Chemical Engineering Thermodynamics
Prof. Sasidhar Gumma
Department of Chemical Engineering
Indian Institute Technology, Guwahati

Lecture – 38
Chemical Reaction Equilibria

Hello and welcome back. In the previous lectures we looked at equilibrium instability involving liquid phases, immiscibility in case of liquid phases etcetera. What we will do in the remaining part of this course is talk about equilibrium in systems involving chemical reactions. The treatment is somewhat similar to what we have done earlier. We look at the minimization of the Gibbs free energy at a given temperature and pressure, the temperature and pressure being the conditions of the reaction in this case.

And so in that sense it would be a natural extension of what we have done in case of liquid equilibrium. But before we do that we need to set a few things in order as far as chemical reactions are concerned. So, we will talk a little bit about chemical reactions and how we treat chemical reactions, so that we can formulate a thermodynamic framework for analyzing the chemical reaction equilibrium. So, let us get started. First thing we define for chemical reactions is what is known as a stoichiometric number.

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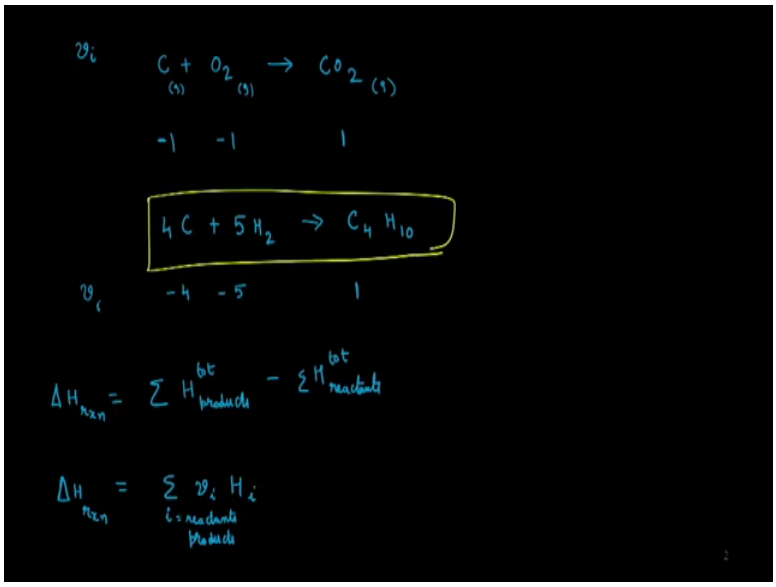

A stoichiometric number is denoted by a symbol nu i and it essentially gives the number of moles of the reactants and products in a balanced chemical reaction. So, for example,

if I have a reaction such as C plus O 2 going to CO 2 all of them in the gaseous phase then the stoichiometric number nu i for C is going to be negative 1 because it is a reactant it has been consumed that is the reason for the negative sign. Similarly, for oxygen it is negative 1 whereas, for CO 2 it is a product it is being produced. So, the sign would be positive and then 1 mole of CO 2 is produced. So, the stoichiometric number for CO 2 is 1, for C and O 2 are negative 1.

In a similar way if I have a reaction 4 between carbon and hydrogen to give butane C 4 H 10 this is what we call as the formation reaction for butane. In this case the stoichiometric number for carbon is going to be negative 4, negative being the sign for the reactant and 4 being the number of moles in the reaction we have shown about, negative 5 for hydrogen and positive 1 for butane and butane. So, these are the stoichiometric numbers for C H 2 and C 4 H 10 in this particular balance reaction and so on. They are going to be and the when we deal with chemical reactions, so let us make a note of that.

Now, once we have a chemical reaction just like heat effects upon mixing or change in enthalpy due to mixing or formation of a solution there is going to be a change in enthalpy when chemical species react and form a new chemical species. It is not just enthalpy other thermodynamic properties such as Gibbs free energy etcetera also change due to the reaction. We need to identify these changes in thermodynamic variables due to the reaction. Let us take an example in this case of enthalpy and discuss how it can be calculated or treated when chemical reactions occur, right.

If I have a reaction such as this one above there is going to be an enthalpy change of one chemical reaction, this enthalpy change essentially is going to be enthalpy of the products minus the enthalpy of the reactants. This is going to be the total enthalpy in Joules or kilo Joules summed over all the products minus summed over all the reactants, and this is what we call as the enthalpy change due to the reaction delta H for the reaction.

Now, we are talking about the total enthalpy. So, if there are 4 moles of carbon, then it is going to be 4 times the molar enthalpy for carbon, if there is 5 moles of hydrogen it is going to be 5 times the molar enthalpy for hydrogen and so on. Now, in terms of stoichiometric numbers this becomes a little easier to write it will simply be sigma nu i H

i over all the reactants and products, i can be reactant, i can be a product and because the negative sign is automatically included in the stoichiometric number for the reactants the above equation will be straightforward and the summation would give what we call as the enthalpy change due to the reaction.

Now, the question is at what conditions is this enthalpy change. Now, if you recall enthalpy is when you be a function of temperature and pressure. So, at what temperature and what pressure are we talking about the heat of the particular reaction? For example, the reactants can enter at a particular temperature and pressure, the products can come out at a different temperature and pressure depending on how much heat is evolved or consumed during the reaction in addition to how much heat is added or removed from the system.

So, in that sense at what conditions are we talking about the heat of the reaction, right. For example, the reactants can enter at the room temperature of 300 Kelvin and they can come out as products at 500 Kelvin. In another scenario they can come out at products at 1000 Kelvin in which case the enthalpy change due to the reaction is going to be different. So, there needs to be a consistent way in which we can talk about these enthalpy changes due to the reaction.

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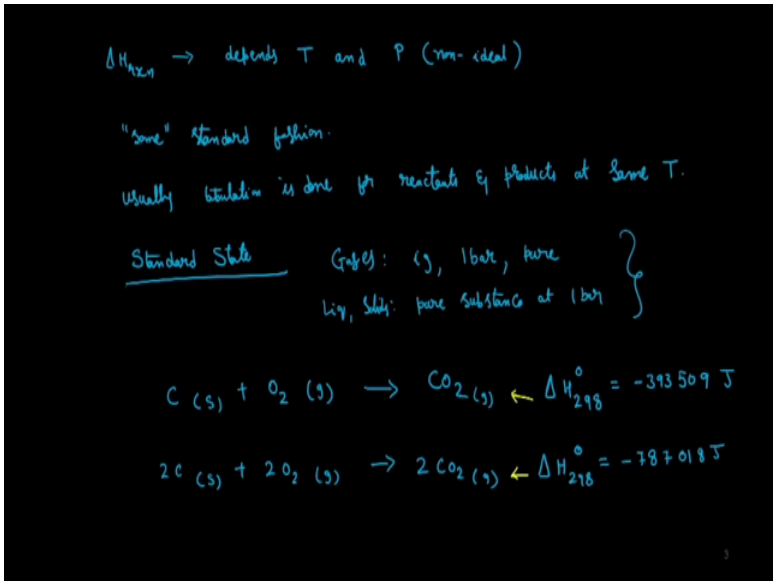

So, in that sense delta H for the reaction is going to depend on temperatures and pressures as well if the gas is non-ideal. The gas is ideal enthalpy is independent of

pressure, but otherwise it is going to be dependent on its going to be dependent on pressure also. So, to come up with a consistent way of expressing these things and each reaction can be carried in a different way it is not possible to tabulate the enthalpy changes due to reaction that are carried out in different ways. So, the usual practice is that two tabulate heats of reaction when they are carried out in some standard fashion, alright.

So, we tabulate heats of reaction if they are carried out in some standard fashion. The usual convention, usual consistent way that is adopted to tabulate them in standard fashion is to tabulate when both the reactants and products are at the same temperature, alright. Usually tabulation is done for reactants and products at same temperature. If they occur at different temperatures then one can easily use the specific heat capacities and take them from the temperature; standard temperature to the temperature of interest. We will see what we mean by that when we solve a problem, alright.

And again the tabulation can be done at various standard temperatures, but the usually adopted convention is that the standard state for tabulating these heats of reaction that is usually accepted is for gases. It is ideal gas at 1 bar, for liquids and solids it is pure substance again at 1 bar. Of course, the gases are also pure ideal gases at one bar these are the usually accepted standard states and we take the reaction occurring at the temperature of interest under these standard state conditions and tabulate the heat of the reaction. If it is occurring at a different condition then one can easily move them to different condition using the processes we already learnt in the change, calculate the change in enthalpy when it goes from the standard condition to a different temperature and pressure, and add the two enthalpies that will give the heat of the enthalpy change due to the reaction at a different condition, alright.

So, what we mean by this is for example, if I consider the reaction C in a solid state plus O 2 in a gaseous state giving CO 2 then the heat of this reaction at 298, this subscript 298 is 4 the temperature, 298 Kelvin and the superscript naught is to indicate that this is a standard state condition, alright. And at this standard state condition which means we are at in an ideal gas state for a gas as a pure substance for the solid carbon then at these standard state conditions and it is occurring at 1 bar at these standard state conditions delta H 298 naught is negative 393509 Joules.

What this means is that if this reaction is carried out at 298 Kelvin, both the reactants C in the solid state oxygen in the gaseous state are entering the reactor at 298 Kelvin and CO 2 the product comes out from the reactor at 298 Kelvin, 1 mole of each of those. Then the change in enthalpy during the process that is occurring at 298 Kelvin is negative 393509 Joules or negative 393.5 kilo Joules for this particular reaction. This is true when 1 mole of carbon in the solid form 1 mole of oxygen in the gaseous form enter react and then 1 mole of CO 2 comes out of the reactor. So, this particular delta H value is at those conditions 298 Kelvin and 1 bar 4 pure substances.

If I change this reaction, right if I change this reaction and say that 2 moles of carbon are reacting with 2 moles of oxygen still in the solid and gaseous wants to give 2 moles of CO 2 in the gaseous form, then the delta H for this particular reaction is going to be twice the previous amount because the size of my system has doubled. So, the change in enthalpy is going to double this is the total change in enthalpy it will double, and it is going to be two times of the above value which is negative 787018 Joules, right.

So, whatever enthalpy change value we are writing is associated with a particular reaction. So, the first one is associated with this reaction, the second one is associated with the reaction written therefore, 2 moles with this reaction, alright. So, writing it independent of the reaction does not make sense we include both of them together.

Not only that, it is also important to identify the state of the reactants in the products. If you notice we said that carbon is in a solid state, oxygen is an gaseous state, CO 2 comes out in a gaseous state at 298 Kelvin and 1 bar.

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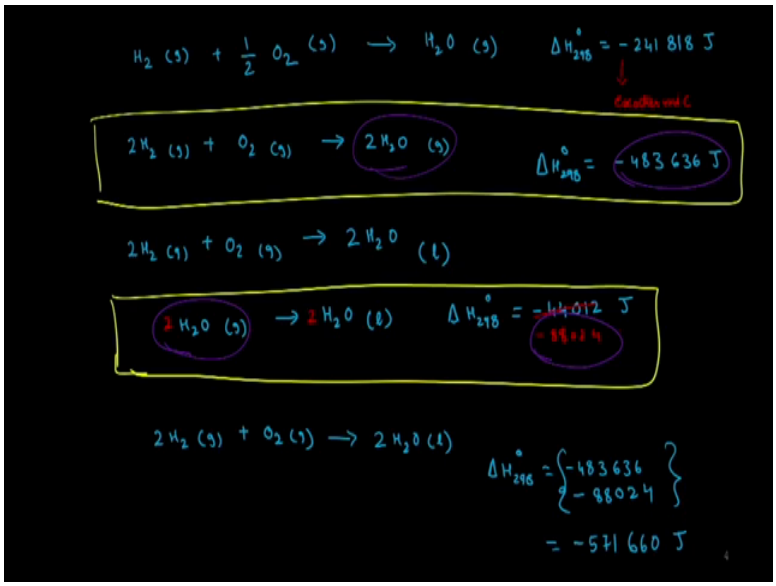

Now, for example, if I have another reaction H 2 in the gaseous form plus half O 2 again in the gaseous form giving H 2 O in the gaseous form, right then the standard enthalpy change for this reaction at 298 Kelvin is negative 241 kilo Joules, 818 kilo Joules or 241 818 Joules, alright. What this means is that if 1 mole of hydrogen and half a mole of oxygen react to give 1 mole of a water in all in the gaseous form and this reaction occurs at 298 Kelvin and that is the enthalpy change due to the reaction.

Now, notice that the negative sign here indicates when we say enthalpy change due to the reaction it is the enthalpy of the products minus the enthalpy of the reactants which means the negative sign indicates that the system of my interest which is the reactants and the products are losing enthalpy or they are losing enthalpy to the surroundings that is what the negative sign here means. If they are losing enthalpy then we call that as a exothermic process. If they again enthalpy then the sign would be positive and we call that as an endothermic process or an endothermic reaction in this case.

Now, if I double the size of this reaction just as we talked earlier, if I react 2 moles of hydrogen still in the gaseous form plus 1 mole of oxygen in the gaseous form to give 2 moles of water in the gaseous form then this delta H 298 would simply be doubled as we discussed earlier and this would be negative 483636 Joules, alright. Now, the state of the system like I said is also important all the reactants and the products are in the gaseous form. Now, consider this reaction, 2 H 2 in the gaseous form plus O 2 in the gaseous

form giving 2 H 2 O, but then this is in the liquid form then what would be the enthalpy change for this particular reaction.

To answer that question what we do is we write the first equation; we will consider the first equation here. And we will write another equation for condensation, let us say 2 moles of water or just 1 mole of water in a gaseous form to go to 1 mole of water in the liquid form this is a condensation reaction, the whole water vapour is condensing into liquid water. And for this the change in enthalpy if this condensation occurs at 298 Kelvin, we can easily look up this value it turns out to be enthalpy of condensation or negative the enthalpy of vaporization it is negative 44012 Joules. This is for 1 mole of water condensing if I have 2 moles condensing, right then it will be twice this value which is negative 88024 Joules, alright.

So, what we will do now, is we will take these two equations, I have put in the boxes, right the first one gives me the gas and the second one is for gas going to the liquid we can add these two equations and once we add the two equations the reaction would look exactly what we want, 2 H 2 integrations form plus O 2 integrations form. Notice that the this here will cancel out with this and on the right-hand side I will be left with the liquid. 2 H 2 O in the liquid and when I add these two the changes in enthalpy are going to be simply sum of this value plus this value, right. That will be the change in enthalpy.

Delta H 298 when I add those two values it is going to be negative 483636, negative 88024 and I add these two this value turns out to be negative 571660 Joules. So, if the state of the reactants or the products changes then accordingly I will have two use the correct state to get the enthalpy change for that particular reaction. Realize there are several thousands or millions of reactions that are occurring and again it is not possible to tabulate heat of reaction for each one of them. So, what we rather do is to resort to a very convenient way, and the way we do that is using a quantity known as heats of formation, alright or enthalpy change for the formation reaction.

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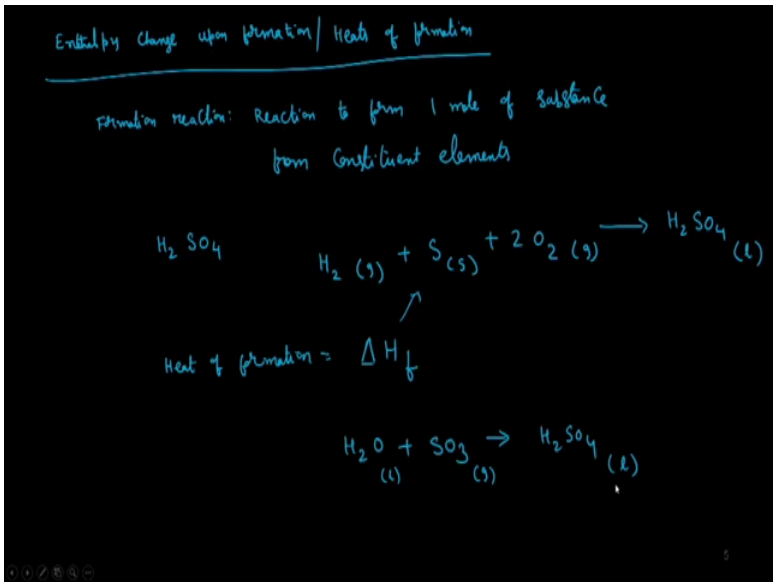

Enthalpy change for upon formation or more commonly called as heats of formation. What these are essentially are the enthalpy changes for the formation reaction? And we define formation reaction as one where 1 mole of the desired compound or substance is formed from its constituent elements. So, formation reaction is defined as reaction to form 1 mole of substance from constituent elements, ok.

So, the constituent elements for example what we mean by this is if I have H 2 SO 4 sulfuric acid then the constituent elements for sulfuric acid are hydrogen, oxygen and sulfur. Their naturally occurring states are hydrogen is in the gaseous form, sulfur is in the solid form, oxygen again is in the gaseous form in the correct stoichiometric ratios. It will be 1 mole of hydrogen 1 mole of sulfur and 2 moles of oxygen giving me H 2 SO 4, right. This is the formation reaction, and if I am talking about liquid and this will be the formation reaction for liquid H 2 SO 4, alright. And the enthalpy change for this reaction is known as the heat of formation, delta and it is denoted by delta H f for this particular reaction, alright.

Now, notice that if I write the reaction H 2 O plus SO 3 giving H 2 SO 4, this is liquid this is gas, this is liquid, then this cannot be a formation reaction because the reactants are not elements, right. H 2 O is a compound, it is not an element, S O 3 is not a element it is a compound. So, the naturally occurring elements in their natural states are hydrogen in the gaseous form sulfur in the solid form and oxygen in the gaseous form. So, those,

when we use them as the reactants to make the compound of interest, we get the formation reaction and the enthalpy change for that formation reaction is what we call as heats of formation or sorry heat of formation.

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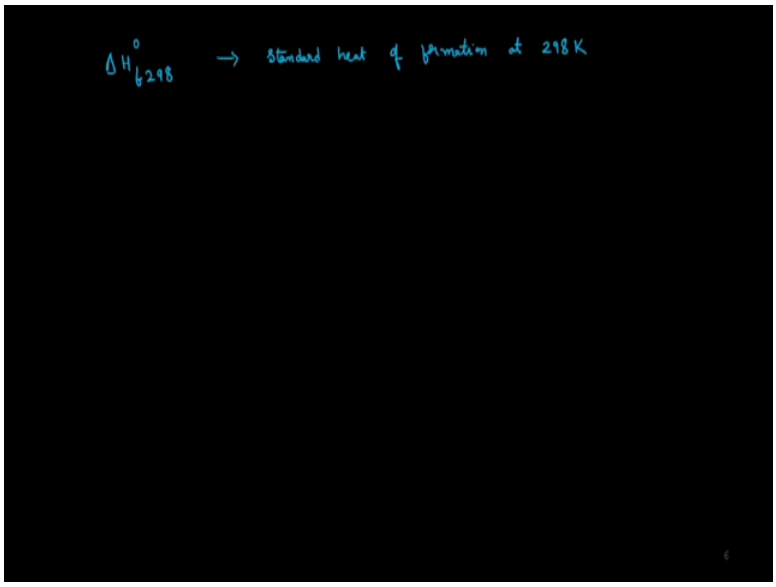

Just like we define the standard heat of reaction we can define a standard heat of formation delta H f. And at some temperature let us say 298 Kelvin as is the convention then delta H f 298 with a superscript naught will indicate standard heat of formation for a species at 298 Kelvin. What this means is that the formation reaction occurs at 298 Kelvin, in it is a standard state and the enthalpy change for that particular reaction is what we call as the standard heat of formation at 298 Kelvin.

Now, why are these heats of formation useful? They are useful because once we tabulate heats of formation for various chemical species; I can use them to calculate enthalpy change for the reactions they are involved in.

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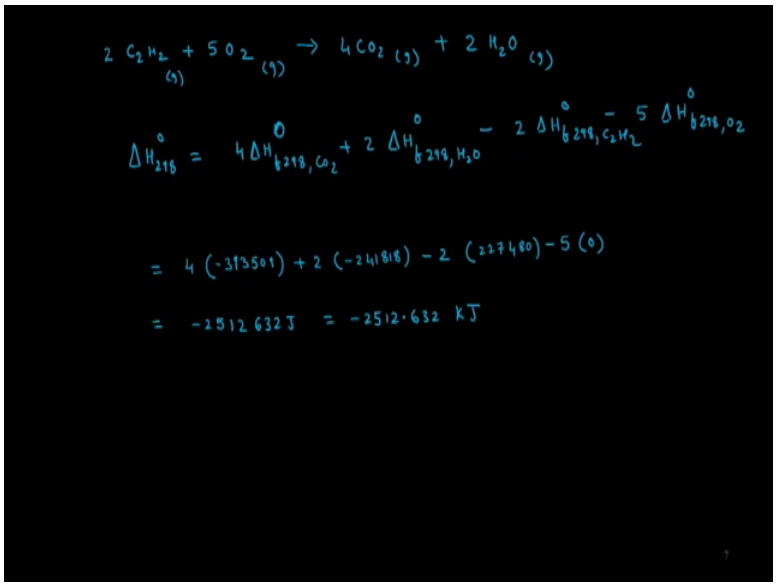

What we mean by that is this. Let us say I have a reaction for acetylene with oxygen both of them are in the gaseous form, reacting to give carbon dioxide in the gaseous form plus water, right. If I have this particular reaction the enthalpy change due to this reaction in its standard state is going to be simply 4 times the heat of formation for CO 2 in its standard state plus 2 times the heat of formation for water.

Obviously, all of these are in gaseous form minus 2 times the heat of formation for acetylene minus 5 times the heat of formation for oxygen. All of these are standard heats at 298 Kelvin. And if I multiply them with the appropriate stoichiometric number and add them that will give me the standard heat of the reaction at the same temperature which is 298 Kelvin in this case.

This will work out because once we write all the formation reactions and add them by weighting them suitably with stoichiometric numbers then we will end up with the particular reaction we are looking at. In this case I can go back to any handbook and look at heats of formation for each of these 4 species and use those numbers to get the enthalpy of this particular reaction. The heat of formation 4 CO 2 is negative 393509 Kelvin plus the heat of formation for water is negative 241818 Kelvin.

Remember this is heat of formation for water in the gaseous form minus 2 times heat of formation for acetylene which is 227480 that is positive quantity minus 5 times the heat of formation for oxygen because it is already in its elemental form heat of formation will

be 0 for oxygen. Once we have that simplify the numericals it turns out to be negative 2512632 Joules or that is negative 2512.632 kilojoules, right. That is the enthalpy of the particular reaction we are looking at which we calculated directly using the heats of formation. So, enthalpy of each and every reaction at its standard state need not be listed, all we need is data for heat of formation of each of the species involved in that particular reaction. Once we have that we can readily calculate heat of the standard heat of that particular reaction, right.

Now, again this is only a standard heat of reaction. What if the reactants and the products are at different temperatures, how do we handle that particular scenario? Let us take an example again. We will hold on to this value which we will use.

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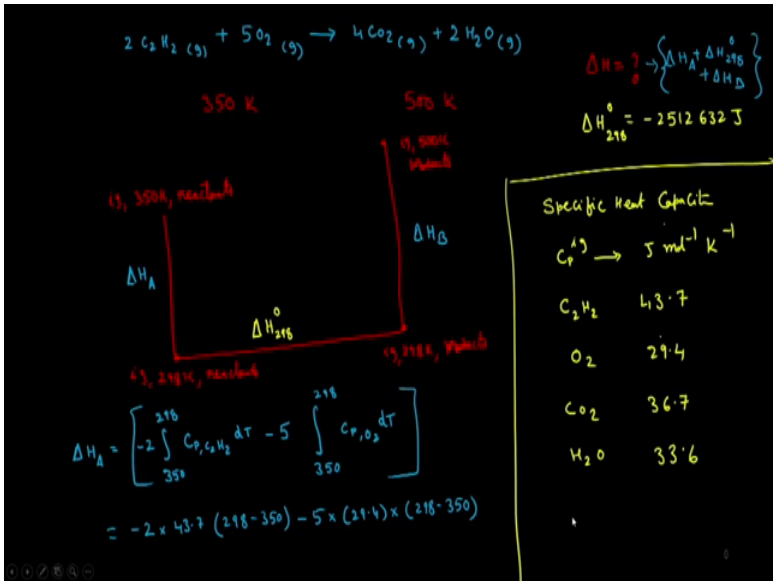

Let us say I have this particular reaction we looked at just now, which is 2 C 2 H 2 in the gaseous form plus 5 O 2 giving 4 CO 2 plus 2 H 2 O. If I have this reaction and if the reactants are entering the reactor at 350 Kelvin, and the products are leaving at let us say 500 Kelvin and we are interested in finding delta H for this particular reaction when the reactants enter at 350 Kelvin and the products leave at 500 Kelvin. How do we do that?

What we do know from our previous experience is that I can calculate this standard heat of reaction at 298 Kelvin which we just did. Let us write that number done. Delta H 298 is negative 2512632 Joules. This I know if the reactants enter at 298 Kelvin and the products leave at 298 Kelvin, I know the enthalpy change due to the reaction. But what if

they enter at 350 and leave at 500 what would be the enthalpy change due to that particular reaction?

To do that what we do is since enthalpy is a state function, we formulate an alternate convenient path to calculate the enthalpy change. By that what we mean is that let us say all of this is ideal gas for now. Let us say I have an ideal gas 350 Kelvin and I have the reactants, what we will do is we will take them to the ideal gas state at 298 Kelvin still as reactants, then we will convert them into products at 298 Kelvin. And then we will take these products back to the desired temperature in this case 500 Kelvin as an ideal gas 500 Kelvin and products, alright.

Now, if you notice I already know this value this is the heat of the reaction at 298 Kelvin, standard heat of reaction at 298 Kelvin because the reactants are at 298 and they are going to products at 298. So, I have that information. What I need is to be able to take the reactants in their ideal gas state two reactants at 298 Kelvin and products from 298 Kelvin to the products in their ideal gas state at 500 Kelvin.

So, let us call this particular quantity as delta H A and this quantity as delta H B, right. In that scenario this delta H, I am looking at here will simply be delta H A plus delta H 298 plus delta H B. If I add these 3 enthalpy changes or the enthalpy changes for these 3 steps then I will end up with the enthalpy I am interested in which is reactants entering at 350 and products leaving at 500. I have the heat of reaction at 298 I need to calculate the other two. How do I calculate delta H A? It is pretty straightforward if I have the information on the specific heat capacities of the reactants and the products.

Let us write some numbers here. Let us say the specific heat capacity data is given. So, the specific heat capacity data is given to us in the ideal gas state for C 2 H 2 O 2 CO 2 and H 2 O and let us say the units given to us are in Joules per mole per Kelvin. Then the values are going to be 43.7 for C 2 H 2, 29.4 for oxygen, for CO 2 is 36.7 and for water is 33.6.

So, the C p ig values are given. Now, recall that cpi g is a function of temperature. For sake of simplicity we have just assumed that it is constant with temperature, but if it is dependent on temperature then we will have to do an integration to get the enthalpy change. For now, let us say they are just constant with temperature so that it makes the calculation a little easier, but otherwise the method involved does not changed.

Now, for delta H A, right it is the reactance 2 moles of C 2 H 2 and 5 moles of O 2 going from 350 to 298 Kelvin, right. It is 2 moles of C 2 H 2 going from 350 to 298 Kelvin C p 4 C 2 H 2 dT plus 5 moles of O 2 going from 350 to 298 C p for oxygen dT and this will get a negative sign because this stoichiometric number is negative for the reactants. So, I am going to put a negative sign instead of 2 I will write it as minus 2 and minus 5 for both of these reactants. Once I do that, I simplify it will be negative 2 times since C p is constant it will be 43.7 times 298 minus 350 minus 5 times the value for a C p of oxygen is 29.4 times 298 minus 350 that is delta H A.

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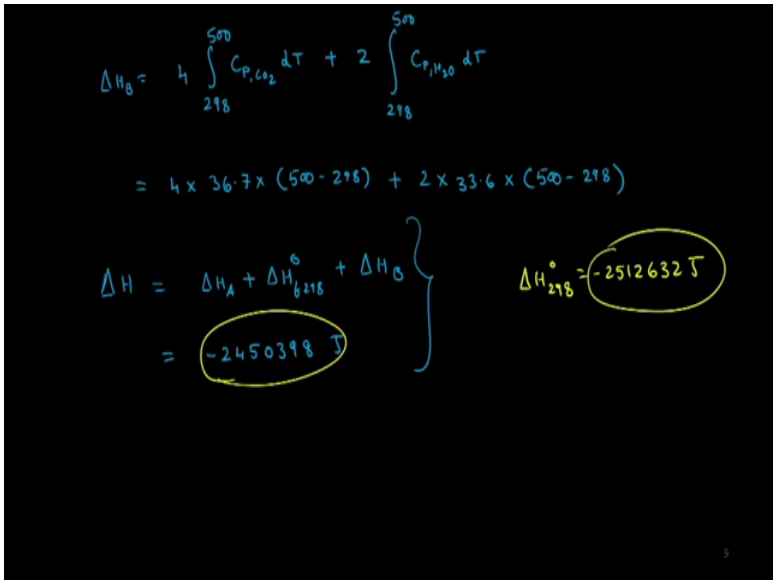

Now, similarly I can write delta H B. It will be the stoichiometric number for the products, right which is 4 times integral of 298 to 500, that is the temperature change for the products, C p 4 CO 2 dT plus the stoichiometric number for water which is two times the integral of 298 to 500 C p for water dT. And if I simplify this integral cp for CO 2 is constant it is 36.7 times 500 minus 298 plus 2 times 33.6 is the C p for water times 500 minus 298. This is the value for delta H B. Now, if I am interested in delta H for the whole process then it is going to be delta H A plus delta H f standard 298 and delta H B. If I add all these values it will be negative 2450398 Joules.

So, this is the change in enthalpy if the reactants are entering at 350 Kelvin and the products leave the reactor at 500 Kelvin. So, all that I needed to calculate this a heat of the reaction is simply the standard heat of the reaction at 298 Kelvin and then the

specific heat capacities I can go ahead and calculate the change in enthalpy due to the reaction at different conditions, right.

Now, notice that if this reaction were occurring at 298 then the change in enthalpy was negative 2512632 Joules. So, that is the difference we are looking at if the temperatures of the reactants and products are different. It is still because the particular reaction is highly exothermic, majority of the contribution for delta H still comes from the reaction, but then the difference in the temperatures manifests itself into delta H in this scenario.

So, with that we looked at calculation of enthalpy changes upon reaction occurring at different conditions. Similar to enthalpy changes one can calculate changes in Gibbs free energy, given the Gibbs free energy of formation at its standard state, one can calculate the change in Gibbs free energy at different conditions from the Gibbs free energy of formation data, just like we have done the calculation for enthalpy changes. When we come back in the next class, we are going to look at how we can use this information of property changes upon reaction to characterize chemical reaction equilibrium.

Thank you.