Basic Principles and Calculations in Chemical Engineering

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Lecture # 19
Standard Heat of Formation

Welcome to massive open online course on basic principles and calculations in chemical engineering. So, you are discussing about the energy and its arms hundred module 6. Now under this module, today we will discuss more about that energy and its forms and we will discuss how about the standard heat of formation.

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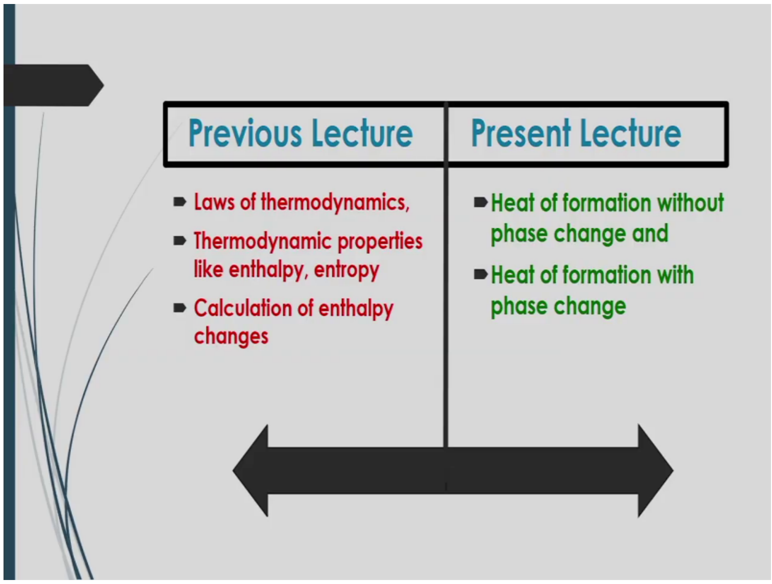

Previous Lecture	Present Lecture
Laws of thermodynamics, Thermodynamic properties like enthalpy, entropy Calculation of enthalpy changes	Heat of formation without phase change and Heat of formation with phase change

In the previous lecture we have law described laws of thermodynamics, in thermodynamic property is like enthalpy entropy and how to calculate that enthalpy change based on you know phase change as well as without phase change based on the material characteristics like specific heat of fluids particular you know temperatures and also specific heat capacity at a particular you know, pressure and you know constant volume.

So, we have discussed and also we have done some, you know, examples and based on who is how to calculate that, enthalpy changes and how this enthalpy changes can be assessed. So, in this case, we will discuss about that, heat of formation when there will be you know, certain you know, chemical reactions and during that reactions how heat will be you know, released or adsorbed and based on that release and absorption of that heat.

how you can calculate that enthalpy for the formation of particular compounds, they are in the reaction and also in necessarily occurring substance what should be that heat of formation that we will discuss here and also how that heat of formation can be calculated, if there is a change your phase of that particular components there in the mixture.

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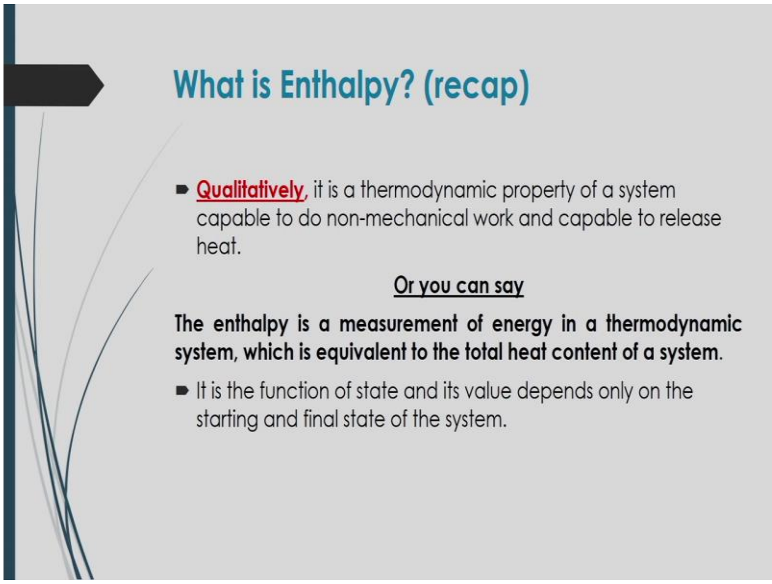

What is Enthalpy? (recap)

- **Qualitatively**, it is a thermodynamic property of a system capable to do non-mechanical work and capable to release heat.

Or you can say

The enthalpy is a measurement of energy in a thermodynamic system, which is equivalent to the total heat content of a system.

- It is the function of state and its value depends only on the starting and final state of the system.

So, before going to that, we have to go through again how that what is enthalpy we have already described about that enthalpy and what is the definition and we have actually narrated about that enthalpy that it can be you know, a you know property of the system, we should be capable to do non mechanical work and capable to release heat and it is generally a function of state and its value depends on you know, the starting end point I will state of the system.

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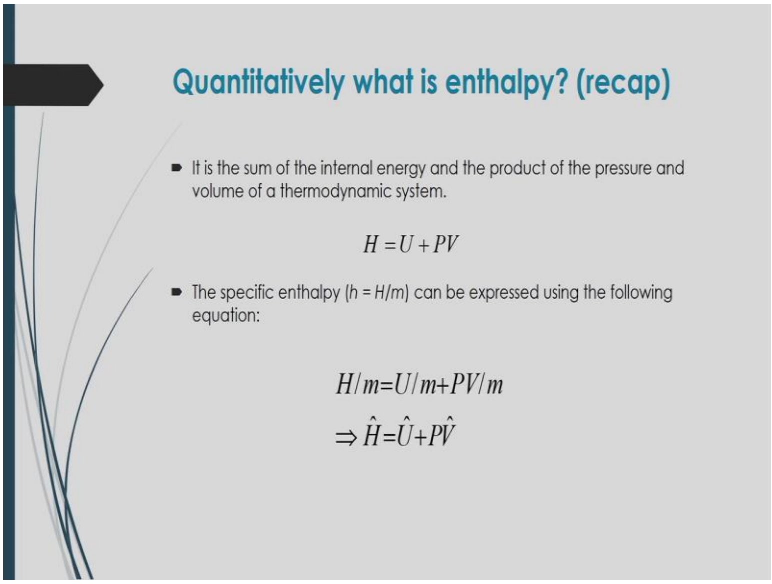

Quantitatively what is enthalpy? (recap)

- It is the sum of the internal energy and the product of the pressure and volume of a thermodynamic system.

$$H = U + PV$$

- The specific enthalpy ($h = H/m$) can be expressed using the following equation:

$$H/m = U/m + PV/m$$

$$\Rightarrow \hat{H} = \hat{U} + P\hat{V}$$

And quantitatively that enthalpy can be calculated based on the you know, what will be the internal you know energy change if any heat or work done by the system or on the system there and also what will be the, you know, through energies you know their change, because of that, if any work by shaft is done on the system or that system is doing some work on a particular fluid element and based on who is how that a flow energy will be changed and based on that internal energy change and flow energy change

How that enthalpy can be, you know, calculated or estimated that we have already given discussed in our previous lectures. They are and based on that enthalpy calculation also how to calculate that the specific enthalpy just you have to you know, divide that in therapy by each you know, moles or mass then you can get that specific enthalpy there.

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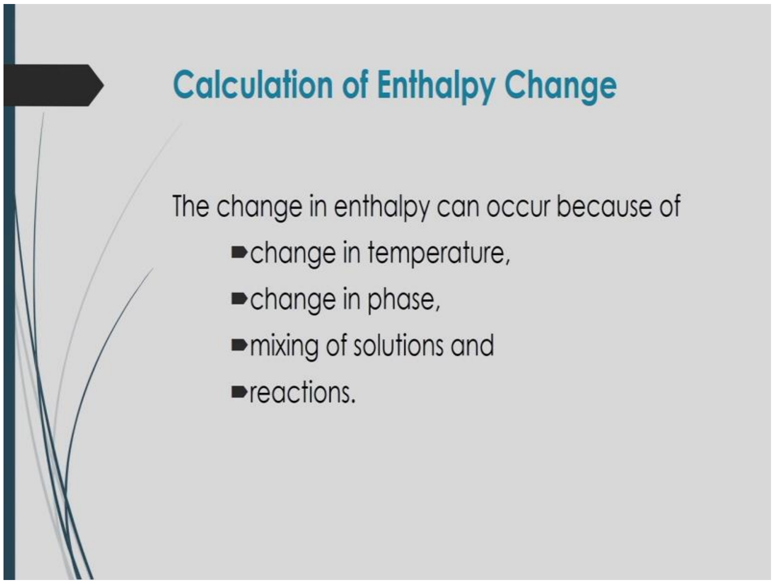

Calculation of Enthalpy Change

The change in enthalpy can occur because of

- change in temperature,
- change in phase,
- mixing of solutions and
- reactions.

And also we told that the change in enthalpy can occur because of that change in temperature, because, specific heat capacity depending on the temperature and also this entropy change can be resulted because of the change in phase and also how that solutions and their components are mixing with other components also, they are it depends on how what the amount of enthalpy is supplied or at least to the system also, the stage of enthalpy can be happened because of that have reactions to that.

So, we will discuss all those things, 1 by 1 already we have discussed that how enthalpy can be you know calculated if there is the temperature change and also how that enthalpy can be calculated, if there is a you know, phase changes. So, still we will discuss here about that.

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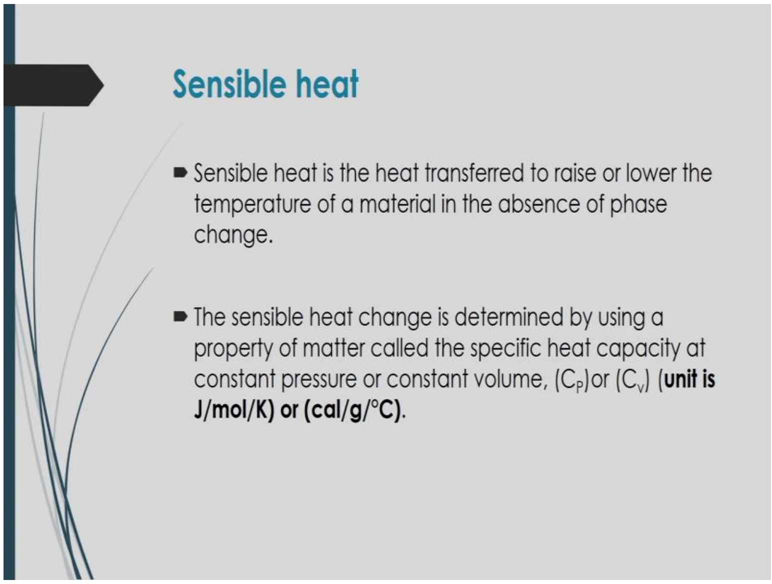

Sensible heat

- Sensible heat is the heat transferred to raise or lower the temperature of a material in the absence of phase change.
- The sensible heat change is determined by using a property of matter called the specific heat capacity at constant pressure or constant volume, (C_P)or (C_V) (**unit is J/mol/K) or (cal/g/°C)**.

Now, we have calculated that sensible heat because of that temperature difference and this is basically enthalpy change, because of that temperature. And when heat is transferred range or allow the temperature of a material in the absence of you know phase change then it will be regarded as sensible heat and, but it depends on that specific you know heat capacity of that material at a constant volume or a constant pressure and it is usually generally joule per mole power k.

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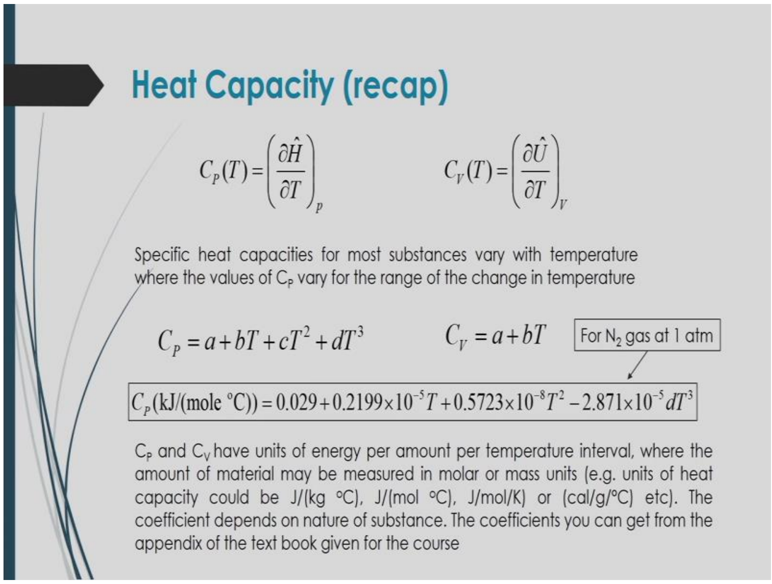

Heat Capacity (recap)

$$C_P(T)=\left(\frac{\partial\hat{H}}{\partial T}\right)_p \qquad C_V(T)=\left(\frac{\partial\hat{U}}{\partial T}\right)_V$$

Specific heat capacities for most substances vary with temperature where the values of C_P vary for the range of the change in temperature

$$C_P=a+bT+cT^2+dT^3 \qquad C_V=a+bT$$

For N_2 gas at 1 atm

$$\boxed{C_P(\text{kJ/(mole °C)})=0.029+0.2199\times10^{-5}T+0.5723\times10^{-8}T^2-2.871\times10^{-5}dT^3}$$

C_P and C_V have units of energy per amount per temperature interval, where the amount of material may be measured in molar or mass units (e.g. units of heat capacity could be J/(kg °C), J/(mol °C), J/mol/K) or (cal/g/°C) etc). The coefficient depends on nature of substance. The coefficients you can get from the appendix of the text book given for the course

And heat capacity of the material this is you know, are defined by that CP is equal to what is the change of entropy per unit change of temperature that will be called as you know, heat capacity and if it is done power unit molar mass, then it will be called a specific heat capacity as similarly, this specific heat capacity you know be assessed for constant temperature and constant pressure and also constant volume. Now, if there is no change of temperature of course, there will be no sensible heat there.

So, we can say that specific heat capacity cannot be changed it will be constant here so specific heat capacity for most substances generally varies with unit temperature values of CP value for the range of change in temperature there so, example is given for nitrogen gas at 1 atmosphere in the slides. These slides also earlier have shown that how specific heat capacity at constant pressure and constant volume depending on that temperature specific heat capacity at constant pressure depends on you know the temperature.

As you know Polynomial function but as specific heat capacity at constant volume actually shows the functionality of temperature as a linear function there.

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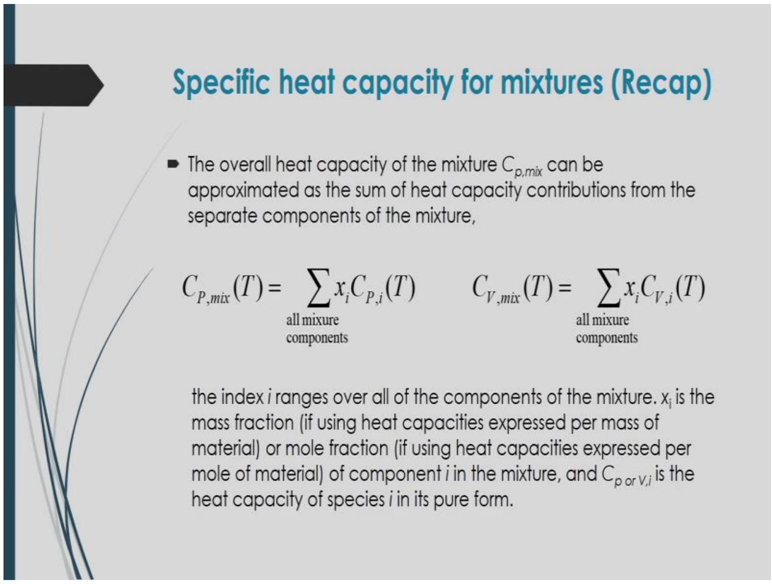

Specific heat capacity for mixtures (Recap)

- The overall heat capacity of the mixture $C_{p,mix}$ can be approximated as the sum of heat capacity contributions from the separate components of the mixture,

$$C_{P,mix}(T) = \sum_{\substack{\text{all mixure}\\ \text{components}}} x_i C_{P,i}(T) \qquad C_{V,mix}(T) = \sum_{\substack{\text{all mixure}\\ \text{components}}} x_i C_{V,i}(T)$$

the index *i* ranges over all of the components of the mixture. x_i is the mass fraction (if using heat capacities expressed per mass of material) or mole fraction (if using heat capacities expressed per mole of material) of component *i* in the mixture, and $C_{p\ or\ V,i}$ is the heat capacity of species *i* in its pure form.

And the specific heat capacity for the mixture we have also discuss about that it is actually depending on that, what is the you know volume fraction or more fraction of that components are present in the mixture. So, it depends on the smaller fraction or mass fraction of these components in the mixture and it can be calculated by you know, the product of that more fraction and the specific heat capacity of the pure substances there.

If there are more than 1 components of course, you will be there are more than 2 components then accordingly you have to you know first find out what truth does more fraction some aspects and then what the you know specific heat capacity for individual components simply by product of those you know variables and summing up you get that was specifically capacity of that mixture.

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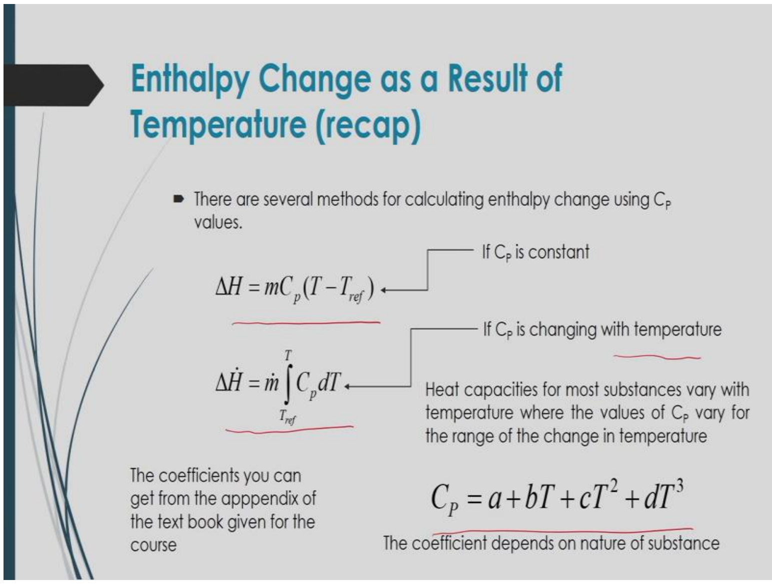

Enthalpy Change as a Result of Temperature (recap)

- There are several methods for calculating enthalpy change using C_P values.

$\Delta H = mC_p(T-T_{ref})$ ← If C_P is constant

$\Delta \dot{H} = \dot{m}\int_{T_{ref}}^{T} C_p dT$ ← If C_P is changing with temperature

Heat capacities for most substances vary with temperature where the values of C_P vary for the range of the change in temperature

$$C_p = a + bT + cT^2 + dT^3$$

The coefficient depends on nature of substance

The coefficients you can get from the apppendix of the text book given for the course

If you know that a specific heat capacity then you can calculate that proximate the enthalpy change. If you know that CP is constant that means specific heat capacity is constant then simply you can calculate that you know enthalpy change by this equation and if you are you know having the change of specific capacity with temperature then you have to you know calculate the enthalpy change.

Based on that integral form of that you know enthalpy just by multiplying molar flow rate or mass flow rate with this you know i integrated value of this you know specific capacity within a certain range of temperature that temperature range can be you know defined from the reference temperature to a certain temperature there. So, this reference temperature maybe you know that for standard from standard condition like it may be you know 30 degree Celsius.

And 1 atmospheric patient or you can take that reference temperature to 73.15 Kelvin or 0 degree Celsius there and the coefficients for that specific heat capacity which are expressed based on polynomial function is that is, depending on that measure of substances there.

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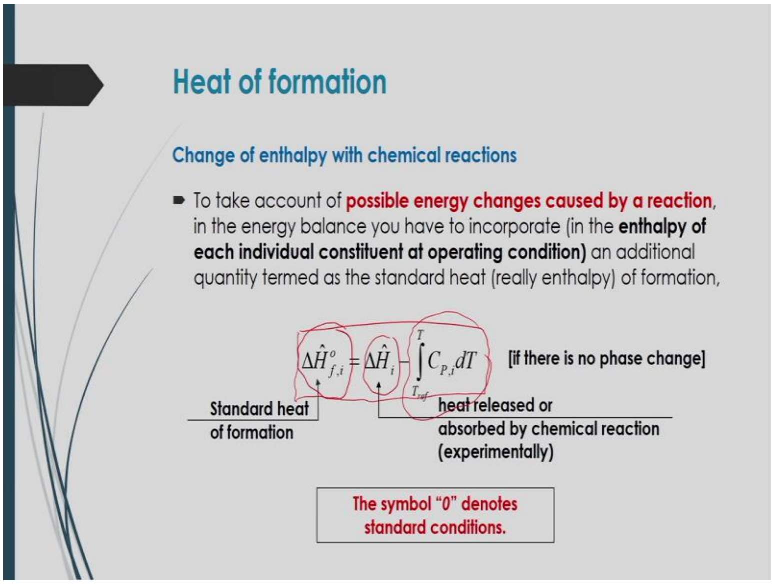

Heat of formation

Change of enthalpy with chemical reactions

- To take account of **possible energy changes caused by a reaction**, in the energy balance you have to incorporate (in the **enthalpy of each individual constituent at operating condition**) an additional quantity termed as the standard heat (really enthalpy) of formation,

$$\Delta\hat{H}^o_{f,i} = \Delta\hat{H}_i - \int_{T_{ref}}^{T} C_{P,i}\,dT$$

[if there is no phase change]

Standard heat of formation

heat released or absorbed by chemical reaction (experimentally)

The symbol "0" denotes standard conditions.

Main focus on this lecture is to you know, estimate the heat of formation they are now, change of enthalpy the chemical reactions if you are talking about that, there is a certain reaction happens there and that reaction is taking place between somewhere you know reactance and which will give you some products. So, in that case you will see that there will be certain changes of you know enthalpy during that reaction.

Now, that change of enthalpy or heat you can say that comes from sensitive heat or also diastral being contributed by you know that heat of formation of that individual components like here react incipit his reactions, then you have to you know considered that heat of formation for this you know, particular you know analyzes often tell people that chemical reactions.

Now, to take account of that possible energy changes caused by a reaction in the energy balance, the new half to incorporate in that enthalpy apiece individual constituent at operating condition and an additional quantity term does a standard heat of formation. So, you have to you know, add that the standard heat of formation with that sensible heat change with respect to temperature. There but to find out that total you know heat up reaction.

Now, how to you know find out that heat of formation of individual components are based on that you know, heat released or heat absorbed during that reaction once you know that amount of heat released or amount of heat absorbed by that reaction from that, you know, heat absorption or heat you know generation you can calculate that heat of permission of that individual constituent or components in the reaction mixture.

So, for that, you can define that heat of formation by this you know equation here your delta H fi at a standard condition that will be close to you know delta H i - you know sensible heat because of that temporary differences. So, this H f i 0 hat is basically the standard heat of formation at a standard condition like you know 298 degrees degree Kelvin and 1 atmospheric pressure and this delta H i is, you know, basically the heat released or absorbed by the chemical reaction that is obtain by experimentation.

And after getting these heat released or absorption by experiment, you have to subtract this sensible heat within a certain range of temperature there. So, after getting these you know, subtraction of this, you know sensible heat from the heat of reaction, you can regard it as a heat of formation of that particular constituents. Now, in this case, we are not considering that there is no phase change, so, within a certain phase that will be you know to be considered, but whenever phase change will be there, then you have to you know consider also that sensible heat for phase change their.

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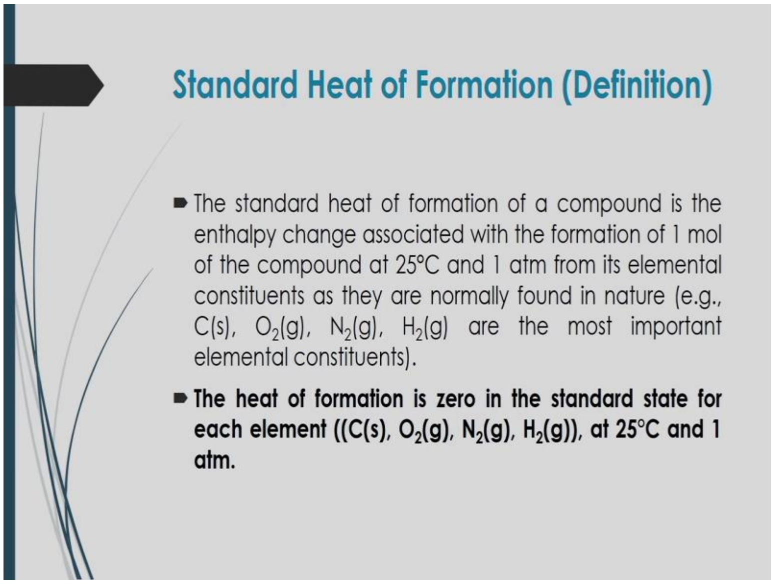

Standard Heat of Formation (Definition)

- The standard heat of formation of a compound is the enthalpy change associated with the formation of 1 mol of the compound at 25°C and 1 atm from its elemental constituents as they are normally found in nature (e.g., C(s), O_2(g), N_2(g), H_2(g) are the most important elemental constituents).
- **The heat of formation is zero in the standard state for each element ((C(s), O_2(g), N_2(g), H_2(g)), at 25°C and 1 atm.**

What is the definition of that heat of formation, standard heat of formation, the standard heat of formation of a compound is the enthalpy change that is associated to the formation of 1 mole of compound at 25 degrees Celsius and 1 atmosphere from its elemental constituents as they are normally found in itself like some compounds carbon, oxygen, nitrogen, hydrogen, they are actually necessarily occurring, you know, compounds are constituents you can say and these are elemental constituents.

So, in this case, all these you know compounds will have that standard heat up formation of you know, 0 because those who are necessarily you know, form that compounds, the heat release to be you know, 0 or permission of that components requiring that heat will be equal to 0. So, that is why you have to define that the standard heat of formation for a particular substance which are not actually necessarily occurring substances.

So, that can be obtained from that particular you know heat release or heat absorption by the reaction of that components with other you know, consequence there.

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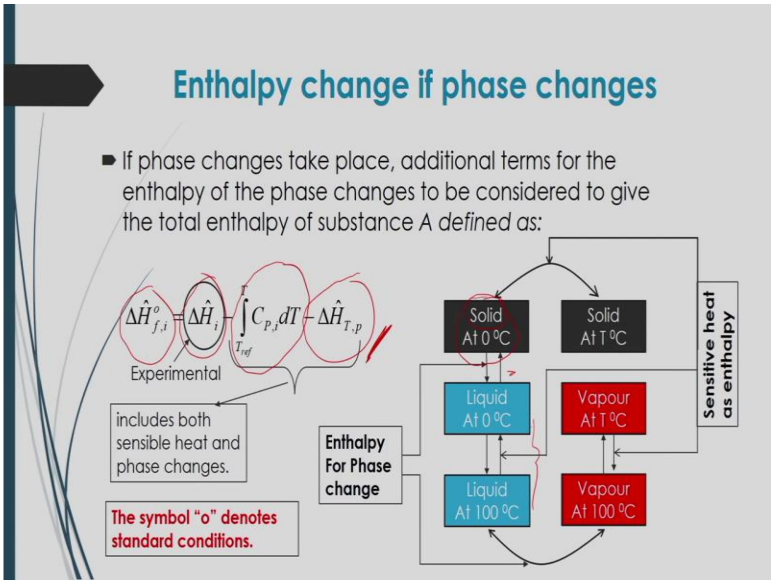

Enthalpy change if phase changes

- If phase changes take place, additional terms for the enthalpy of the phase changes to be considered to give the total enthalpy of substance A *defined as:*

$$\Delta\hat{H}^{o}_{f,i} = \Delta\hat{H}_{i} - \underbrace{\int_{T_{ref}}^{T} C_{P,i}\,dT - \Delta\hat{H}_{T,p}}$$

Experimental

includes both sensible heat and phase changes.

The symbol "o" denotes standard conditions.

So, enthalpy change of the phase change is there. So, in that case, you know that additional terms for the enthalpy of the piece changes to be considered to give the total enthalpy of the substance like here the heat of formation will be physical to here that is experimentally obtained heat released or absorption there and what should be the sensible heat that you have to subtract and also you have to subtract that for to be the enthalpy is change because about a phase change there.

So, this enthalpy change because of that phase change it will be difficult to here delta HTP we have actually discussed about that you know that phase change like you know from solid to liquid and then liquid to vapor there is a transition and for converting that certain moles of liquid to vapor or vapor to solid or even liquid to solid or solid to liquid and that transition heat release or heat requirement for that it is called you know that heat of you know phase change or a discord let it heat up you know certain phase change there.

If suppose all it is converting to you know liquid and it will be called us you know let it heat up, you know, phase change of solid to liquid and even liquid if it is converting to be part and it will be let it job vaporization there. So, in this way again we can say that whenever we are having these patients are during the formation of the compounds and also the reaction then you have to consider that heat of formation.

But just by you know subtracting that you know heat up subtracting that the heat of phase change from that heat of reaction as well as the subtraction of the sensible heat within a certain range of temperature from the heat of reaction there. So, here one you know that systematic you know that conversion of that or you can say that P change is shown here for you know solid to you know vapor how it is actually changing this case.

Generally solid that if we are considering water so, water actually becomes the solid when it is at 0 degree Celsius. Then solid, you know water at 0 degrees Celsius whenever it will be you know becoming to liquid generate that theoretically centigrade you have to you know apply some enthalpy or heat energy there, so, that it will become that you know solid to liquid just by melting. So, these you know converting this solid to liquid at that 0 degree Celsius it would be you know requiring some enthalpy or heat.

So, that heat will be called as let in heat of you know that melting there and similarly, that liquid whenever you know, changing his temperature from 0 degree Celsius to 100 degrees Celsius, then you will see there will be you know sensible heat scenes within this you know temperature range of 0 to 100 degrees Celsius and again at that you know 100 degree Celsius it will see that liquid will you know become vapor.

And during this conversion of these are liquid to vapor at 100 degrees Celsius, there will be some heat, you know required that heat requirement is called latent heat of vaporization. So, these are you know, transition another, you know enthalpy that is latent heat of you know melting or vaporization those are actually happened at a constant temperature there. So, this whenever phase changing will be there, there will be certain heat requirement.

Again, if you are hitting these from hundred degrees Celsius to you know certain temperature like T then there will be again that certain you know, heat, you know requirement and that heat requirement is called that sensible heat within temperature is a range of hundred degree Celsius to temperature T. Now, again you know that if you are converting this you know this vapor to again directly to solid you will see that there will be a latent heat of you know, solidification discord sublimation.

So, again there will be a huge amount of you know heat is required to you know convert this vapor to the solid at that temperature again solid temperature to temperature or to 0 degree Celsius there will be no releasing of heat there then there will be you know that again sensible you know latent heat or sensible heat is required from you know converting this solid at temperature T to 0 Celsius.

So, in this way there will be a cycle and to you know get this you know material so, solid to vapor and vapor to solid like this. So, are these are called that a phase change to this case, how many bargain will be required for to be the enthalpy change that you have to calculate.

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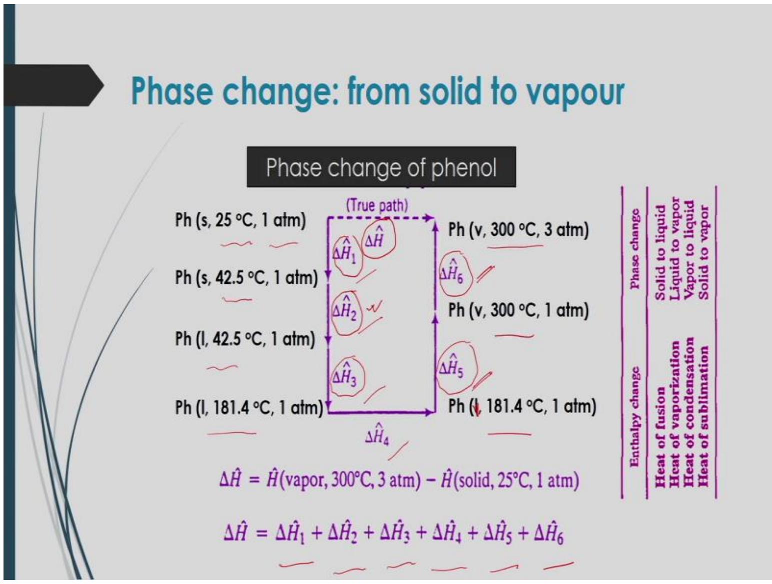

Phase change: from solid to vapour

Phase change of phenol

$$\Delta\hat{H} = \hat{H}(\text{vapor, 300°C, 3 atm}) - \hat{H}(\text{solid, 25°C, 1 atm})$$

$$\Delta\hat{H} = \Delta\hat{H}_1 + \Delta\hat{H}_2 + \Delta\hat{H}_3 + \Delta\hat{H}_4 + \Delta\hat{H}_5 + \Delta\hat{H}_6$$

Phase change	Enthalpy change
Solid to liquid	Heat of fusion
Liquid to vapor	Heat of vaporization
Vapor to liquid	Heat of condensation
Solid to vapor	Heat of sublimation

Now, let us have an example for phase change from solid to vapor for you know phenol. Now, phenol if we consider that at 25 degrees Celsius, you know, at 1 atmospheric pressure, this is a standard condition, this phenol if we you know heat it up to 42.5 degrees Celsius, you will see that this phenol will change its you know, will heat up because of that, you know, sensible heat there.

This phenol basically as a solid we can say that at 25 degrees Celsius and 1 atmosphere and if you heat it up to 42.5 degrees Celsius there will be a certain heat requirement or enthalpy requirement at that entropy requirement is called that you know, heat of you know, sensible to you know converting this material from this 25 degrees Celsius to 42.5 degree Celsius. So, here in this case, some heat is required to you know heated up from this, you know reference temperature to the certain temperature.

After that you will see that, at that fixed temperature of 42.5 degree Celsius at 1 atmospheric pressure, this solid phenol will become to liquid phenol in this case, becoming that solid to liquid at that constant temperature are some heat will be required. So, that heat is called you know latent heat of you know melting, so, this melting latent heat will be regarded Delta H2 here Similarly, at that 42.5 degrees Celsius, when about this solid phenol will be becoming liquid phenol and again it will be heated up to 181.24 degree Celsius.

And that liquid phase at atmospheric pressure for that, you will need some sensible heat opt in phase 3 and again at that particular you know a temperature of 181.4 degrees Celsius This is basically that boiling point of you know phenol. So, at this boiling point of phenol keeping this temperature constant you will see that this liquid will become vapor. So, at that particular temperature of 181.4 degrees Celsius without changing that temperature.

You have to you know supply some energy or it will require some you know energy as an enthalpy change and that entropy change it is called latent heat of vaporization of this phenol. And after that, if you know, want to you know, heat this vapor, you know, this vapor this panel up to you know 300 degrees Celsius, then there will be no some heat is required that is called sensible heat for this vaporization state from 181.4 degrees Celsius to 300 degrees Celsius.

Again at that 300 degrees Celsius if you want to you know, change this up bar up to a certain pressure then you will have you also required some you know enthalpy or supplier P2 there. So, for that, you know that that heat also to be you know, considered for that so totally from this solid phenolic 25 degrees Celsius to you know converted to vapor at 300 degrees Celsius at the atmosphere, there will be a total lie in therapy required a will to delta H 1 + delta H 2 + delta H 3 + delta is you know, 4 + delta is 5 and delta 6. So, total enthalpies declared like this.

Now, if you want to you know directly convert this you know solid phase to that web page hypothetically it will require total you know enthalpy delta So, delta H will be equal to summation of this, you know, ah delta H1 delta H2 delta H3 delta H4 delta H5 delta H6. So, in this way that you have to calculate the enthalpy change, worrying about any materials you know becoming vapor from its solid state or becoming you know solid from its vapor state.

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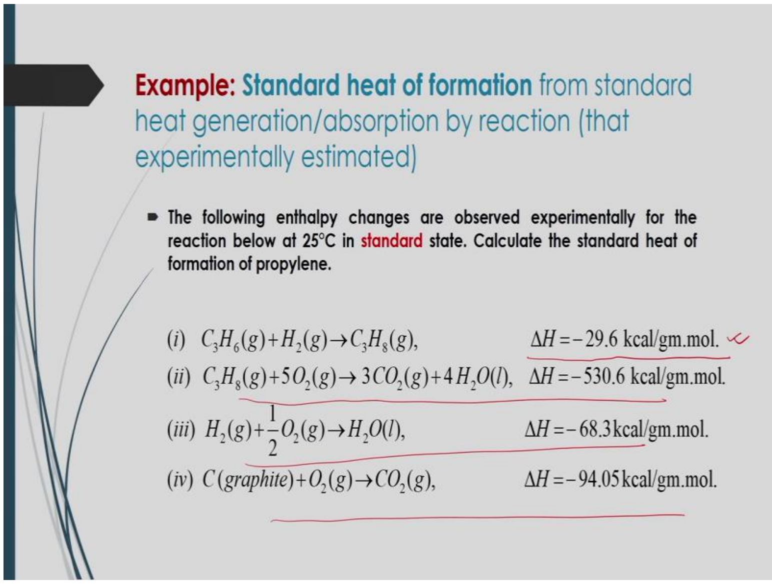

Example: Standard heat of formation from standard heat generation/absorption by reaction (that experimentally estimated)

- The following enthalpy changes are observed experimentally for the reaction below at 25°C in standard state. Calculate the standard heat of formation of propylene.

(i) $C_3H_6(g)+H_2(g)\rightarrow C_3H_8(g)$, $\Delta H=-29.6$ kcal/gm.mol.

(ii) $C_3H_8(g)+5O_2(g)\rightarrow 3CO_2(g)+4H_2O(l)$, $\Delta H=-530.6$ kcal/gm.mol.

(iii) $H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(l)$, $\Delta H=-68.3$ kcal/gm.mol.

(iv) $C(graphite)+O_2(g)\rightarrow CO_2(g)$, $\Delta H=-94.05$ kcal/gm.mol.

Let us do an example for this calculation of standard heat of formation from the standard heat up generation or absorption by reaction that is experimentally estimated. Now, here the following you know reactions, you know 1 to 4, there are some enthalpy changes during this section are observed experimentally at 25 degrees Celsius in a standard state in this case you have to calculate the standard heat of formation of you know this profiling there. So, here profiling is you know converting into you know 4 different components there as part reactions.

Respective reactions will released or absorb some you know that heat energy that is called enthalpy that enthalpy change is given for you know respective you know reactions here in the slides. See, so, from this enthalpy change that is experimentally obtained you have to find out that what should be the you know standard heat of formation from this for this you know profiling substance.

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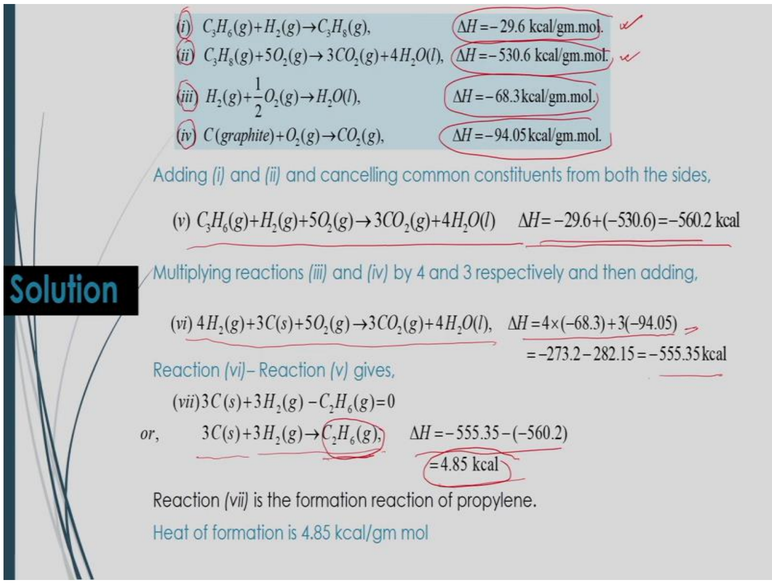

Solution

(i) $C_3H_6(g)+H_2(g)\rightarrow C_3H_8(g)$, $\Delta H=-29.6$ kcal/gm.mol. ✓

(ii) $C_3H_8(g)+5O_2(g)\rightarrow 3CO_2(g)+4H_2O(l)$, $\Delta H=-530.6$ kcal/gm.mol. ✓

(iii) $H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(l)$, $\Delta H=-68.3$ kcal/gm.mol.

(iv) $C(graphite)+O_2(g)\rightarrow CO_2(g)$, $\Delta H=-94.05$ kcal/gm.mol.

Adding *(i)* and *(ii)* and cancelling common constituents from both the sides,

(v) $C_3H_6(g)+H_2(g)+5O_2(g)\rightarrow 3CO_2(g)+4H_2O(l)$ $\Delta H=-29.6+(-530.6)=-560.2$ kcal

Multiplying reactions *(iii)* and *(iv)* by 4 and 3 respectively and then adding,

(vi) $4H_2(g)+3C(s)+5O_2(g)\rightarrow 3CO_2(g)+4H_2O(l)$, $\Delta H=4\times(-68.3)+3(-94.05)$

$=-273.2-282.15=-555.35$ kcal

Reaction *(vi)*– Reaction *(v)* gives,

(vii) $3C(s)+3H_2(g)-C_2H_6(g)=0$

or, $3C(s)+3H_2(g)\rightarrow C_2H_6(g)$, $\Delta H=-555.35-(-560.2)$

$=4.85$ kcal

Reaction *(vii)* is the formation reaction of propylene.

Heat of formation is 4.85 kcal/gm mol

Now, according to this reaction, we right we considered that reaction number 1 reaction number 2 reaction number 3 and reaction number 4 and respective you know that enthalpy of you know reaction or heat of reaction, it is there. Now, according to this law, basically we can get this heat of formation just by you know some adding or subtracting or manipulating like by multiplying subtraction or by addition of this, you know, equation and also corresponding you know enthalpies.

So, in this case if you add this equation number 1 and 2 and canceling the common constituents from both the sides, we can get this equation number 5 by you will see. So, accordingly that enthalpy also will come like it is here delta H will be coming as here, what is the you know the condition of 1 wins here is - 29.6 plus here - 530.6 kilo calorie per gram mole. So, in this way that enthalpy can be you know they are - 560 point 2 kilo calorie.

Now, if we multiply the reaction see and reaction 4 by 4 and 3 respectively and then adding then we can get this equation number 6 here. Now, in this case again that enthalpy correspondingly will be calculated by this you know equation and in this case you have to multiply the enthalpy of this you know say 3rd equation by 4 and the you know by fourth equation by you know 3 and then add it up you will get this final value of 555.25 kilocalorie.

And reaction 6 and reaction 5 if you subtract then it will you know, result this equation on 7 and finally, you know that respective you know that enthalpy change will be coming as like this 4.85 kilo calorie. So, in this case, this equation number seven is basically the formation of violin from this carbon and hydrogen. Now, this carbon and hydrogen are you know, that enthalpy changes, you know that. So, ultimately, what about enthalpy changes for you know that, you know profiling.

So, this profiling formation will, you know required this enthalpy change of 4.85 and that you know standard condition. So, that is why this amount of 4.85 you know kilocalorie for the formation of phenol you know profiling will be regarded as standard heat of formation for this profiling and heat of formation here is you know 4.85 kilo calorie per gram mole and it is a positive so, it is basically you know that endothermic reaction.

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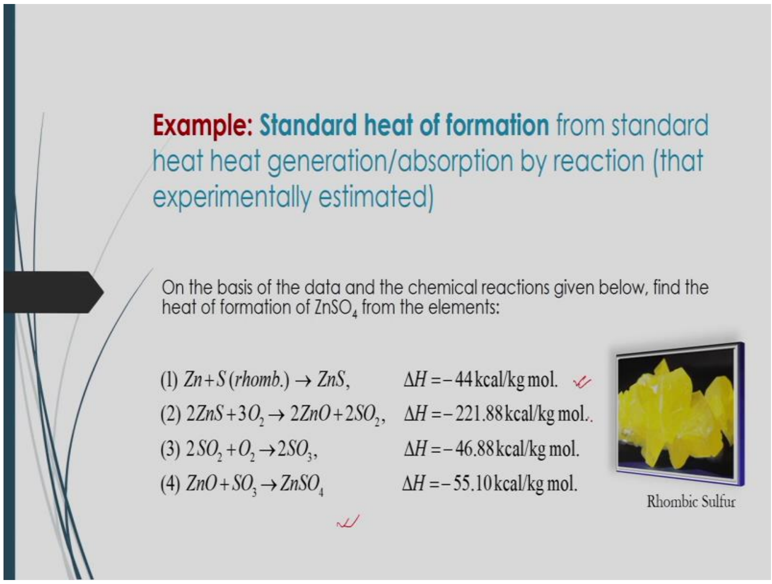

Example: Standard heat of formation from standard heat heat generation/absorption by reaction (that experimentally estimated)

On the basis of the data and the chemical reactions given below, find the heat of formation of $ZnSO_4$ from the elements:

(1) $Zn + S(rhomb.) \rightarrow ZnS,$ $\Delta H = -44\,\text{kcal/kg mol.}$ ✓

(2) $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2,$ $\Delta H = -221.88\,\text{kcal/kg mol.}$

(3) $2SO_2 + O_2 \rightarrow 2SO_3,$ $\Delta H = -46.88\,\text{kcal/kg mol.}$

(4) $ZnO + SO_3 \rightarrow ZnSO_4$ $\Delta H = -55.10\,\text{kcal/kg mol.}$

✓

Rhombic Sulfur

Similarly, another example you can you know do for calculation of standard heat of formation from standard heat generation or absorption by reaction that experimentally estimated now, in this case, an example like on the basis of data and the chemical reactions given below here in the slides and the heat of formation of zinc sulfate from the element exactly the same way what about we have done.

the previous example, we can do we can calculate that you know heat standard heat of formation for this formation of gene south, but there in this case again these 4 reactions are given and respective you know enthalpy you know phase change or this reactions are given here.

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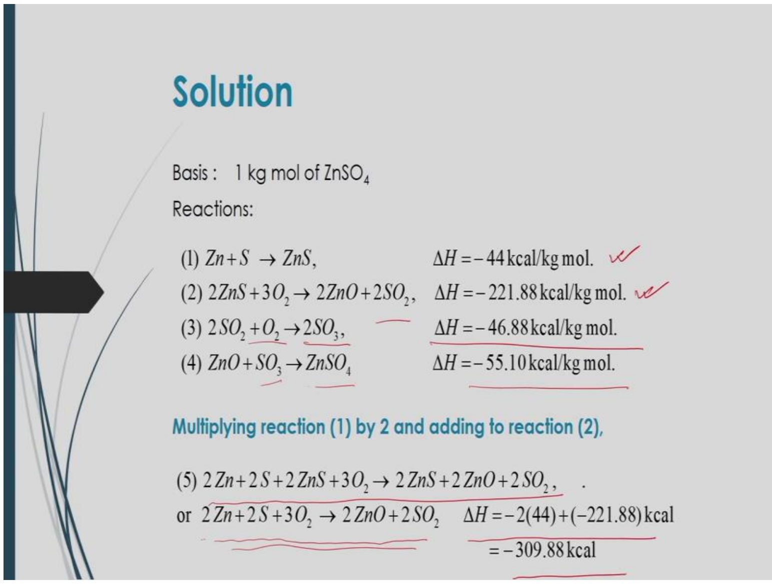

Solution

Basis : 1 kg mol of $ZnSO_4$

Reactions:

(1) $Zn + S \rightarrow ZnS,$ $\Delta H = -44\,\text{kcal/kg mol.}$

(2) $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2,$ $\Delta H = -221.88\,\text{kcal/kg mol.}$

(3) $2SO_2 + O_2 \rightarrow 2SO_3,$ $\Delta H = -46.88\,\text{kcal/kg mol.}$

(4) $ZnO + SO_3 \rightarrow ZnSO_4$ $\Delta H = -55.10\,\text{kcal/kg mol.}$

Multiplying reaction (1) by 2 and adding to reaction (2),

(5) $2Zn + 2S + 2ZnS + 3O_2 \rightarrow 2ZnS + 2ZnO + 2SO_2,$

or $2Zn + 2S + 3O_2 \rightarrow 2ZnO + 2SO_2$ $\Delta H = -2(44) + (-221.88)\,\text{kcal}$

$= -309.88\,\text{kcal}$

And in this case again solution can be you know, obtain based on that some inabilities are these reactions as well as you know enthalpies respective enthalpies and adding or subtracting then we can get that perspective of value of that heat of formation. Now, let us do that here first reaction is zinc + sulfate that will give you the zinc sulfate and zinc sulfide then, it fluid up you know enthalpy of that reaction is this given here.

Even second reactions in south by to lag in time reactive oxygen it will give you a zinc oxide and sulfur dioxide and he talked our reaction is - 2.1 .88 kilo calorie per kg mole and this produced sulfur dioxide again will react to toxins and it will give you the sulfur trioxide and then heat reactions is will be you know that 46.8 kilo calorie per kg mole and then again this zinc oxide will be reacting with this sulfur trioxide which will give you that zinc sulfate by releasing that heat of you know 55.10 kilo calorie per kg mole.

Now, multiplying this reaction 1 by 2 and adding to the reaction to will this you know the action of this here and finally, after you know canceling the terms and the right hand side and left hand side, we can express this equation as zinc + sulfur + oxygen that will give you a zinc oxide +

Dark side and then you can get this you know enthalpy of after adding these enthalpy accordingly, you know there. So it will be coming as - 309.88 kilocalorie.

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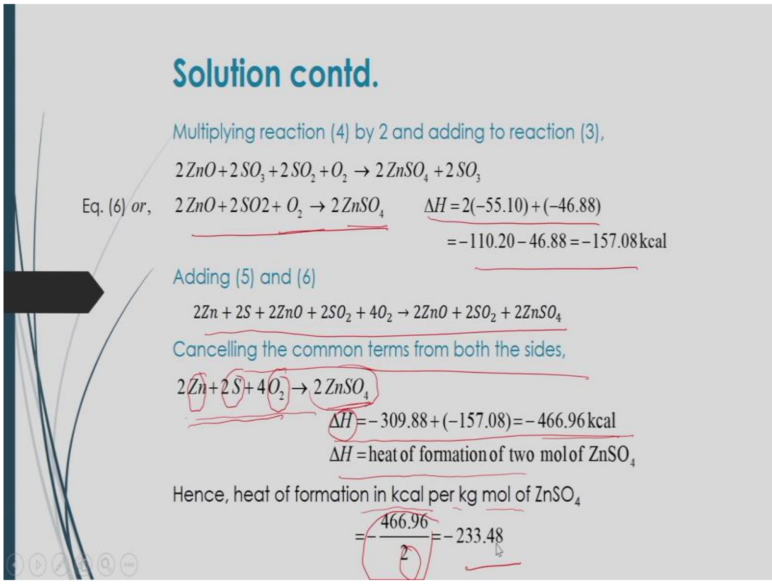

Solution contd.

Multiplying reaction (4) by 2 and adding to reaction (3),

$$2ZnO + 2SO_3 + 2SO_2 + O_2 \rightarrow 2ZnSO_4 + 2SO_3$$

Eq. (6) or, $2ZnO + 2SO2 + O_2 \rightarrow 2ZnSO_4$ $\Delta H = 2(-55.10) + (-46.88)$

$$= -110.20 - 46.88 = -157.08\,\text{kcal}$$

Adding (5) and (6)

$$2Zn + 2S + 2ZnO + 2SO_2 + 4O_2 \rightarrow 2ZnO + 2SO_2 + 2ZnSO_4$$

Cancelling the common terms from both the sides,

$$2Zn + 2S + 4O_2 \rightarrow 2ZnSO_4$$

$$\Delta H = -309.88 + (-157.08) = -466.96\,\text{kcal}$$

ΔH = heat of formation of two mol of $ZnSO_4$

Hence, heat of formation in kcal per kg mol of $ZnSO_4$

$$= -\frac{466.96}{2} = -233.48$$

Now again multiplying the reaction 4 by 2 and adding to reaction 3, we can get this final enthalpy as - 157.08. In this case, the reactions are, you know zinc oxide + SO 2 and + oxygen that will give you that zinc sulfate. Again, if we consider this reaction as you know equation number 6 then adding equation 5 and 6, we can represent this equation like this and canceling the common terms from both sides we can get this zinc + sulfur + oxygen that will give using sulfate there.

Now in this case this zinc is unnecessarily occurring substance sulfur is naturally occurring oscine and also that Nestle offering compound. So, in this case the centerpiece also zero. So, ultimately what happened this zinc sulfate will form that formation of these things help it will give you that heat of formation standard heat of formation of the thing celebrated that standard condition. So, this can be finally, calculated based on this you know his law of the summation of this enthalpy here from this equation from the enthalpy of you know equation of you know 5 and 6 there.

So, this delta S is basically heat of formation of 2 mole of zinc sulfate, since it is produced to more often self at their hands heat of formation in kg more kilo calorie per kg mole off you know zinc sulfate can be often just by dividing this enthalpy by 2 then you can get this up finally - 233 point 3.8. So, in this way you can easily calculate what from the standard heat of formation of a particular substance.

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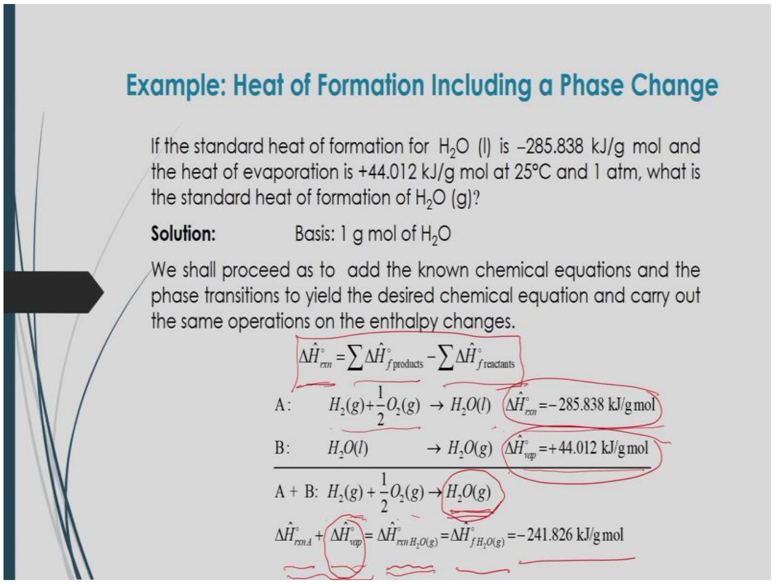

Example: Heat of Formation Including a Phase Change

If the standard heat of formation for H_2O (l) is −285.838 kJ/g mol and the heat of evaporation is +44.012 kJ/g mol at 25°C and 1 atm, what is the standard heat of formation of H_2O (g)?

Solution: Basis: 1 g mol of H_2O

We shall proceed as to add the known chemical equations and the phase transitions to yield the desired chemical equation and carry out the same operations on the enthalpy changes.

$$\Delta\hat{H}^{\circ}_{rxn} = \sum \Delta\hat{H}^{\circ}_{f\,\text{products}} - \sum \Delta\hat{H}^{\circ}_{f\,\text{reactants}}$$

$$\text{A:} \quad H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta\hat{H}^{\circ}_{rxn} = -285.838 \text{ kJ/g mol}$$

$$\text{B:} \quad H_2O(l) \rightarrow H_2O(g) \quad \Delta\hat{H}^{\circ}_{vap} = +44.012 \text{ kJ/g mol}$$

$$\text{A + B:} \quad H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$$

$$\Delta\hat{H}^{\circ}_{rxn\,A} + \Delta\hat{H}^{\circ}_{vap} = \Delta\hat{H}^{\circ}_{rxn\,H_2O(g)} = \Delta\hat{H}^{\circ}_{f\,H_2O(g)} = -241.826 \text{ kJ/g mol}$$

How to calculate that heat of formation including a phase change, let us consider this like, if the standard heat of formation for you know that water liquid is - 285.838 kilo joule per gram mole and the heat of evaporation is 44.012 kilo joules per gram all at 25 degrees Celsius and 1 atmosphere then what is the standard heat of formation of you know, water gas as a gas. So, in this case, first considered that 1 gram mole of water.

In this case we can proceed is as to add the unknown, you know chemical equations and the phase transition to yield the desired chemical equation and K out the same operation on the enthalpy changes. So, in this case standard heat of reaction can be, you know, defined as submission of a standard heat of formation of the products and also, you know, subtracting the summation of the seat of formation of the reactants by this equation as given in the slide.

Now, in this case if we consider that reaction A has here, hydrogen + oxygen that will give you that water just by releasing that heat of reaction as you know - 285 point 838 kilo per gram old at its standard condition. And again, this liquid water height will become that gas was water just by changing its pace. And in that case, latent heat of vaporization at that standard condition is

44.012 kilojoules per gram mole, then we can you know edit up these 2 equations and finally, we can have this you know hydrogen + oxygen that will be due to, you know, water, but that water will be in the vapor stage.

So, finally, we can calculate what should be the standard heat up, you know, reaction for these. So, we can get this standard heat up reaction for this component A and also for this you can see that standard heat of vaporization they are now in this case standard heat up reaction for this component A here reaction A that will be equal to extended heat of reaction for this you know this water formation.

And also you can see that that can be obtained you know that that that you have to add the heat up let me to bear for addition they are then totally you will get this total amount you know, heat up, you know, reaction for this formation of gash was water molecule. So, this is basically the formation of you know gaseous water molecule at this, you know a standard condition. So, this is basically opt in by this enthalpy or enthalpy of the reaction and until we have this vaporization.

Which is called latent heat of vaporization finally, you can get it by just summing up these 2, you can get this - 240 1.826 kilo joule per gram mole.

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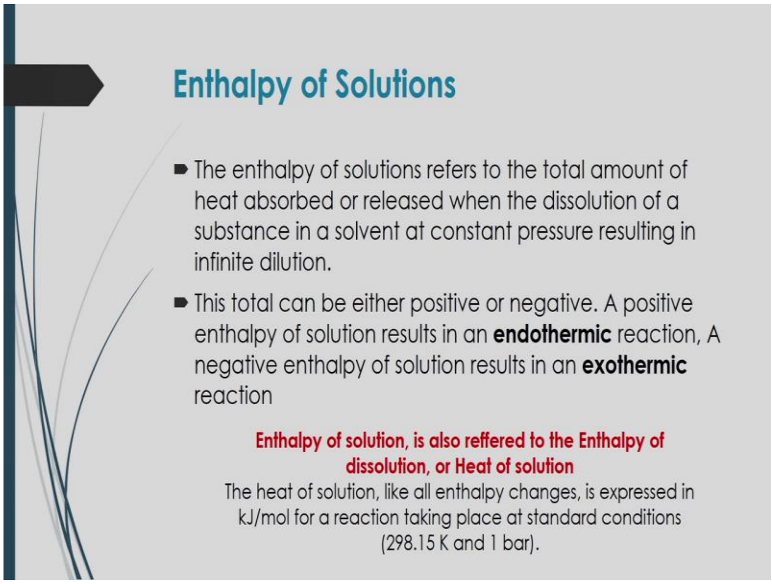

Enthalpy of Solutions

- The enthalpy of solutions refers to the total amount of heat absorbed or released when the dissolution of a substance in a solvent at constant pressure resulting in infinite dilution.
- This total can be either positive or negative. A positive enthalpy of solution results in an **endothermic** reaction, A negative enthalpy of solution results in an **exothermic** reaction

Enthalpy of solution, is also reffered to the Enthalpy of dissolution, or Heat of solution

The heat of solution, like all enthalpy changes, is expressed in kJ/mol for a reaction taking place at standard conditions (298.15 K and 1 bar).

Now, let us consider another thing that enthalpy of solution how to calculate it. Now, the enthalpy of solutions refers to the total amount of heat that is absorbed or released, when the dissolution of a substance in a, you know, solvent at constant pressure that will result in in finite or you know dilution. Now, this total enthalpy can be either Positive or negative, and if there is a positive enthalpy of solution results.

Then you can see that we are endothermic reaction, if there is a negative enthalpy of solution results, then you can see that could be exothermic reaction, sometimes you will see that in therapy of solution is, you know referred to the enthalpy of the solution or heat up solution. Now, this heat of solution like all enthalpy changes is expressed in kilojoules per mole or a reaction that is taking place at standard condition there.

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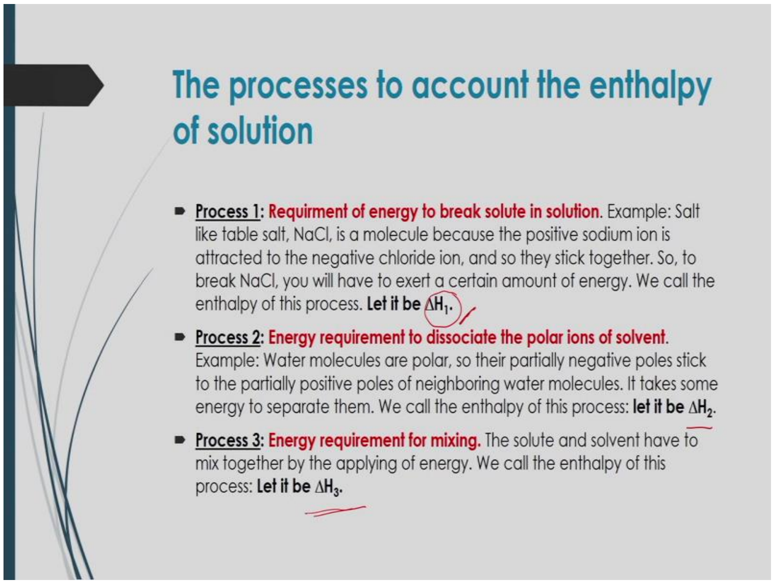

The processes to account the enthalpy of solution

- **Process 1**: **Requirment of energy to break solute in solution.** Example: Salt like table salt, NaCl, is a molecule because the positive sodium ion is attracted to the negative chloride ion, and so they stick together. So, to break NaCl, you will have to exert a certain amount of energy. We call the enthalpy of this process. **Let it be ΔH_1.**
- **Process 2**: **Energy requirement to dissociate the polar ions of solvent.** Example: Water molecules are polar, so their partially negative poles stick to the partially positive poles of neighboring water molecules. It takes some energy to separate them. We call the enthalpy of this process: **let it be ΔH_2.**
- **Process 3**: **Energy requirement for mixing.** The solute and solvent have to mix together by the applying of energy. We call the enthalpy of this process: **Let it be ΔH_3.**

Now, there are you know, different processes actually considered to you know, estimate that enthalpy of solution, there are 3 processes basically happened if there is suppose any salivate are dissolving in a water solution. So, in this case, like sodium fluoride suppose sodium fluoride is you know dissolving in water. So, in that case what are the you know process involves there to get this solution.

Now, that solution sometimes some heat will be required to break the solute in the solution. So, that will be called as process 1 and for the you know breaking up of solute in this case like salt like cable salt, sodium chloride is a molecule in this case because the positive sodium ion is attracted to the negative chloride ion at its you know molecular form and for that if you were the eristic together.

And so, to break that sodium chloride in the solution, you will have to exert a certain amount of energy that energy is called that enthalpy of this process 1 and it is let it be delta H 1. Similarly, the solution you will see that portable solvent being used in this case let it be water. So, you will see that there will be you know that dissociation of the, you know, polar ends of that solvent happens and poured that some energy is required.

So, water molecules are partially that having negative poles that is stick to that partially positive pulls of neighboring water molecules there. So, it takes some energy to separate them. So, we call them in therapy of this process like you know hydrogen and hydroxyl ion there. So, there will be you know, some energy requirement to be suited to dissociate that polar is there again whenever solution to be made, there will be some certain mixing of that solute and solvent.

So, to you know mix that you know; solute and solvent to there will be a certain energy requirement for that mixing. So, for that also have to consider that enthalpy contribution to that entropy of the solution. So, energy requirement for mixing that case a solute and solvent have to mix together by applying some energy. So, we call that in therapy for this process little bit little tasty. So, there are 3 you know enthalpy changes are there.

when is that the enthalpy change for the breaking up of you know, salute in the solution and in therapy change for the you know, dissociation of polar ions of the solvent, that is that delta H 2 and energy requirement for the mixing of solid and salute and let it be delta H3. So, summation of these are you know 3 contribution of you know enthalpy will give you know enthalpy of solution.

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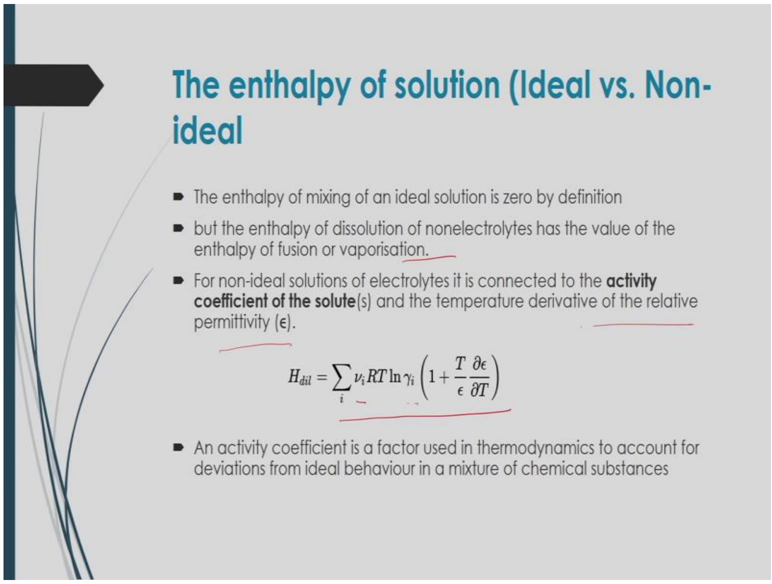

The enthalpy of solution (Ideal vs. Non-ideal

- The enthalpy of mixing of an ideal solution is zero by definition
- but the enthalpy of dissolution of nonelectrolytes has the value of the enthalpy of fusion or vaporisation.
- For non-ideal solutions of electrolytes it is connected to the **activity coefficient of the solute**(s) and the temperature derivative of the relative permittivity (ϵ).

$$H_{dil} = \sum_i \nu_i RT \ln \gamma_i \left(1 + \frac{T}{\epsilon}\frac{\partial \epsilon}{\partial T}\right)$$

- An activity coefficient is a factor used in thermodynamics to account for deviations from ideal behaviour in a mixture of chemical substances

Even the enthalpy of solution that may be you know different for ideal and non-ideal solution that the enthalpy of mixing up an ideal solution basically is zero by definition, but the enthalpy of the solution of non-electrolytes has been you know has the value of the enthalpy of fusion or vaporization or non-ideal solution of electrolytes which is connected to the activity coefficient of the solute and also this you know that breaking up the you know, molecules you know molecules of solvent and solids also.

And the temperature sometimes you know derivative of the relative permittivity up to have the solution there. So, in that case that you know that enthalpy of that total dilution of that you know non ideal solution can be defined by this equation here in this case, you is called activity coefficients and gamma i is basically the surface tension of that particular components and then, here if aslant basically the relative permittivity of that, you know, components there.

So, this is basically change with respect to temperature. So, any activity coefficient is a factor which will actually change that you know enthalpy of that you know valued solution. The activity coefficient is a factor used in thermodynamics to account that deviations from the ideal behavior in a mixture of chemical substance.

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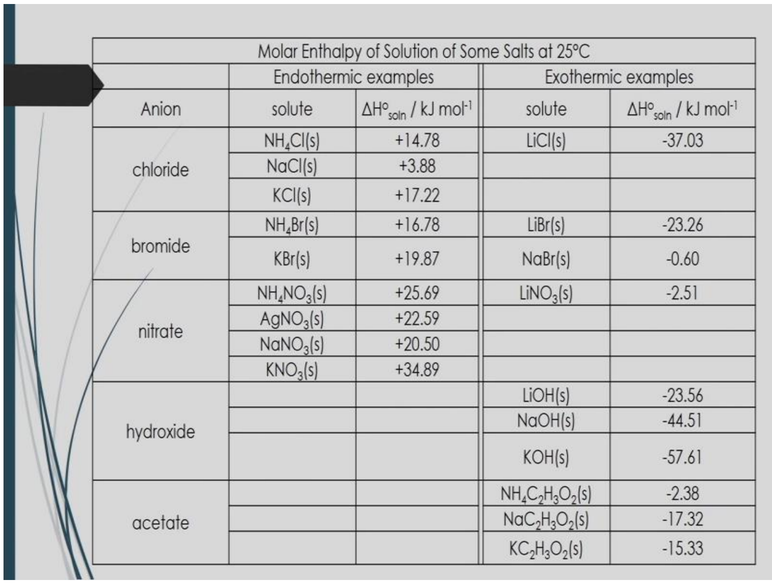

Molar Enthalpy of Solution of Some Salts at 25°C

	Endothermic examples		Exothermic examples	
Anion	solute	ΔH°_{soln} / kJ mol^{-1}	solute	ΔH°_{soln} / kJ mol^{-1}
chloride	$NH_4Cl(s)$	+14.78	$LiCl(s)$	-37.03
	$NaCl(s)$	+3.88		
	$KCl(s)$	+17.22		
bromide	$NH_4Br(s)$	+16.78	$LiBr(s)$	-23.26
	$KBr(s)$	+19.87	$NaBr(s)$	-0.60
nitrate	$NH_4NO_3(s)$	+25.69	$LiNO_3(s)$	-2.51
	$AgNO_3(s)$	+22.59		
	$NaNO_3(s)$	+20.50		
	$KNO_3(s)$	+34.89		
hydroxide			$LiOH(s)$	-23.56
			$NaOH(s)$	-44.51
			$KOH(s)$	-57.61
acetate			$NH_4C_2H_3O_2(s)$	-2.38
			$NaC_2H_3O_2(s)$	-17.32
			$KC_2H_3O_2(s)$	-15.33

And here in this tables, there are some salts at 25 degree Celsius how they are molar enthalpy of the solution, when they will be you know dissolve in water it changing these are given here.

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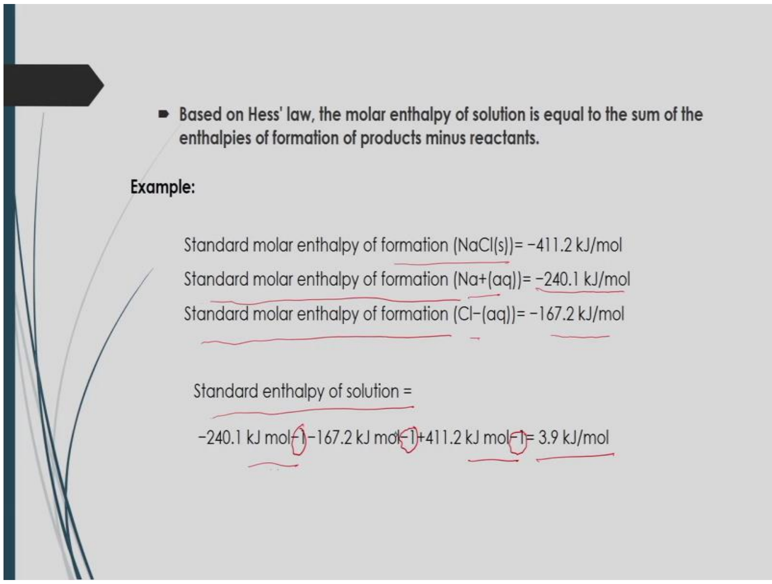

- **Based on Hess' law, the molar enthalpy of solution is equal to the sum of the enthalpies of formation of products minus reactants.**

Example:

Standard molar enthalpy of formation (NaCl(s))= −411.2 kJ/mol

Standard molar enthalpy of formation (Na+(aq))= −240.1 kJ/mol

Standard molar enthalpy of formation (Cl−(aq))= −167.2 kJ/mol

Standard enthalpy of solution =

$-240.1\ \text{kJ mol}^{-1} - 167.2\ \text{kJ mol}^{-1} + 411.2\ \text{kJ mol}^{-1} = 3.9\ \text{kJ/mol}$

And based on Hess' law you will see that mala interpret the solution is equal to the sum of the centerpiece of formation of products the act and that already given example, they are like standard molar enthalpy of formation of sodium chloride to be you know that - 411.2 kilojoules per mole and steady molar enthalpy of formation of sodium ion for the dissociation that will be– 240.1 kilojoules per mole or a standard molar enthalpy of formation for that chloride down, it is - 167.2 kilo per mole.

So, according to that his law that the standard enthalpy of solution to be equal to - 240.1 kilojoules per mole -167.2 kilojoules per mole + 411. 2 kilojoules per mole that will be able to 3.9 kilojoules per mole, here this is - 1 is actually superscripts this - 1 is superficially per mole here. So this is correct here this will be you know, molar per mole here kilojoules per mole this i.

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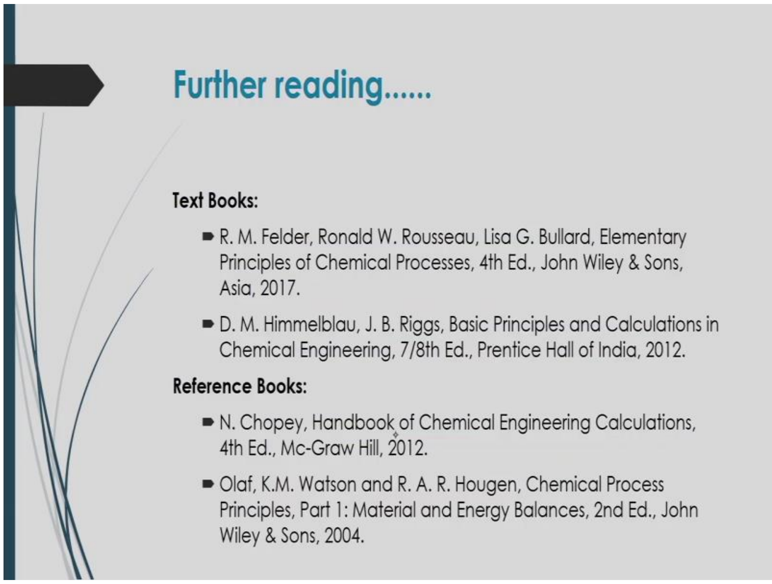

Further reading......

Text Books:

- R. M. Felder, Ronald W. Rousseau, Lisa G. Bullard, Elementary Principles of Chemical Processes, 4th Ed., John Wiley & Sons, Asia, 2017.
- D. M. Himmelblau, J. B. Riggs, Basic Principles and Calculations in Chemical Engineering, 7/8th Ed., Prentice Hall of India, 2012.

Reference Books:

- N. Chopey, Handbook of Chemical Engineering Calculations, 4th Ed., Mc-Graw Hill, 2012.
- Olaf, K.M. Watson and R. A. R. Hougen, Chemical Process Principles, Part 1: Material and Energy Balances, 2nd Ed., John Wiley & Sons, 2004.

So, we have so discuss that how heat of formation can we calculated from the heat of reaction and also how heat of past and that heat of formation can be, you know, calculated from the you know phase changing and also heat up solution how to calculate based on their mechanism of dissociation and mixing and also you can say breakup of salivate solution. So, I would suggest you to go further about this standard heat of formation with some other examples also from this textbook and practice it.

And in the next lecture, we will try to discuss you know, that, about that energy balance, like how to do that mechanical energy balance and also, other you know, energy balance is based on the actions there So thank you for you are kind attention.