Chemical Principles II
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Module 04
Lecture 23
Thermochemistry Part – 02

Okay, so welcome to this module of thermochemistry going ahead so enthalpy of formation and bond energy, so from enthalpy of formation we can get an idea that how much strength is there in a bond formation, just we have seen right one example of CO2 was almost 1600 record right, is it, now we can get a sense of number from any other things.

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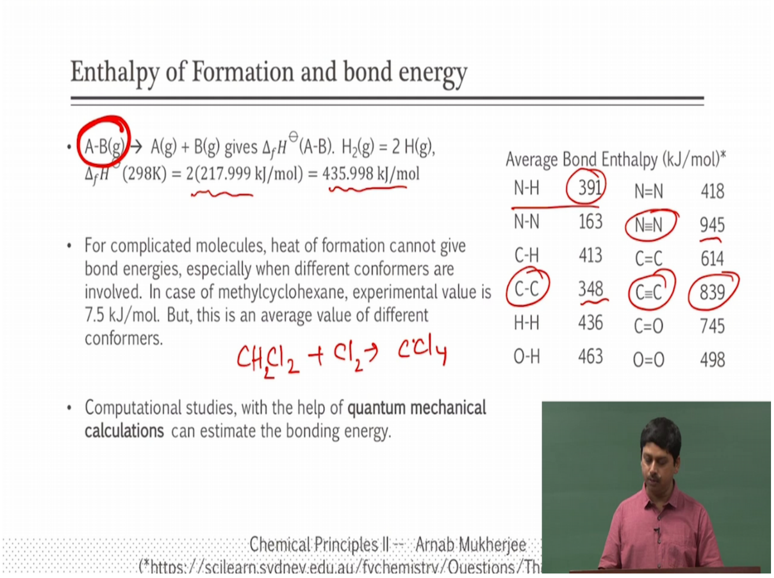

Enthalpy of Formation and bond energy

- A-B(g) → A(g) + B(g) gives $\Delta_f H^{\ominus}$(A-B). H_2(g) = 2 H(g), $\Delta_f H^{\ominus}$(298K) = 2(217.999 kJ/mol) = 435.998 kJ/mol
- For complicated molecules, heat of formation cannot give bond energies, especially when different conformers are involved. In case of methylcyclohexane, experimental value is 7.5 kJ/mol. But, this is an average value of different conformers.

$CH_2Cl_2 + Cl_2 \rightarrow CCl_4$

- Computational studies, with the help of **quantum mechanical calculations** can estimate the bonding energy.

Average Bond Enthalpy (kJ/mol)*

N-H	391	N=N	418
N-N	163	N≡N	945
C-H	413	C=C	614
C-C	348	C≡C	839
H-H	436	C=O	745
O-H	463	O=O	498

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(*https://scilearn.sydney.edu.au/fychemistry/Questions/Th

So let say we are talking about A, B formation from A and B, now looking at the enthalpy of formation of A, B, if the A and B are in standard states they will get the bond energy of A, B, so for example H2, H2 is forming from 2HG like two hydrogen atom and enthalpy of formation is typically 2 into 217 so giving rise to 435.998 kJ per mole, so that is the formation of hydrogen molecule from hydrogen atom or rather it is getting stabilised, so it is the other way down, we have written the question from H2 to 2H, which is that means this much energy has to be supplied but remember this is at 298 that is not the bond energy, that is at a finite temperature, for bond energy we have to calculate the value at 0 Kelvin that is an intrinsic part energy right.

So how do you calculate the 0 Kelvin will come back to that but before that will give you some more numbers, which will give you an idea, for example NH is 391, it is actually smaller than H2 and the reason is a there is a heated O atomic system, so electron is more towards nitrogen, look at, carbon carbon 348 and C triple bond C 839, so we knew right the double, triple bond is more stable than the double bond and double bond is more stable than the single bond and all that.

Nitrogen triple bond very strong you see, triple bond nitrogen more stable compound, one of the most stable compounds and that has like 945 kilojoule per mole strength and this data I have got from this site here mention, so idea is that from heat of formation we can get that but only when there are very simple molecules like you know a diatomic molecule we are talking about.

Okay, so you see that for complicated molecules this bond energy calculation will be very difficult, for example, we can let say, if I talk about CH CI 2 plus Cl now this kind of processes if you see or let say CH 2 Cl 2 you are going to see CCL4, so we have to understand that all other connectivity that are there, so we cannot calculate the CH bond strength by this because there are other residue substitutions involved in this process right, so it is very difficult to get only the CH bonds energy by heat of formation method.

Similarly, sometimes there are more than one confirmation are possible, for example, methylcyclohexane, methylcyclohexane can be there in both actual and equatorial position right, so in that case, they will have different heat of formation and we are only going to get an average value, so therefore you know quantum calculations are helpful which can give you from ab initio method this bond energies, so we have studied the energy of hydrogen atom right.

Similarly we can study energy of hydrogen molecule, you have also studied hydrogen molecule right, bonding energies and the bonding values of hydrogen molecule is very close to our calculation, will talk about that, so you see 435.998 Kelvin right, at 0 Kelvin it is around 432 which is very, very close to the quantum chemical calculation, okay so quantum mechanics can give you an idea about this bonds strength which can be experimentally verifiable using this kind of systems.

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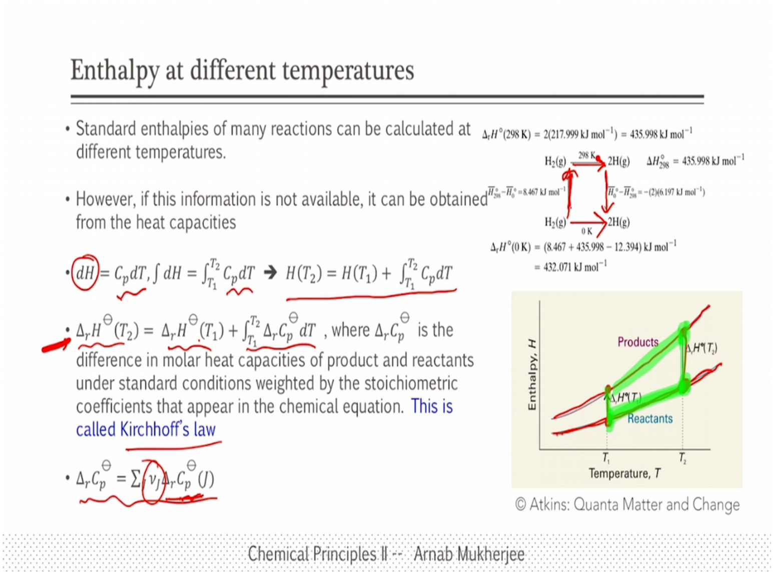

Enthalpy at different temperatures

- Standard enthalpies of many reactions can be calculated at different temperatures.
- However, if this information is not available, it can be obtained from the heat capacities
- $dH = C_p dT, \int dH = \int_{T_1}^{T_2} C_p dT \rightarrow H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$
- $\Delta_r H^{\ominus}(T_2) = \Delta_r H^{\ominus}(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^{\ominus} dT$, where $\Delta_r C_p^{\ominus}$ is the difference in molar heat capacities of product and reactants under standard conditions weighted by the stoichiometric coefficients that appear in the chemical equation. This is called Kirchhoff's law
- $\Delta_r C_p^{\ominus} = \sum \nu_J \Delta_r C_p^{\ominus}(J)$

$\Delta_r H°(298\ \text{K}) = 2(217.999\ \text{kJ mol}^{-1}) = 435.998\ \text{kJ mol}^{-1}$

$H_2(g) \xrightarrow{298\ \text{K}} 2H(g) \quad \Delta H^{\circ}_{298} = 435.998\ \text{kJ mol}^{-1}$

$\overline{H}^{\circ}_{298} - \overline{H}^{\circ}_{0} = 8.467\ \text{kJ mol}^{-1}$

$\overline{H}^{\circ}_{0} - \overline{H}^{\circ}_{298} = -(2)(6.197\ \text{kJ mol}^{-1})$

$H_2(g) \xrightarrow[0\ \text{K}]{} 2H(g)$

$\Delta_r H°(0\ \text{K}) = (8.467 + 435.998 - 12.394)\ \text{kJ mol}^{-1}$
$= 432.071\ \text{kJ mol}^{-1}$

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Now how do you get enthalpy and different temperature, so in order to understand that we have to see that standard enthalpies are define only for 1 bar pressure but it can be at any different temperature right, so standard enthalpy of many reactions can be calculated at different temperatures, however if this information is not available it can be obtained from the heat capacities, how? Let say we already know that Delta H or DH is CPDT, so which means that, by indicating this particular quantity we are going to get the enthalpy at different temperature right, for any system we can heated up and depending on its own heat capacity we are going to get the change in enthalpy from one temperature to another temperature.

So it is like this, you imagine that we are talking about reactant and the reactant has different values are different temperature right and this is a product which also has different enthalpy at different temperature, now what we are observing at one temperature like this and another temperature like this will be only different by the differences in CPs, so if I now take the difference in CPs then we can get the difference in enthalpies at two different temperature you see.

So and that is what it is mention here, which is called the Kirchhoffs law, so reaction at one temperature T2 is equal to reaction at, sorry heat of formation, heat of reaction at one particular temperature T2 is equal to heat of formation at a particular temperature T1 plus integration of the T1 to T2 Delta R CP, so it is now the difference in the reactions of CP which means that the same way we calculate reaction enthalpy we are calculating the reaction CP.

Okay, and that and the reason is and graphically shown here and once you do that we are going to use that Delta CP to calculate the process and again we can write in general Delta R CP as the stoichiometric, so CPs difference in CPs multiplied by their style stoichiometric coefficient, just like we did for reaction enthalpy same thing, but for CP once you get the CP we multiplied by the temperature and added the enthalpy of one value.

So also to be clear here, you see here we know the value of heat of formation of hydrogen atom from hydrogen molecule at 298 Kelvin okay and we also know the heat capacities of hydrogen gas from, so we can calculate the enthalpy change from 0 Kelvin to 298 Kelvin, we can calculate that, similarly we can calculate by knowing the heat capacity of hydrogen atom we can calculate the difference in it, from 298 Kelvin to 0 Kelvin.

Now having those all these three values we can calculate the change in enthalpy at a 0 Kelvin is called a thermodynamic cycle, so cycle means there is a cyclic step out of which you do not know only one value, you know all the other three, from all other three we can actually calculate the last one, so using exactly this things, so we know this point, will use different color, we know this point, we know this point, we know this point, we have to know only that, we know this step, we know this step, we know the steps, so we can calculate that, 1, 2, 3, this three we know only thing we are calculating is the last one, this one.

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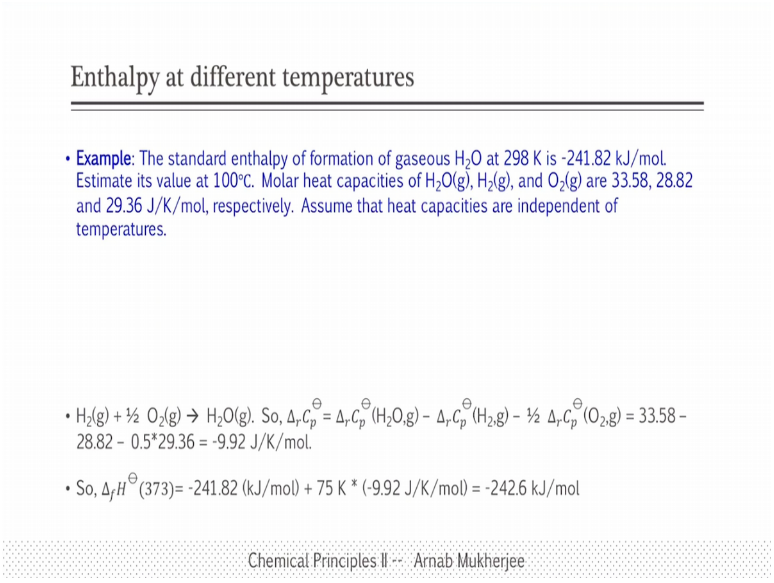

Enthalpy at different temperatures

- **Example**: The standard enthalpy of formation of gaseous H_2O at 298 K is -241.82 kJ/mol. Estimate its value at 100°C. Molar heat capacities of $H_2O(g)$, $H_2(g)$, and $O_2(g)$ are 33.58, 28.82 and 29.36 J/K/mol, respectively. Assume that heat capacities are independent of temperatures.

- $H_2(g) + ½\ O_2(g) \rightarrow H_2O(g)$. So, $\Delta_r C_p^\ominus = \Delta_r C_p^\ominus(H_2O,g) - \Delta_r C_p^\ominus(H_2,g) - ½\ \Delta_r C_p^\ominus(O_2,g) = 33.58 - 28.82 - 0.5*29.36 = -9.92$ J/K/mol.
- So, $\Delta_f H^\ominus(373) = -241.82$ (kJ/mol) + 75 K * (-9.92 J/K/mol) = -242.6 kJ/mol

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Now this is just a simple example that the standard enthalpy of formation of gaseous H2O at 298 is this much value, estimate its value at 100°C. Okay, so 298 Kelvin and 100° 373 Calvin right, so molar heat capacities of water, hydrogen and oxygen are given, assume the heat capacity is independent of temperature that we have to otherwise we cannot subtract them because they are going to change right.

So that formula is very clearly here, so first we right down the reaction is $H_2 + O_2$ is H_2O, than we calculate the delta R CP that means reaction heat capacity, so which is given by terms in there with the coefficient as the stoichiometric values and that is giving us that R CP as -9.92, now how much change in temperature is that from 298 to 373 that it will be 75°, so 75 multiplied by 9.92 and at the value whatever it is that as 241.82, once you do that will get -242.6 kilojoule.

So that is how knowing the heat of formation or heat of reaction at one temperature we can calculate that, in other temperature and like that we can also you know we can now calculate a heat of formations for all possible systems for reactions, for physical changes, for biochemical reaction and also by knowing that we have a sense of the internal energy of particular system and remember that once we understand the in their energy of a particular system that is stored we can get an understanding that which can give us heat and therefore which we can use for work.

That is why we are storing methane right, people are nowadays trying to store methane why? Because methane can give us energy, water, it cannot but water is more stable but hydrogen is less stable, which means, hydrogen has more internal energy which can be extracted, so that is why people are trying to split water into hydrogen and oxygen, so that hydrogen can be used as a fuel, so basically somehow the energy that is their if you can use that and store it, just like a battery, so if you can store methane than it will be use as a source like a battery in future right.

So all ideas of doing that is that, so and these are we call as chemical energy that you are storing, for example, food gives us the energy right, glucose because it is not as stable as carbon dioxide and water it can be decomposed into that and given as the energy, if it would be very, very stable we cannot extract any energy out of that, it can only go lower spontaneously okay, so that is why this very important and this kind of ends the first law of thermodynamics.