**Material and Energy Balance Computations**
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**Lecture-51**
**Energy Balance with Chemical Reactions-I**

Welcome back, now we are into the $11^{th}$ week of the course. And today we are going to start as promised in the previous class something very interesting. And that is we are now going to talk about energy balance with chemical reactions. So, far if you look into the discussion, we did not talk about any chemical reaction. And this part of energy balance is something very special to chemical engineers as you can understand from the name because as a community the chemical engineers only deal with reacting systems.

So, for example energy balance, these types of thermodynamics, mechanical engineers also do a lot because they design turbines, wheels, engines, etcetera**.** But there it is more like a change of phase is more important. So, you use super heated steam, that has certain amount of energy, it has certain amount of enthalpy. So, it rotates a turbine, loses some amount of energy, transfer that energy to the turbine and therefore it becomes it is degree of super heat reduces, it is pressure reduces.

But if you have looked into all the calculations that we have done so far using the steam table, there was no chemical reaction. And from our basic chemistry, we all know about chemical reactions, it is not that I have to teach you chemical reactions. And you are also educated enough to remember that there can be two types of chemical reactions, exothermic and endothermic. And what happens in exothermic reactions?

Heat gets released, so the reacting vessel often becomes hot. And again, as a chemical engineer or as an engineer it might be your responsibility to maintain constant temperature. So, that there is not an overshooting of the temperature in the reactors. Why? Because if you do not take care of the heat that is getting generated the reactor temperature will keep on increasing and the biggest problem is that might actually lead to material failure. So, as I always tell as an engineer you must worry about the practical aspects. Therefore, often what happens? You see that there is a reactor which comes with a cooling jacket. In fact, I remember in the tutorial we took up a problem where it was very interesting that steam was used as the cooling medium. So, it must have been a very high temperature reaction, so that heat needs to be extracted out. So, these are something that you will learn in your subsequent courses; may be on ‘process equipment design’ and ‘reactor design’ etc. But more importantly what exactly is happening in a endothermic reaction and an exothermic reaction?

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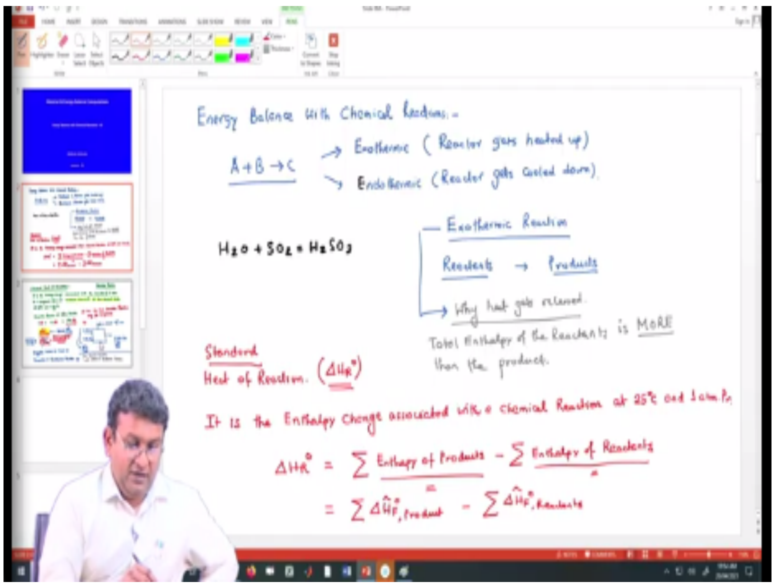


So, in fact this is the class we all look forward to energy balance with chemical reactions. So, typically you can write some reaction like this and it can either be exothermic where heat, I will not say heat gets generated or the reactor or your beaker in which you have done all your reaction so far gets heated up. Other is endothermic, where the reactor gets cool down, one can also write let us say an actual chemical reaction let us say $H_2O$ + $SO_2$ = $H_2SO_3$ or something like this.

So, how do we define it? Let us try to understand what exothermic reaction is. So, what exactly is happening in exothermic reaction? So, you see the reactor gets heated up. So, in a reaction what you have? You have the reactants which eventually results into products. Of course, there can be additional complexities that there is not 100% conversion etcetera.

We will talk about that; we will learn how to handle those are not big problems. So, why does heat get released? So, critical question to ask is rather than just knowing that you have endothermic reaction and exothermic reaction probably many of you know but it is not a bad idea to ask the critical question, why heat gets released? And the simple answer to this is the total enthalpy of the reactant is more than the product.

So, essentially what it means? That more amount of energy was initially stored energy in whatever form energy within course, we will discuss how to quantify this. More amount of energy was initially stored in the reactants and when the product forms less amount of energy is stored into it, so what happens? This difference in the total energy of the reactants minus the energy of the product actually gets released and therefore your reactor gets heated up.

This is essentially the physics of exothermic reaction. Question to ask is how do we define this energy associated with each reacting species? There is a specific terminology for that which we will talk about. And so essentially what also is happening? You have the heat of reaction, so the energy that is the energy change that takes place because of a chemical reaction is what is known I mean we will talk about the formal definition is what is known as the heat of reaction.

So, now what you can also understand? You can very well tell what happens in an endothermic reaction. Endothermic reaction, whatever is the energy that was initially stored in the reactants, more energy is stored in the product. So, from where does this more additional energy come? This additional energy comes from the surrounding and therefore the surrounding medium becomes cold in an endothermic reaction.

So, how do we quantify what is exothermic reaction, what is endothermic reaction etcetera? So, in order to quantify that we essentially need to define a parameter called heat of reaction. Typically, we define the standard heat of reaction ($\Delta H_{R0}$). So, what is standard heat of reaction? So, when you are talking about standard heat of reaction, it is the enthalpy change associated with a chemical reaction at 25°C and 1 atm pressure. So, loosely writing is equal to summation of enthalpy of products - summation of enthalpy of reactants. Now the question is how do we write the enthalpy of the reactant or these products?

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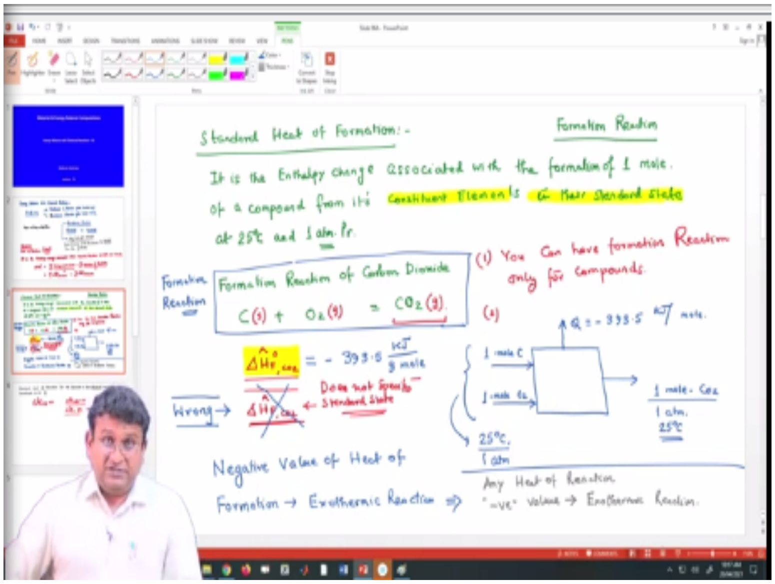


And in order to do that we need to define a parameter which is known as the standard heat of formation. This is a very interesting concept because many of us often forget and what is even more interesting the assumptions associated with standard heat of formation. Because many of us when we are talking about heat of reaction, we talk, we know, loosely we all know it is the enthalpy change associated with the chemical reaction.

But we often miss out that this so-called enthalpy change is defined or quantified in terms of standard heat of formation. And as you will soon understand the standard heat of formation actually comes has certain degree of assumptions. So, let us understand standard heat of formation carefully. And this will also allow you to learn about a special type of chemical reaction which is known as the formation reaction. So, let us see how it goes?

So, standard heat of reaction is the enthalpy change associated with the formation of 1 mole of a compound from it is constituent elements in their standard state at 25°C and 1 atm pressure. Now this is very interesting, so what it means is the heat of formation is essentially the heat of reaction associated for the formation of a particular compound from it is elements in their standard state.

So, the formation reaction of carbon dioxide for example, carbon (C) and oxygen ($O_2$) reacts to form carbon dioxide ($CO_2$) is getting generated. But remember if you write this equation only, this is not the appropriate formation reaction, why because there is a specific condition for formation reaction, for a reaction to be considered as the formation reaction. The constituent elements must be in their standard state, so this is very important.

And you specifically write therefore in order to write a formation reaction that carbon must be solid, oxygen must be gas and carbon dioxide also must be gas, this must be written. So, first thing is the formation reaction is valid only for compounds, so you can have only for compounds, this is number 1. And it has to start from it is elements in their standard form. So, now the heat of formation data for carbon dioxide turns out to be, so this cap stands for molar 1 mole and the 0 stands for standard state.

Typically, in principle you can have this value or this symbol also; but they are not same. Because this is the heat of formation of carbon dioxide, but this does not specify standard state. So, you might independently, does not specify standard state, you might independently write that you have done let us say the combustion reaction between carbon and oxygen at certain temperature and pressure and this is the enthalpy change associated.

So, you can say that at that condition this is the heat of formation but that is not the standard value. The standard value is accepted everywhere, and you need it for calculating the heat of reaction which you will also understand is the heat of formation at the standard state. So, it is like this $H_{F0}$ cap for the particular compound. So, it turns out that the value of $H_{F0}$ cap, so this is actually wrong and therefore I will not remove it, but this will remain as something that is wrong.

And this value turns out to be as from the literature it is -393.5 kilo joule per gram mole. So, this is analogous to as if 1 gm mole of carbon and 1 gm mole of $O_2$ both at 25°C and 1 atm pressure are entering a reactor to produce 1 gm mole of carbon dioxide, again at 1 atmosphere and 25°C. And there is a reaction, however the reactant and products enter and leave at the same temperature, so some heat must get liberated. And the amount of that heat is -393.5 kilo joule per gram mole.

There are certain riders in formation reaction, what you may please remember? A negative value of heat of formation means essentially exothermic reaction. In fact, this is not a convention in fact I must tell the full thing we are still not discuss the heat of reaction in detail. Even for any heat of reaction negative value means exothermic reaction and why is it so?

It is because you see the way heat of reaction is defined; it is the total enthalpy of the products - total enthalpy of the reactants. And now probably you can understand once you already know the heat of formation, so the heat of reaction is nothing but the summation of all the standard heat of formation of the products - standard heat of formation of the reactants. So, this is how it goes.

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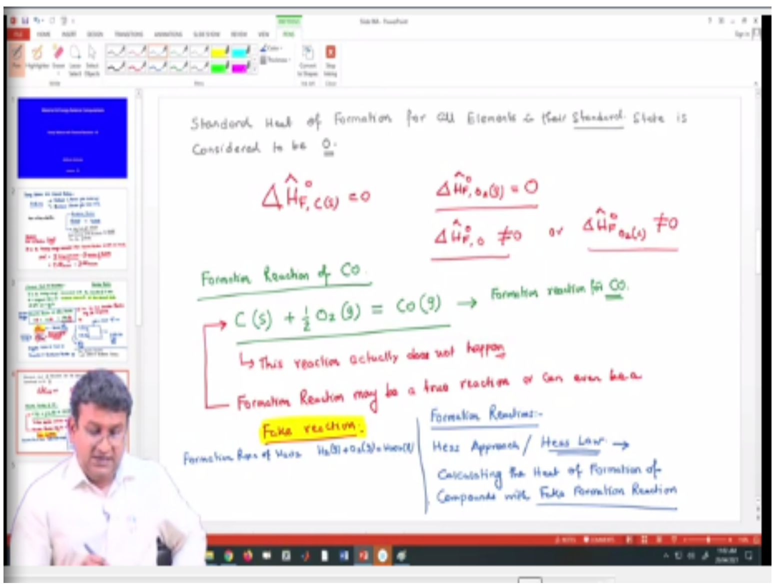


Now there are certain additional things you may want to recall; or you may want to remember or learn. The standard heat of formation for all elements in their standard state, this is extremely important is considered or assumed to be 0. Now this is something we often forget; you must remember that whatever heat of reaction value or heat of formation value you are writing this write on this assumption. So, what does it mean?

If you write something like standard heat of formation of carbon which is solid at room temperature, it must be solid, this is equal to 0. But please do remember or let us say heat of formation of oxygen and it is a diatomic oxygen which is the stable standard state is 0. But, so what I have written? So, if you are talking about standard heat of formation of liquid oxygen for example it is not 0, why it is not '0'?

Because liquid oxygen is not in it is standard form. Similarly heat of formation of O for example ion that is not $O_2$, because that is not in it is standard form. So, any reaction that sort of, so this type of a reaction is known as the formation reaction where we talk about the formation of a compound in it is standard form at 25°C and 1 atm pressure from it is elements in their respective standard form at 25°C and 1 atm pressure.

So, this is what is known as a formation reaction. And the very next example gives you a very fascinating aspect about formation reaction. Let us try to write down the formation reaction of carbon monoxide. So, how will it look like? It will look like carbon in solid form plus if you write stoichiometrically half oxygen in gaseous form leading to CO in gaseous form. So, this is the absolutely correct formation reaction for carbon monoxide, but what is the problem?

Problem is as follows, this reaction does not happen, actually does not happen, why? Because if in a reactor you take carbon and half the number of moles of oxygen and react, you know what will happen? Half the amount of carbon will get converted to carbon dioxide and the other half of carbon will remain unreacted, but you cannot get CO. However, that is not the consideration while writing the formation reaction.

Formation reaction must be written in the form of the product forming from it is constituent elements in their standard form. So, CO, the formation reaction is CO whatever we have written is absolutely correct. And that tells us that the formation reaction may be a true reaction or can even be a fake reaction, this is very interesting. So, formation reaction may not happen, it might be a fake reaction but does not matter when you are writing the formation reaction, this is how it should go.

So, one can write formation reactions let us say of several compounds, how to calculate these numbers? Well, it is a tricky thing, heat of reaction you can in principle measure in a calorimeter. So, you can actually perform a reaction and from there you can measure the amount of heat that is getting generated, it is possible. Now you must remember then in that case to measure the heat of reaction using a calorimeter the reaction must take place.

So, therefore the formation reactions of compounds that are true, the formation reaction takes place, well, they can be measured. But for compounds which have a fake formation reaction, it is actually a problem. And essentially there are other routes to find out the heat of formation of such compounds following some other approach or an approach called Hess law or Hess approach.

So, that is something very important and maybe I will start afresh in the next class or Hess law as they call it. So, this is very interesting and is extremely helpful in calculating the heat of formation of compounds with fake formation reaction and the list is pretty exhaustive. So, you can try to write down for example the formation reaction of $H_2O_2$ and it will be $H_2(g) + O_2(g) = H_2O_2$ (l) and stuff like that. So, quickly before we finish today's class let us have a quick look at 'Hess law'.

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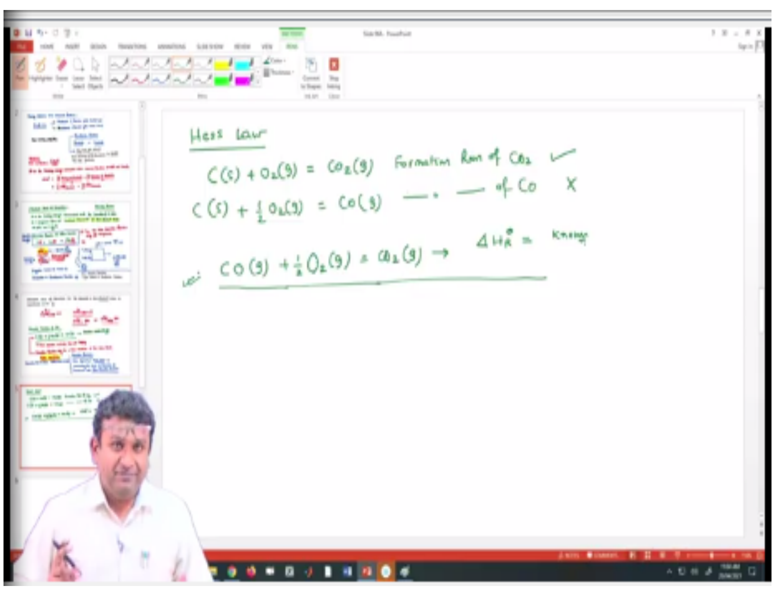


So, what we have understood that? This is a formation reaction of carbon dioxide and this is true, this is the formation reaction of carbon monoxide and this is false. However, another reaction takes place and that reaction is oxidation of carbon monoxide. So, this reaction, this is not a formation reaction, this reaction can be performed, and it is heat of reaction value is known. So, what Hess law suggests? And I will pick up in the next class from here.

That the heat of formation of carbon monoxide or in other words what it suggests is whatever is the thermal heat change associated with the forward reaction, the backward reaction has exactly the same amount of heat associated with a negative sign. So, I will start from here; let us not get into the details because we are running really out of time today. And from here we will pick up in the next class and show you how to calculate using Hess law?

This is a very, very useful formulation. How to calculate using Hess law the heat of formation of materials or compounds which have a fake formation reaction? And this concept we will extend in extracting heat of formation data from other reactions like combustion reactions or other reactions that might be happening. Thank you.