Introduction to Chemical Thermodynamics and Kinetics

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Lecture – 10
First law – part 5

Now, in many chemical reactions heat is either absorbed or heat is either released. So, based on that we can divide the chemical reactions into 2 categories and most of the cases this heat transferred is done at constant pressure.

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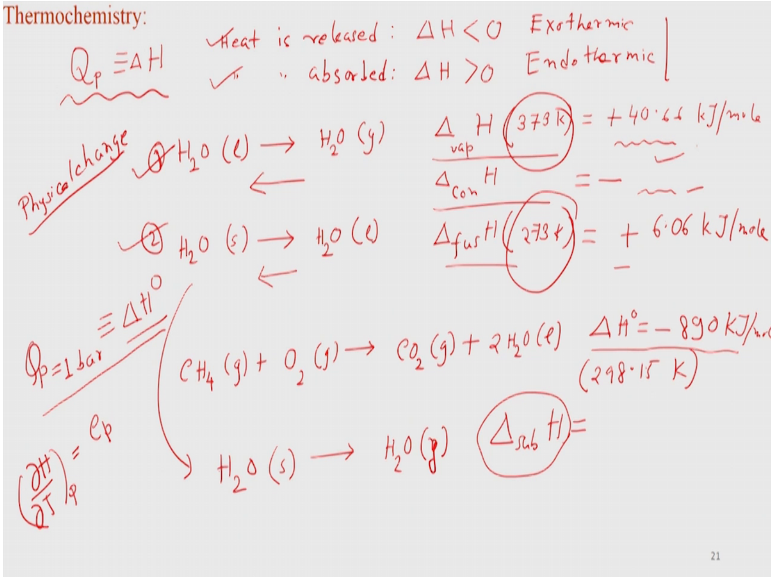

Thermochemistry:

$Q_p \equiv \Delta H$

✓ Heat is released : $\Delta H < 0$ Exothermic

✓ " absorbed: $\Delta H > 0$ Endothermic

Physical change

① $H_2O(l) \rightarrow H_2O(g)$ $\Delta_{vap}H\,(373\,K) = +40.66$ kJ/mole

$\leftarrow$ $\Delta_{con}H = -$

② $H_2O(s) \rightarrow H_2O(l)$ $\Delta_{fus}H\,(273\,K) = +6.06$ kJ/mole

$\leftarrow$ $-$

$Q_{p=1\,bar} \equiv \Delta H^0$

$CH_4(g) + O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H^0 = -890$ kJ/mol $(298.15\,K)$

$H_2O(s) \rightarrow H_2O(g)$ $\Delta_{sub}H =$

$\left(\frac{\partial H}{\partial T}\right)_p = C_p$

So, then the quantity we have to look at is nothing, but the change in enthalpy for that process. Now if heat is released in the environment say heat is released, then delta H should be negative because by convention we took that heat absorbed by the system or when heat transferred from the surrounding to the system is positive.

So, this should be negative and if heat is absorbed by the system then we take delta H to be positive the reactions where heat is generated overall heat is generated is called as Exothermic reaction and the reaction where the heat is absorbed is called Endothermic reaction. Now this exothermic or endothermic based on their classification we can actually study the chemical reaction or the heat change associated with the chemical reactions.

Now, let us take an example now when a physical change is happening by physical change we mean that you know chemical reaction is happening for example, say boiling of water or freezing of water into ice something like that. So, suppose water is liquid water is getting evaporated to water vapor which is gas or vapor and the associated enthalpy change will write it as delta vaporization we never write 8 suffix vaporization it is vaporization is a process or vaporization is denoting the way that change was happened.

So, we keep a suffix after delta. So, delta vaporization age that at some temperature which is 373 kelvin which is at 100 degree centigrade is plus 40.66 kilo joule per mole usually we will use the kilo joule per mole unit here. So, it is plus in the sense that the reaction is endothermic. So, heat is absorbed by the system. So, it is obvious that you have to supply heat in order to boil the water which means when water condenses if we had considered the reverse process the delta condensation of water convinced recession of water or the delta condensation of the enthalpy change will be nothing, but the negative of the same number 40.66 kilo joule per mole.

Now, this means actually there is a reversibility already established here and it makes sense because we are just considering the changes of phase or at that temperature where basically the phase change is happening and also keeping the pressure constant. So, similarly you could write that water when liquid water is freezing into say ice or say the ice is actually melting into liquid water so, that melting process we usually call it as fusion that fusion now the temperature is 0 degree centigrade that is also positive because heat is absorbed and then ice melts and that value is 6.06 kilo joule per mole.

So, what we see here is that the fusion process similarly you could also ask the freezing process which is the opposite of that and then it will be just minus. So, the reaction will be endothermic. So, when water freezes into ice some heat is released similarly when water vapor condenses into liquid water some heat is released. So, the reaction is exothermic, always these kind of changes are at equilibrium because we are keeping the pressure constant otherwise we cannot write it in terms of the enthalpy.

Because enthalpy is heat change at constant pressure and always also the temperature also kept same because we are only considering the heat change keeping the temperature constant which means these processes we are discussing are reversible in nature now you can actually this constant pressure you could actually make this constant pressure as the standard pressure which is one bar. So, in that case the associated enthalpy change you could write it as a standard enthalpy change.

Now, for example, you can ask this question of this combustion of methane for methane gas reacts with oxygen which is also in gas to form carbon dioxide which is gas plus water, but the water actually forms as a liquid and that H 0 delta H 0 for this process is nothing, but minus 890 kilo joule per mole and this is also done at a particular temperature remember and this is perhaps taken at 298 degree centigrade 298 Kelvin which is 25 degree centigrade or to be more precise it is probably 298.15 Kelvin.

Now this is the delta H 0 of this reaction which means actually this delta H 0 corresponds to the heat change when the pressure was kept constant at one bar pressure now keeping on this discussion you can think that whether where is the heat change there is a reversibility we are assuming and you can think that we could write associated heat change for this process say for example, when the ice is going into water paper, this is known as the sublimation.

Now this sublimation the question is can we actually write the sublimation as a subtraction of these 2 processes which is basically it is going from solid to gas. So, we could actually add these 2 processes which is the vaporization and fusion. So, basically it is it fuses first and then it vaporizes. So, we are asking this question right now if the ice could directly could sublime into a pepper that will not happen at constant at normal temperature and pressure which is one atmosphere and 25 degree centigrade safe, but that may happen we can make that happen, when the pressure and temperature I mean are adjusted in such a way that water can directly is sublime into ice, ice can directly sublime into water vapor and that we will discuss when we discuss phase diagram for water.

But this is possible and since these are all energy terms delta H is also additive because you remember that delta H is a state function and it only depends on the final and the initial states. So, here the final state was water vapor and the initial state was liquid, here the final state is liquid and initial state is solid. So, you can just argue that if this thing happens the sublimation then we can also write that this will be nothing, but the differences between the delta H vaporization not difference it is addition plus delta H fusion, but there is a caveat here the balance which we are writing here at 2 different temperatures.

So, delta H is of course, will vary with temperature because you already calculated that these if we change the temperature keeping the pressure now constant that is nothing, but equal to C p because that is the heat change at constant pressure. So, we have to also calculate take into account the value of C p for example, if you are doing it at say 273 degree centigrade you make a fusion of the ice and then you have to raise it to 373 degree centigrade.

So, you have to warm the water over a range of 100 degree centigrade and which means you have to now take all the C p d T values which are at different temperatures and then you can calculate the heating of water how much heat is involved and then at 373 degree centigrade you can actually do this process. So, this will be the entire change from going from solid ice to water vapor, but right now we are not considering that we are asking this question if we happen to have a situation like the ice is directly going into vapor then what will happen, but then we can actually use this equation which is basically vaporization plus the fusion of that process.

But keeping in mind all of them has to be at some same temperature at and not normal pressure which is one atmosphere this would not happen because the ice directly does not go into the vapor you have to go to the liquid phase you have to heat up the liquid and then you have to do the fusion. So, there will be some additional hitting thing which is nothing, but integral of C p d T going from say 273 degree centigrade to 373 degree centigrade, but when you consider the sublimation if you have the values of delta H vaporization and delta H fusion at that pressure and at that temperature then only you can make an addition.

Now this concept which we are building tells us that if I have a particular process and if I can divide the process into many other process then we can probably add all of them together to get a overall value of this process something like we just said that can we actually calculate the sublimation of delta H sublimation for ice going into the water vapor and similar way we can also think of it the and we answered that the pressure and temperature has to be constant only then we can measure it.

So, there is a law that is associated with this and the law is known as Hess's law and which states that the standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions in which into which the reactions may be divided.

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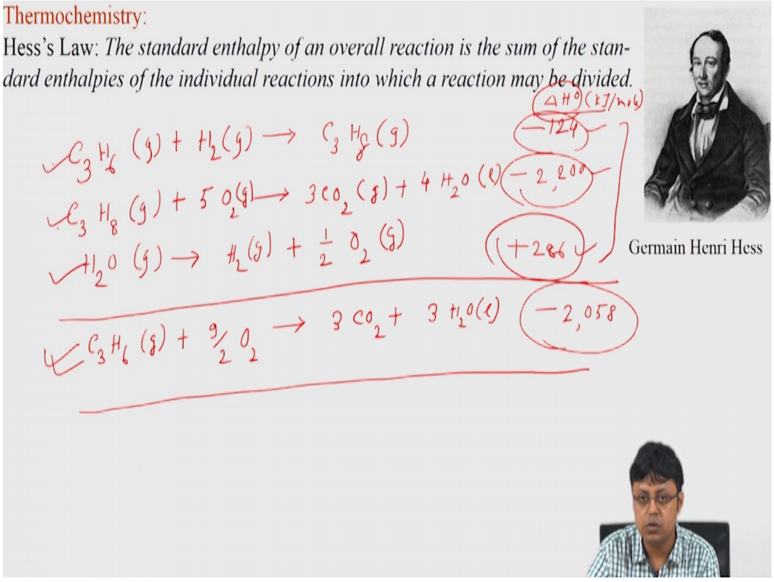

Thermochemistry:

Hess's Law: *The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.*

$\Delta H^0 (kJ/mol)$

$C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g)$ -124

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ $-2,200$

$H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ $+286$

$C_3H_6(g) + \frac{9}{2}O_2 \rightarrow 3CO_2 + 3H_2O(l)$ $-2,058$

Germain Henri Hess

Now let us take an example let us say we have this hydrocarbon which is propylene and then we are reducing it to make propane C 3 H 8 which is also a gas and then we are considering another reaction where say C 3 H 8 gas plus 5 O2 is going into it is basically combustion reaction.

And that is giving hydrocarbon combustion will always give you the values which are you always get carbon dioxide if it is a complete combustion will always get carbon dioxide and water if it is incomplete combustion you might get carbon monoxide and then we have water and H 2 giving half, this is this would be water plus water going into H 2 plus half O 2.

So, we have the thermo chemical data which says it will be minus. So, these are all delta H 0 of the respective reaction and these are all reported in kilo joule per mole. So, first reaction is minus 124, the second one is minus 2200 you can see that it is heat is released in this 2 reaction because we are doing a combustion here and this is also hydrogenation which this double bond going into the alkyne. So, it is a heat is released and then we have for this reaction it is an endothermic reaction it has to be supplied to the system.

Now, if we just add all of them you can actually get a very interesting equation which is C 3 H 6 in gas phase and there is 9 by 2 O 2 that is going into carbon dioxide and 3 water molecule liquid you can also measure it or you can if you know all these other reactions you could also just add the standard enthalpies for those reactions and could calculate it because it just follows because energy is additive, but the conditions have been kept same because these are all delta H 0 in the sense that the pressure was kept constant.

In the sense that the all these reactions were done at one atmosphere one bar pressure and then only you can write a big equation for which you probably could not carry out, but you know that there are other reactions and this reaction which you want to study can be decomposed into these all other reactions for which this delta H 0 s are known they you can calculate the delta H 0 for the unknown reaction and that is known as Hess's law.

Now in a similar way we can also think about the standard enthalpy of formation.

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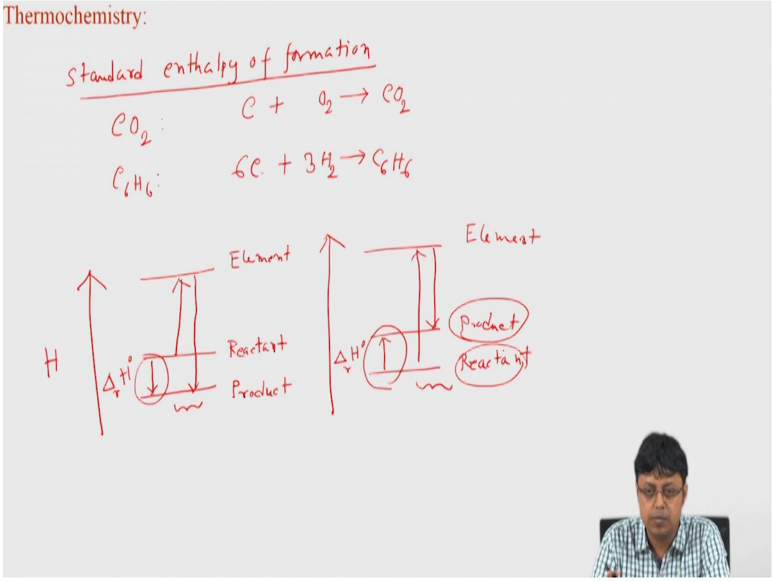

Thermochemistry:

Standard enthalpy of formation

CO_2: $C + O_2 \rightarrow CO_2$

C_6H_6: $6C + 3H_2 \rightarrow C_6H_6$

So; that means, suppose we have carbon dioxide now we are asking what is the energy associated with if we had made carbon dioxide from it is constituent elements meaning if we just do this reaction if we break everything apart and if we do this reaction what will be the standard enthalpy associated with this or say for example, if we talk about benzene, the question is if we had done this reaction, can you calculate the standard enthalpy of formation.

Now this conceptually is very interesting suppose we have some reactant and some product and in this case the way I have drawn it is that this is basically the their relative enthalpy and the product is lower in energy which means when the reactant goes into the product. So, the reactant has a higher enthalpy than the product which means the heat will be released in this case and we are making a reaction like this and this is the standard enthalpy say for the reaction that is why I am writing a delta suffix r.

Similarly, you could also think that the product is energy content wise higher and the reactant is energy content wise lower, which means you have to supply energy to go from reactant to product that is also fine. Now you could think instead of going directly from reactant to product we could first break the reactant into it is elements and that; obviously, will be a energy consuming process because you have to break some bonds and then suppose all these elements you are again putting together to form now the product.

And you can easily see these 2 arrows if you just add since one is upward and one is a downward arrow, the difference will always be equivalent to this arrow. It is just addition of energies or the conservation of energies similarly if the product lies above we could also ask the same question if we actually can calculate the delta H of formation of that particular reactant and the product and then you could if we could take the difference of them then we could actually calculate the delta H for the reaction. So, you can actually if you know the standard enthalpy of formation which means actually a formation of the reactant and the product this will be reactant.

If we know the reactant and the products standard enthalpy of formation then you can actually calculate what is the standard enthalpy associated going from the reactant to the product. So, that actually immediately follows from Hess's law you can easily figure that out and we will have will give you some examples or as well as some numerical problems or it will be asked to calculate these standard enthalpies of formation or and use that to calculate the standard enthalpies associated with some reaction involving reactants and products whose standard enthalpy of formation will be provided.

Thank you.