Fundamentals Of Combustion – I

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Lecture – 11
Thermo chemistry

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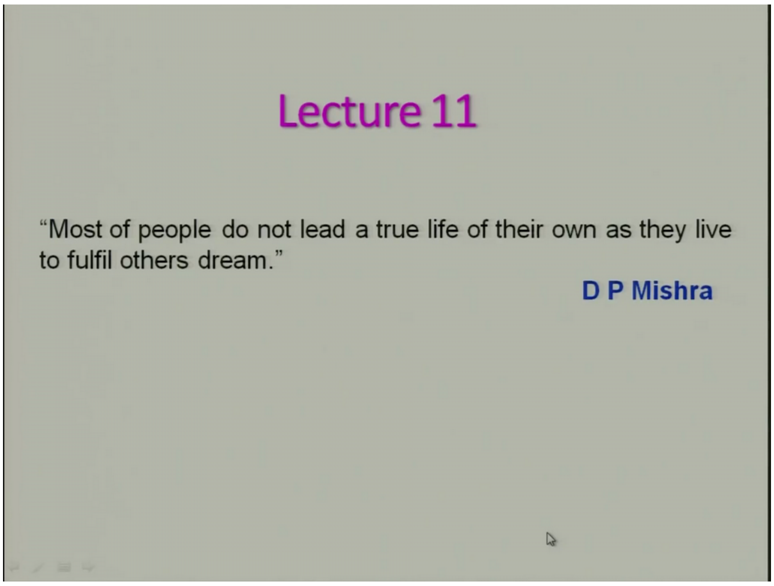

Lecture 11

"Most of people do not lead a true life of their own as they live to fulfil others dream."

D P Mishra

So, let us start this lecture with a thought process. Most of people do not lead a true life of their own, as they live to fulfil others dream. Particularly, nowadays, the market forces are making our dreams. They are influencing our dreams. We do not have our own dream because, we do not have time to think and take a proper step. So, you people should be very careful about it. And what in our scripture (Refer Time: 00:44) So, (Refer Time: 00:46); that means, you should have your own swadharma; means characteristics, right.

So, in the last lecture, basically we discussed about how to handle the mixture fraction, right? Or the fuel air ratio particularly when we are handling in the diffusion flame and we define a mixture fraction. We also related that to the equivalence ratio. And I also told it is a conserved scalar which is having a lot of ramification particularly for diffusion flame which we will be discussing later on.

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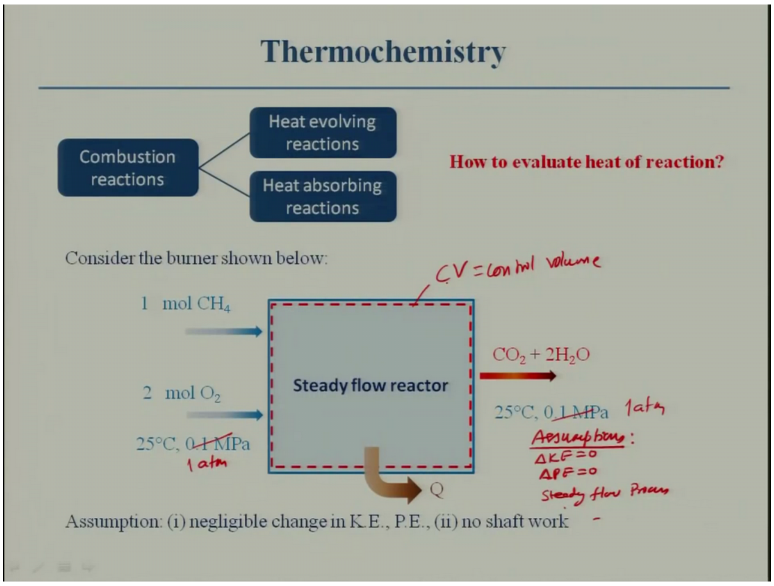

Thermochemistry

Combustion reactions

Heat evolving reactions

Heat absorbing reactions

How to evaluate heat of reaction?

Consider the burner shown below:

CV = control volume

1 mol CH_4

2 mol O_2

25°C, 0~~.1 MPa~~ 1 atm

Steady flow reactor

$CO_2 + 2H_2O$

25°C, 0~~.1 MPa~~ 1atm

Q

Assumptions:
$\Delta KE = 0$
$\Delta PE = 0$
Steady flow Process

Assumption: (i) negligible change in K.E., P.E., (ii) no shaft work -

And now, we will be continuing, how to look at this combustion reactions, right? And combustion reaction basically it evolve during the reaction. And heat can be absorbed during the reactions, right? And if it is evolved, what we call? We call it as an exothermic reaction; if it is absorbed we call it an endothermic reaction.

So, question arises if it is the case some heat being evolved and we need to find it out during certain reactions, right? Then we will have to find out heat of the reactions, right? Question arises how we will find out heat of reactions, right? Let us look at a burner which is I have shown here. One mole of methane is reacting with 2 moles of oxidizer. Of course, it is going to the product very well. That it will be, one mole of carbon dioxide and 2 moles of water, right?

And keep in mind that it is this fuel and oxidizer entering into this reactor or the burner at 25 degree Celsius and 0.1 mega Pascal. It is also reaching the 25 degree Celsius and 0.1 mega Pascal. It is not really 0.1 mega Pascal; I would suggest that it should be one atmospheric pressure. One atmospheric pressure means 101325 Pascal. And you might be wondering, why I have taken this, any idea? Because, see we are talking about heat of reaction, there should be some standard state you know. So, therefore, I have taken that right, because, the standard state is your 25 degree Celsius and one atmospheric pressure; not 0.1 mega Pascal, are you getting?

So, and of course, if it is reacted and some heat being evolved, then heat can be transferred that is Q.

Now, I need to find out how much heat is evolved. Because, whatever the heat is released, that is going out; that is the balance. So, for this, what I will have to do? How I will go about it? I will have to do basically carry out a heat balance, right? So, how I am going to do or this? Any idea? Very simple questions. So, what we will do? We will have to make some assumptions, and we will have to apply which law? First law of thermodynamics, right?

And what are the assumption we are saying? Change in kinetic energy is 0, change in potential energy is also 0 and steady state, steady flow process. In this example, these are assumptions, right? And there is no work done. The shaft work is 0. So, with these assumption we can find out basically, which is very easy. So, therefore, if you look at that, we need to invoke the first law of thermodynamic for a control volume. If you look at control volume is, this is your control volume; this dash line, right? And in that, we need to apply the first law of thermodynamics, right? This is nothing but your control volume. Of course, what I have shown is a control surface, but total is control volume, fine.

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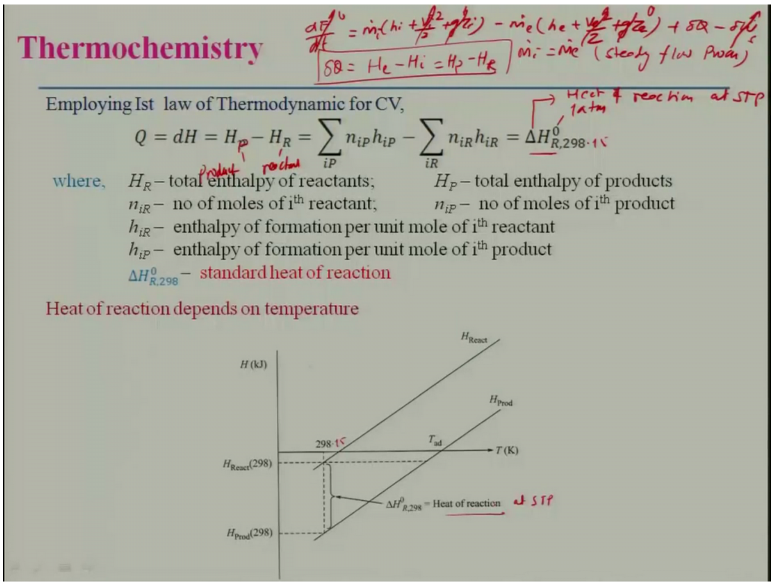

Thermochemistry

$$\cancel{\frac{dE}{dt}}^{0} = \dot m_i\left(h_i + \cancel{\frac{V_i^2}{2}} + \cancel{g z_i}\right) - \dot m_e\left(h_e + \cancel{\frac{V_e^2}{2}} + \cancel{g z_e}^{0}\right) + \delta Q - \cancel{\delta W_s}$$

$$\boxed{\delta Q = H_e - H_i = H_P - H_R}$$

$\dot m_i = \dot m_e$ (steady flow Proces)

Employing Ist law of Thermodynamic for CV,

Heat of reaction at STP

1 atm

$$Q = dH = \underset{\text{Product}}{H_P} - \underset{\text{reactant}}{H_R} = \sum_{iP} n_{iP} h_{iP} - \sum_{iR} n_{iR} h_{iR} = \Delta H^0_{R,298\cdot 15}$$

where, H_R – total enthalpy of reactants; H_P – total enthalpy of products

n_{iR} – no of moles of i^th reactant; n_{iP} – no of moles of i^th product

h_{iR} – enthalpy of formation per unit mole of i^th reactant

h_{iP} – enthalpy of formation per unit mole of i^th product

$\Delta H^0_{R,298}$ – standard heat of reaction

Heat of reaction depends on temperature

So now, I will have to apply the first law of thermodynamic for a control volume. What it would be?

Student: (Refer Time: 05:14)

It would be d e by d t is equal to m dot I am just writing full thing and you should keep in mind that whole thing minus this is I;. I; is the inlet. This is exit h e plus v e square divide by 2 plus the z e. This is I; plus delta Q minus delta w right, this is 0, this is 0 and I am saying the change in kinetic energy and change in potential energy is also 0, right. And keep in mind that, what we are doing? We are assuming that m dot I; is equal to m dot e that is, for steady flow process, what is he saying? The mass is conserved continuity equation basically.

And by that, what you are getting? You are getting basically delta Q is nothing but, what is that? Is H e minus H I; and what is e? E is your nothing but H P product minus H reactant. Yes or no?

Student: Yes.

And that is, the thing what you are getting from this expression. H means, how we are getting H? H is the enthalpy, right mass flow rate into H right? This will be steady flow process. So, therefore, it will be second. Second will cancel it out; that is the thing you will get.

So, therefore, Q is nothing but d H change in enthalpy. See that is a very simple thing you are taking about. And H P, minus H R. H P is basically enthalpy of product minus enthalpy of reactant. What is enthalpy product? It is nothing but summation of n I; P into h I; P minus n I; R h I; R and this is for the basically product side. This is your P stand for product, R is reactant. And keep in mind that, this R if all these R at 298. 0 means, one atmospheric pressure. This is not exactly 298. It is 298.15 kelvin, right? Exactly then, we call this as a heat of reaction. This is your heat of reaction at STP standard temperature and pressure, right. This is n I; R is a number of moles in the I; th reaction. Reactant can be anything like for example, methane, it can be methane and oxygen, nitrogen, right? I; can stand for anything right? And similarly, n I; P is a number of moles of the I; th product. Product means carbon dioxide. And in this example, water, right? You keep in mind that, we have taken only oxidizer; not air. So, therefore, nitrogen would not come into picture.

So, h I; R enthalpy of formation per unit mole of I; th reactant and h I; P is the enthalpy of formation for unit mole of I; th product. And this I, as I told you, it can be depending on this participating species in the reactant and also the product.

So, heat of reaction basically depends on the temperature right, isn't it? But, heat of reaction at standard state will be basically at the 298.15 kelvin. So, if you look at this, is your enthalpy of the product right and enthalpy of reactant is higher. So, therefore, enthalpy of product minus enthalpy of reactant will be negative. Therefore, it is an exothermic reaction and this deference is basically, heat of reaction at S T P.

Now, if you look at I have drawn this 2 parallel lines. Will it be parallel? Will it be; it would not be provided if C P is not a function of temperature, then it can be parallel. If C P is a function of temperature, it would not be. What would it be? You people think about it. We will discuss little later on. Why I am not giving the answer right now? Because, you will think. Are you getting my point? So, this is basically heat of reaction at standard temperature and pressure.

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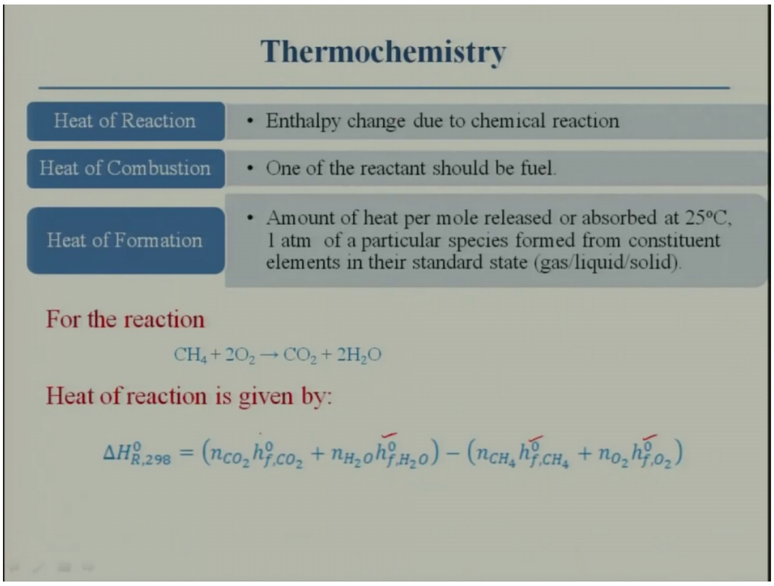

Thermochemistry

Heat of Reaction	• Enthalpy change due to chemical reaction
Heat of Combustion	• One of the reactant should be fuel.
Heat of Formation	• Amount of heat per mole released or absorbed at 25°C, 1 atm of a particular species formed from constituent elements in their standard state (gas/liquid/solid).

For the reaction

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Heat of reaction is given by:

$$\Delta H^0_{R,298} = (n_{CO_2} h^0_{f,CO_2} + n_{H_2O} h^0_{f,H_2O}) - (n_{CH_4} h^0_{f,CH_4} + n_{O_2} h^0_{f,O_2})$$

So, if you look at heat of reaction, is basically enthalpy change due to a chemical reaction, right? It need not be only for our combustion reaction. It can be for any chemical reaction and generally it is reported at the standard temperature and pressure. So, heat of combustion, particularly when there is a fuel right, and we call basically heat of combustion is nothing but heat of reaction divided by the fuel and that is generally, is this can be heat of reaction can be positive, it can be negative.

If it is exothermic, it will be negative; if it is endothermic, it will positive by the convention. But, heat of combustion generally, not all the time because in some book, you may find heat of combustion also negative they are giving. So, generally, we assume it to positive in our calculations. We will be using as positive right, all the time. Because, we take mode of heat of reaction divided by the either in the moles or in the mass of the fuel right.

So, it will be mega joule per k g, right? If it is a k g or mega joule per mole, you know na right? Roughly some number? What will be methane heat of combustion or any hydrocarbon? What it would be? Any idea? You do not have idea. We will see, will take an example and see.

So, if you look at, if I am looking at the heat of reaction right, evaluate a heat of combustion because, if I do not know the heat of reaction, I cannot find out heat of combustion. For that, I need to use heat of formation, isn't it? Without that, I cannot calculate right. So, therefore, it is very important and keep in mind that, when you talk about heat of combustion, we call it as also calorific value. When you talk about calorific value, we can say low heating value or low calorific value. High calorific value you remember we discussed earlier right. So, that way one has to aware about this thing.

So, for this reaction, one mole of methane is reacting with 2 moles of oxidizer or oxygen rather reacting given to the product of one mole of carbon dioxide and 2 moles of water. And heat of reaction will be basically is, n C O 2, that is, n moles of carbon dioxide with the heat of formation of carbon dioxide 0 corresponding to one atmospheric pressure and of course, this correspond to 298.15 kelvin into n moles of water into heat of formation of water minus the n moles of methane into heat of formation of methane plus n moles of oxygen into heat of formation of oxygen; that means, I should know these values right. Of course, these values how I will know this from the table? I will have to use it or is there any other way I can get, right?

Student: (Refer Time: 13:41)

Yes. That again you will have to do that. Say and number of moles of course, you can get from here in this case, number of moles is one mole here right, water is 2 moles right, and methane is one mole oxygen is 2 mole. So, you know this thing. So, if you know these values, you can calculate very, easily right?

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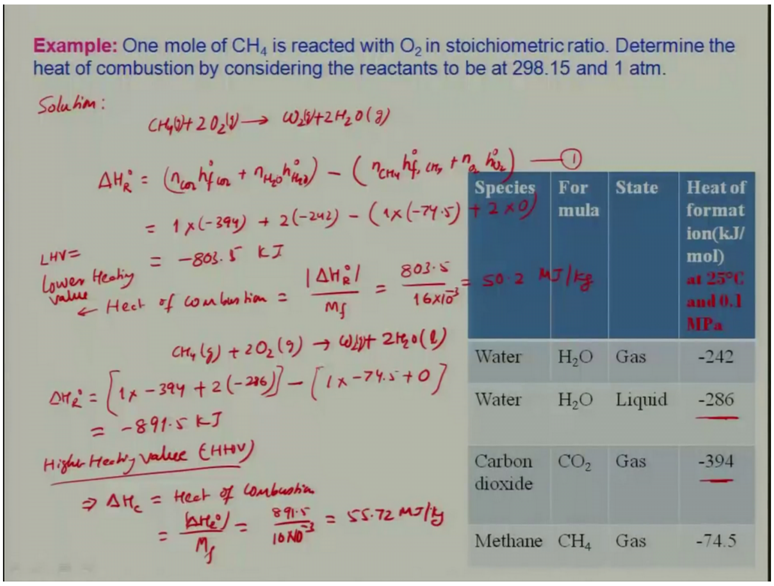

Example: One mole of CH_4 is reacted with O_2 in stoichiometric ratio. Determine the heat of combustion by considering the reactants to be at 298.15 and 1 atm.

Solution:

$$CH_4(g)+2O_2(g) \rightarrow CO_2(g)+2H_2O(g)$$

$$\Delta H_R^\circ = (n_{CO_2} h^\circ_{f,CO_2} + n_{H_2O} h^\circ_{H_2O}) - (n_{CH_4} h^\circ_{f,CH_4} + n_{O_2} h^\circ_{O_2}) \quad \text{①}$$

$$= 1\times(-394) + 2(-242) - (1\times(-74.5) + 2\times 0)$$

$$= -803.5 \text{ kJ}$$

LHV = Lower Heating value ← Heat of combustion $= \frac{|\Delta H_R^\circ|}{M_f} = \frac{803.5}{16\times10^{-3}} = 50.2$ MJ/kg

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta H_R^\circ = [1\times -394 + 2(-286)] - [1\times -74.5 + 0]$$

$$= -891.5 \text{ kJ}$$

Higher Heating value (HHV)

$\Rightarrow \Delta H_c$ = Heat of Combustion $= \frac{|\Delta H_c^\circ|}{M_f} = \frac{891.5}{16\times10^{-3}} = 55.72$ MJ/kg

Species	Formula	State	Heat of formation(kJ/mol) at 25°C and 0.1 MPa
Water	H_2O	Gas	-242
Water	H_2O	Liquid	-286
Carbon dioxide	CO_2	Gas	-394
Methane	CH_4	Gas	-74.5

Let us consider an example, like one mole of methane is reacting with the certain amount of oxygen in a stoichiometric ratio. Determine the heat of combustion. Consider a reactant to be 298.15 kelvin and one atmospheric pressure right.

So, what you will have to do? Basically, heat of combustion and when you talk about heat of combustion, we will be looking at both; that means, lower heating values or the higher heat of combustion, lower heat of combustion or higher heat of combustion.

So, stoichiometric you know C H 4 and oxygen will be right? What it would be? C H 4 plus 2 oxygen going to the C O 2 plus water. Water is basically 2 and keep in mind, all are in gas. We are considering as a gas right. So, change in enthalpy of heat of reaction. If you look at, we need to find out first heat of reaction, right? Heat of reaction would be, what it would be? It will be m C O 2 plus h f C O 2 plus n water h water, right? So, from this table for the heat of formations we can get this values right. So, for this case what will be? This will be one mole of carbon dioxide. So, one into 394 kilo joules per mole, right? You can say or plus n s 2, this will be 2 into minus 242. This is basically corresponding to gas right. So, minus n C H 4 is one into 74.5 plus n what this will be basically 2 into this will be 0. So, this turns out to be something 803 kilo 803.5 kilo joule.

Now, heat of combustion if you look at, I am taking mod of delta H are not divided by the mass of fuel, right? I can also express some, in terms of moles also. I can do that people do report, but this is little easier to keep in mind. Also, easier to use. Therefore, I have used this here. 803.5 mod means, it will be positive. Although it is negative, this will be positive divided by mass of fuel. How I will find it out molecular weight of fuel into the one mole? So, that will be 16. So, this happens to be 50.2, right? And this will be 10 power to minus 3 this will kilo joule. This will be mega joule per k g, which is a very big amount of energy being released. Just burn one k g of methane, you will get around 50.2 mega joule mega means 10 power 6 joule; it is a very huge amount.

And if it is a liquid, instead of gas, right? If it is a liquid, what will happen? This C H 4 this will be gas. Definitely oxygen carbon dioxide to water. It can be liquid. This is your gas. Now, this why you are doing because, this heating value is basically lower heating value I have given table here. You can look at maybe, I will use this is basically lower heating value is equal to this.

Now, I can do use the same expression here. If I say, this is equation one for that I can use, so for this, what I will have to do? I will have to use this values, right? And n will be one mole into same thing 394. If you look at this is carbon dioxide is 394 kilo joule per mole, this is kilo joule per mole is a one mole. If you take this is minus 394 plus 2 into what I will have to do?

Now, I will have to, because a liquid. So, 286 for the water minus this will be same right? One into minus 74.5 plus 0 because, 0 is like heat of formation of oxygen is not given here, but this is 0 that happens to be something minus 891.5 kilo joule and heat of combustion of the higher heating values H H V is equal to delta H C. I can write down heat of combustion right is equal to delta H R naught divided by M M F equal to 891.516 into 10 power take minus 3 is equal to 55 point 72 mega joule per k g. If you look at there, is increase in energy therefore, it is known as higher heating values.

So, if you look at, like we have learnt, now, how to calculate the heat of combustion? Heat of reaction of course, using the heat of formations, this is the one method of calculating the heat of reaction.

Now, question arises is, there any other method of heat of reactions provided heat of formation is not there or it is a new compound you have developed, how you are going to do that calculation? Because, I am, we are interested to calculate heat of combustion. So, therefore, we need to know to calculate the heat of reaction how we are going to do? We are going to discuss that in the next class.

Thank you very much.