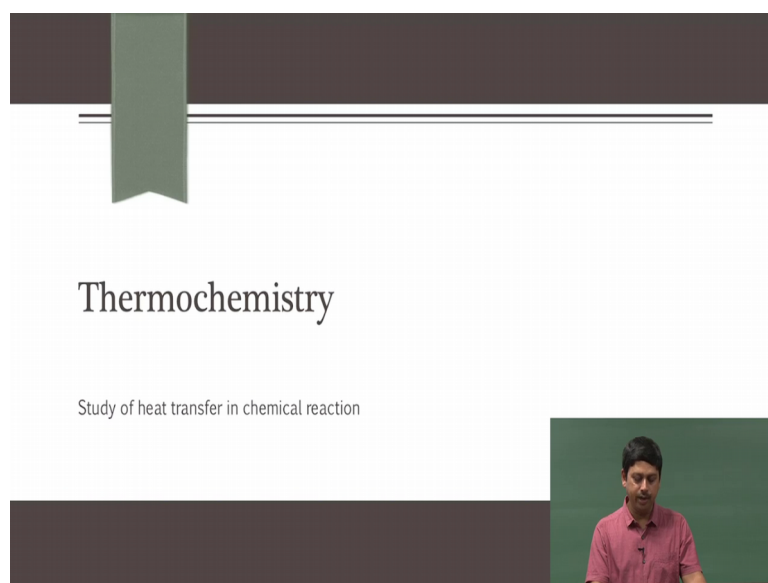


Chemical Principles II
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Module 04
Lecture 22
Thermochemistry Part – 01

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Okay, so welcome to this module of thermochemistry, so thermochemistry deals with the study of heat transfer in chemical reactions.

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Enthalpy Change and Standard State

- $\Delta H = q_p \rightarrow$ Heat measured at constant pressure is enthalpy



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Enthalpy Change and Standard State

- $\Delta H = q_p \rightarrow$ Heat measured at constant pressure is enthalpy
- Since one can measure only the **change** in enthalpy, we need to establish a **reference state** w.r.t. which we will measure the enthalpy for any change. The reference state of an element is its most stable state (**standard state**) at 1 bar at the specified temperature.
- **Standard state** of a system is its pure form at 1 bar pressure at a specified temperature.
- All calculations involve **standard enthalpy change** ΔH^\ominus , which by definition is the enthalpy difference of for a processes where initial and final substances are in their **standard state**.
- **Standard enthalpy of formation of an element, $\Delta_f H^\ominus$, in their reference state is 0 at all temperatures.** For example, reference state of nitrogen $N_2(g)$ not N. Therefore, formation of $N_2(g)$ from $N_2(g)$ is like a null reaction.

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Heat transfer at constant pressure is called a no change in enthalpy that we already know and we have already defined at earlier, so therefore, in order to calculate the change in enthalpy we need to calculate the process in constant pressure, temperature is not required to be like, temperature can be anything we can define any particular temperature for that, it is not important to be a particular value.

Now since it is an enthalpy change we have to talk about reference state with respect to which will calculate the change and that is called the reference state and typically when we calculate the change in enthalpy we calculate from something called standard states and then that gives us standard enthalpy and that at a 1 bar pressure and that we specify temperature.

So what is a standard state? Standard state of a system is its pure form at 1 bar pressure at a specified temperature, so for example nitrogen at 298 Kelvin at 1 bar pressure will be in gases form, carbon will at the same temperature at 1 bar pressure will be in graphite, in solid form, mercury will be in liquid form, water will be in liquid form, hydrogen will be in gas form, so those are you know standard states at 1 bar pressure at a you know specified temperature.

However, water will not be liquid at a very high temperature right, in that lets a 373 Calvin, 378 Kelvin let say, at 378 Kelvin at 1 bar pressure water will be in vapour form, so those thing we have to considered that what is most stable form at a specified temperature at 1 bar pressure and with respect to that we are going to calculate the change in enthalpy, which will give us the heat of formations, which will give us this, you know, enthalpy change and that is what thermochemistry is all about.

So all and when you calculate is enthalpy change we always use the standard states so that we get standard enthalpy change, so standard enthalpy change is denoted as Delta H with this particular sign, which by definition is the enthalpy difference for a process where initial and final substances are in their standard states.


So that automatically means that standard enthalpy of formation of an element in their reference state is 0 because there is a reference point from where we are starting, so nitrogen, formation of nitrogen gas at 1 bar pressure will be 0 because there is a reference state.

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Enthalpy Change and Standard State

The image contains two diagrams illustrating enthalpy change. The left diagram shows an exothermic reaction where the reactant level (R) is higher than the product level (P), with a downward arrow indicating heat release ($\Delta H < 0$). The right diagram shows an endothermic reaction where the reactant level (R) is lower than the product level (P), with an upward arrow indicating heat absorption ($\Delta H > 0$).

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So here we are, we already discussed about and exothermic and endothermic reactions, but here we are going to specify once more, so look at this particular profile, enthalpy profile Y axis will be enthalpy and X axis will be reaction coordinate and this particular process reactant is getting converted to product and the enthalpy is becoming lower, so in this process, the ΔH is negative, which means that, that same amount of heat is going to be released, so because the heat is getting released in this particular process we call that as exothermic reaction.

In this particular process again, this much amount of heat needs to be supplied for the reaction to happen, ΔH is positive and heat is going to be, you know take a in my the system is called endothermic reactions.

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Hi, welcome to chemistry Department of IISER, Pune we are right now in the 3rd floor of the chemistry wing, I am going to take you to one of the organic chemistry lab you can see the wonderful instruments at the used in order to carry out their research work, however we are going to use very simple instrument and simple experiment in order to demonstrate exothermic and endothermic reactions.

Okay, so in the class I have discussed about the exothermic and endothermic reactions, now we are going to demonstrate exothermic and endothermic processes this particular lab and you see this is a and organic chemistry lab and you can see there are a lot of equipments and other things are there, however we are not going to use such a complicated thing.

In order to demonstrate the exothermic reactions you going to use sodium hydroxide beads as you can see here, they are called pellets, sodium hydroxide pellets and normal water, so you know what happens in exothermic reaction that when two things mixed together, then it goes to a more stable state and releases heat, now you can understand the release of heat by measuring the temperature.

First what we are going to do is that, we are going to demonstrate you the experiment, so I first pour water in a beaker and measure the temperature, so as you can see the temperature of the water is 25°C currently, now I am going to drop some sodium hydroxide pellets in the water and you will see that the heat is going to be released because sodium hydroxide and water will form solutions of sodium hydroxide in water, I will drop all of them actually and they are going to react and they are going to go to more stable state and therefore they are going to release heat and that heat can measure by using temperature.

So I am going to start it now just to make the process a little bit faster, otherwise also it will dissolve after sometime, now you see it is almost becoming a saturated sodium hydroxide solution and I can see the temperature increasing a little bit, I will start a little bit more just to dissolve it and you can see the temperature is already become 41°C , so just tell you the temperature of this particular room is however you know normal 25°C or 24°C and that as we have demonstrated in Zeroth Law of thermodynamics that everywhere here touches the surface will have the similar temperature.

I can show you that as you can see it is 24.4° and let us measure the temperature of the wall, as you can see it is 23.9° and any surface that we can think of, for example I measure the temperature of the floor see 24.1° and now when I go back to the solution. Hopefully the temperature is increased even further, now the temperature is 38.4° , yes, so now says it is resolved now what is going to happen is that slowly the temperature will come down to the normal room temperature because the exothermic reaction, so the heat is released to the environment and thereby the initial temperature that is so or the initial heat that we saw by measuring the temperature is going to get lower and lower and the temperature is going to go to equilibrate to normal room temperature.

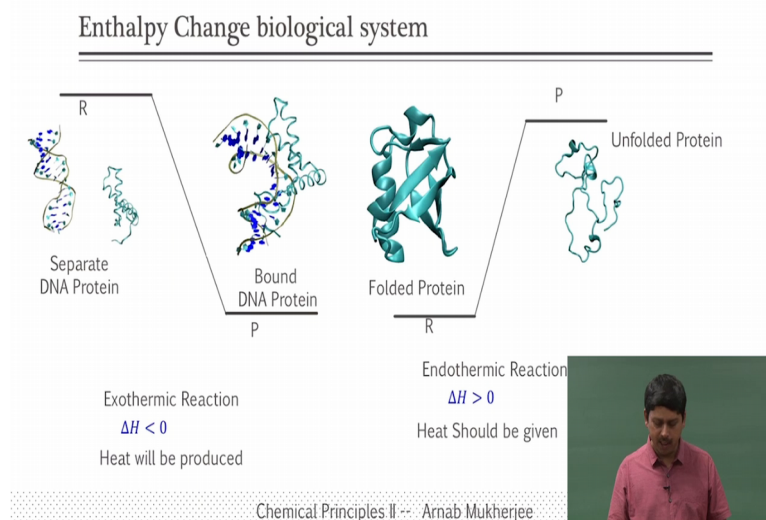
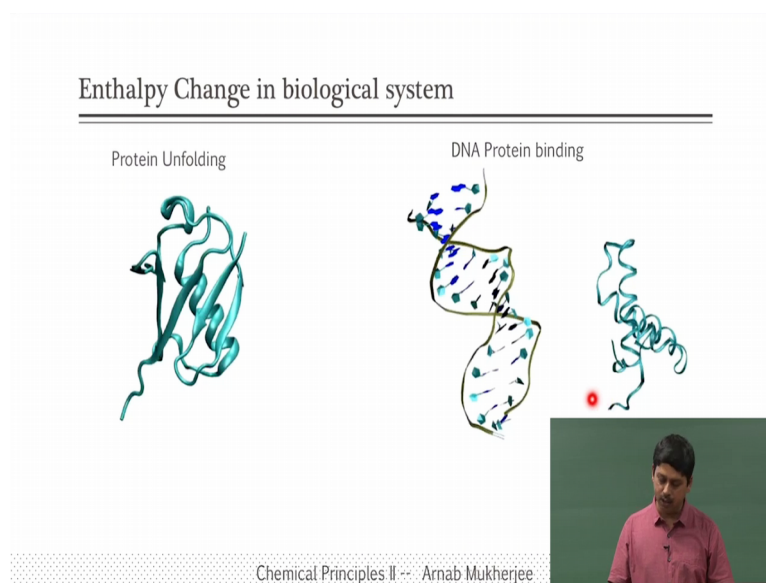
Now we are going to show an example of an endothermic reaction and for that what we are going to use is ammonium chloride as you can see here, we have taken already some ammonium chloride the piece of paper and this is just a plain water, remember last time when you put sodium hydroxide the temperature increased, now in this particular case, the

temperature should decrease, so we will measure the temperature first of the normal water and you can see the temperature is 23.3.

Now we are going to add ammonium chloride okay, I am going to put all of that and will start little bit, I can feel the temperature decreased already just to show you the temperature of ammonium chloride itself is actually 24°, however, when you do that for the water and you can see it has already come down to 12°, so when we dissolve little bit more the temperature will decrease further as you can see the temperature 10.9° and further studying temperature is still decreasing.

However, after sometime what will happen is at the temperature will equilibrate to the normal temperature of the room and it will come to the equilibrium with the surrounding but right now the beginning of this reaction as a reaction is progressing the temperature is getting down, and that is an example of an endothermic reaction.

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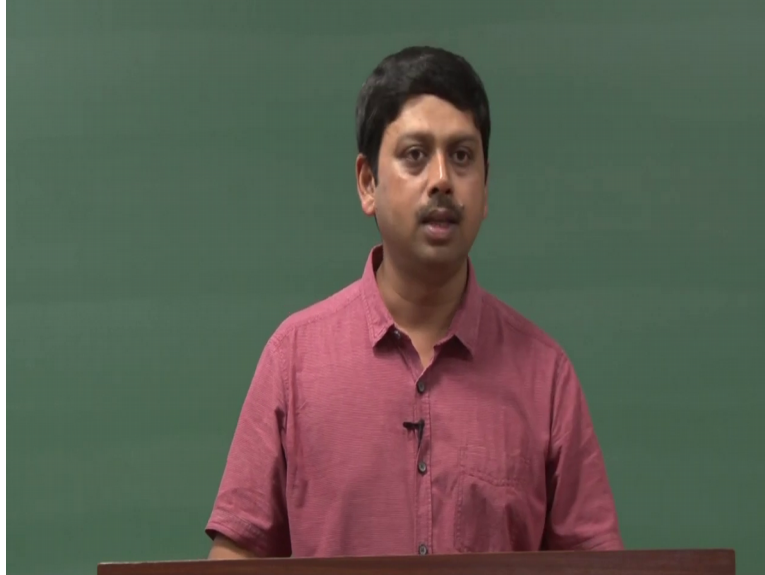


So in our body there are a lot of reaction always is happening and there are you know proteins and DNA which are biomolecules which carry out a lot of different functions, we are showing a particular structure of a protein which normally in the folded state is functional and in the un-folded state is not functional and this folding, unfolding process keep on happening in our body and those process is essentially involve a change in enthalpy.

Similarly proteins bind the DNA and carry out lot of functions and they are also the same thing will happen, so you are there is an example where we are showing that binding of a protein to the DNA, we are showing as an enthalpically favourable process. However, it did not be, we are just giving one example, similarly we are showing an unfolding of protein as an enthalpically you know forbidden process or not forbidden, but enthalpically you know

costly process ΔH is negative, positive which means we have to put that you know heat in to the system, it may or may not be the case, it is just a prototype example.

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So the point is to show that even for this kind of conformational changes there will be a change associated with you know with the enthalpy.

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Enthalpy Change biological system

Monomer Dimer

R P

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Different types of changes ΔH_{trs}

- Standard enthalpy of transition ($\Delta_{tr}H^\ominus$): Physical Changes such as vaporization, fusion, sublimation
- Standard enthalpy of formation ($\Delta_f H^\ominus$): Formation of CO_2 from carbon and oxygen $C(s) + O_2(g) \rightarrow CO_2(g)$
- Standard enthalpy of reaction ($\Delta_r H^\ominus$): Any chemical change where molecules react to form a different set of molecules: $\Delta_r H^\ominus = \sum_{products} \nu \Delta_f H^\ominus - \sum_{reactants} \nu \Delta_f H^\ominus$

such as for this reaction, $2A + B \rightarrow 3C + D$, $\Delta_r H^\ominus = \{3 * \Delta_f H^\ominus(C) + 1 * \Delta_f H^\ominus(D)\} - \{2 * \Delta_f H^\ominus(A) + 1 * \Delta_f H^\ominus(B)\}$

$$\Delta_r H^\ominus = \sum_j \nu_j \Delta_f H_j^\ominus$$

Transition	Process	Symbol
Transition	Phase $\alpha \rightarrow$ phase β	$\Delta_{tr}H$
Fusion	$s \rightarrow l$	$\Delta_{tr}H$
Vaporization	$l \rightarrow g$	$\Delta_{tr}H$
Sublimation	$s \rightarrow g$	$\Delta_{tr}H$
Mixing	Pure \rightarrow mixture	$\Delta_{tr}H$
Dilution	Solute \rightarrow solution	$\Delta_{tr}H$
Hydration	$X^+(g) \rightarrow X^+(aq)$	$\Delta_{tr}H$
Atomization	Species(α, l, g) \rightarrow atoms(g)	$\Delta_{tr}H$
Ionization	$X(g) \rightarrow X^+(g) + e^-(g)$	$\Delta_{tr}H$
Electron gain	$X(g) + e^-(g) \rightarrow X^-(g)$	$\Delta_{tr}H$
Reaction	Reactants \rightarrow products	$\Delta_r H$
Combustion	Compound(α, l, g) + $O_2(g) \rightarrow CO_2(g)$	$\Delta_r H$
Formation	Elements \rightarrow compound	$\Delta_f H$
Activation	Reactants \rightarrow activated complex	$\Delta^\ddagger H$

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Same is true for formation of a Dimer from Monomer and again it is shown as enthalpically favourable process, so in the macroscopic level, there are many different changes happen, one can categorise that those changes has enthalpy of transition and you see the transition is written as you know, Delta TRS H with that sign, so earlier notation was, it was Delta H TRS, but since we are talking about a particular type of change therefore the notation is, current notation is associated with delta itself, so physical changes can be of different types such as vaporisation, fusion, sublimation all those are physical changes where there is no such chemical reaction is happening, water is going from ice to water, there is no chemical reactions going is just that the phase is going changes from one form to another form, just like you know in confirmation, one confirmation is changing from one confirmation to the

another one, there are also an enthalpy as changes associated with that here also the same thing, enthalpy changes associated with that.

Second type would be an enthalpy of formation, denoted as $\Delta_f H$ formation of CO_2 from carbon and oxygen, so, carbon is in the solid state, oxygen will be in the gases state and forming as CO_2 in the gases state, this will be a reaction and this is basically, if you calculate this reaction enthalpy we are going to get heat of formation of CO_2 , so essentially, there is no difference between all the different forms but we have to only look at a process that is happening.

Standard enthalpy of reaction is when we calculate the total change in the enthalpy of formation of all the products minus enthalpy of formation of all the reactance multiplied by the stoichiometric ratios, for example, in this reaction $2\text{A} + \text{B} \rightarrow 3\text{C} + \text{D}$, we are going to calculate the total change in the standard enthalpy of reaction as 3 multiplied by formation of C, 1 multiplied by formation of D and subtract it from 2 multiplied by heat of formation of A and 1 multiplied by heat of formation of B.

So and we can in general, we can of course write down the whole process as this one new, new J is the coefficient and then heat of formation, standard heat of formation of all the components, where we have to know that new J is are negative for reactance and this will give us the reaction enthalpy, standard reaction enthalpy and the notation is slightly different, it is this, the notation is this basically.

Okay any here you see several different other types of a transitions are mentioned, for example, there is a phase transition from alpha to beta we can call that as know, transition enthalpy then there is a fusion which is going from solid to liquid, vaporisation from liquid to gas, sublimation solid to gas, mixing then you know solution, for example put some sugar in water, it will be dissolved, so there will be an enthalpy change associated with that as well, so we and for the protein and other things you showed binding enthalpies, you showed confirmation enthalpies, those are also there.

So, any processes you can think of, for example, hydration something is going from gas state to aqua state sodium hydroxide, let say going from solid state to aqua state, atomisation, ionisation, electron gain, reactions, combustion, formation, so all different processes can have their own enthalpy changes and wherever you consider an overall change we have to see

what kind of processes is happening and added them together to get the total change of the enthalpy.

(Refer Slide Time: 15:38)

$A \rightarrow B \rightarrow C$

Enthalpy is a State Function

- Enthalpy is a state function. So, one can combine the two different processes such as fusion and vaporization to get the overall enthalpy change for solid \rightarrow vapor transition, called sublimation.

$\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)} \quad \Delta_{\text{vap}}H^\ominus(373 \text{ K}) = +40.66 \text{ kJ mol}^{-1}$

$\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)} \quad \Delta_{\text{fus}}H^\ominus(273 \text{ K}) = +6.01 \text{ kJ mol}^{-1}$

$\Delta_{\text{fus}}H^\ominus + \Delta_{\text{vap}}H^\ominus = \Delta_{\text{sub}}H^\ominus$

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- Hess's law states that enthalpy change of an overall reaction is the sum of the standard enthalpies of the individual reactions

- The process is reversible. So, $\Delta H^\ominus(A \rightarrow B) = -\Delta H^\ominus(B \rightarrow A)$

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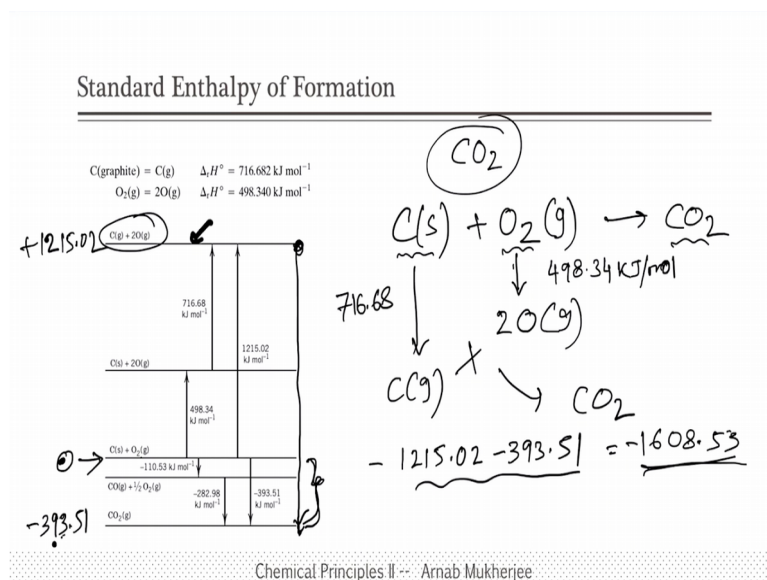
Now we can do that, I said, we have to add up right, I said that in a hurry we can do that because enthalpy is a state function. That is when it goes from A to B to C we do not have to care how it is going, we just have to calculate the difference between B and A and will get a value and then C and B and will get a value and will add them together because it is the state function.

So, enthalpy is the state function, so one can combine the two different processes such as fusion and vaporization let say, to get the overall change for solid to vapor, we know solid to liquid, we know let say we know liquid to gas which is vaporization, we know solid to liquid which is melting, solid to liquid is a melting and opposite processes is fusion right and then we can add them together here, so let say you can add this two processes and you can get the combined process for sublimation and Hess's law says that in very similar terms that you can do even for not for phase change, you can do that for reaction as well, you can combine one or more reactions to get an overall change in the you know initial and final reactions and we are going to use that a lot in order to calculate the enthalpy in different processes reactions.

And also it is reversible because again it is a state function, it does not matter, so for example here we are talking about solid to liquid as 6.01 kJ per mole right, similarly liquid to solid will be -6.01 kJ per mole, so solid to liquid you can say it is melting similarly liquid to solid

will be you know fusion, it will be just the negative of that and that you can do again because it is a state function.

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Now we are going to give you an example, so we are going to talk about heat of formation of CO₂, so what are the components involve in that, so we, see the standard state of carbon is graphite, which is a solid and standard state of oxygen is gas, so you to start from their because they are 0 right, so that is here you see but in order to form CO₂, in order to form CO₂ we need to have the oxygen from O₂ molecule to oxygen atom, so you have to break the bond and that cost energy how much, so you can see that going from O₂ gas to O it cost for 98.34 kJ per mole, again, carbon also need to be go from solid state to gases state right and that requires 716.68,

So these are endothermic processes because we have to supply enthalpy but then once we get this two things we can add them together and it will form CO₂ which, however, is an exothermic processes because where does this form? Actually why is a exothermic process? Due to the bond formation, it has become more stabilized and therefore it will be released and how much is that you can see that, now if you start from state like this state it comes all the way here which is 1215.02 - 393.51, this is the total amount of bonding energy that we get by making C and O and how did I calculate that because I know from this is 0 and this is a plus 1215.02 and this is my negative 393.51 right.

So I am now taking a difference from here to here therefore it will be 393 minus this one, and that is how we get is total number right, we can calculate that, I do not know whether I did it

right or not, but this is like I just summed both this. Okay, this is how we get the heat of formation of, so remember where our 0 is, that is very important we need to know that 0, heat of formation of CO₂ because we are going to start from the standard state of C, standard state of oxygen and standard state of CO₂.

Therefore, this is our 0, so since this is our 0, so heat of formation is only this much, sorry this is the only, it of formation is -393.51, however, the bonding energy that we get between gaseous, carbon and you know gaseous atomic oxygen is this much, because this is a 0, so standard state of carbon and oxygen we are getting this much stabilization so that is a heat of formation -393.51 that is not a problem but we have to supply energy to go to this state, you have to supply the energy to go to the state and that is a positive value and bonding overcomes that positive value and comes to negative, so the bonding has to be stronger than even the energy, the enthalpy required to you know supplying the or put the carbon in the gaseous state and making oxygen atomic okay.

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Combining Various Enthalpies of Formation

	$\Delta_f H^\circ / (\text{kJ mol}^{-1})$
H ₂ O(l)	-285.83
H ₂ O(g)	-241.82
NH ₃ (g)	-46.11
N ₂ H ₄ (l)	+50.63
NO ₂ (g)	33.18
N ₂ O ₄ (g)	+9.16
NaCl(s)	-411.15
KCl(s)	-436.75

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$$U = q_w$$

$$H = q_p$$

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So I guess that is clear, now combining various enthalpies of formations is possible, so for example, these are different formation enthalpies for water -285.83, so we remember we discussing about which is more you know stable, methane or water right, we can get that from heat of formation, so what are heat of formation is -285.83 and methane is approximately -74 and we know that if we burn methane will get carbon dioxide and water right, both of which are more stable than methane.

So that is where we can actually understand which is having higher internal energy and which is having a lower internal energy, so we can see what are in the gaseous state also and then different things, so we are going to only show, talk about the formation of KCl, what other things involved in formation of KCl.

So for KCl again we start from this is our 0 state, where potassium is a solid and chlorine is a gas in Cl₂, so in order to make it from potassium solid to gas you need to supply +89 and then in order to break the bond in chlorine you need to supply +122 and then there is an electron transfer that has to happen between chlorine and potassium right, that becomes K⁺ and Cl⁻ and that is again and enthalpically you know endothermic process have to supply that.

Once you form that than, no so that to just take out the electron from potassium, however, when you, when chlorine takes in the electron, so what is that call you know right, when you take out electron from an atom, ionization energy, so this is the typical ionization energy that is required and then this thing will form where potassium and so that is the stabilization, that is called, when it will take the chlorine will take the electron, electron affinity.

So because chlorine has higher electron affinity it will become there and then finally you are getting you know interactions you to ironing interaction between the K⁺ and Cl⁻ forming this thing, so if I ask you how much is the formation, heat of formation for potassium chloride, what will be the value? It is only this much okay, because it started from there and we ended up here, but here I ask you that okay, what is the you know interaction enthalpy between potential iron and chloride iron, then it is this much okay.

So by writing them along the enthalpy axis you will be able to figure out all possible contributions to overall change in the enthalpy and remember enthalpy and internal energy are very similar, except there is a difference, one is internal energy is heat at a constant volume and enthalpy is heat at a constant pressure and between them, there is just work done PV and that is actually very small, so often from heat of you know heat of formation we can understand, the internal energy of the system. Okay.

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Hess's Law (One More Example) Tutorial Problem example

How many meters of stairway could a 70 kg man climb (the energy available in metabolizing an 18g spoonful of glucose work? (Heat of formation of glucose is -1275 kJ/mol, CO₂ is -393.5 kJ/mol)

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O(l)$$

$$\Delta_r H = \Delta_f H(CO_2) \times 6 + \Delta_f H(H_2O) \times 6 - \Delta_f H(C_6H_{12}O_6) - 6 \times \Delta_f H(O_2)$$

$$= (-393.5 \times 6 - 283.5 \times 6 + 1275 + 0)$$

$$= -2361.0 - 1701.0 + 1275$$

$$= -2787 \text{ kJ/mol}$$

$$\begin{array}{r} -2361 \\ -1701 \\ \hline -4062 \\ +1275 \\ \hline -2787 \end{array}$$

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Hess's Law (One More Example) Tutorial Problem example

How many meters of stairway could a 70 kg man climb (the slope of the stairway is 30°) if all the energy available in metabolizing an 18g spoonful of glucose to CO₂ and H₂O could be converted to work? (Heat of formation of glucose is -1275 kJ/mol, CO₂ is -393.5 kJ/mol and water is -283.5 kJ/mol)

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$\Delta H = -2787 \text{ kJ/mol}$
 18 gm Sugar
 M_w of C₆H₁₂O₆ = 180
 18 gm C₆H₁₂O₆ = 0.1 mol
 $\Delta H = -278.7 \text{ kJ}$

$$h = x \sin 30^\circ$$

$$(x \sin 30^\circ) \times 70 \times 9.8$$

$$= \frac{x}{2} \times 70 \times 9.8 \text{ J}$$

$$\frac{x}{2} \times 70 \times 9.8 = 278.7 \times 10^3$$

$$x = \frac{2 \times 278.7 \times 10^3}{70 \times 9.8} = 812.5$$

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Now that is been done, there is a problem here, so the title is not correct but we just one tutorial problem let say for example, so what it says that, that how many meters of stairway could a 70 KG man climb with the slope of the 30° , if all the energy available in metabolizing 18 g glucose to CO_2 and H_2O could be converted to work? So what it is saying is that, so glucose is $\text{C}_6\text{H}_{12}\text{O}_6$ and it requires some oxygen to form CO_2 and H_2O , so that is the combustion of you know glucose or metabolization of glucose.

Let say everything is converted to energy, how much energy it will give us? Since it is a heat of reaction, we can get a heat of reaction from balancing the equations, we have to balance the equation first, so we can say 6CO_2 , so it will give us 12 oxygen and you have 6 oxygen here, so that will give us that but we need 6 H_2O in order to get 12 hydrogen, we got that and now how many oxygens, so $12 + 6$, 18 oxygen we have only 6, so we need the 12 so this will be 6. Okay, so now this reaction is balance, now in order to get the enthalpy of this reaction we need to have enthalpy of formation of CO_2 multiplied by 6 plus enthalpy of formation of H_2O multiplied by 6 minus enthalpy of formation of $\text{C}_6\text{H}_{12}\text{O}_6$ minus 6 into enthalpy of formation of O_2 correct.

Now we have got the values here -393.5 into 6 minus 283.5 into 6 minus minus is plus now 1275 and what is the enthalpy of oxygen? 0, good, so that will be 0, so can you tell me the value here, just calculate that and tell me, so I can also do that, I do not want to, so I am getting this value current, so this is the kilojoules per mole that is energy available to us right, now let us see that how much we can climb with that.

So I am going to delete everything else remember 2787, so this a good point, so we are getting -2787 kilojoule per mole of energy or enthalpy let say, so that is for a particular mole, now we are using how much sugar we are using 18 g of sugar, now what is the molecular weight of glucose? I will write it that so molecular weight of 180, so therefore 18 g $\text{C}_6\text{H}_{12}\text{O}_6$ is equal to 0.1 mole, so therefore the enthalpy change for 18 g, 278.7 K kilojoule per mole, so this must energy is available to us, because we only took 18 g okay.

18 g is just one spoonful, now we are going to climb up, 70 kg man is going to climb up with an angle of 30° , so let say climb up X distance, X metre right, so if it climbs up X metre, what is the height that is going to be change? That is $X \sin 30^\circ$, so $X \sin 30^\circ$ is our H, $\sin 30$ is how much? Half, so $X \sin 30$ is this one, then mass is 70 kg and G is 9.8 metre per second square right, so which is X by 2 into 70 into 9.8 is equal to or we can actually you know, we can do that right away, so now X by 2 into 70 into 9.8 is now equal to 278.7, so

negative am not using because that negative is basically giving us energy, so that is a positive now.

So how much X we are getting 278.7 okay, by the way, this is kilojoule, so we have to add this much because this is joule right and this is kilojoule okay, just calculate that and let me know how much we are getting 812.5 m and that means the height that it is climbing is half of that almost 400 meter and that is higher than the Eiffel tower or the Empire State building of New York which is around 380.

So sugar is that much, you know giving us that much energy, so ideally is not the thing because that, of course you calculate the energy why it is coming out the same but in this energy is you know as if somebody is lifting you, so let say a left is pushing you up that much, that is the energy that is going to spend, however when we take a step or climb a stair than in our body there are a lot of muscles, lot of other things that are working continuously, so it is not just the gravitational work that our body is doing, our bodies also going a lot of internal muscle work at a molecular level that spends a lot of energy, our blood pressure is going to be higher and are muscles going to be stiffened you know and many other things that are.

So therefore ultimately actually are going to use more calories by climbing that much but even then there is a importing thing to understand more or less the ballpark number that we get from that, so the amount of energy that actually is there, you know, one spoonful of sugar.