Material and Energy Balance Computations
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Lecture-53
Energy Balance with Chemical Reactions-III

Welcome back, now to the 53rd lecture of the course. We have already started to discuss energy balance with chemical reactions. And in the previous lecture we have learnt a very important law which is essentially the 'Hess law'. And we have seen how Hess law can be used to circumvent the problem associated with calculation of the heat of formation of compounds which have a fake formation reaction, which we have already noticed. What we plan to do now?

We will continue with Hess law or rather it will be primarily based on application of Hess law, where we will show, or I will teach you how one can calculate the heat of formation? Not only from heat of formation of other compounds which have real formation reaction but even other type of reactions whose heat of reaction values can be easily measured. And one such type of reaction is of course the combustion reaction. We have this so called concept of standard heat of combustion.

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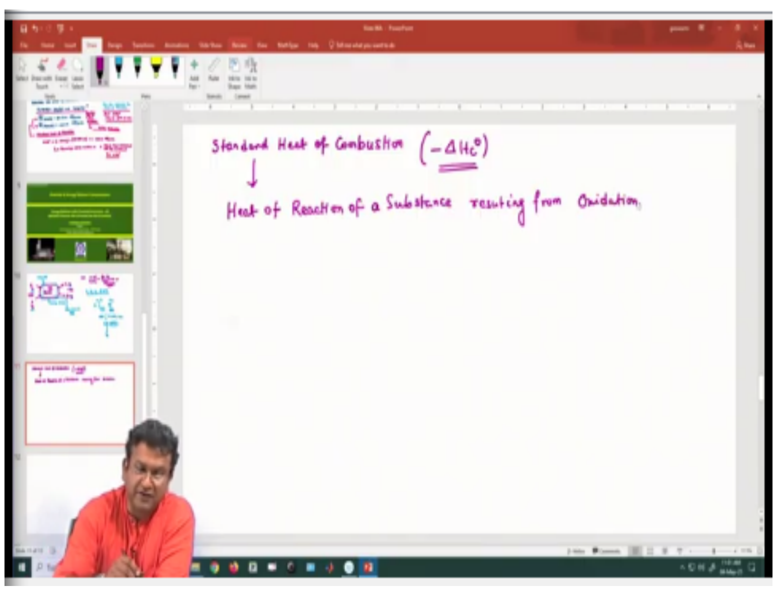
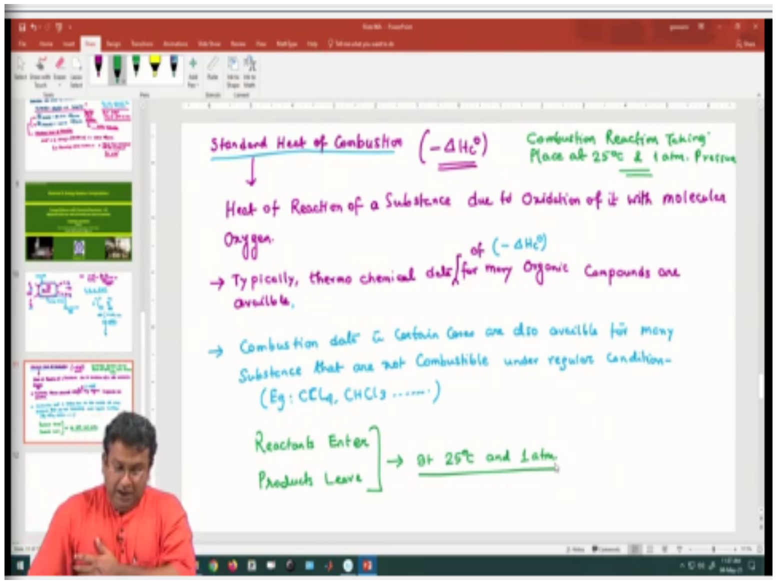


Typically, it is represented by ($-\Delta H_c^0$), so this is essentially nothing but the heat of reaction of a substance resulting from oxidation with molecular oxygen. **(Refer Slide Time: 02:30)**



So, here what we essentially do? We have a combustible compound and what you essentially look at is the heat of reaction associated, if you burn it or combust it or oxidize it in stoichiometric oxygen only. You do not consider any excess air; or you do not consider presence of nitrogen in air etc.

So, when you are calculating the heat of combustion, please do understand that you are not talking about the air that you are pushing into the reactor or the combustion chamber because oxidation reaction only takes place with molecular oxygen and in stoichiometric amount and this can be measured. So, typically most organic compounds are combustible and therefore the thermo chemical data for many organic compounds are reported or easily available in the form of heat of combustion.

Typically, thermo chemical data for many organic compounds are available. Data for heat of combustion ($-\Delta H_c^0$) for many organic compounds are available. However, for many of them the direct heat of formation data is not available. And very interestingly even the combustion data in certain cases are also available for many substances that are not combustible under regular condition which include CCl_4, chloroform ($CHCl_3$) etc. Of course, when we are talking about the standard heat of combustion, it now should immediately come to the mind of this class that we are essentially talking about this combustion reaction.

What is the condition at which the combustion reaction is taking place? The condition is 25°C and 1 atm pressure. So, the reactants enter, and products leave at 25°C and 1 atm. So, typically what you need to understand that since all the combustion reactions are exothermic, so heat gets generated. And therefore, the flue gas that eventually comes out of the combustion chamber is typically hot.

Even if you hold your hand in the exhaust, in front of the exhaust of your car or bike, you will see that a hot gas is coming out, so that is nothing but flue gas. So, whatever you have studied as flue gas, one of the classic examples is that the exhaust that is coming out from an automobile engine is actually flue gas. And many times, you might have noticed particularly for our students who are joining from the northern part of the country that in winter months some water drips out of this exhaust chamber. So, now this class should immediately understand what it is? It is nothing but the H_2O, the water present in the exhaust has condensed into water because of low temperature outside. And under what condition this condensation takes place? We will learn when we talk about humidity. So, the take home message is that in a combustion reaction energy gets generated. Some part of this energy is used in driving a motor or moving a shaft etc. So, that is essentially an internal conversion of energy from one form to the other. But more importantly the products are coming out at a higher temperature.

So, here if you are willing to measure the standard heat of combustion, you need to ensure that the products are also coming out at 1 atm pressure and 25°C. So, essentially you have to cool down the products and therefore based on that the total heat that gets generated by the system can be measured and that is essentially the heat of combustion.

Now what I will do? As I already promised in the initial introductory part of this lecture, that I am going to pick up an example of a unique system. Let’s say for chloroform, the heat of combustion data is available, but the heat of formation data is difficult to obtain.

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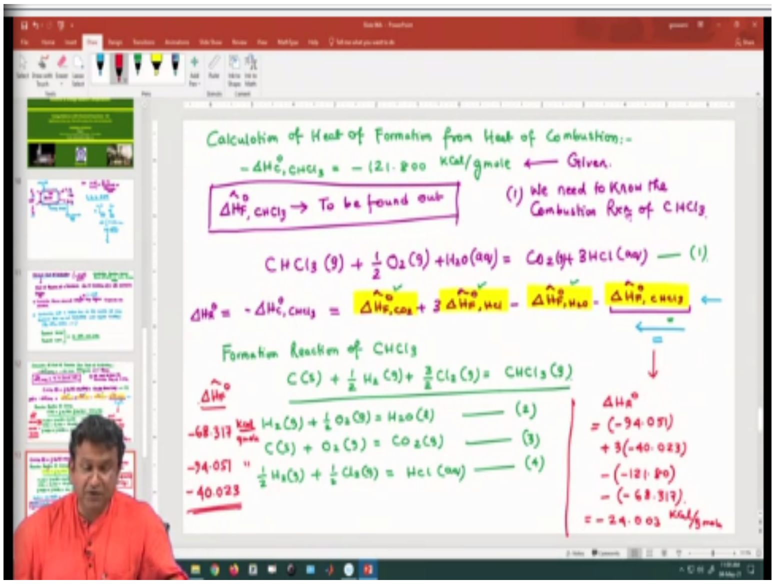

So, essentially the problem we are talking about is application of Hess law and it is calculation of heat of formation from heat of combustion. So, the heat of combustion for chloroform $(-\Delta H_{c, CHCL3}^{0})$ is given and you are told to find out the heat of formation (ΔH_F^0 cap). Now I am going to show how to tackle this problem step wise very slowly, so that you understand, and you all pick up how we are applying Hess law. And then subsequently you can solve this for other type of compounds, which I will try to give some examples in your assignments. So, in order to solve this problem, we essentially need to know certain things: (1) the combustion reaction of chloroform, which is not a very straight forward reaction (Have you ever heard that chloroform is being used as a fuel? The answer is no.),

$CHCL_3$ (g) + ½ O_2 + H_2O (aq) = CO_2 (g) + 3HCl (aq)------------------------- (1)

So, what exactly is given to you is the heat of reaction of this particular reaction. So, when you say that heat of combustion of chloroform is given, that means actually what you have is the heat of reaction for the above reaction. And this turns out to be the heat of combustion of $CHCl_3$ in this particular case = heat of formation of CO_2 + 3*heat of formation of HCl - heat of formation of H_2O - heat of formation of $CHCl_3$.

So, this is what you need to find out. And of course, in order to progress, we now understand that we need to have the heat of formation data of carbon dioxide HCL and water. So, I am going to show it in terms of 'Hess law'.

So, what we also need to know the formation reaction of chloroform. So, the formation reaction of chloroform is as follows, so this is how it goes. So, from this equation you can write that heat of formation of chloroform = heat of formation of carbon dioxide + 3* heat of formation of HCl - heat of formation of water - the heat of combustion of chloroform. So, you can straight away calculate that. But I am going to show you how you get that in terms of 'Hess law'.

So, let us see how we get it? So, this is the formation reaction of chloroform,

$$C(s) + 1/2H_2\ (g) + 3/2\ Cl_2\ (g) = CHCl_3\ (g)$$

Also we have,

$$H_2(g) + 1/2O_2\ (g) = H_2O\ (l)\text{-----------------------------------}(2)$$

$$C(s) + O_2\ (g) = CO_2\ (g)\text{---}(3)$$

$$1/2H_2\ (g) + 1/2Cl_2\ (g) = HCl\ (aq)\text{-------------------------------}(4)$$

And let us also look into the formation reactions of these 3 compounds i.e. water, hydrochloric acid and carbon dioxide. So, the whole purpose of this problem is essentially to showcase to you the application of Hess law. It may not be useful in this particular case but there are situations where you might have to solve stuff like this. So, what are we trying to get?

We are essentially trying to get an expression for the heat of formation of chloroform through the heat of combustion data that is available to us. And for that let us see what we are going to write? We are essentially going to use 'Hess law'. So, we know that we can add on or subtract equations.

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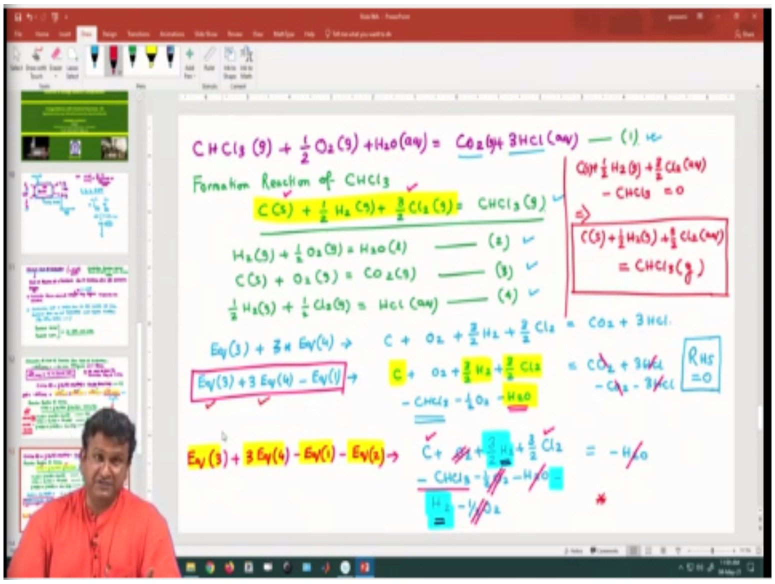

The reason I am taking this longish route is to demonstrate where Hess law comes into picture. So, what we have to do first? We try to match these righthand sides of the equations, so we do, so that you can get if you write and for Hess law you essentially treat the chemical reactions as sort of algebraic equations. So, if you do

Eq 3 + 3* Eq 4 $\rightarrow$ $C + O_2 + 3/2H_2 + 3/2Cl_2 = CO_2 + 3HCl$

As finally we need to have an expression for heat of formation of chloroform, we should bring in the heat of formation of chloroform here, by introducing or subtracting the heat of formation. So,

Eq (3) + 3* Eq (4) – Eq (1) $\rightarrow$ $C + O_2 + 3/2H_2 + 3/2Cl_2 - CHCl_3 - 1/2\ O_2 - H_2O$

$= CO_2 + 3HCl - CO_2 - 3HCl = 0$

So, now you see what are we trying to get? We are trying to recombine these equations, these 3 ‘heat of formation reaction’s and 1 combustion reaction to get essentially the formation reaction of chloroform.

So, you now see that you already have chloroform. So, definitely chloroform is going to be on the right-hand side. But what you also observe is in this composite equation? You actually have water sitting on the left-hand side. So, you need to eliminate this water because water is not there in your formation reaction of chloroform. So, what do we do now? So, how can we eliminate water? We can eliminate water if we do something like add or subtract something to this composite equation now and this is what is the composite equation turn into,

Eq (3) + 3* Eq (4) – Eq (1) – Eq (2) $\rightarrow$ $C + O_2 + 3/2H_2 + 3/2Cl_2 - CHCl_3 - 1/2\ O_2 - H_2O - 1/2\ H_2 - 1/2\ O_2 = -\ H_2O$

Or, $C + H_2 + 3/2Cl_2 - CHCl_3 = 0$

Or, $C + H_2 + 3/2Cl_2 = CHCl_3$, which is the formation reaction of chloroform ($CHCl_3$).

So, finally what we get? What we are learning here is a direct application of 'Hess law', where you can essentially get not only the value but you also learn how to get the heat of the formation reaction using the heat of the combustion reaction of that particular compound along with certain other. So, byproducts or other reactants or whatever you have thus their formation reaction. So, I hope all of you are clear as to why we are doing this laborious exercise.

Because finally as far as the numerical part is concerned, we will actually get these heat of formation values of each component of eq (1) and you could have simply plugged in those numbers and obtained the final value for heat of formation for chloroform. But the whole purpose of this lecture is to demonstrate the applicability of Hess law in a broader perspective.

And as I have repeatedly told in the context of Hess law, you actually treat the chemical reactions just the way that they are as an algebraic equation. So, you are very much allowed in this context to write, sorry, this is not aqueous, this gas chloroform is gas. So, now what is the take home message? We are reaching the end of this class, but what is the take home message? Take home message is that this is the way to essentially by which I have shown how you can get the formation reaction from combustion reaction.

And what are the operations you have done? You have done equation 3 + thrice equation 4, sorry I should look into here, you have done equation 3 + thrice into equation 4 - equation 1 - equation 2. So, all you need to do is you simply add up heat of formation of carbon dioxide + thrice the heat of formation of hydrochloric acid - the heat of combustion of chloroform - heat of formation of water.

And you see that is exactly the expression you have over here for the one step calculation to find the heat of formation. So, where you can simply plug in these numbers and you can just do it yourself. As the heat of formation value of water is -68.317 kilo calorie per gram mole, that for carbon dioxide is -94.051 and that for hydrochloric acid is -40.023. So, if you know these numbers you can straight away calculate. But what I have demonstrated how you can take advantage of Hess law in generating reconstructing the formation reaction. So, I request all of you to kindly practice this and with other compounds to get a better feel of applicability of Hess law. Thank you.