Chemical and Biological Thermodynamics: Principles to Applications

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Lecture - 05
Tutorial – 2

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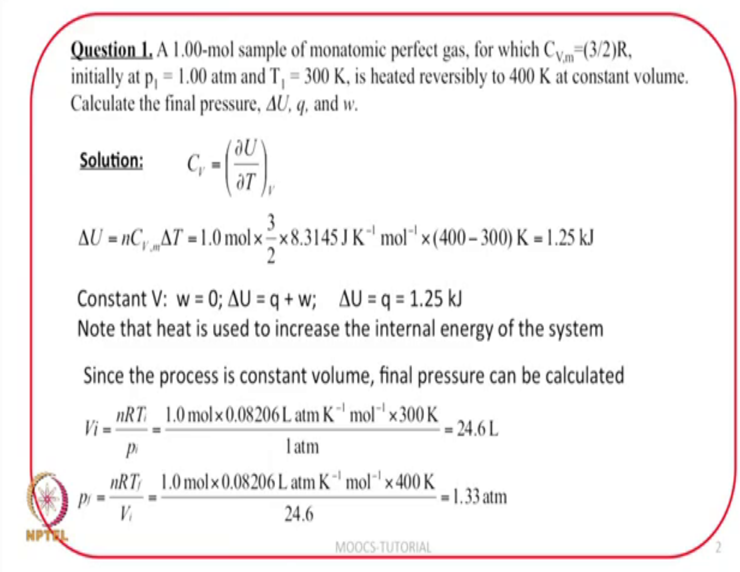

Question 1. A 1.00-mol sample of monatomic perfect gas, for which $C_{V,m}=(3/2)R$, initially at $p_1 = 1.00$ atm and $T_1 = 300$ K, is heated reversibly to 400 K at constant volume. Calculate the final pressure, ΔU, q, and w.

Solution: $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

$$\Delta U = nC_{V,m}\Delta T = 1.0\,\text{mol} \times \frac{3}{2} \times 8.3145\,\text{J K}^{-1}\,\text{mol}^{-1} \times (400-300)\,\text{K} = 1.25\,\text{kJ}$$

Constant V: w = 0; ΔU = q + w; ΔU = q = 1.25 kJ
Note that heat is used to increase the internal energy of the system

Since the process is constant volume, final pressure can be calculated

$$Vi = \frac{nRT_i}{p_i} = \frac{1.0\,\text{mol} \times 0.08206\,\text{L atm K}^{-1}\,\text{mol}^{-1} \times 300\,\text{K}}{1\,\text{atm}} = 24.6\,\text{L}$$

$$p_f = \frac{nRT_f}{V_i} = \frac{1.0\,\text{mol} \times 0.08206\,\text{L atm K}^{-1}\,\text{mol}^{-1} \times 400\,\text{K}}{24.6} = 1.33\,\text{atm}$$

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In this lecture, we will discuss some numerical problems based on first law of thermodynamics, and see how the concepts developed on changing internal energies connection with the heat and work can be applied. Let us take a look at this question number 1. A 1 mol sample of monatomic perfect gas, for which the constant volume heat capacity is equal to 3 by 2 R, initially at p 1 equal to 1 atmosphere and T 1 equal to 300 Kelvin is heated reversibly to 400 Kelvin at constant volume. Calculate the final pressure change in internal energy, q and work. So, first of all let us see what is the information given to us. The gas is monatomic and perfect, the value of C v is given even if it was not given we know that the value of C v for a monatomic perfect gas is equal to 3 by 2 R.

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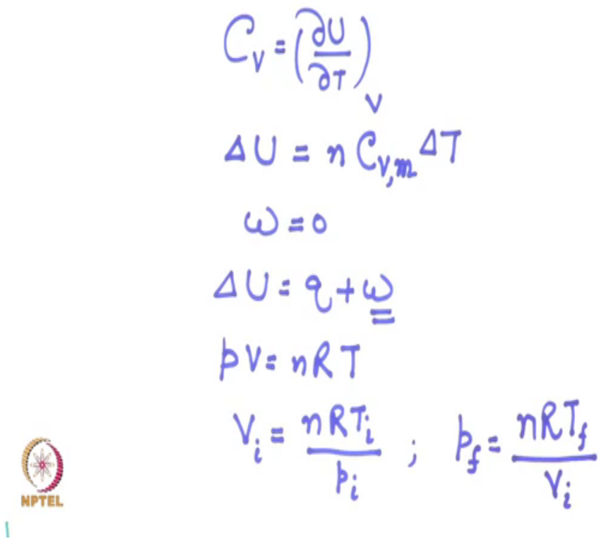

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\Delta U = n\, C_{v,m} \Delta T$$

$$w = 0$$

$$\Delta U = q + \underline{\underline{w}}$$

$$pV = nRT$$

$$V_i = \frac{nRT_i}{p_i} \; ; \quad p_f = \frac{nRT_f}{V_i}$$

Now, as we discussed in the previous lecture that C v is equal to dou U by dou T at constant volume it is always true for perfect gas. We can use this equation to get delta U is equal to n times C v m into delta T, where n is the number of moles and C v, m is the molar constant volume heat capacity. So, from this, we can easily get the value of delta U. Let us take a look at the slide n which is one mol given information is given, C v is 3 by 2 R, and I will use the value of R in Joules per Kelvin per mol, because finally I would like to have the answer in Joules, and the temperature difference is 400 minus 300. So, therefore, the value of delta U after I convert into kilo Joules come out to be 1.25 kilo Joule very easy. Second, also note that the heating is done at constant volume. So, for any constant volume process connected with the p v changes of a gas, if the volume is held constant, there is no work done.

So, straight away, we can set w is equal to 0. So, if w is equal to 0, then I use the first law delta U is equal to q plus w, and immediately we get to know that delta U is equal to q. And let us see the calculations. Since, delta U and we have just calculated to be 1.25 kilo Joules. So, q is also equal to 1.25 kilo Joules. Please note here that the heat is used to increase the internal energy of the system here, since no work is done; whatever heat is supplied that is directly getting converted into change in internal energy that is adding up to the internal energy of the system.

Now, the only thing which is remaining is to calculate the final pressure. The gas is ideal. So, whenever a gas is ideal, I can use the expression p V is equal to n R T. And initial volume can be calculated from n R T i upon p i all the information is given n is given, R we can choose of some suitable units, and initial temperature and initial pressure are given. Let us take a look at the calculations; n is 1 mol. And here I will use R in the units of liter atmosphere Kelvin inverse mol inverse because the pressure given to me is in atmosphere.

So, after substitution, we get a volume initial volume of 24.6 liter. The given information is that the system is heated reversibly at constant volume. And here you see since the system is heated reversibly that means, it must be the pressure or the temperature not the pressure because if you change the pressure the volume will change. Here the temperature is being changed in a reversible manner in an infinitesimally small amounts. So, in order to get now the final pressure p f will be equal to n R T f, and since it is a constant volume process I can use V I, which I just calculated look at the slide V i comes out to be 24.6 liter. And the final pressure from this expression n R T f by V i will come out to be 1.33 atmosphere. So, the temperature is being increased the volume is being held fixed, so obviously, the pressure is going to increase. So, the pressure has increased from 1 atmosphere to 1.33 atmosphere.

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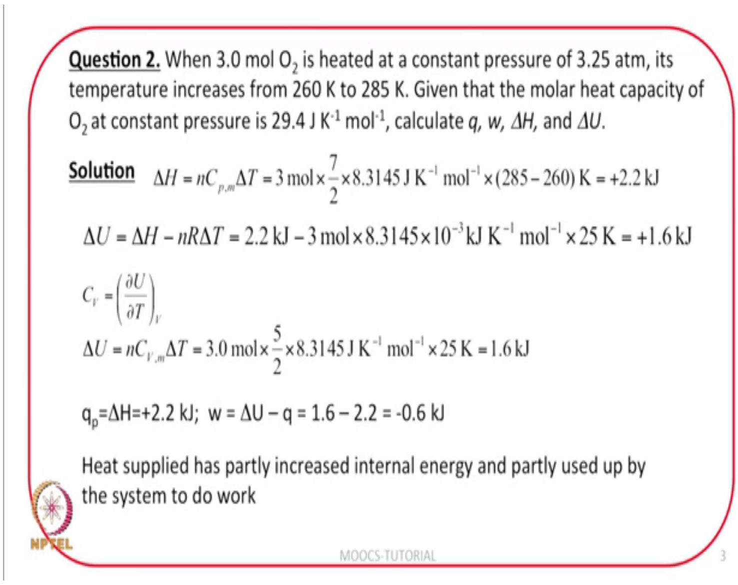

Question 2. When 3.0 mol O_2 is heated at a constant pressure of 3.25 atm, its temperature increases from 260 K to 285 K. Given that the molar heat capacity of O_2 at constant pressure is 29.4 J K^{-1} mol^{-1}, calculate *q, w, ΔH,* and *ΔU*.

Solution $\Delta H = nC_{p,m}\Delta T = 3\,\text{mol} \times \frac{7}{2} \times 8.3145\,\text{J K}^{-1}\,\text{mol}^{-1} \times (285 - 260)\,\text{K} = +2.2\,\text{kJ}$

$$\Delta U = \Delta H - nR\Delta T = 2.2\,\text{kJ} - 3\,\text{mol} \times 8.3145 \times 10^{-3}\,\text{kJ K}^{-1}\,\text{mol}^{-1} \times 25\,\text{K} = +1.6\,\text{kJ}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\Delta U = nC_{V,m}\Delta T = 3.0\,\text{mol} \times \frac{5}{2} \times 8.3145\,\text{J K}^{-1}\,\text{mol}^{-1} \times 25\,\text{K} = 1.6\,\text{kJ}$$

$q_p = \Delta H = +2.2$ kJ; $w = \Delta U - q = 1.6 - 2.2 = -0.6$ kJ

Heat supplied has partly increased internal energy and partly used up by the system to do work

Now, let us take a look at a different type of question, and see how to address that. Now, it is a question when the pressure is held constant when 3 mol of oxygen is heated at a constant pressure of 3.25 atmosphere, its temperature increases from 260 Kelvin to 285 Kelvin. Given that the molar heat capacity of oxygen at constant pressure is 29.4 Joules per Kelvin per mol, calculate q, w, delta H and delta U. And also let us assume that the oxygen gas is behaving ideally. So, what is the information given, we are given that the process is a constant pressure process, and we also are given the increase in temperature. So, we can easily get delta H for this process from this expression.

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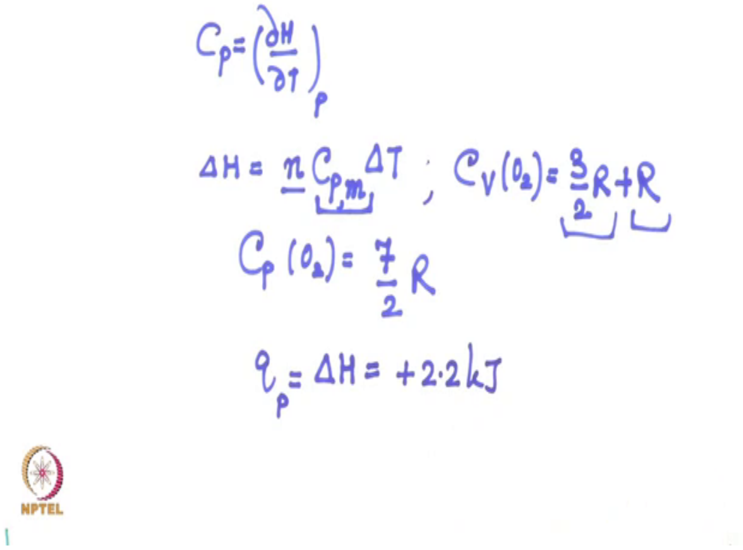

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

$$\Delta H = \underline{n}\,\underbrace{C_{p,m}}_{}\,\Delta T \; ; \; C_v(O_2) = \underbrace{\frac{3}{2}R}_{} + \underbrace{R}_{}$$

$$C_p(O_2) = \frac{7}{2}R$$

$$q_p = \Delta H = +2.2\,kJ$$

C p is equal to dou H by dou T at constant pressure, so delta H is equal to n times C p m into delta T. If I take dT to other side integrate and treat heat capacity at constant pressure as a constant quantity means independent of temperature then I can write this equation. The value of n is given the value of C p m heat capacity at constant pressure for oxygen. Oxygen is a diatomic gas, for a perfect monatomic gas the value of C v is 3 by 2 R, and C p is 3 by 2 R plus R, which is 5 by 2 R. And here oxygen will diatomic, therefore the value of C p for oxygen will be equal to 3 by 2 R contribution to C v comes from translational degree of freedom and being a linear molecule.

Another R contribution comes from the rotational degree of freedom. So, C v for oxygen gas will be 3 by 2 R plus R, this is due to translational degree of freedom this is due to rotational degree of freedom which is 5 by 2 R. And if you add another r to this because c p minus C v is equal to R or if I take the difference in molar heat capacities C p m minus C v m is equal to R. So, C p is going to be 7 by 2 R, 5 by 2 R plus R is equal to 7 by 2 R.

So, I use this information to calculate delta H, let us take a look at the slide delta H is equal n times C p m times delta T, and is 3 mol C p m as I just discussed is 7 by 2 into R. Let us choose the units to be 8.3145 Joules per Kelvin per mol. And the difference in temperature is 285 minus 260 Kelvin. A point to be noted here is when you are using the difference whether you use the temperatures in Kelvin or you use the temperature in degree Celsius, it does not matter. And the calculation suggests that the number turns out to be plus 2.2 kilo Joules. And immediately we can from here only say that q is equal to it is a constant pressure process is equal to delta H. So, this turns out to be also plus 2.2 kilo Joules.

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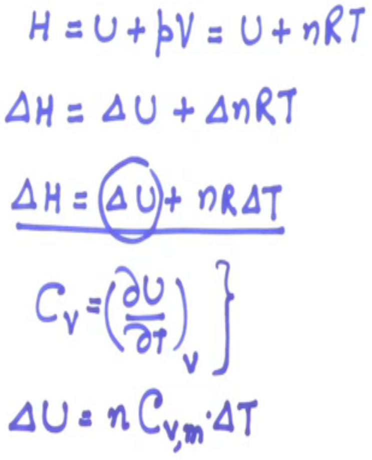

$$H = U + pV = U + nRT$$

$$\Delta H = \Delta U + \Delta n RT$$

$$\underline{\Delta H = \Delta U + nR\Delta T}$$

$$\left. C_V = \left(\frac{\partial U}{\partial T}\right)_V \right\}$$

$$\Delta U = n\, C_{V,m} \cdot \Delta T$$

Now, how do you calculate the value of delta U? There are two ways of calculating the value of delta U over here. One is that we know H is equal to U plus p V; and if I use it for a gas perfect gas U plus n R T. So, delta H will be equal to delta U plus delta n R T and here the temperature is changing. So, delta H will be equal to delta U plus n r delta T, this equation can be used to get the value of delta U.

Now let us go back to the slide. So, delta U is equal to delta H minus n R delta T, we substitute the value of delta H as 2.2 kilo Joules, n is equal to 3 mol, R is equal to 8.3145 and I divide by 1000 to convert into kilo Joules per Kelvin per mol. And delta T is 25 Kelvin you see, delta U is turning out to be plus 1.6 kilo Joules. I can also get the same number from the definition of C v because C v is equal to dou U by dou T at constant volume. Although here the volume is constant, but as I discussed in the previous lecture that this equation holds true for perfect gases whether the pressure is held constant or volume in held constant does not matter.

So, therefore, delta U from this equation will be equal to n times C v m into delta T. And if I substitute the values n as 3 mol, C v is 5 by 2 R, for the reasons that I just discussed and temperature difference is 25 Kelvin and you see you get the same number 1.6 kilo Joules. Whether you use the equation delta U is equal to delta H minus n R delta T or delta U is equal to n times C v m delta t you get the same answer.

Now, q is equal to plus 2.2 kilo Joule that we have already discussed because it is a constant pressure process. So, the all the heat which is supplied at constant pressure is equal to delta H. And the value of work can be obtained by using the first law that is delta U is equal to q plus w. And I seen on the slide that w is equal to delta U minus q which is equal to 1.6 minus 2.2 is equal to minus 0.6 kilo Joule. These are the numbers.

But let us look at the meaning coming out from these number. The heat supplied is 2.2 kilo Joules and though change in internal energy is 1.6 kilo Joules that means, all the heat which is supplied has not led to increase in the internal energy, some of it has been used to do the work that means, the system has done some work. And that work of driving back the surroundings is equal to minus 0.6 kilo Joules known this is the negative sign which tells that that the system has done the work. So, yes, I always have mentioned earlier that in thermodynamics, it is not just the numbers, but the sign also carries a lot of meaning.

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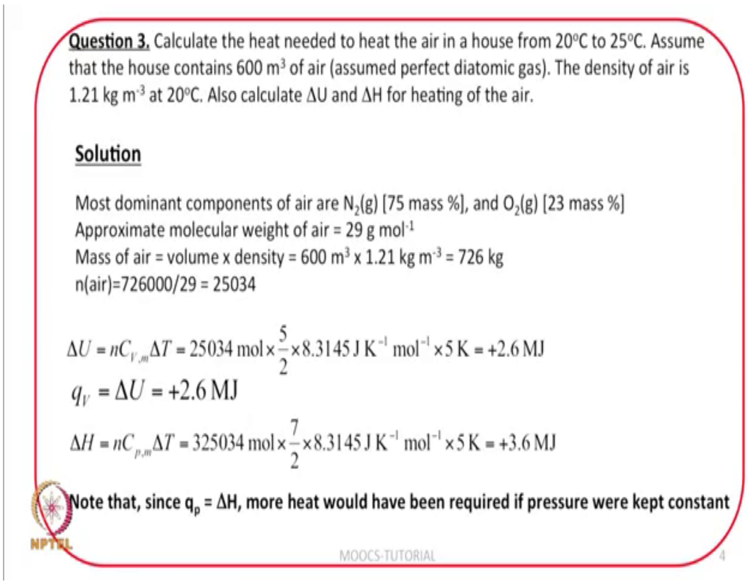

Question 3. Calculate the heat needed to heat the air in a house from 20°C to 25°C. Assume that the house contains 600 m^3 of air (assumed perfect diatomic gas). The density of air is 1.21 kg m^{-3} at 20°C. Also calculate ΔU and ΔH for heating of the air.

Solution

Most dominant components of air are $N_2(g)$ [75 mass %], and $O_2(g)$ [23 mass %]
Approximate molecular weight of air = 29 g mol^{-1}
Mass of air = volume x density = 600 m^3 x 1.21 kg m^{-3} = 726 kg
n(air)=726000/29 = 25034

$$\Delta U = nC_{V,m}\Delta T = 25034\ \text{mol} \times \frac{5}{2} \times 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1} \times 5\ \text{K} = +2.6\ \text{MJ}$$

$$q_V = \Delta U = +2.6\ \text{MJ}$$

$$\Delta H = nC_{p,m}\Delta T = 325034\ \text{mol} \times \frac{7}{2} \times 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1} \times 5\ \text{K} = +3.6\ \text{MJ}$$

Note that, since q_p = ΔH, more heat would have been required if pressure were kept constant

Now, let us take another type of question. Calculate the heat needed to heat the air in a house from 20 degree Celsius to 25 degree Celsius. Assume that the house contains 600 meter cube of air assumed perfect diatomic gas. The density of air is 1.21 kilo Joules per meter cube at 20 degree Celsius; also calculate delta U and delta H for heating of the air. It is an interesting question, and will lead us to the calculation of the amount of heat needed to just increase the temperature from 20 to 25 degree that just 5 degree centigrade change in temperature of the house. And the volume of air in the house if we consider that the whole house is filled with air of house it is that means, it is about one bedroom hall kitchen kind of apartment 600 meter cube of the volume. So, here I need to calculate heat.

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$$\underbrace{q_v} = \underbrace{\Delta U} = \overset{\checkmark}{\underline{\underline{n}}}\,\overset{\checkmark}{C}_{v,m}\,\underbrace{\Delta T}$$

$$\Delta H = \underbrace{n} \cdot \underbrace{C_{p,m}} \cdot \Delta T$$

So, heat we need to decide under constant pressure condition or under constant volume condition. A house has a constant volume, the volume of the house does not change pressure can change that means, we should target q v which is equal to delta U, this is what we need to calculate. And delta U means we should now focus on heat capacity at constant volume. So, this will be equal to n times C v m into delta T that means, now I need to calculate the number of moles. And in order to calculate number of moles, I need the weight of air, the mass of air present in the house. Since, we know the density I can easily calculate the mass. Mass is equal to volume into density. And once I know mass, and if I know the molecular weight of air, I can easily calculate the mass of air or number of moles of air present in the house.

Now, what does the air contain air contains nitrogen and oxygen in majority. Let us say about 75 mass percent nitrogen and about 23 mass percent oxygen, and remaining there are other gases. The approximate molecular weight of air is 29 gram per mol and mass of the air can be calculated from volume and density, mass is equal to volume times density which is 600 meter cube into 1.21 kilogram per meter cube, which is 725 kilogram. And then the number of moles of air will be equal to the weight divided by molecular weight the mass of the air is 726 kilogram which is 726 into 10 raise to the power 3 gram divided by 29 gram per mol. So, the number of moles come out to be 25034.

So, once I have n then I need the value of C v m. And since it is assumed a perfect diatomic gas, so therefore, C v m has to be used as 5 by 2 R; we just discussed in question number 2. So, I have the information on C v m and we are already told that we need to calculate the value of q for just a 5 degree centigrade change in the temperature. And just take a look at the calculations, delta U which is equal to n times C v m times delta T, you substitute the values of n 25034 mol, C v m as 5 by 2 R, and temperature change as 5 Kelvin. The value of delta U comes out to be plus 2.6 mega Joule and that is what our target was to find out. The heat supplied at constant volume that means, the amount of heat that must be supplied simply to change the temperature from 20 degree centigrade to 25 degree centigrade in a house of fairly 1 BHK, you require 2.6 mega Joule of heat. And then you know by using appropriate equations you one can even try to find out the electricity bill that will come to just provide this much heating in the house.

Next is to calculate delta H, and it can be calculated in the same way as we calculated earlier that delta H can be calculated from n into C p m into delta T. Now, we have the value of n C p m will be 7 by 2 R then delta t is same that is 5 Kelvin. And let us take a look at the slide the value of delta H comes out to be 3.6 mega Joule. So, you see the first law of thermodynamics allows us to find out many useful thermodynamic parameters which are either connected with internal energy or connected with heat and also one can connect this with the work. Suppose, if the pressure work kept constant, you know in the house we discussed that the volume is held constant. So, we need to calculate q v. If pressure were held constant, you see how much amount of heat would have required, you would have required more heat 3.6 mega Joule.

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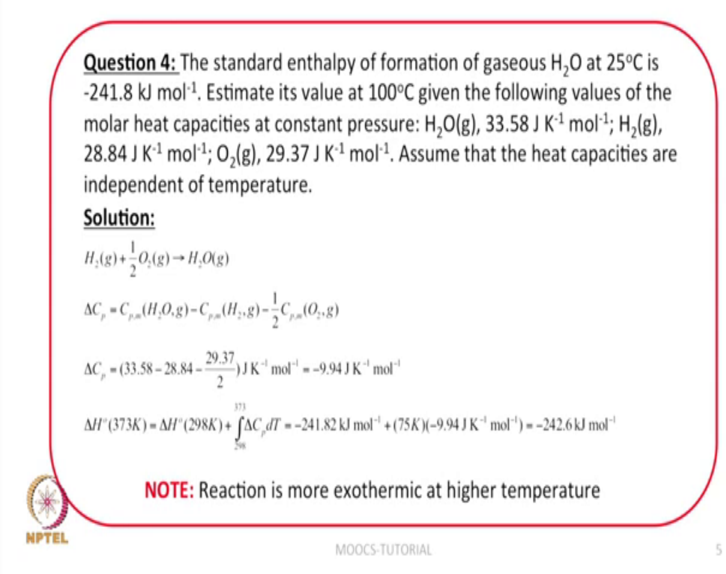

Question 4: The standard enthalpy of formation of gaseous H_2O at 25°C is -241.8 kJ mol^{-1}. Estimate its value at 100°C given the following values of the molar heat capacities at constant pressure: $H_2O(g)$, 33.58 J K^{-1} mol^{-1}; $H_2(g)$, 28.84 J K^{-1} mol^{-1}; $O_2(g)$, 29.37 J K^{-1} mol^{-1}. Assume that the heat capacities are independent of temperature.

Solution:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$$

$$\Delta C_p = C_{p,m}(H_2O,g) - C_{p,m}(H_2,g) - \frac{1}{2}C_{p,m}(O_2,g)$$

$$\Delta C_p = (33.58 - 28.84 - \frac{29.37}{2})\,\mathrm{J\,K^{-1}\,mol^{-1}} = -9.94\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

$$\Delta H^{\circ}(373K) = \Delta H^{\circ}(298K) + \int_{298}^{373}\Delta C_p dT = -241.82\,\mathrm{kJ\,mol^{-1}} + (75K)(-9.94\,\mathrm{J\,K^{-1}\,mol^{-1}}) = -242.6\,\mathrm{kJ\,mol^{-1}}$$

NOTE: Reaction is more exothermic at higher temperature

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Let us now solve the last question of this tutorial, which is the standard enthalpy of formation of gaseous water at 25 degree Celsius is minus 241.8 kilo Joules per mol, estimate its value at 100 degree Celsius. Given the following values of the molar heat capacities at constant pressure water vapors is 33.58 Joules per Kelvin per mol, hydrogen gas is 28.84 Joules per Kelvin per mol, oxygen gas is 29.37 Joules per Kelvin per mol, and assume that these heat capacities are independent of temperature. So, the information given is the enthalpy of formation or delta H of the reaction at 25 degree centigrade, and we are asked to find out the value of delta H at 100 degree centigrade.

So, in order to connect these two parameters, we need the values of heat capacity. And the heat capacities let us see how to get the value of delta C p for the reaction. This is the reaction representing the formation of gaseous water, hydrogen gas plus half oxygen gas forming H 2 O gas. Delta C p can be calculated from the molar heat capacities at constant pressure of product minus that of the reactants. And all the values are given after you substitute these values, delta C p comes out to be minus 9.94 Joules per Kelvin per mol the value turns out to be minus. So, therefore, try to assign some meaning to the minus sign. Using Kirchhoff's law that is standard enthalpy of reaction at 373 Kelvin is equal to standard enthalpy of reaction at 298 Kelvin plus integration from 298 to 373 delta C p d T. And since it is given that the heat capacities are independent of temperature delta C p can come out of integral and then this calculation suggests that the answer comes out to be minus 242.6 kilo Joules per mol.

So, you see the value of delta H at 25 degree centigrade was minus 241.8 kilo Joules per mol. And the value of enthalpy change at 373 Kelvin is minus 242.6 kilo Joules per mol which is more exothermic than the one at 25 degree centigrade. Although in this example the difference is not very very large, but this difference is actually decided by the connector delta C p; because the delta H at a final temperature is equal to delta H at an initial temperature plus if I treat delta C p to be independent of temperature T f minus T i.

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$$\Delta H(T_f) = \Delta H(T_i) + \underbrace{\Delta C_p}_{}(T_f - T_i)$$

So, it is this value which is a main decider for how the enthalpy of the reaction will be affected, when the temperature is changed. So, I hope that these numerical problems have made the concepts more clearer. In case there are any queries and questions, please do write them down and ask us during the help session.

Thank you very much.