Jet and Rocket Propulsion
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Lecture - 32

Very good morning. So, we are continuing our discussion on the chemistry of chemical rockets. In the last class we have discussed the different definitions of fluid layer ratio, fluid oxidizer ratio and all, and also we defined the standard of heat of formation.

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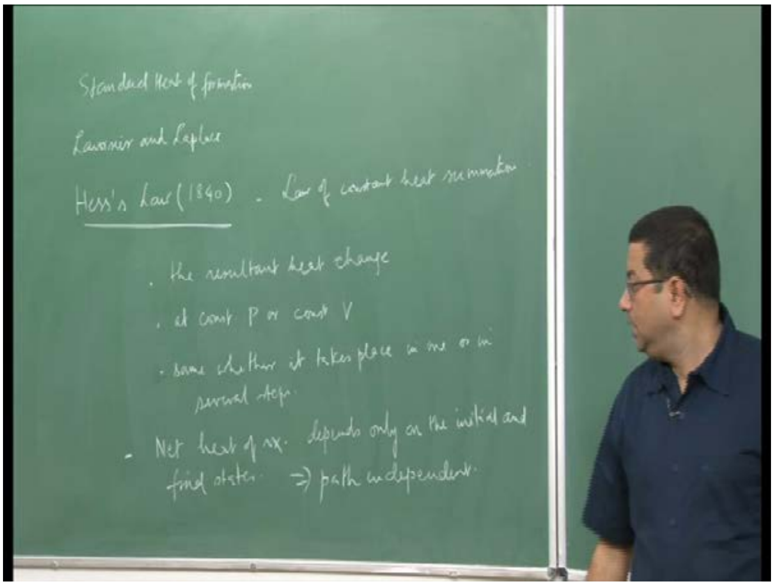

Standard Heat of formation

Lavoisier and Laplace

Hess's Law (1840) . Law of constant heat summation

. the resultant heat change

. at const P or const V

. same whether it takes place in one or in
several steps.

- Net heat of rx. depends only on the initial and
final states ⇒ path independent.

And after that we started discussing ((Refer Time: 00:47)) chemical laws; we have discussed the law of proposed by Lavoisier and Laplace; we states that the quantity of heat which must be supplied to decompose the compound into its elements is equal to the heat evolved when the compound is found from its elements. Now, to continue our discussion on thermo chemical laws, next let us discuss another law which is Hess's law. This was proposed in 1840 by Hess; this is also called law of constant heat summation. Now, this law states that the resultant heat change at constant pressure or constant volume, that is either isobaric process or isochoric process. In a given chemical reaction is the same whether it takes place in 1 or in several steps; that is whether the reaction takes place in one step or in multiple steps it does not matter as long as the process is carried out at constant pressure and constant volume. The resultant heat change is the sum of the heat change for all the process that is taking place.

So, essentially the net heat of reaction depends only on the initial and final states; it does not depend on the past taken by the reaction to reach the final state, it depends only on the initial and the final states. Therefore, it is path independent, and because of this what is proposed is that the thermo chemical reactions are thermo chemical equations for different reactions can be either added or subtracted like algebraic equations.

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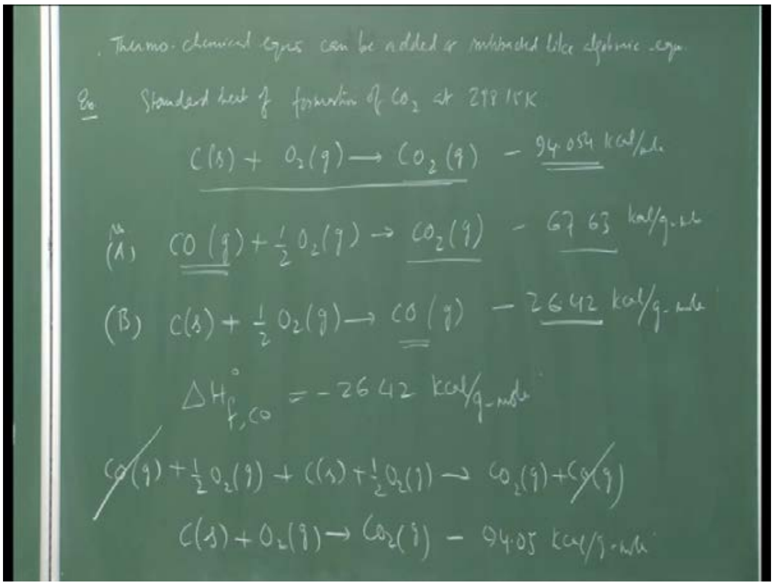

. Thermo-chemical eqns can be added or subtracted like algebraic eqn.

Ex Standard heat of formation of CO_2 at 298.15K

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad -94.054 \text{ kcal/mole}$$

$$(A) \quad CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad -67.63 \text{ kcal/g-mole}$$

$$(B) \quad C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \quad -26.42 \text{ kcal/g-mole}$$

$$\Delta H^{\circ}_{f,CO} = -26.42 \text{ kcal/g-mole}$$

$$\cancel{CO}(g) + \frac{1}{2}O_2(g) + C(s) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) + \cancel{CO}(g)$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad -94.05 \text{ kcal/g-mole}$$

So, the thermo chemical equations can be added or subtracted like algebraic equations. Now, this is the very important law and allows us to estimate the heat of reaction or for different complex reactions without going into the complexity. Instead what we can do is we can break a complex chemical reaction into several smaller or simpler reaction steps; and then add all of them together to get the final heat of reaction. Now, let us explain it by taking an example. Let us consider that we want to estimate the standard heat of formation of CO 2 at 298.15 degree Kelvin; we want to estimate the standard heat of formation carbon dioxide at 298.15 degree Kelvin. We have seen it in the previous class that the standard heats of formation of this form its elements; if you estimate it from its elements this is equal to 94.054 kilo calorie per mole; we have seen this at the previous class.

Now, let us estimate the same from some other path. Let us consider the reactions that it is form from say carbon dioxide burning in oxygen giving carbon dioxide gas. Now, for this reaction it can be estimated that the heat of this reaction is equal to 67.63 kilo calorie per gram mole.

Now, if I look at this reaction although we are forming carbon dioxide gas this is not a formation reaction. Because of the fact that CO carbon monoxide is not an element it is a molecule; where as we have defined the formation reaction or heat of formation as the heat involved when the molecule is formed from its elements. So, therefore, that is why there is a discrepancy between this 2. But we can take care of this discrepancy by using Hess's law. Let us consider the formation reaction for carbon monoxide. So, if carbon mono oxide is formed from elementary carbon and oxygen through a reaction like this. Then, the heat evolved for this process is 26.42 kilo calorie per gram mole; this if I look at this reaction this is the formation reaction for carbon monoxide. Because carbon and solid is element and oxygen in its molecular form is also element.

So, therefore this is the formation reaction for carbon monoxide. So, we can write the formation reaction for carbon monoxide under heat of formation for carbon monoxide is 26.42 kilo calorie per gram mole. Now, as we can see here in this reaction both of this are really at their standard state but not in this reaction. So, in order to get this reaction if I look at this 2; if I just add this 2 algebraically then I get this. So, if I add let me call this reaction A and this reaction B. If I add reaction A and B what I would get is CO gas plus half O 2 gas plus C (s) plus half O 2 gas giving me CO 2 (g) plus CO g. Now, CO g can be cancel form here; what I get is c s plus O 2 (g) giving CO 2 (g). So, what I see here is that if I add reactions A and B algebraically I get the formation reaction for CO 2 which has been shown earlier. Therefore, from Hess's law; now the heat of formation or the heat of this reaction which is the heat of formation form carbon dioxide is nothing but the algebraic sum of this 2. So, if I add this 2 heating values; then this comes out to be equal to minus 94.05 kilo calorie per gram mole.

So, what we are seeing here is that this is exactly equal to the heat of formation that we had earlier discussed. Therefore, what we see is that either we take this step or we follow little more complex step; we get the same heat of reaction as long as this process is carried out at standard temperature sorry constant pressure or constant volume we get the same value of heat of reaction. So, this law called Hess's law is a very important law which helps us in estimating the heat of formation or heat of reaction of more complex reactions starting from basic elementary states. Now, taking this forward now this discussion forward we have to get now; what can say see that if we are looking at very complex reaction consisting of many many molecules; we can get the heat of formation values for different molecules. Because as I have said in the previous class; this values are tabulated in some more chemical tables.

So, we can take those values and then form the complex chemical reaction by algebraically adding or subtracting those reactions and we get the required value. So, then what we have to get now is the standard heat of formation. So, far we have said that the standard heat of formation that we are getting here is the heat evolved. Now, how do we get this heat evolved; we can either do a calorimetric, and estimate the heat evolved or there may be some more simpler steps. So, next we discuss a simpler method or for estimating the standard heat of formation or heat of formation that comes from bond energies.

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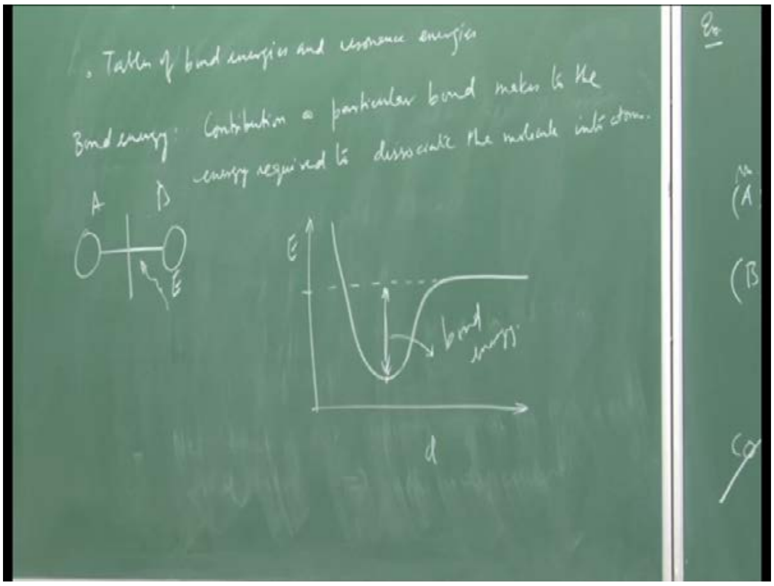

. Tables of bond energies and resonance energies

Bond energy: Contribution a particular bond makes to the energy required to dissociate the molecule into atoms.

So, we discuss bond energies and heats of formation. In this method we can estimate the standard heat of formation by using tables of bonds and resonance energies. So, we can use the tables of bond energies and resonance energies. Let me explain what is bond energy; before that first let me say that where they are useful? This method can be very useful for compounds which have not been synthesizes before. For example, here if we are talking about the heat of formation these are for the compounds which have been synthesize before we know the heating the heat of formation values or the heat of reaction values. So, these are tabulated in thermo chemical tables.

But if you are looking for a new compound which has not been synthesize before; then in order to we are estimate what will be the heat of formation for that; we can use the bond energies method. Secondly, there may be some reactions which are not suitable for burning in a calorie meter; in that case also this method using bond energies is more applicable. So, first let us define what is bond energy? Bond energy is the contribution particular bond makes to the energy required to dissociate the molecule into atoms. So, as we know that all the molecules are made up of several atoms; and this atoms are kept together by the inter molecular bond. Now, if you have to break this molecule into its constraints atoms; we have to supply some amount of energy. Now, the bonds that are there in the in the molecule all of them are not same every bond is little different.

So, the contribution of a individual bond or the amount of energy required to break this individual bond is the bond energy for that particular bond; and the total bond energy is the summation of the bond energy of individual bonds. So, if the 2 molecules are together; let us say I am looking at molecule A and B they are together; because of certain inter molecular bond. If you have to break them apart we have to supply some amount of energy.

So, this energy that we need to supply to break this bond is the bond energy for this bond between A and B. So, therefore this the energy required to pull the 2 atoms apart. Now, this bond energy from modern physics can be shown to be function of the distance between this 2 atoms. So, if I plot a general energy verses distance curve you have seen that before in physics; it looks like something like this. So, this is the bond energy when the molecules are infinitely apart; as we bring them together the intermolecular forces increase; there is a distance at a point where the bond the energy requirement is minimum.

So, therefore the molecule will be formed at that distance. So, this is the energy difference between the inter molecular forces at a when a molecules are infinitely apart; and this is the minimum distance or value at the potential minimum related to. So, therefore the value of this potential minimum with respect to the distance when the molecules are infinitely apart is essentially the bond energy. Now, this bond energies so this is my bond energy; once again the bond energies are also fundamental properties of the bonds. So, they are also tabulated in thermo chemical tables. So, we can get this information from the tables. And, then use that to estimate the bond energy; I would like to point out here one thing; that while considering this bond energy we should also take into account the possibility of resonance. Let me explain what is resonance?

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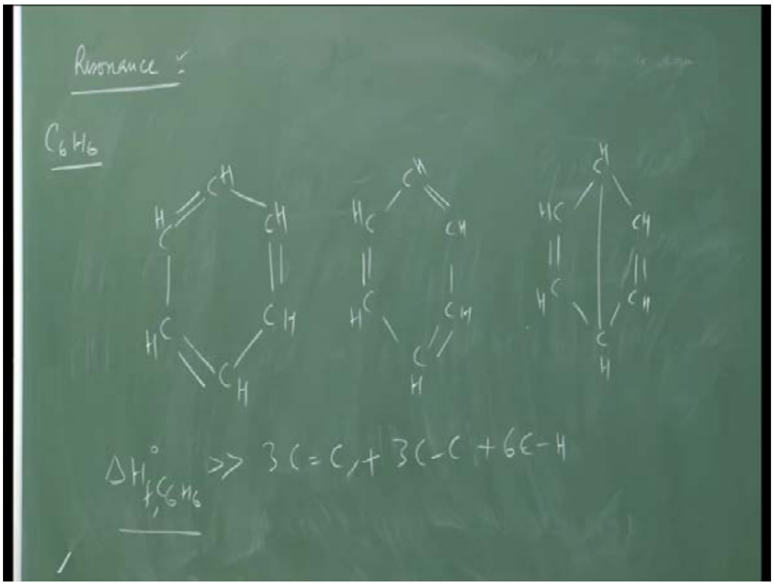

So, in order to estimate the bond energy for a particular bond for a molecule in a molecule; we have to take in to account the possibility of resonance; in order to estimate particularly the heat of formation. Let us understand resonance with an example. Let us consider benzene for aromatic hydro carbon; it can have various structures, it can have like this and few double bonds or it can be like this; and not this bonds the double bonds can be at different carbons. So, it can be here, here, here. Similarly, we can have another structure and the location of this double bonds may be different. For example, we can have it here and you can have it here, you can have it here.

So, as you can see similarly there are other possibilities also. So, what we are saying is you are seeing is that we have the same molecule which is benzene molecule C 6 H 6. However, the orientation of the bonds are the final structure can be different. So, all of them represent the same molecule but with different structure. So, this multiple structures are called resonance. Now, due to this resonance the actual heat of formation of benzene is going to be much much higher than what we estimate from the bond energies; that is the actual heat of formation for benzene is much much higher than the standard. As we can see here what we have is 1, 2, 3; 3 C double bonds and then 1, 2, 3; 3 single bonds for carbon carbon and 6 C H bonds; this are the standard the bonds that we have. However, because of this possibility of multiple structures called resonance; the actual heat of formation is going to be much much higher. Then what we estimate from just looking at the bond energies.

So, both the bond energy and the resonance energy then must be considered for calculating the heat of formation for a particular molecule. The resonance energies are also tabulated in thermo chemical tables in the hand books. I like to emphasize one more thing here that the bond energy the way we have defined is essentially the negative of the energy required to form the bond. Because the way we have defined the bond energy is energy required to break the bond. Therefore, from the thermo chemical laws we have just discussed it is equal to the negative of the energy required to form the bond. Now, let us again try to understand its by looking at an example because that is the best way to explain the processes. So, let us look at an example that how do we use this concept of bond energy to estimate the heat of formation?

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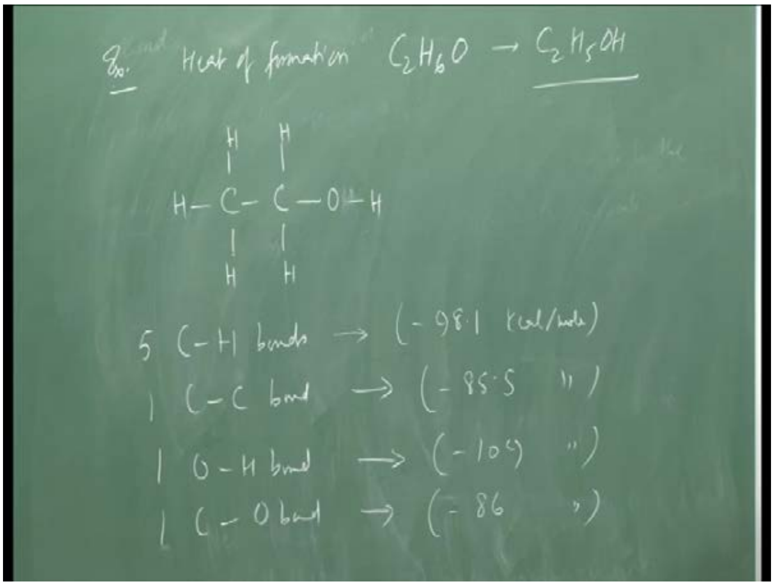

Ex. Heat of formation $C_2H_6O \rightarrow C_2H_5OH$

5 C–H bonds → (−98.1 kcal/mole)

1 C–C bond → (−85.5 ")

1 O–H bond → (−109 ")

1 C–O bond → (−86 ")

So, for the example it is consider that we want to estimate the heat of formation for ethanol is also written as C 2 H 5 O H; this is the alcohol we want to estimate the heat of formation for that?

So, first let us look at the molecular structure O H. So, this is the molecular structure of ethanol. Now, is let us count the number of bonds that we have we have 1, 2, 3, 4, 5. So, we have 5 C H bonds then we have 1 C C bond; then we have 1 O H bond and 1 C O bond. Now, from the thermo chemical tables we can get the bond energies for this; bond energy for a C H bond is 98.1 kilo calorie per mole, for C C it is minus 88.5 kilo calorie per mole, for O H it is minus 109 kilo calorie per mole; and for CO it is minus 86 kilo calorie per mole; notice that all the bond energies are negative. Now, we want to estimate the bond energy for this? So, essentially rather the heat of formation for ethanol; essentially what we are interested is to find out the energy required to form 1 mole of ethanol. So, first let us estimate from the bond energies what is the energy required to form one mole of ((Refer Time: 22:10)).

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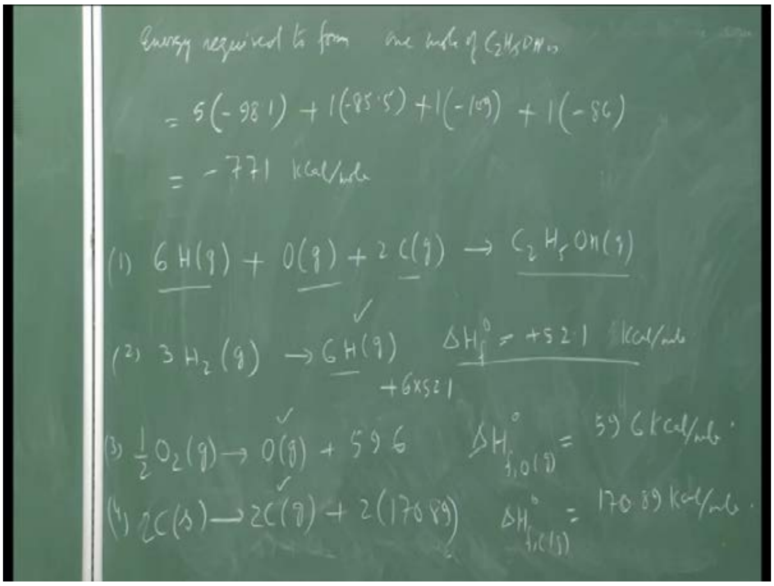

Energy required to from one mole of $C_2H_5OH_{(l)}$

$$= 5(-98.1) + 1(-85.5) + 1(-109) + 1(-86)$$

$$= -771 \text{ kCal/mole}$$

(1) $\underline{6H(g)} + \underline{O(g)} + 2\underline{C(g)} \rightarrow \underline{C_2H_5OH(g)}$

(2) $3H_2(g) \rightarrow \underline{6H(g)}$ $\underline{\Delta H_f^0 = +52.1 \text{ kCal/mole}}$ $+6\times52.1$

(3) $\frac{1}{2}O_2(g) \rightarrow O(g) + 59.6$ $\Delta H^0_{f,O(g)} = 59.6 \text{ kCal/mole}$

(4) $2C(s) \rightarrow 2C(g) + 2(170.89)$ $\Delta H^0_{f,C(g)} = 170.89 \text{ kCal/mole}$

So, energy required to form one mole of C 2 H 5 O H is nothing but the energy required to form 5 C H bonds plus 1 C C bond plus 1 O H bond plus 1 C O bond. So, the total energy is just the algebraic some of all this; this is equal to 771 kilo calorie per mole. Now, if I write this as a thermo chemical reaction equation; then this is equal to 6 H (g) plus O (g) plus 2 C (g) giving us C 2 H 5 O H (g); because here we have 6 hydrogen plus 1 oxygen plus 2 carbon. So, this is the formation reaction. And, the bonds are formed from this; remember that in order to form the bonds we have to supply all this in their atomic state. So, therefore this is the basic constituents of this molecule. So, we write this equation like this. Now, if I look at this equation; this gives me the formation of alcohol either ethanol from this basic steps or other basic elements. But these are particularly hydrogen, oxygen or carbon in the gaseous states and not in their elementary state. Therefore, it cannot call this reaction as the formation reaction for ethanol. So, what we have do is first to get the formation reactions.

So, the atomic hydrogen will come from a formation reaction; and that formation reaction will be breaking taking 3 molecules of hydrogen and then breaking it into 6 hydrogen atoms in their gaseous state. This is then going to been my first reaction of which gives be hydrogen atoms. And, the heat of formation for hydrogen atom can be obtained from the thermo chemical tables is an endothermic reaction requiring 52.1 kilo calorie per mole and 6 times this actually. Because heat of formation of this equal to this; since we have forming 6 of this. So, this is equal to 6 time 52.1 because heat of formation for atomic hydrogen from molecular hydrogen is 52.1. So, therefore this reaction will requires 6 times 52.1 amount of heat. Similarly, we have to form the atomic oxygen from molecular oxygen through this reaction and the heat is equal to 59.6. Because the heat of formation of atomic hydrogen gas sorry at atomic oxygen gas is 59.6 kilo calorie per mole.

Similarly, here we have carbon in its gaseous state but the element the standard state of carbon acts under temperature and pressure is solid. So, we have to first convert solid carbon into gaseous carbon and we have two of them. So, we take 2. So, that also requires some heat we have to supply some heat to evaporate the solid carbon into gaseous carbon. And, the heat required for that reaction is 170.89 that is heat of formation for carbon gas is equal to 170.89 kilo calorie per mole. So, now if I look at these 3 reactions; these are formation reactions for atomic hydrogen, atomic oxygen and gaseous carbon. So, if I now add this 4; let me call this 1, 2, 3 and 4; if I now add these 4 reactions what we get is the formation reaction for ethanol.

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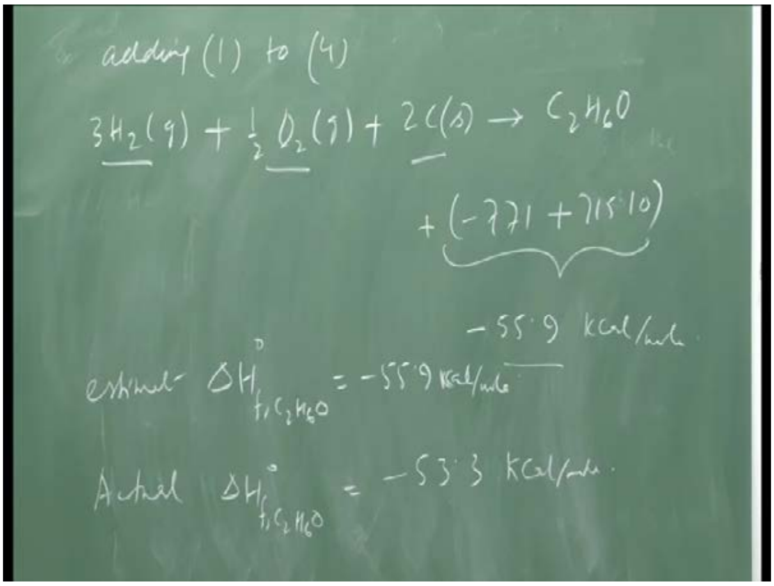

adding (1) to (4)

$$3H_2(g) + \frac{1}{2}O_2(g) + 2C(s) \rightarrow C_2H_6O$$

$$+ \underbrace{(-771 + 715.10)}_{-55.9 \text{ kCal/mole}}$$

estimated $\Delta H^\circ_{f,C_2H_6O} = -55.9$ kcal/mole

Actual $\Delta H^\circ_{f,C_2H_6O} = -53.3$ kCal/mole

So, adding this 4 reactions we get adding 1 to 4 we get 3 H 3 (g) plus half O 2 (g) plus 2 C (s) giving as C 2 H 6 O. So, this is the formation reaction because now hydrogen is is in the standard state at standard temperature and pressure, oxygen is the standard state and carbon is also in its standard state. So, therefore this is the formation reaction for the molecule we are looking for which is ethanol. Therefore, we can also just do and algebraic summation for all of this; for this reaction delta H is minus 771. So, if I just add all the heats minus 771 plus 715.1 that is if I add this, this plus this I get 715.1. So, this gives me the total now heat of formation for this; this comes out to be equal to minus 55.9 kilo calorie per mole. So, if I can summarize that the estimated heat of formation for ethanol from the method we have just; the estimated delta H f C 2 H 6 O is equal to minus 55.9 kilo calorie per mole; whereas we can estimate it using calorimetric and get the actual value which is also present in thermo chemical tables.

So, the actual value of heat of formation for ethanol is minus 53.3 kilo calorie per mole. So, what we have seeing here is that there is a slight difference between the estimated value and the actual value all of this difference is quite small is a very small difference. But this difference do exist and this difference between the estimated value and the actual value is primarily because of the fact that the bond energy is that we have taken here are the average bond energies. But bond energy for all the bonds are not same because if I look at a C C bond on one side of it; if we have a oxygen bond or other side it has a hydrogen bond then there they will exact different type of pulls. Similarly, for different bonds we can have different type of bond slightly different bond energies depending on the composition. So, therefore the overall bond energy for individual bond is slightly different from the average bond energy. Now, since we have used the average bond energy; therefore there is a small discrepancy between our estimated value and the actual value.

So, this tells us how to estimate the heat of formation. So, if we know the composition either the molecular structure we can estimate the heat of formation using this method. Now, heat of formation is not what we are looking for. Finally, for our estimation of final temperature in the combustor we need to know the heat of reaction; that is the energy that reaction is going to release where it is in that conditions at which the reaction is occurring. So, the next thing that we have to do is estimate the heat of reaction; which in order to estimate that we will use the concept of heat of formation. So, next let us look at the heat of reaction and try to find out a method to estimate the heat of reaction from the concepts that we have discuss so far which will be then useful in estimating the final temperature. So, the next topic we are going to discuss is our heat of reaction.

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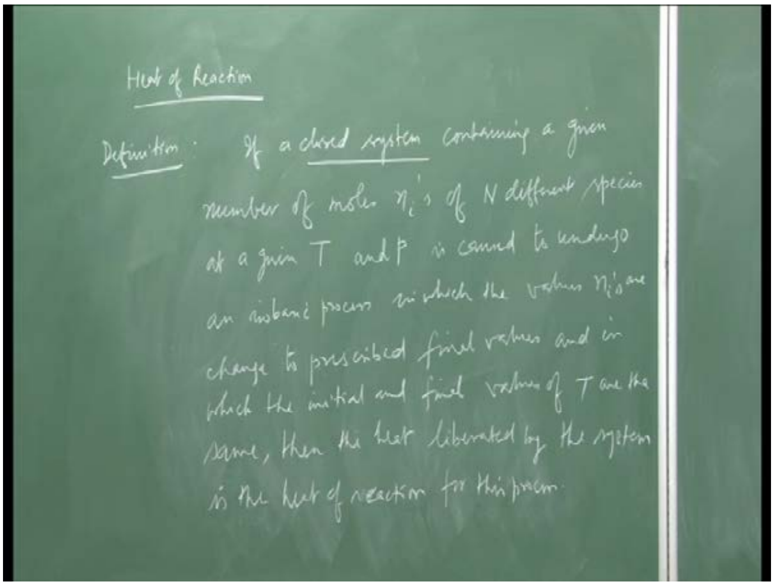

Heat of Reaction

Definition: If a closed system containing a given number of moles n_i's of N different species at a given T and p is caused to undergo an isobaric process in which the values n_i's are change to prescribed final values and in which the initial and final values of T are the same, then the heat liberated by the system is the heat of reaction for this process.

Now, if we are since we are talking about combustion; in order to estimate the temperature and the final composition combustion is concerned with the heat changes associated with the combustion reaction; it deal with the conversion of chemical energy into heat energy. So, we want to estimate how much heat is produced when we have a combustion reaction? Now, the heat change associated with a chemical reaction is an indefinite quantity and it depends on the path taken; whereas so far we have discussed for the path independent properties. So, if the reaction takes place at constant pressure and or constant volume the heat change has a definite value. Now, if the process is specified then and only then the heat change will have a definite value; if the process is not specified it is going to be not a specific value. So, fortunately if we know at the process the path that the process takes whether is a constant pressure or constant volume or constant temperature whatever; if we know the path taken if the process is specified then we can estimate the heat of reaction using the large we have just discussed, so therefore since the heat of reaction as we have said depends on the path taken.

Now, the easiest of the processes are either constant pressure process or constant volume process. Therefore, heat of reactions are the heat changes associated with chemical reactions are primarily measured at either constant pressure at constant pressure and constant volume. So, let us now look at the definition of heat of reaction? If a closed system if we consider a closed system containing a given number of moles that is n i’s of N different species at a given temperature and pressure is caused to undergo an isobaric process in which the values n i’s are changed to prescribed final values. And, in which the initial and final values of temperature are the same; then the heat liberated by the system is the heat of reaction for this process. So, let us understand what this definition says; first we are considering a closed system. So, therefore the system is not interacting with the surrounding. Secondly, this system contains a given number of moles of N different species. So, the composition is specified; initial composition is specified and the system is at a given temperature and pressure.

Now, what we are seeing is that; this system is allowed to undergo an isobaric process; isobaric process is a constant pressure process. So, therefore the pressure remains same and molecules are allowed to react with each other but the final value of the temperature is also same. So, therefore the temperature does not change. So, now we do not have the change in pressure, we do not have change in temperature only chemical composition changes. And, which comes to a different values of n i’s and this n i the final composition is also prescribed. So, we know the final composition also; under the circumstances the heat liberated for this process is called the heat of reaction for this process ok. So, this is the definition of heat of reaction.

So, when a system makes these changes it goes from initial stage to a final stage; then it may lose some energy, it may gain some energy the energy transformation can be either heat or work. Now, the chemical reaction typically undergo the changes under no velocity change. So, this is a closed system there is no change in velocity. So, we can neglect the potential energy and kinetic energy changes. So, this is and further more this is the constant pressure process.

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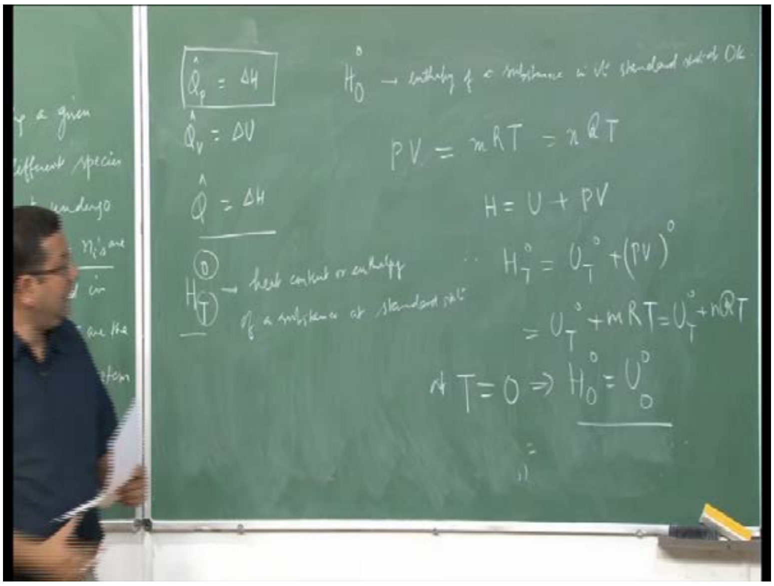

From thermodynamics we know that for a constant pressure process the rate the change in heat is equal to the change in enthalpy, the heat transfer is equal to the change in enthalpy. So, for a constant process no flow reaction heat liberated is equal to the change in enthalpy; this we have seen in basic thermodynamics. On the other hand for a constant volume process where heat liberated is equal to change in its internal energy; that also we have seen in thermodynamics. For a reacting flow if we neglect the potential energy and kinetic energy term and we consider there are no work other than the flow work that is P d v work; then the net change in enthalpy is equal to the heat of reaction. So, if we are talking about a reacting flow then this condition is also valid.

So, therefore for our cases we are talking about reacting flows. So, therefore the change in heat is nothing but change in enthalpy. It is a common practice first of all I would like to point out here that this is a common practice to deals wth moles in closed system and mass in closed systems to designate the amount of species involve in the process. Now, coming back to our description of heat of reaction we are dealing with notations.

So, the notation for heat content or enthalpy of a system; first of all at its standard state can be designated as H T naught. So, this is the notation for heat content or enthalpy of a substance at standard state. Here, the index o superscript o specified the standard state and that T is the temperature in Kelvin. So, at a given temperature if the element is it standard state there is a sudden heat or enthalpy associated with that system. So, for example if I write H 0 0; then this is the enthalpy of a system or a substance in its standard state at 0 Kelvin at absolute 0 temperature.

Now, we are dealing with gaseous species. So, first let us define now the equation of state? So, for a gaseous species the equation of state can be defined as a and we are considering a perfect gas. So, this is my equation of state the P V equal to m R T; where m is the mass of the system, R is the gas constant, T is the temperature in Kelvin; this is pressure, this is volume; it can also written as the number of moles the universal gas constant times temperature. And, enthalpy is defined as U plus P V this is standard thermodynamic definition.

Therefore, the standard heat content can be written as the heat content its standard state is the internal energy at its standard state plus P v at its standard state. Now, P V as I can write here as m R T. So, this can be written as m R T or it can also be written as m R T. Now, at absolute 0 temperature which we have defined here; since from this equation of state this term the P V worked on term is a function of temperature ((Refer Time: 42:03)) goes to 0 this term goes to 0. So, at time at 0 temperature we can show that we have shown that the standard enthalpy of substance and standard state at 0 degree Kelvin is equal to its internal energy at that condition. So, that has been shown here. Therefore, the 0 degree Kelvin can be considered to be a good datum to start our discussion. Now, in thermodynamic as we see here all the parameters are given in terms of delta H or delta U; essentially the change in state from state 1 to state 2; whereas this definition for at a particular state.

So, therefore if we know condition at a particular state that does not help us; we have to describe in terms of in the change in properties. So, if we are talking about the change in properties we need to know at initial condition. Now, from this description since we are showing that the enthalpy and internal energy at absolute 0 temperature are same; that can be considered to be a good initial condition. Then, from there if I look at the change in properties with respect to absolute 0 that gives me good description of the system. So, let me consider, let me put this equation 1, this as equation 2 and this as equation 3.

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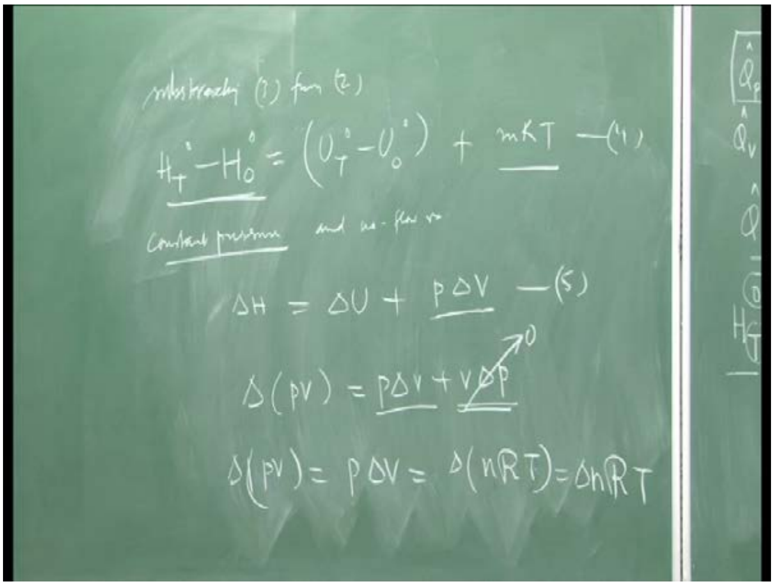

subtracting (3) from (2)

$$\underline{H_T^0 - H_0^0} = (U_T^0 - U_0^0) + \underline{mRT} \quad \text{—(4)}$$

Constant pressure and no-flow rx

$$\Delta H = \Delta U + \underline{P\Delta V} \quad \text{—(5)}$$

$$\Delta(PV) = \underline{P\Delta V} + \underbrace{V\cancel{\Delta P}}_{} \xrightarrow{} 0$$

$$\Delta(PV) = P\Delta V = \Delta(nRT) = \Delta n RT$$

$\hat{Q}_P$

$\hat{Q}_V$

$\hat{Q}$

H_T

So, now if I substrate 2 from 3 from 2. So, subtracting 3 from 2 gives me H T naught minus H 0 naught is equal to U T naught minus U 0 naught and plus m R T; let me call this equation 4. Now, let us look at this equation if we consider constant pressure because that is how we have defined our heat of reaction and no flow reaction. Then, this is my delta H the change in enthalpy is equal to the change in internal energy.

So, this is delta U plus the m R T term which is equal to the P d V work; let me call this equation 5. Now, if V is the volume of 1 mole of any ideal gas at constant pressure and temperature; if V is the volume of one mole of any ideal gas then delta P V is equal to can be written as P del V plus V del P. But since we are considering a constant pressure process this term is 0. So, therefore del P V is equal to P del V. Therefore, that is why this term was del P V which is equal to P del V from here; that is how we get this relationship. Now, for an ideal gas we have already shown here that P V is equal to m R T. So, P del V will be equal to nothing but the change in this property. So, let me just look at del P V is equal to P del V which is equal to del n R T. However, for the heat of reaction we said the temperature remains same only the changes in n. So, I can write this as del n R T; where this R is my universal gas constant.

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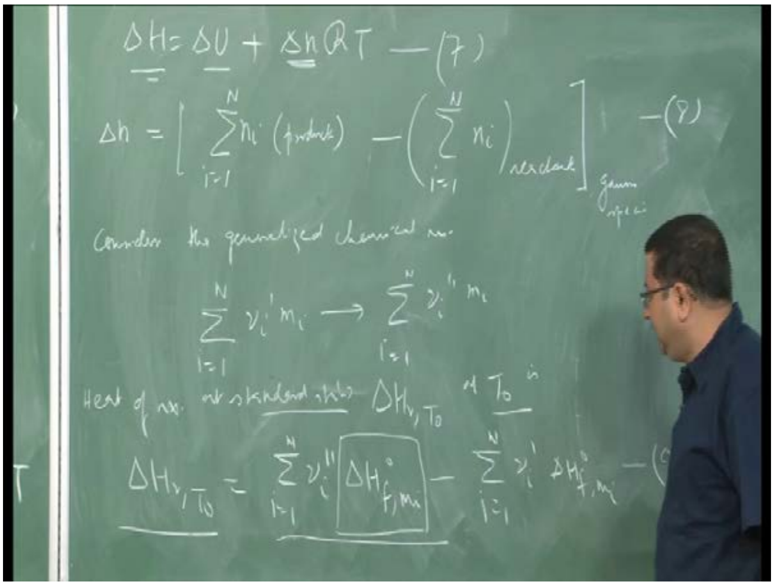

$$\underline{\Delta H} = \underline{\Delta U} + \underline{\Delta n} R T \quad \text{— (7)}$$

$$\Delta n = \left[\sum_{i=1}^{N} n_i \,(\text{product}) - \left(\sum_{i=1}^{N} n_i \right)_{\text{reactant}} \right]_{\text{gaseous species}} \quad \text{— (8)}$$

Consider the generalized chemical rxn.

$$\sum_{i=1}^{N} \nu_i' m_i \longrightarrow \sum_{i=1}^{N} \nu_i'' m_i$$

Heat of rxn. at standard state $\Delta H_{r,T_0}$ at T_0 is

$$\Delta H_{r,T_0} = \sum_{i=1}^{N} \nu_i'' \boxed{\Delta H^0_{f,m_i}} - \sum_{i=1}^{N} \nu_i' \Delta H^0_{f,m_i} \quad \text{— (}$$

So, now if I put it back into this equation; my expression for change in enthalpy becomes equal to delta H is equal to delta U plus delta n R T. Let me call this; this was 5, let be the equation 6, this is equation 7. So, now we have represented the change in enthalpy as change in internal energy and change in number of moles. Now, let us look at this term little more closely the change in number of moles; what is delta n? It is essentially the total number of moles of the products minus the total number of moles of the reactants and of course everything is a gaseous species; let me call this equation 8. So, now let us look back at our definition of heat of reaction; we said that it has to be at the constant pressure which we have in corporate here; it has to be at the initially and final stage of temperature are same. So, that has curve been included here. Now, the only change is in the number of moles. So, that represented through this expression or the changing number of moles is the total number moles for the product minus the total number of moles for the reactants. So, this gives me delta n.

Now, if I consider the generalized chemical reaction which we have expressed earlier also; it will be given by this expression. Then, for this chemical reaction the heat of reaction at standard state; that is delta H r at standard state T naught; where T naught is the standard temperature is given by delta H r T naught now is equal to nothing but the change in enthalpy of the products minus change in enthalpy of the reactants in its formation state. Let me call this equation 9. So, this is the heat of reaction act it standard temperature also T naught. So, at standard temperature now initially we had been considering the reaction at constant pressure. If this pressure happens to be the standard temperature at standard pressure; and the temperature that we are at which we working also happens to be the standard temperature. So, if the reaction takes place have standard temperature and pressure. Then, the total heat of reaction at the standard temperature and pressure is equal to the heat of formation for the products minus the heat of formation for the reactants, why? Because the heat of formation now in this case becomes equal to the heat of reaction.

So, delta H f m i is the heat of reaction for the products total enthalpy of the products at the standard state minus the total enthalpy of the reactants are the standard state. Since, both of them are define in the case for the standard state. Therefore, the total sheet of reaction at the standard state is nothing but the total enthalpy at the standard state for the products minus total enthalpy at the standard state for the reactants. So, this is how we get the heat of reaction. Now, in many here the heat of reaction is define at the standard temperature T naught. But many cases we would like to define it not at standard temperature T naught but some other temperature the system temperature. So, if instead of T naught if this temperatures are the heats are either the reactions are occurring at some other temperature T 2; then we can estimate that as well. So, let us say that in this description we are considering the reaction is occurring at standard temperature T naught we said that ok; it is not t naught it is the any temperature T 1.

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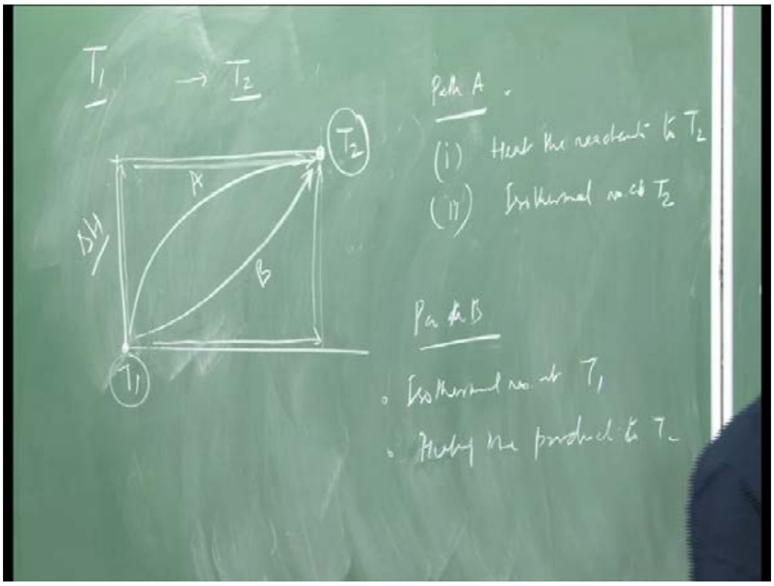

So, the initial reactions are occurring at any temperature T 1 and we know the heat of reaction for that temperature T 1; we want to estimate what will be the temperature sorry what will be the heat of reaction? If the reaction occurs not at T 1 but some other temperature T 2. So, for that let me draw path diagram; let us say that our reactants where initially at this point. Now, after the reactions they go to this point; this is my condition T 2. Now, this is my delta H both of this states; this was my temperature T 1 initially this was at temperature T 1 for the reaction happens and it goes to temperature T 2; this and this 2 states are also equilibrium states let us say.

Now, we want to find out if this conditions I defined T 1 what will be conditions at this temperature T 2? As we can see here now we can take 2 different paths; actually it can be multiple different path; I am considering 2 different paths this path A and this path B. In path a what I am saying is that the molecules other the products which were initially at temperature T 1 are first heated two temperature T 2; and then we along the reaction at the constant temperature at T 2. So, the paths taken is path A first of all is first heat the reactants which are initially at temperature T 1 to temperature T 2. And, then second we have isothermal that is the constant temperature reaction at T 2. So, now with following this path we reach this condition. So, now I products are at temperature T 2 and we want to estimate the enthalpy here? Similarly, we can have another path; path B where we can have the isothermal reaction at temperature T 1, so we come here and then heating the products to T 2; from here to here.

So, in following in both the paths we reach the final state T 2 from the initial state T 2. Now, we have to find out the heat change is associated with that; and as the diagram shows the total heat change will be same. So, we are running out of time today. So, I will stop here today. In the next class we will first revised this portion and then continue from here with our description of heat of reaction.

Thank you.