h}_f^\circ + \underline{\bar{h} - \bar{h}^\circ}\right)_R = \sum N_P\left(\bar{h}_f^\circ + \underline{\bar{h} - \bar{h}^\circ}\right)_P + Q_{out}$$

$$T = T^\circ = 25\,^\circ C$$

$$-Q_{out} = \sum N_P \bar{h}^\circ_{f\,P} - \sum N_R \bar{h}^\circ_{f,R}$$



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$$a_{th} = 2$$

$$CH_4 + 2(O_2 + 3.76\,N_2) \rightarrow CO_2 + 2H_2O + 5.64\,N_2$$

So what is happening in the combustion chamber? Methane is being burned with air ok, it is entering into the combustion chamber at 25 degree centigrade and leaving it at 25 degree centigrade as well ok and the combustion is being done at 1 ATM. So we have to determine the amount of heat coming out of this combustion chamber, since temperature is constant, so it will lose its energy to the surrounding.

So that heat can be obtained by energy balance on this combustion chamber, so from the energy balance what we get E in minus E out equal to delta E of this system ok? And here we assume that air behaves as an ideal gas ok and we know that delta E system is nothing but delta of the internal energy plus delta of kinetic energy plus delta of potential energy and we also assume that change in kinetic energy is 0 potential energy is 0, since temperature is constant so this delta will also be 0.

That means energy in will be equal to energy out. Since there is no set works so this is W dot will be 0, so the total heat coming into the chamber is the heat of the reactant ok, so the heat of reactant is nothing but the number of moles of reactant times enthalpy of formation of reactant at that reference temperature plus enthalpy at working temperature minus enthalpy at reference temperature ok will be equal to number of moles of product stream times, enthalpy of formation plus enthalpy at working temperature. So that is H minus H not of the product.

Since working temperature and reference temperature are same in this case ok, T equal to T not which is 25 degree centigrade ok one more thing is missing here, Q is coming out ok, so Q out will be there. So after solving it and rearranging we get Q out equal to number of moles of product times enthalpy of formation of product minus number of moles of reactant times enthalpy of formation of reactant because these terms will be 0 since working temperature and reference temperatures are same.

So we need to find out Q out so that heat of formation data for all the substances are given here ok? So utilising these heat of formation data we will calculate Q out ok?

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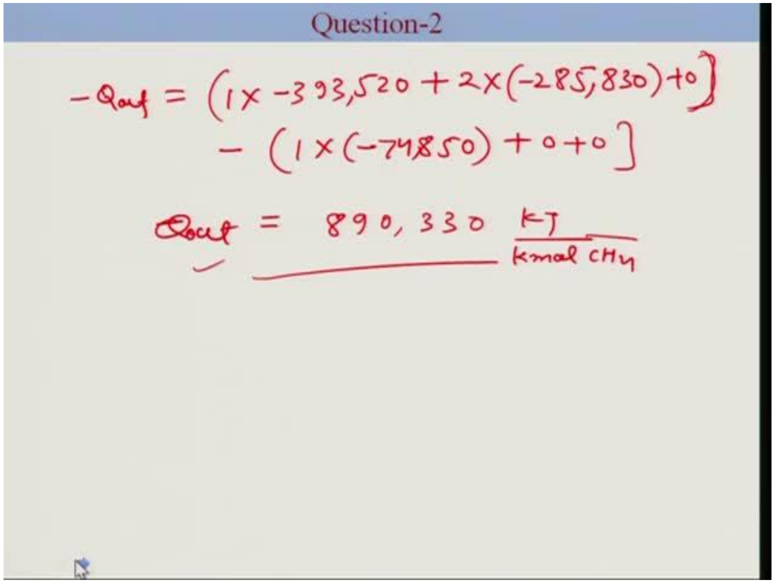

Question-2

$$-Q_{out} = (1 \times -393{,}520 + 2 \times (-285{,}830) + 0]$$

$$- (1 \times (-74850) + 0 + 0]$$

$$Q_{out} = 890{,}330 \ \frac{kJ}{kmol\ CH_4}$$

So after plugging all the heat of formation data which is Q out equal to 1 into 393520, these are the enthalpy of product streams 2 times minus 285830 minus enthalpy of the reactant, 1 into 74850 plus because naturally occurring gases will have 0 heat formation like nitrogen and oxygen. So after solving it Q out will be 890 kilo joule per kilo mole of CH4 ok. So this much of heat will come out of the combustion chamber, it has also been asked if we use 100 percent of excess air then what will happen to the this energy?

So if combustion is achieved with 100 percent excess air, the answer would be the same, since it would enter and leave at 25 degree and have no energy, so answer remains same.

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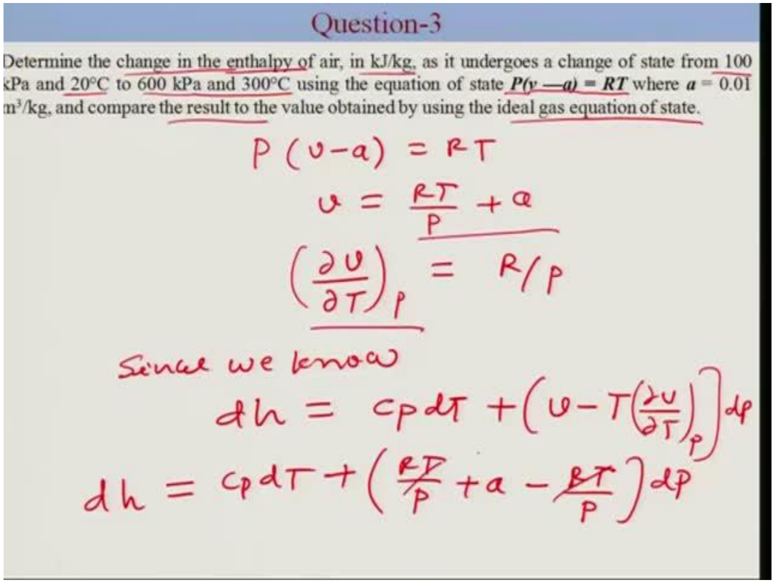

Question-3

Determine the change in the enthalpy of air, in kJ/kg, as it undergoes a change of state from 100 kPa and 20°C to 600 kPa and 300°C using the equation of state ***P(v — a) = RT*** where ***a*** = 0.01 m³/kg, and compare the result to the value obtained by using the ideal gas equation of state.

$$P(v-a) = RT$$

$$v = \frac{RT}{P} + a$$

$$\left(\frac{\partial v}{\partial T}\right)_P = R/P$$

Since we know

$$dh = c_p\,dT + \left(v - T\left(\frac{\partial v}{\partial T}\right)_P\right) dP$$

$$dh = c_p\,dT + \left(\frac{RT}{P} + a - \frac{RT}{P}\right) dP$$

So moving to the next question, determine the change in enthalpy of air in kilo joule per kg as it undergoes a change of state from 100 kilo Pascal and 20 degree centigrade to 600 kilo Pascal and 300 degree centigrade uing the equation of state PV minus A equal to RT where A value is given 0.01 meter per kg and compare the results with the ideal gases equation of state. Since equation of state is given which is equal to PV minus A equal to RT, so after solving it for V, we get V equal to RT by P plus A ok.

First we get derivative of volume with respect to T keeping pressure constant and from here we get R upon P. Now we will utilise this, this expression to get enthalpy. Since we know DH change in enthalpy is equal to CP DT plus V minus T times del V upon del T at constant P. So this is a general expression for any equation of state, so substituting this value here, we get BH equal to CPDT plus volume, volume is RT by P, ok RT by plus A minus RT by P ok.

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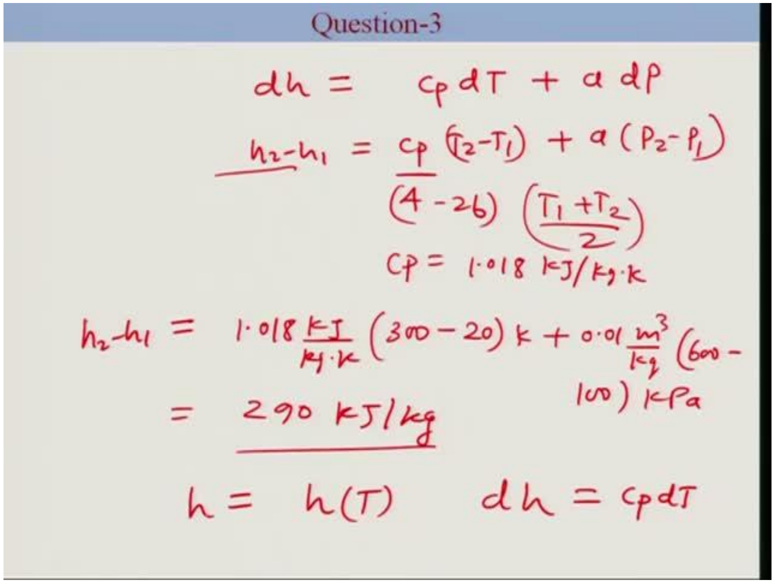

Question-3

$$dh = c_p dT + a\, dP$$

$$\underline{h_2 - h_1} = \underline{c_p} (T_2 - T_1) + a (P_2 - P_1)$$

$$(A-26) \quad \left(\frac{T_1 + T_2}{2}\right)$$

$$c_p = 1.018 \text{ kJ/kg}\cdot\text{K}$$

$$h_2 - h_1 = 1.018 \frac{\text{kJ}}{\text{kg}\cdot\text{K}} (300 - 20)\,\text{K} + 0.01 \frac{\text{m}^3}{\text{kg}} (600 - 100)\,\text{kPa}$$

$$= \underline{290 \text{ kJ/kg}}$$

$$h = h(T) \qquad dh = c_p dT$$

So this gets cancelled out and what we get from here is DH equal to CPDT plus A times DP, after integrating it we get H2 minus H1 equal to CP T2 minus T1 plus A times P2 minus P 1 ok. CP can be obtained from the table A to B ok and this can be obtained at average temperature T1 plus T2 by 2, so since temperature is changing ok it is not constant, so corresponding CP is equal to 1.018 kilo joule per kg calorie ok.

So after substituting all these values in this expression we get H2 minus H1 equal to CPDT. That means 1.018 kilo joule per kg times delta T which is 300 minus 20 calorie plus value of A is given which is 0.01 meter cube per kg times delta P is 600 minus 100 kilo Pascal. So after solving it we get 290 kilo joule per kg ok, so this much of enthalpy will change. We have to compare this result with ideal gas equation of state. Since we know enthalpy of ideal gas is function of temperature only ok and from there we get DH equal to CPDT ok.

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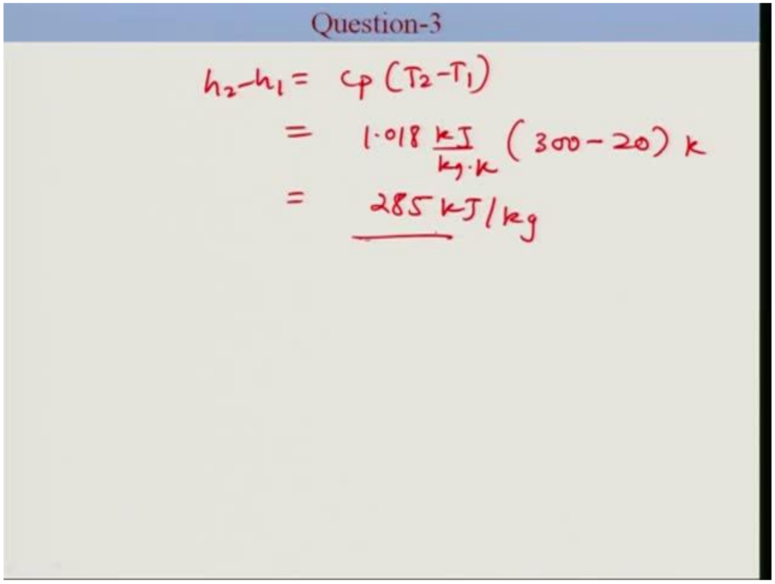

Question-3

$$h_2 - h_1 = c_p (T_2 - T_1)$$

$$= 1.018 \frac{kJ}{kg \cdot K} (300 - 20) K$$

$$= \underline{285} \, kJ/kg$$

After integrating we get H2 minus H1 will be equal to CP T2 minus T1, so we know CP value 1.018 kilo joule per kg times 300 minus 20 calorie. So this gives 285 kilo joule per kg, now you can see the difference, here change in enthalpy is less than that of the previous case ok.

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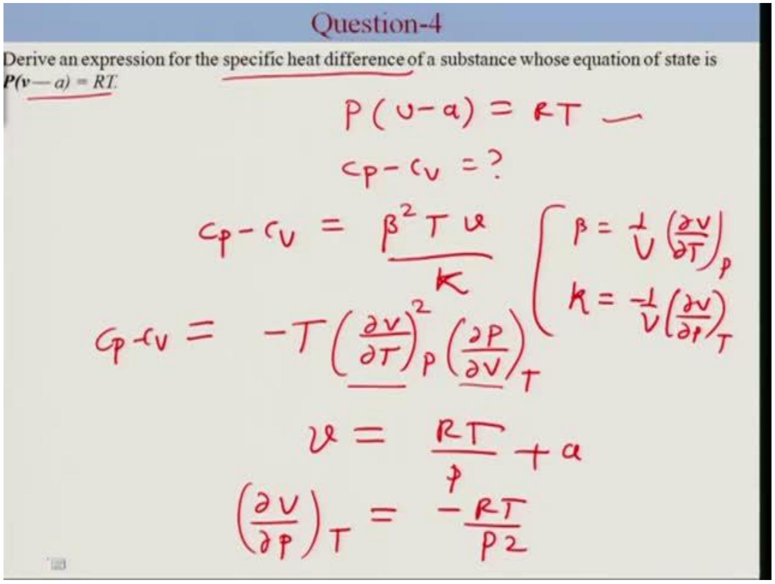

Question-4

Derive an expression for the specific heat difference of a substance whose equation of state is *P*(*v* — *a*) = *RT*.

$$P(v-a) = RT$$

$$c_p - c_v = ?$$

$$c_p - c_v = \frac{\beta^2 T v}{K} \quad \left\{ \begin{array}{l} \beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \\ k = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \end{array} \right.$$

$$c_p - c_v = -T \underline{\left(\frac{\partial v}{\partial T}\right)_p^2} \underline{\left(\frac{\partial P}{\partial v}\right)_T}$$

$$v = \frac{RT}{p} + a$$

$$\left(\frac{\partial v}{\partial p}\right)_T = -\frac{RT}{p^2}$$

Now moving to the next question, derive an expression for specific heat difference of a substance whose equation of state is this, so it is given that equation of state is PV minus A equal to RT, now we have to determine CP minus CV value ok. Since we know CP minus CV is equal to beta square TV upon cuppa where beta is volumetric spencer coefficient ok cuppa is isothermal compressibility factor, so if you see beta is equal to 1 by V del V upon del T at constant pressure, whereas cuppa equal to minus 1 by V del V upon del P at constant temperature right.

So if we insert it here we get CP minus CV equal to minus T del V upon del T at constant pressure square then del P upon del V at constant T. Since equation of state is given, we need to find del V by del T and del P by del V from this equation of state, so solving this equation of state for V which is specific volume V will be equal to RT upon P plus A ok.

Taking derivative with respect to P, del V upon del P at constant T will give us minus RT upon P square ok but we need del P upon del V right?

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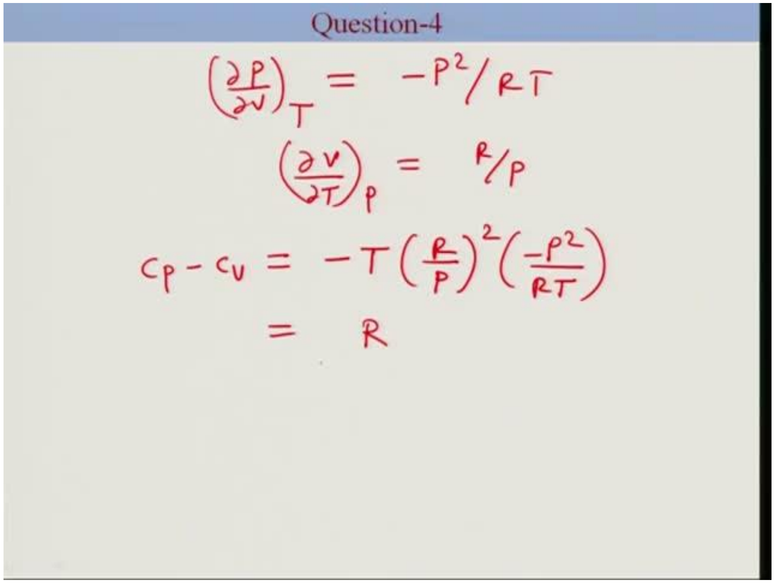

Question-4

$$\left(\frac{\partial P}{\partial v}\right)_T = -P^2/RT$$

$$\left(\frac{\partial v}{\partial T}\right)_P = R/P$$

$$c_p - c_v = -T\left(\frac{R}{P}\right)^2\left(\frac{-P^2}{RT}\right)$$

$$= R$$

So after solving it we get del P upon del V at constant T equal to minus P square upon RT right and taking derivative with respect to T of that equation of state at constant pressure will give us R upon P.

So substituting all these values we get CP minus CV minus T times R by P square into minus P square upon RT, so this gives R ok. So CP minus CV will be equal to R, so with this we have completed this course, hope you have enjoyed this course, thank you.