Fundamentals of Combustion

Prof. V. Raghavan
Department of Mechanical Engineering
Indian Institute of Technology, Madras

Lecture – 10

First Law and Second Law of Thermodynamics Applied to Combustion - Part 2
Enthalpy Calculation

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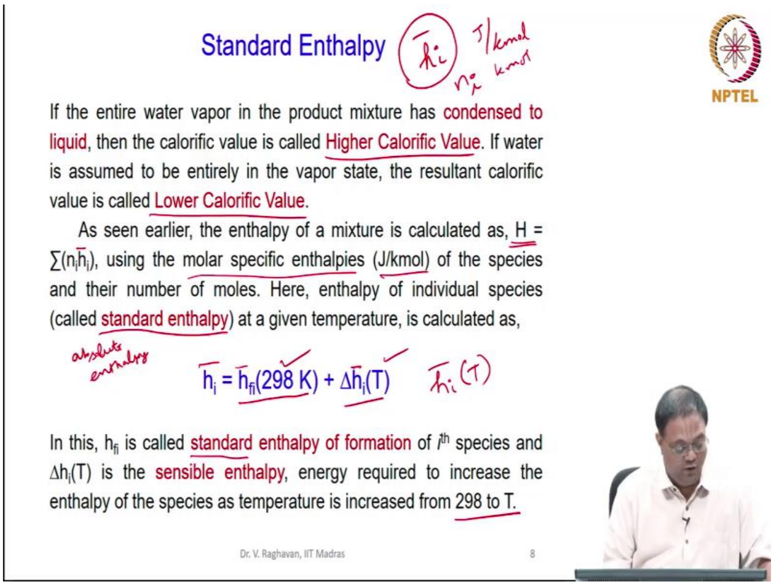

Standard Enthalpy $\bar{h}_i$ J/kmol n_i kmol

If the entire water vapor in the product mixture has condensed to liquid, then the calorific value is called Higher Calorific Value. If water is assumed to be entirely in the vapor state, the resultant calorific value is called Lower Calorific Value.

As seen earlier, the enthalpy of a mixture is calculated as, $H = \sum(n_i\bar{h}_i)$, using the molar specific enthalpies (J/kmol) of the species and their number of moles. Here, enthalpy of individual species (called standard enthalpy) at a given temperature, is calculated as,

absolute enthalpy

$$\bar{h}_i = \bar{h}_{fi}(298\ K) + \Delta\bar{h}_i(T) \qquad \bar{h}_i(T)$$

In this, h_{fi} is called standard enthalpy of formation of i^{th} species and $\Delta h_i(T)$ is the sensible enthalpy, energy required to increase the enthalpy of the species as temperature is increased from 298 to T.

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Now, if the entire water vapor in the product mixture has condensed to liquid; that means, that vapor’s enthalpy also we are trying to extract out. The calorific value now what we get is called higher calorific value because we are also adding the latent heat of vaporization of water vapor.

So, water vapor condensing to liquid that heat also I am extracting. That is called higher calorific value or higher heating value. On the other hand, the other extreme is if water is assumed to be entirely in vapor state, I do not condense even a bit of that then what we get is called the lower calorific value.

Please understand the calculations. We know the products what is the product enthalpy we are going to substitute there?

Whether it is vapor’s enthalpy see for example water, what enthalpy value I will substitute whether it is corresponding to the vapor’s enthalpy or liquids enthalpy that will make this difference basically. The difference between the higher calorific value and the lower calorific value is nothing, but the latent heat of vaporization of water at the given pressure.

Now, this gives some definitions like heat of reaction, negative of that is heat of combustion. When you do the reaction in controlled manner so that the reactants enter at 298 and finally, products are cooled to 298 Kelvin it is called standard heat of reaction. So, negative of that is the standard heat of combustion or calorific value or heating value. In the calorific value or heating value you have two values based upon whether the water in the products is in liquid or vapor state. If it is in liquid, then you have already extracted the latent heat of the water also to the surroundings. So, what we have extracted is will contribute to what is called higher heating value or higher calorific value.

When the water is entirely in vapor state, it is lower calorific value, but you can see that some water may condense and some may remain in vapour state. So, we will get the values in between these two. The difference in between these two is only the latent heat of water.

Now, how will you calculate the enthalpy of the mixture. We already seen that molar specific enthalpy h_i as I said I can also put the overhead bar. I have dropped it for convenience. Molar specific enthalpies in J/kmol of each species, when I say h_i bar overhead bar, I mean this is the molar specific enthalpy of the ith species in J/kmol.

Now, number of moles of ith species is n_i. Then I multiply these two so, this is in kmol. When I multiply this, I get the net enthalpy of the ith species so add like that for all the species. So, $\sum n_i \overline{h_i}$ that will give the mixtures enthalpy in J. So, J or kJ.

Now, for this how will you calculate? So, by equation you know what are the n_i values that itself is not so easy, we will see that the product is not so straightforward to calculate the n_i's.

That involves what is called chemical equilibrium and so on. Let us see that later but how will you first calculate $\overline{h_i}$ or h_i. So, just for convenience, I am leaving the overhead bar.

Whenever there is a molar base quantity, it is customary to put overhead bar like this. For convenience, I am dropping it while writing the equation.

$$h_i = h_{fi}(298\ K) + \Delta h_i(T)$$

Now, if you see this, the enthalpy of a particular species is called absolute enthalpy; absolute enthalpy or standard enthalpy. So, standard enthalpy is calculated as the sum of two terms; one is called h_{fi} enthalpy of formation f is formation of the i^{th} species and this is calculated at a temperature of 298 Kelvin.

This is the enthalpy of formation of the i^{th} species plus delta h_i at a temperature of T. That means, if you add heat so that the temperature of the species increases from the reference state of 298 to any given temperature T.

Now, you are adding some sensible enthalpy to this. So, this part is the sensible enthalpy part. This is the enthalpy inherent when the species is at 298 Kelvin. This enthalpy is this energy is processed by the particular species.

So, that is the enthalpy of formation of the species when the species forms and it is at 298 K, reference state.

But when you heat this, you are adding some more energy to the species that is called sensible enthalpy. If you add these two together, you get the h_i calculated at any temperature T. So, this is what is this. This is calculated at any temperature T.

I have told that enthalpy of individual species called standard enthalpy, you can also say absolute enthalpy is the sum of enthalpy of formation we call this standard enthalpy because it is at 298 Kelvin and sensible enthalpy.

Sensible enthalpy of the i^{th} species is the energy added in order to increase temperature from 298 K to a given temperature T.

This is the definition of the absolute enthalpy, enthalpy of formation of the particular species plus its sensible enthalpy.

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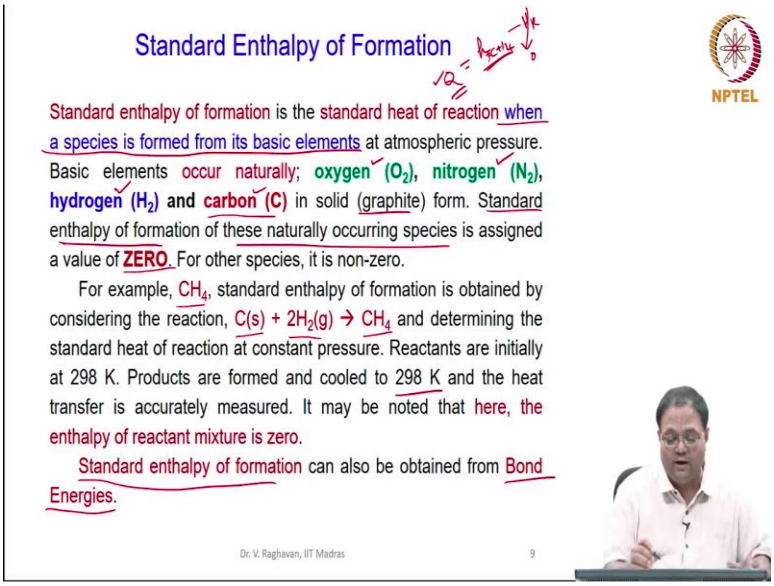

Standard Enthalpy of Formation

Standard enthalpy of formation is the standard heat of reaction when a species is formed from its basic elements at atmospheric pressure. Basic elements occur naturally; **oxygen (O_2), nitrogen (N_2), hydrogen (H_2) and carbon (C)** in solid (graphite) form. Standard enthalpy of formation of these naturally occurring species is assigned a value of **ZERO**. For other species, it is non-zero.

For example, CH_4, standard enthalpy of formation is obtained by considering the reaction, $C(s) + 2H_2(g) \rightarrow CH_4$ and determining the standard heat of reaction at constant pressure. Reactants are initially at 298 K. Products are formed and cooled to 298 K and the heat transfer is accurately measured. It may be noted that here, the enthalpy of reactant mixture is zero.

Standard enthalpy of formation can also be obtained from Bond Energies.

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Now, how to find these values? Let us take enthalpy of formation. Standard enthalpy of formation is the standard heat of reaction so when I form a species by a standard method then I get standard enthalpy of formation.

Now, we have to define some basic elements. The basic elements what we define are oxygen O_2 oxygen molecule. Please understand O, oxygen atom, is not a basic element oxygen molecule is defined as a basic element.

Similarly, nitrogen molecule hydrogen molecule these three are the gas element molecules which are defined as basic elements and solid, carbon graphite is also defined as a basic element. So, 1 solid and 3 gaseous substances are defined as basic elements because they occur naturally.

You can see that in air, O_2 and N_2 are present. Hydrogen is also present in water, too much of hydrogen is present in water if you can get this, but anyway the methods of getting that is different but what I am saying is these are all the molecules which are naturally occurring.

Similarly, carbon in solid form is naturally present. So, these are all the basic elements for which we assign the standard enthalpy of formation value. For these naturally occurring species is assigned value of zero. So, they do not form, they already exist.

But all other species or all other compounds etcetera form from these elements, and when they form from these elements, you have to involve a reaction in which the basic elements are supplied as reactants and you ignite it. Ignition occurs and the products are formed, a particular product is formed.

The product is then cooled to 298 Kelvin, standard temperature, and they extract all the heat and precisely measure what is the heat evolved that is the standard heat of formation.

So, example let us take methane into consideration. Methane standard enthalpy of formation is obtained by considering the reaction between solid carbon and hydrogen molecules ok gas to form CH_4.

$$C(s) + 2H_2(g) \rightarrow CH_4$$

Now, these are the reactants for which enthalpy formation is zero. So, graphite solid, carbon or hydrogen gas enthalpy formation of zero. The reactants are at 298 Kelvin so their enthalpy is zero because the enthalpy formation is set to zero already.

Now, products are formed. So, you know what is the heat we are extracting from this. Apply first law to this reaction for example, Q will be equal to H CH_4 minus the reactants. I will write then this is small h CH_4 minus H reactant.

This is capital H reactant they are mixture because it is a mixture here now this is 0 because it is supplied at 298 Kelvin and at 298 Kelvin only heat of formation is going to be substituted but as I told earlier, for the basic elements H_2 and C the standard enthalpy of formation is defined as 0. So, H_R equal to 0.

So, whatever Q I measure out of this experimental setup that is nothing, but the enthalpy of formation so, I will put a formation here because this is formed from the elements and this is a formation reaction. This is the only species which is formed. $\Delta h_{f,CH_4}$ will be equal to the Q, The Q what we measure precisely.

So, consider this reaction and ignite it, reactant are initially at 298 Kelvin so that the enthalpy of the reactants is 0 products are formed and I exact the heat so that they cooled to 298 K, the only product is this CH_4 here.

So, we can say product is formed and it is cooled to 298 Kelvin and the heat transfer is accurately measured, Q is measured accurately. Once the Q is measured, that Q is equal to the enthalpy of formation of CH_4 that is called standard enthalpy of formation of CH_4.

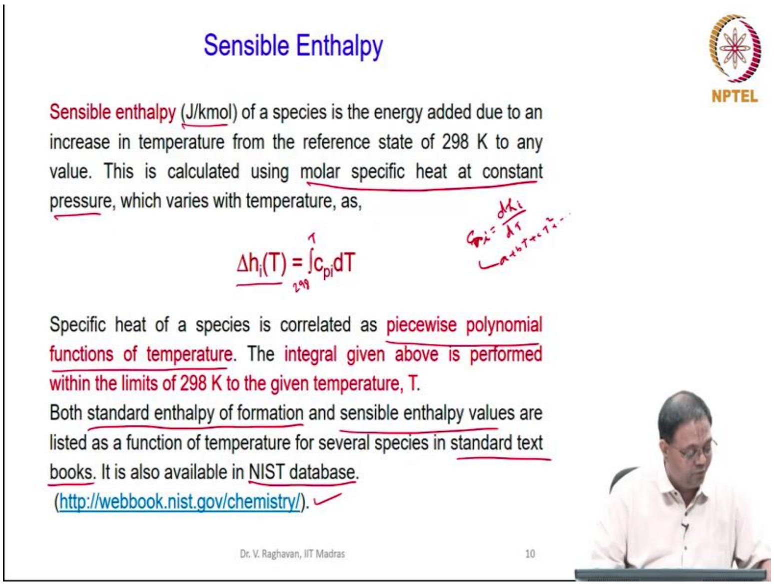
Now, you can note that the enthalpy of reactant mixture is zero because the constitution of that mixture is basically from the naturally occurring elements and it is supplied at 298 Kelvin.

But if you see that if you increase the temperature of the reactants then the enthalpy of reactant will not be zero because the sensible enthalpy will be added to that. Since, they are supplied at 298 Kelvin, only enthalpy of formation which is assigned value of zero contribute to H_R so, the value is 0, the mixtures value is 0. Now, this is one of the techniques.

Another technique is you can use bond energies to determine the enthalpy of formation. So, chemists do that. Bond energy is basically you know if you break a bond, some amount of heat has to be supplied. When a bond forms, then some heat is released and so on. So, based upon this say for example, again the energy of the bond is determined by whether it is a single bond, double bond, triple bond and so on.

So, again there is a way to calculate the standard enthalpy of formation using bond energies. So, I am not going to go into detail of this, but you have to understand that enthalpy of formation of a particular species is nothing, but the standard enthalpy of reaction when the species is formed from its basic elements and the product is cooled, the product is the same species its cooled to the reference temperature of 298 Kelvin.

So, that is the enthalpy of formation, the first part of the enthalpy which is contributing to the standard enthalpy or the absolute enthalpy. (Refer Slide Time: 13:07)



Sensible Enthalpy

Sensible enthalpy (J/kmol) of a species is the energy added due to an increase in temperature from the reference state of 298 K to any value. This is calculated using molar specific heat at constant pressure, which varies with temperature, as,

$$\Delta h_i(T) = \int_{298}^{T} c_{pi} dT$$

$c_{pi} = \frac{dh_i}{dT}$

$a + bT + cT^2 \ldots$

Specific heat of a species is correlated as piecewise polynomial functions of temperature. The integral given above is performed within the limits of 298 K to the given temperature, T.

Both standard enthalpy of formation and sensible enthalpy values are listed as a function of temperature for several species in standard text books. It is also available in NIST database. (http://webbook.nist.gov/chemistry/).

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Now, sensible enthalpy, again its molar based J/kmol, of a species is the energy added during the increase of temperature from 298 Kelvin to the given temperature T.

Now, we can say that this Δh_i can be written as. So, this is an $\int c_p\, dT$, c_p is the specific heat at constant pressure that itself is a function of temperature we have seen that.

Since h is a function of temperature c_p is a ordinary derivative because of the ideal gas assumption so, c_p is ordinary derivative. So, c_p of any species we can write as dh_i / dT so, this is used here.

Any difference in this so, for temperature we say 298 Kelvin to any temperature this integration is done and c_p itself is a function of temperature.

This can be a polynomial. So, $a + bT + cT^2$ etcetera. So, substitute this and integrate this between these two temperatures, you get the sensible enthalpy. You can also use tables; we will come to that later.

So, sensible enthalpy of a species is the energy added due to an increase in the temperature from the reference state of 298 Kelvin to a given value of T.

This is calculated using molar specific heat, molar specific heat of the species at constant pressure is defined as a polynomial. Normally, the specific heat of the species is correlated as a piecewise polynomial function of temperature.

Say for example, from 200 Kelvin to 1000 Kelvin it may have 1 equation its coefficients have one particular set of values. Similarly, when a temperature range increases from 1000 Kelvin to say 3000 Kelvin, you will have another set of values for the coefficients. So, this is piecewise polynomial.

Such correlations are available for every species, several species like say for example, it may be CO_2, CO, CH_4 and so on for every species we get this. Once you know that, you can find the sensible enthalpy or you can also use tables where the sensible enthalpy itself is tabulated as a function of temperature. Both can be done.

Similarly, the standard enthalpy of formation also well it is the constant value you know at 298 K only one value that is also available for several species.

For example, if we take our standard textbook what we have suggested like Stephen Turns, an Introduction to Combustion, in the appendix part of that several tables are given listing the enthalpy of formation as well as the sensible enthalpy values or you can also choose NIST database which is actually available in this website.

webbook.nist.gov, if you go here and type this what you want you will get all the details about that whatever state you want in that say for example, gas or liquid anything and you can find this correlation etcetera.

So, these are normally used. We will actually use the standard textbooks for our calculations and end of the textbook, appendix will give the values of these .

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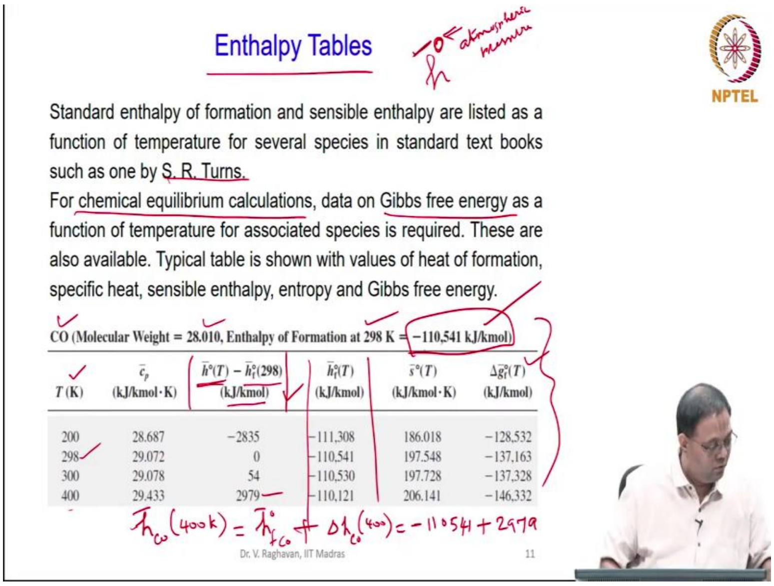

Enthalpy Tables

$\overset{o}{h}$ ← atmospheric pressure

Standard enthalpy of formation and sensible enthalpy are listed as a function of temperature for several species in standard text books such as one by S. R. Turns.

For chemical equilibrium calculations, data on Gibbs free energy as a function of temperature for associated species is required. These are also available. Typical table is shown with values of heat of formation, specific heat, sensible enthalpy, entropy and Gibbs free energy.

CO (Molecular Weight = 28.010, Enthalpy of Formation at 298 K = −110,541 kJ/kmol)

T (K)	$\bar{c}_p$ (kJ/kmol·K)	$\bar{h}^o(T) - \bar{h}^o_f(298)$ (kJ/kmol)	$\bar{h}^o_f(T)$ (kJ/kmol)	$\bar{s}^o(T)$ (kJ/kmol·K)	$\Delta \bar{g}^o_f(T)$ (kJ/kmol)
200	28.687	−2835	−111,308	186.018	−128,532
298	29.072	0	−110,541	197.548	−137,163
300	29.078	54	−110,530	197.728	−137,328
400	29.433	2979	−110,121	206.141	−146,332

$$\bar{h}_{CO}(400K) = \bar{h}^o_{f_{CO}} + \Delta h_{CO}(400) = -11054 + 2979$$

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I am just trying to explain the list of tables from that particular textbook for example, you take Turns textbook this is the way they give; this is the table which you will see in the end of the textbook in appendixes.

Let us take one particular species here say CO carbon monoxide. So, molecular weight is given, accurate molecular weight, then the enthalpy of formation. Enthalpy of formation basically when I say enthalpy of formation at 298 K, it refers the standard enthalpy of formation.

We can also do this experiment in some other temperature you know so, that is what gives the differences, but we do not want any difference, we want only at that 298 Kelvin reference state for which we are going to do all the calculations.

So, this is standard enthalpy of formation of this particular species in kJ/kmol you can see -110541 kJ/kmol for CO it is a negative meaning the heat of reaction is negative; that means, when the CO forms it has a lower energy level than the reactants. For example, what surrounding is going to take is positive.

Now, this is the typical table, actually it runs from 200 Kelvin to 5000 Kelvin. So, you can see the temperature 200 and the reference state also is given here and the temperature increases slowly, I have not given the full table here what they have given here is c_p as a function of temperature then the enthalpy at a particular temperature minus this enthalpy standard enthalpy of formation.

So, that difference they are given that is nothing but Δh. So, this is what Δh is. This Δh is given here. One more nomenclature when you follow Stephen Turns is, see I have already defined the nomenclature of overhead bar which is the molar specific it is in kJ/kmol.

So, molar specific quantities we use overhead bar. What is the meaning of overhead 0 here? Overhead 0 or overhead o this is the atmospheric pressure. So, this represents the atmospheric pressure. The experiment has been done in one atmospheric pressure that is what it means. Anyway, when it is an ideal gas, enthalpy does not depend on the pressure. It is only temperature based.

Now, for us, this column is more important, other columns are not important for us, we do not normally use it. Entropy sometimes we use but this column is not required for us we do not need to use it. Actually, they are trying to list the enthalpy of formation h_f (T) as a function of temperature.

This is the total enthalpy or what it is not cleared actually, not clearly defined but we do not normally use this in any calculation. So, we use the enthalpy of formation what is given here plus the sensible enthalpy which is given here.

Now, to calculate the absolute enthalpy or the standard enthalpy of a species at a particular temperature, let us take enthalpy of CO at 400 Kelvin will be equal to this. The absolute enthalpy will be equal to enthalpy of formation $h_{f,CO}$ plus Δh_{CO} at 400 so, from this table it is written as -110541 which is enthalpy of formation it is given here plus we can say take the value of Δh here itself so, 2979 at 400 Kelvin, plus 2979 that will be the value of h_{CO}.

So, for each species at a particular temperature, I can get the enthalpy by adding the enthalpy of formation which is given here plus sensible enthalpy corresponding to the temperature, you take the third column value that you add to this. So, if you add these two, you will get the enthalpy of the particular species at a particular temperature. So, this is for the heat calculation, I need enthalpy data to do this.

Now, if we go to chemical equilibrium calculations. We will see next that. You need Gibbs free energy value. The Gibbs free energy value as a function of temperature, we need that, that is what is given here. This we will use in our calculation.

Please understand that there is a definition of what is called Gibbs free energy of formation. Like we have enthalpy, enthalpy of formation, Stephen Turns also define a quantity called Gibbs free energy of formation.

So, you have to be very careful when you use some other table rather than Stephen Turns, you can also calculate this Gibbs free energy I will come to that little bit later. When you use this table, you have to use the corresponding values of this table only for all the species when you do the calculations you cannot interchange the tables.

For enthalpies, you can interchange the tables, you will not get much difference but when you use Gibbs energy, in all other textbooks or the NIST etcetera, you do not get the Gibbs energy of formation.

But here in Stephen Turns, basically they give the Gibbs energy, free energy of formation so, using that also you can do the equilibrium calculations which you will see little bit later. So, this is the typical table what we will use for all the species. See this is for CO, similarly you will get for O_2, CO_2, H_2O, H_2, OH, N_2 etcetera. So, based upon that, you will be able to select.

So, if you take for example, instead of CO you take O_2 you will see that enthalpy of formation of O_2 at 298 will be 0. So, based upon these tables, you can do the calculations.

We will come to that little bit later when we do the problems. Enthalpy tables are used to calculate the enthalpy, standard enthalpy or absolute enthalpy of each species and you calculate the enthalpy of the mixture.

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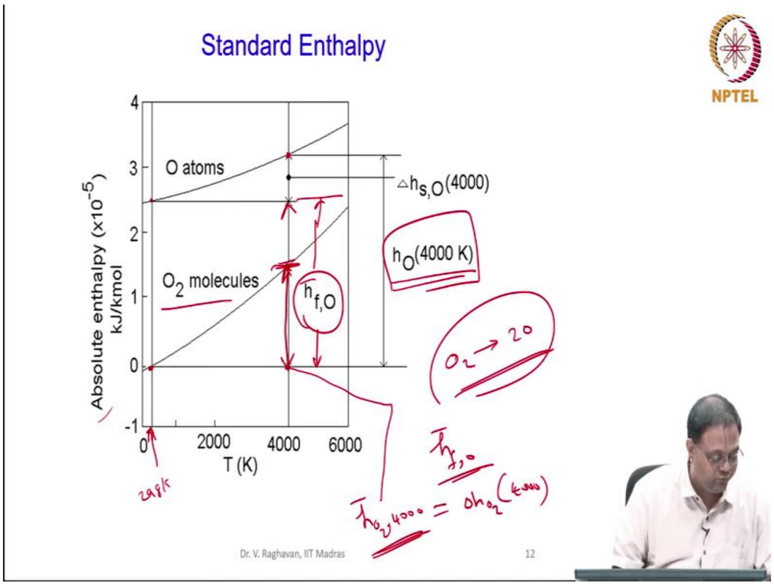

Standard Enthalpy

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Now, I will give this graphically. See for example, I have O_2 when we say absolute enthalpy or standard enthalpy that versus temperature, you will see enthalpy increases with the temperature like this. Now, I have taken two things, one is O_2. So, this is the 298 line. So, this is 298 Kelvin line vertical line.

Now we can see that for O_2, the absolute enthalpy value is 0 at 298 Kelvin, but for O it is not so because O is formed from O_2. O_2 is basic element which is naturally occurring. So, it has a 0 value at 298 Kelvin.

On the other hand, this is the value at 298 Kelvin for O. So, heat of formation of O is this value what I have put here. So, O is formed from O_2. So, $O_2 \rightarrow 2O$. This dissociation reaction requires energy from the ambient so, this is positive. the enthalpy of formation of O is positive.

So, $h_{f,O}$ is obtained from this equation so that is positive basically. When you have to supply heat to break both the atoms, you will get O. Now, let us take some temperature, say 4000 Kelvin temperature line and try to get the value of h for O_2 and O. For example, here, this will be the h of O_2 at 4000 Kelvin, this is the value of enthalpy.

So, 0, enthalpy of formation plus sensible enthalpy. When the temperature rises from 298 Kelvin to 4000 this is the value here. So, this value I would take from this y axis and that will be the h for O_2 at 4000.

Similarly, what is Δh of O for example? So, Δh of O_2 so, this is nothing, but Δh of O_2 where temperature is at 4000 because h_f is 0. Now, if you take the value of absolute enthalpy or standard enthalpy for the O, you have enthalpy of formation.

This will be this adds up two things enthalpy of formation of O is like this here, enthalpy of formation of O plus the sensible enthalpy from this point, whatever be this value at 4000.

You have to add these two to get this h of O at 4000. So, even if we take standard, basic elements like O_2, N_2, H_2 and graphite, when they are at 298 Kelvin its enthalpy is referred like assigned a value of 0, but when they are heated up to higher temperatures, you get values of enthalpy. So, you have to add sensible enthalpy to that.

So, absolute enthalpy of species is the sum of the standard heat of formation and the sensible enthalpy when the temperature is different from 298, sensible enthalpy has to be added so, that is the thing here. For a particular species, you can take this. You have to refer tables or NIST database to extract these values and substitute in your calculations.