Concepts of Chemistry for Engineering
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Lecture 52
Enthalpy, Hess's Law

Hello, welcome back to the next segment of Thermodynamic Discussion. So, far we have discussed the important thermodynamic properties, work, energy and heat, and how they are connected to each other with the first law of thermodynamics. So, in the next part, we will discuss one important parameter enthalpy, let us take a look into that.

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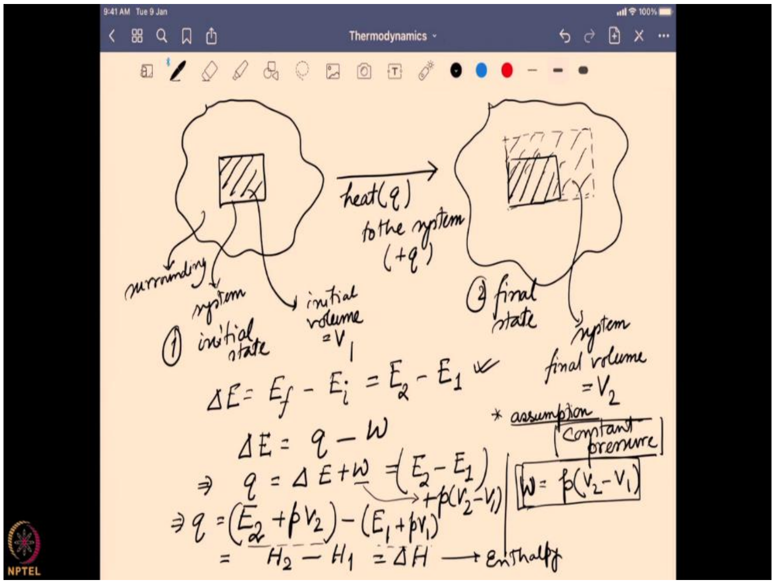

$$\Delta E = E_f - E_i = E_2 - E_1$$

$$\Delta E = q - w$$

$$\Rightarrow q = \Delta E + w = (E_2 - E_1) + p(V_2 - V_1)$$

$$\boxed{w = p(V_2 - V_1)}$$

$$\Rightarrow q = (E_2 + pV_2) - (E_1 + pV_1)$$

$$= H_2 - H_1 = \Delta H \longrightarrow \text{enthalpy}$$

So, now say we have a particular surrounding and over there we have a system, where the system is expandable, say it is a gas. So, this system has an initial volume of V_1, then we are making some changes, in this full system where the initial system was this and now we are expanding the system, and now the system has increased its volume and we say it is the final volume after we completed that process is equal to V_2.

And in this process to make sure that this volume change happens, we have to give some heat to the system, and as we have discussed earlier, we will say that as +q because the heat is going inside the system. Now, what is the overall energy change when we go from the initial state to the final state? So, it is given by energy of the final (E_f) state minus energy of the initial state(E_i). This particular system we are actually trying to find out.

Now, over here, let us say I am writing this as E_2-E_1 where 1 is the initial state, whereas 2 is the final state. Now, over here with respect to first law of thermodynamics we can write it is q-w, we are writing as -w because the volume has increased and that increase has happened because the system itself is doing the work, and when system does the work, we put it a minus sign, so it is q-w.

Now, if I rewrite that as $q= \Delta E + w$, so it is just bringing the w from the right hand side to the left hand side and I am writing that again. Now, over here what is ΔE? It is nothing but E_2-E_1 as it is given over here. Now, what is the overall work done, so over here the work done is actually the increase of volume, and now say I am assuming is very critical assumption is that this process actually taken place at constant pressure.

So, if that process actually happened under constant pressure, then the work done can be given in the form of $p(V_2-V_1)$. So, the volume change that we did during that process into the pressure, with respect to that I can again rewrite $q = (E_2-E_1) + p(V_2-V_1)$. So, this is I am expanding that w. Now, over here the q becomes $(E_2+pV_2) – (E_1+pV_1)$. So, I am just putting all the things with subscript 2 at one side, all the things with subscript 1 into the other side.

So, with respect to that, I can say these parameters are giving me the idea what is happening in the final state and these parameters are giving me what is happening in the initial state. So, instead of writing (E_2+pV_2) or (E_1+pV_1). I can write a totally new parameter which actually come with both these things combined together and I write it as H, and writing H_2 to correspond with that two state our final state and this is H_1 or the initial state.

And this is I can write it is a change in this particular parameter H, and this H factor is known as the Enthalpy. Again coming back to this particular system, we have a system where it is surrounded by surrounding I am giving it to some heat and at constant pressure it is increasing the volume from V_1 to V_2, during that pressure, constant pressure when it is increasing the volume the overall work done is $p(V_2 – V_1)$.

And over there during this process, what is happening following the first law of thermodynamics the heat that is actually given to the system can be explained as a difference of a new factor a new property known as H, and this H is known as enthalpy which is mathematically written in the form of $E + pV$.

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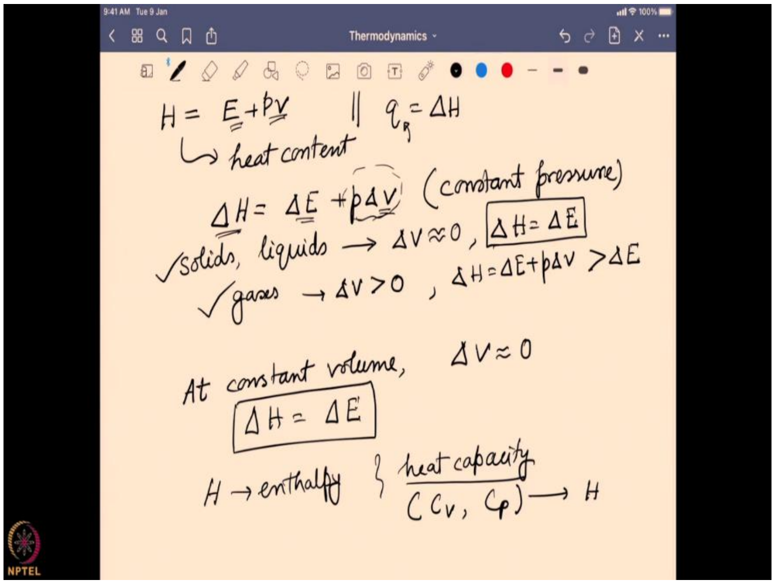

$H = \underline{\underline{E}} + p\underline{\underline{V}}$ || $q_p = \Delta H$

↳ heat content

$\underline{\underline{\Delta H}} = \underline{\underline{\Delta E}} + \underline{p\Delta V}$ (constant pressure)

✓solids, liquids → $\Delta V \approx 0$, $\boxed{\Delta H = \Delta E}$

✓gases → $\Delta V > 0$, $\Delta H = \Delta E + p\Delta V > \Delta E$

At constant volume, $\Delta V \approx 0$

$\boxed{\Delta H = \Delta E}$

$H \rightarrow$ enthalpy } $\frac{\text{heat capacity}}{(C_v, C_p)} \longrightarrow H$

So, when we discussed about enthalpy and I am saying H is equal to E + pV, what does this particularly mean and as we just say that q is nothing but ΔH we can say this enthalpy factor has something to do with the factor heat and that is why we can say H or enthalpy is nothing but the heat content of that particular system, because it is given by the heat parameter. And it is a combination of energy and work done of the volumetric work where it is getting expanded all together connected to this enthalpy.

So, now if we want to discuss furthermore, we can take a look that the ΔH is equal to nothing but ΔE + pΔV which is nothing but $E_2 – E_1$ and V_2-V_1, that you have done earlier and over there again the assumption still correct is that we have done that under a constant pressure. Now, was this particular parameter we got ΔE + pΔV we can say the change in enthalpy ΔH is nothing but change in energy plus the expansion work done over here.

Now, consider three different states, solids, liquids and gas, what happens over there? In the case of solids and liquids, we know the change in volume is pretty low, so over there ΔV almost close to 0, so in that scenario ΔH becomes ΔE, because this particular factor over there pΔV it actually goes to close to 0.

So, over there we can say in this case the enthalpy is nothing but a change in the energy of the system. So, that is giving us an idea what is happening inside the system during the process. So, enthalpy is a very intrinsic process intrinsic parameter for a particular system. Now, what happens for gases we know ΔV is greater than 0, so over there what will happen? ΔH will be equal to $\Delta E + p\Delta V$.

So, we can say at this case it will be greater than ΔE. So, in case of the gases some work can be done by the system that means a gaseous system and in that case the enthalpy change will be higher than the energy change. Whereas, in the solid it will be almost equal to the energy change. So, that is a big difference over there, when we are doing this system under constant pressure and we are doing that for different systems like solids or liquids or gases, so with respect to that we can connect enthalpy to the energy change, and the possible work can be done by that system itself.

Now, we go in other system when if we do the same system at a constant volume, so over there I am not changing the volume at all, so that means ΔV is equal 0. And in that case, ΔH is again going to become ΔE. So, in the case of a constant volume system, the enthalpy change will be equal to the energy change of the system no matter what whether it is a gas, liquid, or solid state.

So, that is a background of the enthalpy change, and the enthalpy change is directly connected to the overall energy change and we can connect it to the heat, so that is why H or enthalpy is nothing but connected to the heat content of the system. And this H or enthalpy can be used to figure it out what will be how much energy the system can take or give in the context of heat or heat capacity.

So, this particular heat capacity is directly connected to the enthalpy factor, and this is beyond the scope of this particular module, but later you can find it out all this heat capacities we found C_v at constant volume or C_p at constant pressure, they can be connected to this enthalpy factor. And their actual derivation of their expression is directly connected to the enthalpy.

So, that is why another reason to think about the enthalpy has nothing but giving you an idea how much heat a system can actually hold or during a process how much heat it can get exchanged with the surrounding. So, that is why enthalpy becomes a very crucial factor. Now, we will go a little bit on some applications of that enthalpy factor.

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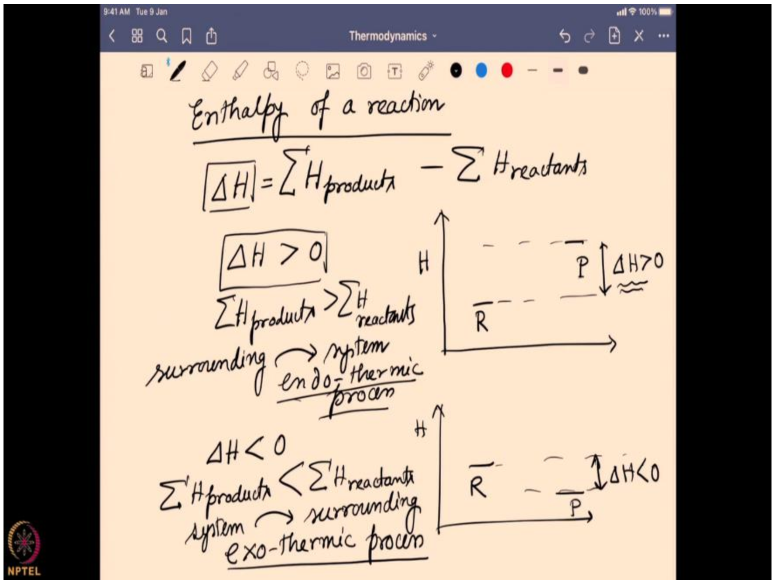

Enthalpy of a reaction

$\boxed{\Delta H} = \sum H_{products} - \sum H_{reactants}$

$\boxed{\Delta H > 0}$

$\sum H_{products} > \sum H_{reactants}$

surrounding → system

endo-thermic process

$\Delta H < 0$

$\sum H_{products} < \sum H_{reactants}$

system → surrounding

exo-thermic process

So, now when we talk about enthalpy, we talk about the enthalpy of a particular process, so let us say we are looking into enthalpy of a reaction, so how do I define an enthalpy of a reaction? So, enthalpy of a reaction is nothing but equal to enthalpy change during that reaction, and we can figure it out by adding all the enthalpy value of all the products we are forming, summing that up, minus all the enthalpy of the reactants.

And whatever the value we will get, that is going to be the enthalpy change for this particular reaction. Now, this is very important, because that is going to connect with the exothermic and endothermic reaction that we have discussed earlier. We have discussed earlier, that endothermic reaction is what where the energy is getting absorbed into the system following a process, for a exothermic process is where the energy is getting released, following that process.

So, over here we can easily find if our ΔH>0, that means the enthalpy of the product is higher than the reactant, how we can do that? So, that means if I draw in a scale where I am drawing enthalpy and in this *x* axis I am drawing where the reactants or the products are, if this is my reactant and I am saying ΔH>0 that means ΔH of products is greater than ΔH of the reactants.

And this can happen when the product enthalpy is higher, and then I can subtract the product enthalpy to the reactant enthalpy and I can say ΔH is greater than 0. For these things to happen, my enthalpy of the product should be higher, so I have to give this extra enthalpy to the system, and where it will be going to come from? That is going to come from the surrounding to the system, so that means system is actually nothing but absorbing energy.

So, is ΔH equal to 0 system represents a endothermic system or endothermic process. So, when a ΔH is greater than 0 that means product enthalpy is higher than the reactant that extra enthalpy going to the product has to be supplied from somewhere and it is actually coming from the surrounding. And this actually signifies there is energy absorption during that process or nothing but endothermic process.

So, this is for endothermic process and very similarly if we have a ΔH less than 0 that means summation of my enthalpy of my product is actually lower than the summation of the enthalpy value of the reactants, that means over here if I want to draw there is my reactant, my product is actually now low, and that is why my ΔH will be less than 0.

And over there during this process what is happening my product is actually going down in enthalpy, so it is releasing some of the enthalpy what was there in the reactant. So, from the reactant to product some of the enthalpy is lost and this enthalpy goes from the system to the surrounding that is the excess energy released, so that is why this is nothing but an exothermic process.

So, previously we have discussed what is endothermic and exothermic process, now we have a parameter that we can easily measure or easily quantify that can give me an idea whether I am having an endothermic process or an exothermic process. And it is happening with respect to enthalpy, the enthalpy change we are going to measure which is nothing but enthalpy of the products minus enthalpy of the reactants and if this value is actually greater than 0, then this is endothermic process, if it is less than 0 it is exothermic process.

So, do I need to remember it or we just need to remember the logic? The logic is products minus reactant, if the product is higher that means it needs extra enthalpy, so it is going to absorb some energy from the surrounding, endothermic process. And if my product is lower than the energy of the reactants, so it is actually getting stabilized and releasing some energy that energy is going to be released it is exothermic process. So, that is why enthalpy we can use in the form and over there we can find out whether it is endothermic or exothermic process. So, some example of endothermic and exothermic processes are as following.

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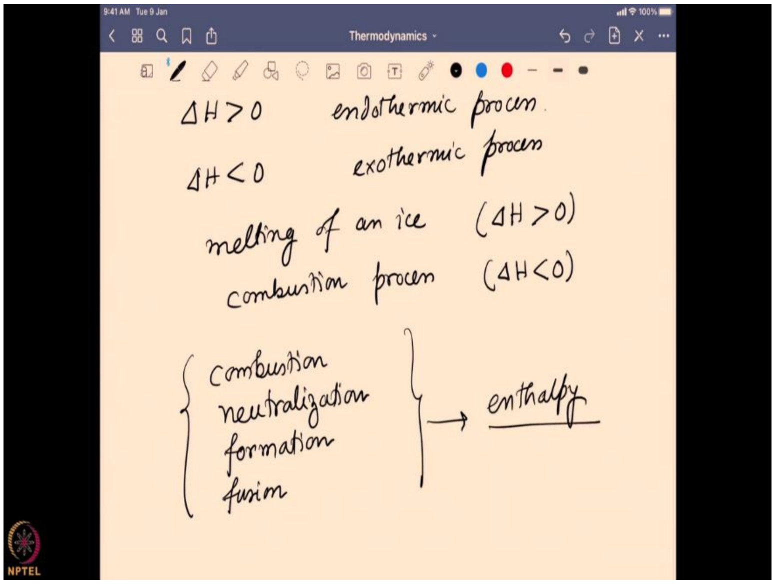

$\Delta H > 0$ endothermic process.

$\Delta H < 0$ exothermic process

melting of an ice $(\Delta H > 0)$

combustion process $(\Delta H < 0)$

$$\left\{\begin{array}{l}\text{combustion}\\ \text{neutralization}\\ \text{formation}\\ \text{fusion}\end{array}\right\} \rightarrow \underline{\text{enthalpy}}$$

So, as we just said ΔH greater than 0, it is an endothermic process and also ΔH less than 0 it is an exothermic process. So, over here for an example, if we look into the melting of an ice, this has a ΔH value greater than 0, so it is an endothermic process, so some energy has to be absorbed in that system.

Similarly, when we are looking into a combustion process, in that case the delta H is actually less than 0, so it is generally an exothermic process. So, in that way for different systems, for different processes physical or chemical processes, we can find out what is the overall energy change and that we can directly connect it with respect to the enthalpy.

And that is why we can find for different processes combustion, we can find neutralization when an acid base reaction is happening over there, there is a change of the enthalpy with respect to the initial acid and base and when the formation of the water and the salt happens. So, over there some of the enthalpy change can give you an idea whether it is a very favorable process or not.

Similarly, formation of different compounds from its original constituents' elements that you can also find out with respect to enthalpy, and also fusion or melting processes, for all these systems we can find a particular enthalpy change. And that enthalpy change give us an idea whether or not the products are forming with respect to enthalpy it is higher or lower than the enthalpy of the reactant systems.

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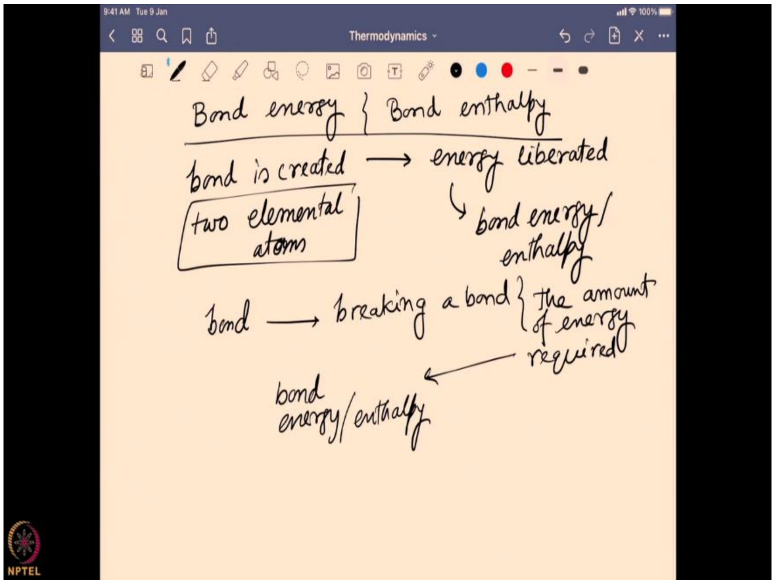

Bond energy { Bond enthalpy

bond is created → energy liberated

two elemental atoms

↳ bond energy/enthalpy

bond → breaking a bond { the amount of energy required

bond energy/enthalpy

Now, this enthalpy change is very critical because it can give us a very good idea with respect to a very important parameter as we know is known as bond energy or in thermodynamic term we can say it is a bond enthalpy. So, what is a bond energy or bond enthalpy, so when we are actually creating a bond, so when a bond is created and the amount of energy liberates during the bond formation and during that we are considering that the bond is forming from the two elemental atoms, so from its elemental form when it is forming during that the energy liberated is nothing but the bond energy or bond enthalpy.

So, it is nothing but we are measuring the bond enthalpy or the overall enthalpy of the system of the product and the reactant, reactants are of the two elemental atoms and product are the product we are forming. So, one example we are combining carbon and oxygen and producing carbon dioxide, so you are going to measure the enthalpy of the carbon dioxide as a product and subtract the enthalpy of the initial reactants that means the carbon and oxygen together and finding out what is the overall enthalpy change, so that is going to give me the bond energy or bond enthalpy of each of the carbon oxygen bonds.

Over there another example of this bond energy can be given in a way that considering the other direction, the bond is already there, now I am breaking the bond, I am breaking a bond and the amount of energies required to break that bond it is nothing but the bond energy or bond enthalpy.

So, we are looking this system in two different ways, either I have the elements and making the bonds, so how much energy is liberated that is the bond enthalpy, and sometimes we have the bond and we are breaking that down and going to the elements, and the energy released it is known as the bond enthalpy or bond energy.

So, we can explain that in either of the direction. So, that is known as the bond energy or bond enthalpy. So, all the bond energy we are actually use all the times in chemistry, physics and all the different requirements, when we are actually using a chemical process, all this bond energy is nothing but a manifestation how the bond enthalpies actually been measured. So, bond energy is nothing but a direct representation of bond enthalpy change during the process of the bond formation. Now, we go back to a very important term and how it is very much connected.

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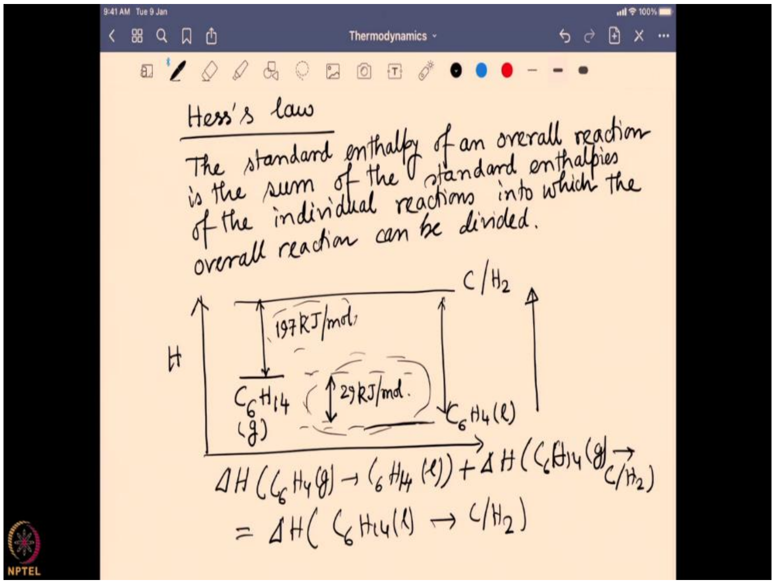

Hess's law

The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which the overall reaction can be divided.

$$\Delta H(C_6H_4(g) \rightarrow C_6H_4(l)) + \Delta H(C_6H_{14}(g) \rightarrow C/H_2)$$
$$= \Delta H(C_6H_{14}(l) \rightarrow C/H_2)$$

So, it is found by a scientist named Hess and he named this law as Hess's law, and I am going to write this and let you guys understand how we can actually follow this bond enthalpy to find out bond energies or the chemical energies or the enthalpy change for a particular process. So, it is given as the standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which the overall reaction can be divided.

So, that is a very important law and that is very important in the terms of measuring the enthalpy, because sometimes we find that we are doing a particular reaction and we are starting from A and B and going to C, and I am want to find out what is overall enthalpy change for this process. But sometimes it is very tricky, and what we can connect it and expand it further the formation of A, formation of B and their enthalpies and all those enthalpies can be connected together, to give you an example, let us take an example of the enthalpy change of C_6H_{14} which is a hexane.

And this hexane is in the gaseous form. And in this gaseous form if I want to go to its original elements, carbon and hydrogen, the enthalpy change is 197 kilojoule per mole that is a unit kilojoule is the energy unit and per mole is giving like per mole of compounds, so we know exactly how much compound we are talking about.

So, it is the hexane, we are actually breaking down to its original form of carbon hydrogen and 197 kilojoule is the difference between them. Now, we know if I go from the liquid state of the hexane to the gaseous state, their energy difference is 29 kilojoule per mole. So, from the gaseous hexane to the liquid hexane, it is 29 kilojoules per mole and liquid hexane has lower enthalpy than the gaseous one.

Now, if I want to find, what is the enthalpy for changing the liquid directly to the original carbon and hydrogen how we can do. So, you can just take a look into this figure and find it out the enthalpy change for the C_6H_{14} gaseous to C_6H_{14} or the Hexane liquid that means for this particular process, plus the enthalpy of the gaseous hexane to its original form, if we add them up together, it is nothing but the enthalpy change for the liquid hexane to its elemental form change.

And over here you can see this is nothing but we can actually put these things up together and find out what will be the overall enthalpy change. So, you have to just add it up and you can find out what will be the enthalpy change for the liquid to the original elemental form. So, that is why Hess's law gives us a very good tool to connect all the enthalpies connected in a particular reaction.

So, in the later stages, we will do some problems where we will use this Hess's law to find out the enthalpy changes of a particular reaction and connect it to the standard reaction that enthalpies are already known and we can connect them all together and find out the enthalpy change for the full particular process.

So, in this particular segment, so far, we have find out what is the connection between the enthalpy with the energy, heat and the work, and we find out enthalpy is nothing but can be shown as an expression of $E+pV$, so it is actually nothing but a heat content of the system it is connected to the heat capacities, and enthalpy of the system is a very important but because this is actually giving us an idea of whether it is an endothermic or exothermic reaction.

For endothermic reaction, ΔH is greater than 0 that means the product enthalpy is higher than the reactant one. Whereas, for exothermic reaction, it is just the opposite ΔH is less than 0, and the enthalpy of my product is actually lower than the enthalpy of my reactants. And we can also use the bond enthalpy to find out the bond energies of different systems, and we can connect the bond enthalpies of different reactions with the standard reaction with the help of the Hess's law. So, that will be here for this particular segment. Thank you.