Basic Principles and Calculations in Chemical Engineering
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Lecture - 24
Energy Balance with Heat of Reaction

Welcome to massive open online course on Basic Principles and Calculations in Chemical Engineering. We are discussing about that basic principles based on material balance and energy balance equation.

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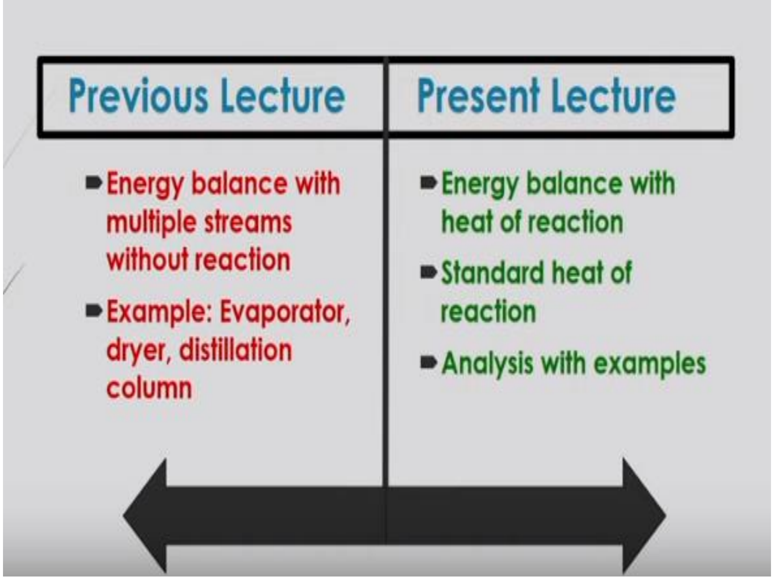

Previous Lecture

- Energy balance with multiple streams without reaction
- Example: Evaporator, dryer, distillation column

Present Lecture

- Energy balance with heat of reaction
- Standard heat of reaction
- Analysis with examples

So in the previous lecture we have discussed about the energy balances with multiple streams without reactions and also the analysis of this energy balance equation based on the examples on evaporator, drier, distillation column, etc. So in this lecture we will try to again discuss about that energy balance with heat of reaction.

So in this lecture, we will discuss the heat of formation, standard heat of reaction and also how to analyze those standard heat of reaction based on the heat of formation and also with some examples.

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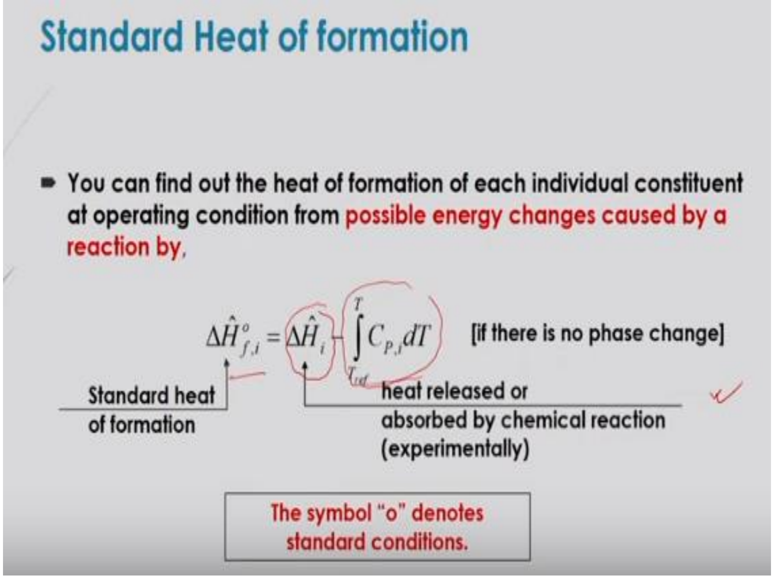

Standard Heat of formation

- You can find out the heat of formation of each individual constituent at operating condition from possible energy changes caused by a reaction by,

$$\Delta\hat{H}^{o}_{f,i} = \Delta\hat{H}_{i} + \int_{T_{ref}}^{T} C_{p,i}\,dT$$ [if there is no phase change]

Standard heat of formation

heat released or absorbed by chemical reaction (experimentally)

The symbol "o" denotes standard conditions.

Now you have to know what is that standard heat of formation because one of the important you know aspect of energy balance when reactions will be involving in a particular process. So for that you have to know that, how that chemical compounds to be formed and during that formation, what will be the energy released or what will be the energy you know are required to form that particular you know compound.

Now that will be actually regarded as standard heat of formation and here standard means that is at a you know standard temperature and pressure what will be the heat is actually required to form that particular compound it is called standard heat of formation. Now this standard heat of formation you can actually estimate based on the you know enthalpy or energy required for a particular reaction.

And by which that you know reaction is carried out and in that case the heat of formation of you know each individual constituent that take part for that reaction at a particular operating condition. If you know that enthalpy released or energy changes caused by that reaction, then you can find out what should be the you know, formation of that particular you know condition like, if it is at a standard temperature and pressure then it will be called as standard condition.

So at that standard condition, what will be the you know energy required to form that particular constituents which are actually taking place, which are actually participate for that particular reaction. If I consider that there will be a certain change of enthalpy due to the temperature change. So that will be regarded as sensible heat.

So if you know that sensible heat for that particular enthalpy change and if you know that you know heat of reaction for that particular you know reaction then from that heat of reaction if you subtract that you know sensible heat, you will get that you know heat of formation of that constituent. So here in this slide it is shown that here that heat of formation of any constituent which will be denoted by that delta H f i 0 hat.

Here see that this hat is basically that specific you know heat formation and 0 here denotes the standard condition, f for formation, i for you know constituents or you know that species there.

So delta H hat 0 f i, it is basically that standard heat of formation of a constituent i but at the specific you know condition that is a standard condition and also at specific you know terms like per unit mass or per unit mole what should be that you know energy required or energy released for that formation of that constituent. Now this delta H i, if I consider that the you know it is the heat released or absorbed by that chemical reaction there.

Then we can have this standard heat of formation just by subtracting this you know enthalpy change or you can say that sensible heat change by the change of temperature from its you know standard condition if is there. Then you have to subtract this. So from this subtraction of this you know energy from this heat of reaction, you can easily calculate what will be the heat of formation there.

So to find out that heat of formation basically you need first to you know allow reaction and then measure the that heat of reaction that is released. That should be find out experimentally. So from that experimental value, then you can find out what should be the heat of formation by this equation. And in this case, if you are changing, you are seeing that, that is there any phase change there, then you have to include all that enthalpy change because of that phase change.

So that is heat of you know vaporization, heat of sublimation, heat of you know melting. So all those terms to be included also if there is a phase change there. If there is no phase change then you have to easily you know omit those terms there.

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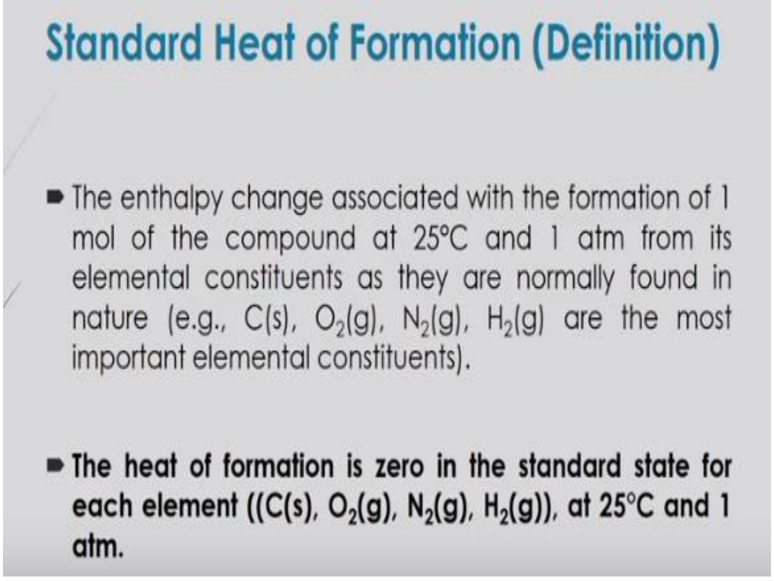

Standard Heat of Formation (Definition)

- 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.**

Now, basically how you will define that standard heat of formation. So it is basically defined as the enthalpy changes, which is associated with the formation of one mole of the compound at 25 degrees Celsius and one atmospheric condition. This is called standard condition from its element constituents as they are normally found in nature like you know carbon, oxygen, nitrogen, hydrogen.

They are you know most important element constituents which are naturally occurred. Now the heat of formations to be you know zero in this standard state for each element of this carbon, oxygen, nitrogen hydrogen at 25 degrees Celsius and one atmosphere. So which constituents are naturally occurring substituents or constituents those you know heat of formation to be regarded as 0.

Whereas if any chemical compound is formed based on some other element then you have to you know consider what should be the heat of formation for that particular compound. We will do some example for this understanding.

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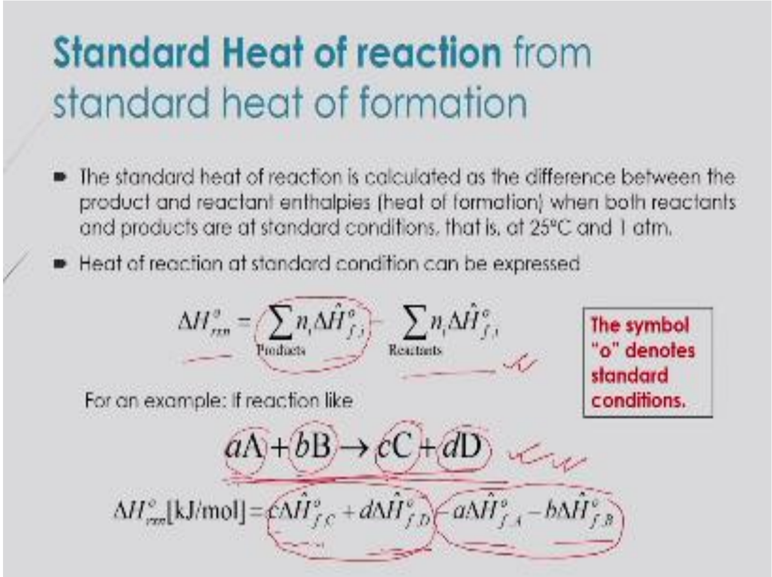

Standard Heat of reaction from standard heat of formation

- The standard heat of reaction is calculated as the difference between the product and reactant enthalpies (heat of formation) when both reactants and products are at standard conditions, that is, at 25°C and 1 atm.
- Heat of reaction at standard condition can be expressed

$$\Delta H^o_{rxn} = \sum_{Products} n_i \Delta\hat{H}^o_{f,i} - \sum_{Reactants} n_i \Delta\hat{H}^o_{f,i}$$

The symbol "o" denotes standard conditions.

For an example: If reaction like

$$aA + bB \rightarrow cC + dD$$

$$\Delta H^o_{rxn}[\mathrm{kJ/mol}] = c\Delta\hat{H}^o_{f,C} + d\Delta\hat{H}^o_{f,D} - a\Delta\hat{H}^o_{f,A} - b\Delta\hat{H}^o_{f,B}$$

Now before going to that, also you have to know at a standard condition, what should be the heat of reaction and how to estimate that heat of reaction from the standard heat of formation there. The standard heat of reaction is calculated as the difference between the product and reactants enthalpies or you can say that heat of formation when both reactants and products are at a standard conditions.

That is at 25 degrees Celsius and one atmosphere. Now suppose, there is a reaction like here aA +bB which will give you the products of C and D. With this you know that stoichiometric coefficient as shown, you know the reaction equation here in the slide. So in this case, you can find out the heat of reaction at this standard condition by this explanation here given in the slide like here delta H rxn 0.

This is basically that enthalpy change or you can say that heat of reaction at a standard condition, zero means here standard and rxn means reaction. So delta H rxn 0 this is basically standard heat of reaction. And this can be calculated based on the difference of total heat of formation of the products and the total heat of formation for the reactants.

So total heat of formation for the products can be you know calculated by this you know terms here. This is basically a summation of all heat of formation of the products components. Now here n i is the number of ith components in the products and here H f i. This is basically the heat of formation for that ith component. So in the products if there are n number of components there.

So we can have this you know total you know heat of formation just by multiplying this you know standard heat of formation of each components by the number of that components there. And similarly, you can get that total enthalpy of formation just by you know multiplying that heat of formation that is specific heat of formation with the number of moles in reactants.

Now, if we consider this reaction equation where you will see that the reactants are A and B as given here in the slide and products are C and D. Whereas they are you know stoichiometric coefficients are aA, B, C and D. Now in this case, you will see that heat of reaction for this reaction, it will be as you know number of moles for products here C and D for C and D respectively here.

Then we can calculate the heat of formation for the c as c into delta H f c. This will give you the heat of formation for this component c. Similarly, heat of formation for the component d in the products that will be your d into delta H f d and then you have to subtract this enthalpy you know enthalpy of that reactants a and b as per this a into delta H f 0 minus delta H f 0 b here.

So what these up to this here, this is the you know total enthalpy of formation for this products and this is basically the you know total enthalpy for you know that you know reactants for the formation at that standard condition. So just by subtracting this total heat of formation of the reactants from the products, you can get that heat of reaction at standard condition.

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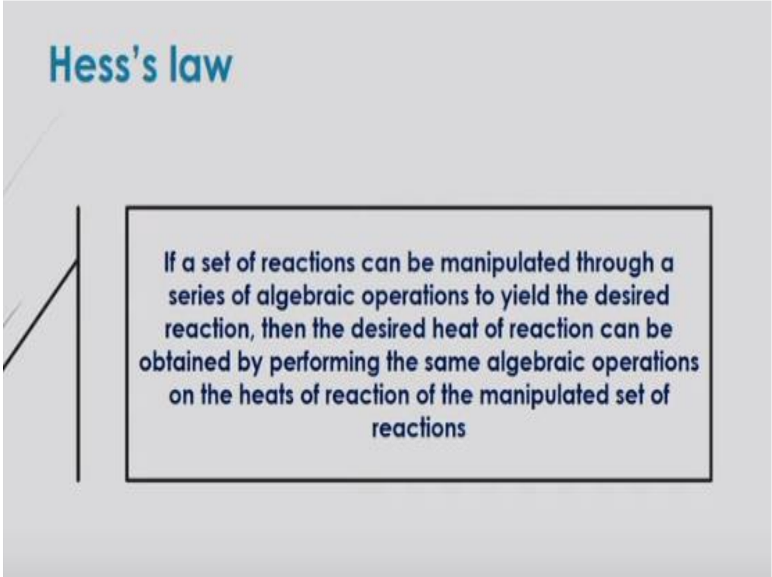

Hess's law

If a set of reactions can be manipulated through a series of algebraic operations to yield the desired reaction, then the desired heat of reaction can be obtained by performing the same algebraic operations on the heats of reaction of the manipulated set of reactions

In this regard if you have more than one reaction, then you have to apply you know Hess laws. According to Hess law, it is basically if a set of reactions can be manipulated through a series of algebraic operations, which will give you the desired reaction, then the desired heat of reaction accordingly can be obtained by performing the same algebraic operations on the heats of reaction of the manipulated set of reactions.

That means here if you have more than one reactions like reaction one, reaction two, reaction three, reaction four like this. And if you are having the respective heat of reactions, like heat of reaction one, heat of reaction two, heat of reaction three, heat of reaction four and so on.

Then, you can find out the you know the total or desired heat of reaction just by performing just by manipulating by the heat of reaction by subtracting those or either one from another one in this way. So this is called Hess law.

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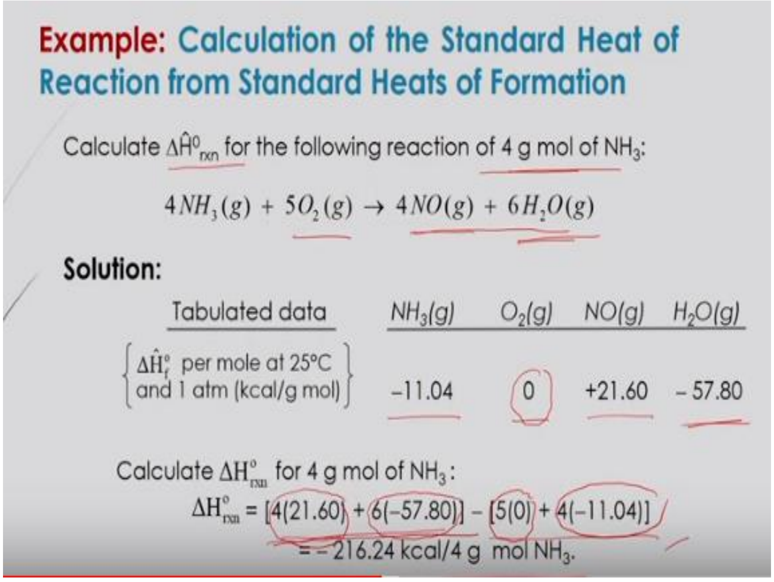

Example: Calculation of the Standard Heat of Reaction from Standard Heats of Formation

Calculate $\Delta\hat{H}^0_{rxn}$ for the following reaction of 4 g mol of NH_3:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Solution:

Tabulated data	$NH_3(g)$	$O_2(g)$	$NO(g)$	$H_2O(g)$
$\left\{\Delta\hat{H}^\circ_f$ per mole at 25°C and 1 atm (kcal/g mol)$\right\}$	−11.04	0	+21.60	− 57.80

Calculate ΔH°_{rxn} for 4 g mol of NH_3:

$$\Delta H^\circ_{rxn} = [4(21.60) + 6(-57.80)] - [5(0) + 4(-11.04)]$$
$$= -216.24 \text{ kcal/4 g mol } NH_3.$$

Let us do an example first giving only one reaction. This is not Hess law as per that from the standard heat of reaction how to calculate the standard heat of reaction. In this example, it is given calculate here the standard heat of reaction for the following reaction given where this reaction ammonia is reacting with oxygen which will give you that you know nitrous oxide with water.

Now in this 4 gram mole of ammonia is participating to react with oxygen to give the production of nitrous oxide and you know that water. In this case, heat of formation at standard condition in kilocalorie per gram mole is given as for ammonia -11.04, for oxygen it is given 0, for nitrous oxide it is given 21.60 and for you know water it is given -57.80.

Now as for you know that heat of reaction according to that principles of finding out the heat of reaction from the heat of formation. So we can find out what should be the heat of you know formation for this product side. It is basically here since the product side is nitrous oxide and water. So here 4 moles of nitrous oxide that will require, that will you know require that heat of formation is you know per mole it is 21.60.

So for 4 moles it will be 4 into 21.60. Similarly, for you know that for water, it is given per mole that heat of formation is -57.80. Then what should be the total heat of formation for six moles of water it will be 6 into -57.80. This is for simply you know product side. Similarly, in the reactant side this you know ammonia, 4 moles of ammonia there since it is naturally occurring.

So we can say that since oxygen is as naturally occurring so for that the heat of formation for naturally occurring you know compound it will be zero. So we can say right here 5 into 0 that will be your heat of formation for this oxygen. Whereas for ammonia, 4 moles of the ammonia, heat of formation will be is equal to 4 into -11.04 as per mole of ammonia formation, it is required -11.04 you know kilocalorie heat.

So after simplification, we can say that the heat of reaction just by subtracting this you know product side to the reactant side. So here we can get this amount minus 216.24 kilocalorie per 4 gram mole of ammonia. So in this way we can calculate the standard heat of reaction from the standard heat of formation.

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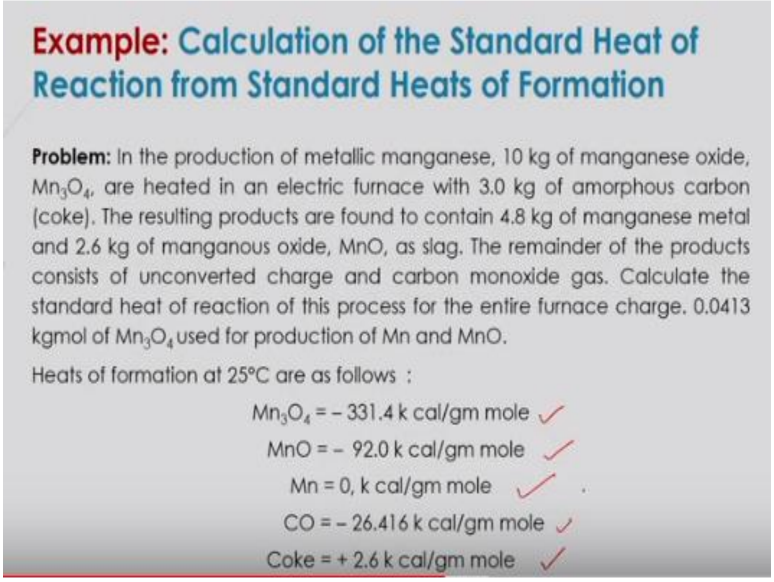

Example: Calculation of the Standard Heat of Reaction from Standard Heats of Formation

Problem: In the production of metallic manganese, 10 kg of manganese oxide, Mn_3O_4, are heated in an electric furnace with 3.0 kg of amorphous carbon (coke). The resulting products are found to contain 4.8 kg of manganese metal and 2.6 kg of manganous oxide, MnO, as slag. The remainder of the products consists of unconverted charge and carbon monoxide gas. Calculate the standard heat of reaction of this process for the entire furnace charge. 0.0413 kgmol of Mn_3O_4 used for production of Mn and MnO.

Heats of formation at 25°C are as follows :

Mn_3O_4 = – 331.4 k cal/gm mole ✓
MnO = – 92.0 k cal/gm mole ✓
Mn = 0, k cal/gm mole ✓
CO = – 26.416 k cal/gm mole ✓
Coke = + 2.6 k cal/gm mole ✓

Let us do another example here to calculate the standard heat of reaction from the standard heats of formation. Now in this case, if you consider that if production of metallic manganese that 10 kg of manganese oxide are heated in an electric furnace with 3 kg of amorphous carbon that is coke. In this case, it will give you the results as a products which will contain 4.8 kg of manganese metal and 2.6 kg of manganese oxide as a slack.

The remainder you know of that products consists of here unconverted charge of that you know manganese and carbon monoxide gas which is actually produced during that you know heating or there is a you know combustion of that manganese oxide with that carbon. Then carbon will be you know producing carbon monoxide which will be inoxidized based on that oxidation process in the furnace.

And then, according to this problem at a standard you know condition there you will see that what should be the standard heat of reaction of this process for the entire you know furnace charge you have to calculate. In this case it is given that 0.0413 kg mole of manganese oxide used for the production of one mole of manganese and one mole of manganese oxide.

As a data we can say that heats of formations at standard conditions are required. It is given here the standard heat of formation for this manganese oxide it is given -331.4 kilocalorie per gram mole. Similarly, other you know heat of formations for manganese oxide, manganese, carbon monoxide and coke are given here in the slides.

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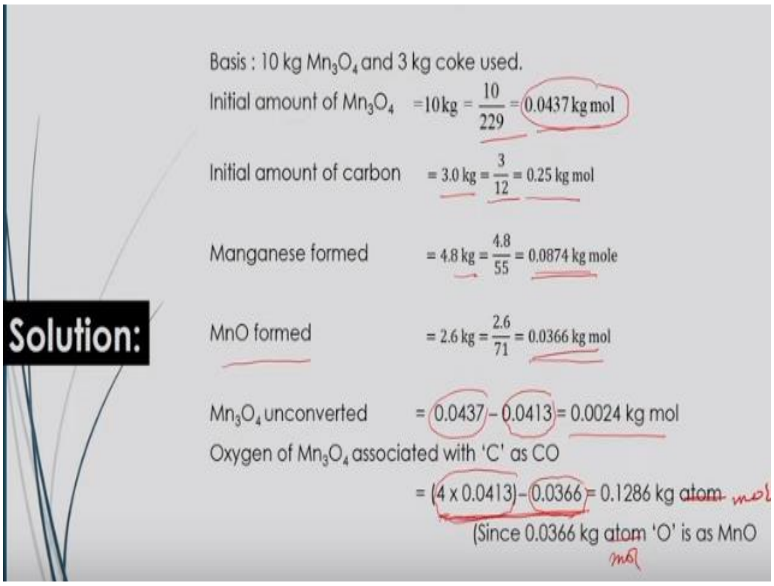

Solution:

Basis : 10 kg Mn_3O_4 and 3 kg coke used.

Initial amount of Mn_3O_4 $= 10\text{kg} = \frac{10}{229} = 0.0437 \text{ kg mol}$

Initial amount of carbon $= 3.0 \text{ kg} = \frac{3}{12} = 0.25 \text{ kg mol}$

Manganese formed $= 4.8 \text{ kg} = \frac{4.8}{55} = 0.0874 \text{ kg mole}$

MnO formed $= 2.6 \text{ kg} = \frac{2.6}{71} = 0.0366 \text{ kg mol}$

Mn_3O_4 unconverted $= 0.0437 - 0.0413 = 0.0024$ kg mol

Oxygen of Mn_3O_4 associated with 'C' as CO

$= (4 \times 0.0413) - 0.0366 = 0.1286$ kg ~~atom~~ mol

(Since 0.0366 kg ~~atom~~ mol 'O' is as MnO

And based on this heat of formation of all those you know components you have to you know calculate what should be the heat of reaction for this whole processes. Now, in this case basis we can consider that since here 10 kg of manganese oxide and 3 kg coke is used for this production of different components of you know that manganese, manganese oxide, even carbon monoxide there.

So you have to first you know convert this you know in unit which will be consistent in all cases. Now since it is given in terms of you know mole here in this case for heats of formation at standard condition, but your charge is given in kg so you have to convert it to moles first. So, initial amount of manganese oxide in you know it is given in kg that is 10 kg it is given. So you have to convert it to moles or kg moles just by dividing this 10 kg by its molecular weight. So it is coming as 0.0437 kg mole. Initial amount of carbon it is 3 kg.

Then after conversion or it will be 0.25 kg mole just by dividing its molecular weight and then manganese formed it is 4.8 kg. You will get 0.0874 kg mole just by dividing its molecular weight. Similarly manganese oxide formed it will be 0.036 kg mole. Now these are the you know components which are formed from this manganese oxide.

You will see that there will be no hundred percent conversion of this manganese oxide. There will be some unconverted manganese oxide to be remained in that furnace. So what is that unconverted manganese oxide? Since this you know one mole of manganese and manganese oxide formed you know has like this here, this amount and this amount, that is 0.0874 and 0.036 mole there.

So for that, this 0.0413 kg moles of manganese oxide is required. Whereas, the manganese oxide supplied as here 0.0437 kg mole. So what will be the unconverted manganese oxide there? Just subtracting it you will get that 0.0024 kg mole. Now, for this oxygen of this manganese oxide which is associated with that carbon to give you that carbon monoxide which will be coming out from that furnace can be calculated by this what will be that?

That that will be you know 4 into 0.0413 here. Here 4 means here 4 moles of oxygen is required for that one mole of you know that manganese oxide conversion and then you can say that 4 into 0.0413 and then minus here what will be the you know manganese oxide form and here from that you can subtract this amount then what will be the you know oxygen for that manganese oxide actually is required to you know oxidize that carbon to carbon monoxide.

So here please correct it here 0.1286 kg it will be kg mole and since the you know that 0.0366 kg you know mole of oxygen is as manganese oxide. So we can say that this amount will be subtracted from this total amount of you know that manganese oxide and remaining amount will be you know used for conversion of carbon to carbon monoxide.

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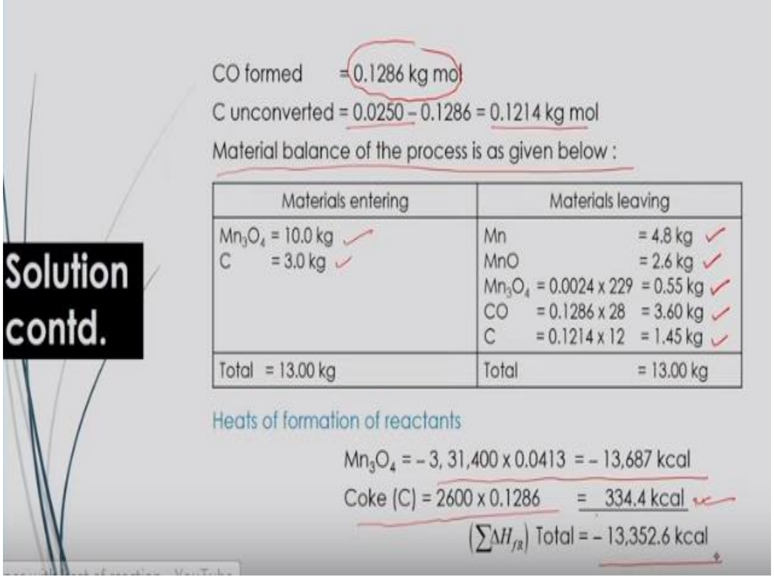

Solution contd.

CO formed = 0.1286 kg mol

C unconverted = 0.0250 – 0.1286 = 0.1214 kg mol

Material balance of the process is as given below :

Materials entering	Materials leaving
Mn_3O_4 = 10.0 kg ✓ C = 3.0 kg ✓	Mn = 4.8 kg ✓ MnO = 2.6 kg ✓ Mn_3O_4 = 0.0024 x 229 = 0.55 kg ✓ CO = 0.1286 x 28 = 3.60 kg ✓ C = 0.1214 x 12 = 1.45 kg ✓
Total = 13.00 kg	Total = 13.00 kg

Heats of formation of reactants

Mn_3O_4 = – 3, 31,400 x 0.0413 = – 13,687 kcal

Coke (C) = 2600 x 0.1286 = 334.4 kcal

$(\sum \Delta H_{fR})$ Total = – 13,352.6 kcal

Carbon monoxide form that will be is equal to then 0.1286 kg mole based on that amount of oxidized oxygen and carbon and converted it will be simply subtracting this you know conversion of carbon monoxide to that you know supplied carbon there. So it will be you know 0.1214 kg mole.

Now as per that material balance of the process we can write this amount of you know material is supplied or entering to that furnace, that is manganese oxide 10 kg, carbon is 3 kg. Whereas materials that are leaving it will be as manganese is 4.8 kg, manganese oxide 2.6 kg, manganese oxide here you know 0.55 kg, carbon monoxide 3.60 kg whereas carbon will be 1.45.

So this will be leaving from that furnace or you can say these are you know at the outlet stream of that process unit. Now heats of formation of that reactants simply here what will be that, manganese oxide. This is your heat of formation of this reactant of manganese oxide and similarly heat of formation of this coke it will be you know this amount.

So total heat of formation for this you know reactants it will be your -13.352 sorry 13352.6 kilocalorie.

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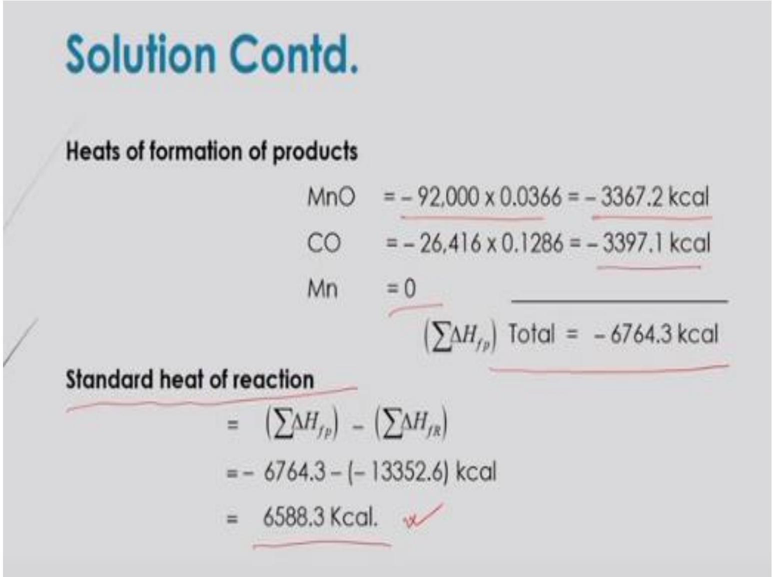

Solution Contd.

Heats of formation of products

MnO = – 92,000 x 0.0366 = – 3367.2 kcal
CO = – 26,416 x 0.1286 = – 3397.1 kcal
Mn = 0
$(\sum \Delta H_{fp})$ Total = – 6764.3 kcal

Standard heat of reaction

$= (\sum \Delta H_{fP}) - (\sum \Delta H_{fR})$
$= -6764.3 - (-13352.6)$ kcal
$=$ 6588.3 Kcal.

And heats of formation of that production then this manganese oxide it will be you know 3367.2 kilocalorie and then carbon monoxide it will be you know that 3397.1 kilocalorie and manganese is zero. So finally, total heat of formation for this product side it will be -6764.3 kilocalorie.

Now as per that you know equation of that standard heat of reaction from that heat of formation of that products and reactants, you can get this value of 6588.3 kilocalorie after substitution of the values of that, you know heater formation for the products and the reactants there. So in this way you can calculate you know heat of reaction from the heat of formation of the constituents.

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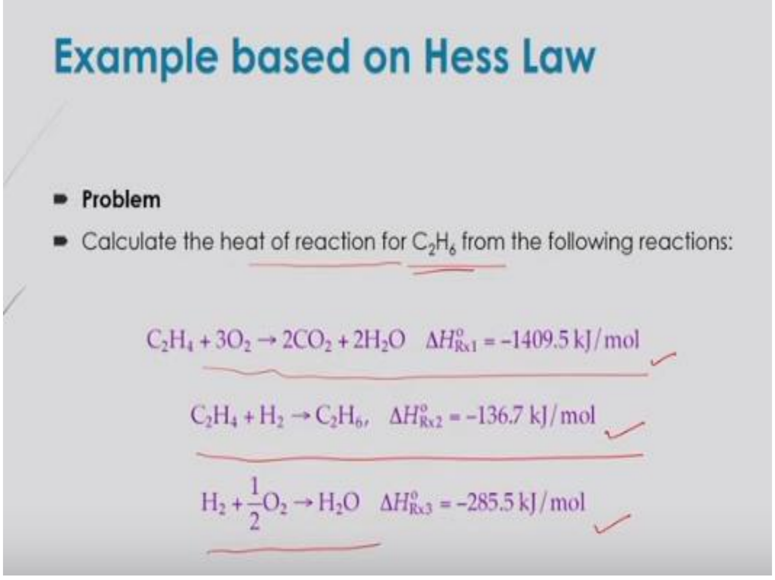

Example based on Hess Law

- **Problem**
- Calculate the heat of reaction for C_2H_6 from the following reactions:

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad \Delta H^o_{Rx1} = -1409.5\ kJ/mol$$

$$C_2H_4 + H_2 \rightarrow C_2H_6, \quad \Delta H^o_{Rx2} = -136.7\ kJ/mol$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Delta H^o_{Rx3} = -285.5\ kJ/mol$$

Now example based on Hess law, let us do this example here. In this case you have to calculate heat of reaction for this C 2 H 6 from the following reactions. Here, you will see that this first reaction that heat of, standard heat of reaction for this first reaction is given to you. And the standard heat of reaction for the second reaction it is given to you. Similarly, for third reaction this heat of reaction is given to you.

Now based on this, you know reaction one, two, and three you have to calculate the heat of reaction for this ethylene to form this products of this here along with this water, carbon dioxide and this.

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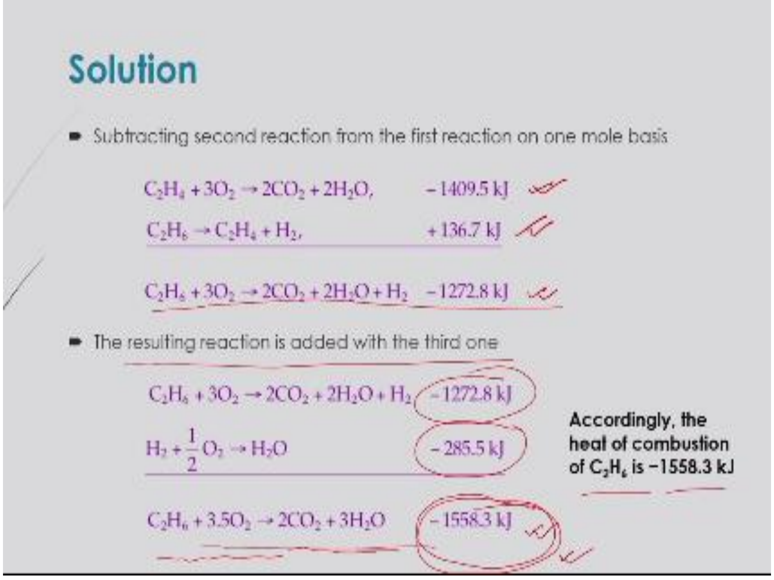

Solution

- Subtracting second reaction from the first reaction on one mole basis

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O, \quad -1409.5\ kJ$$
$$C_2H_6 \rightarrow C_2H_4 + H_2, \quad +136.7\ kJ$$
$$C_2H_6 + 3O_2 \rightarrow 2CO_2 + 2H_2O + H_2 \quad -1272.8\ kJ$$

- The resulting reaction is added with the third one

$$C_2H_6 + 3O_2 \rightarrow 2CO_2 + 2H_2O + H_2 \quad -1272.8\ kJ$$
$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad -285.5\ kJ$$
$$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O \quad -1558.3\ kJ$$

Accordingly, the heat of combustion of C_2H_6 is −1558.3 kJ

So in this case, we can manipulate this you know reaction just by subtracting and accordingly that heat of reactions just by adding, subtracting according to that Hess law. So here also we can do the same fashion based on that Hess law that subtracting the second reaction from the first reaction on one more basis, then we can have this here just subtracting this equation from this first equation, then we can get this.

So here whenever you are subtracting this equation, accordingly you have to subtract that heat of reaction also. So finally, we can get this here for this subtraction. Again, this resulting reaction is to be added with the third one. This is why convention, you have to think about how to do this to get this final equation for this ethane for conversion.

Now in this case, you will see that again if you, you know add this third you know reaction, you know with this resulting reaction, then you can have this final reaction as C 2 H 6 + 3.5 O 2, which will give you that carbon dioxide and water and accordingly then you have to add this you know that is heat of reaction and finally you can get this you know this heat of reaction like this.

So it is coming as 1558.3 kilojoule. Now, accordingly heat of combustion of this you know C 2 H 6 then it will be -1558.3 kilojoule.

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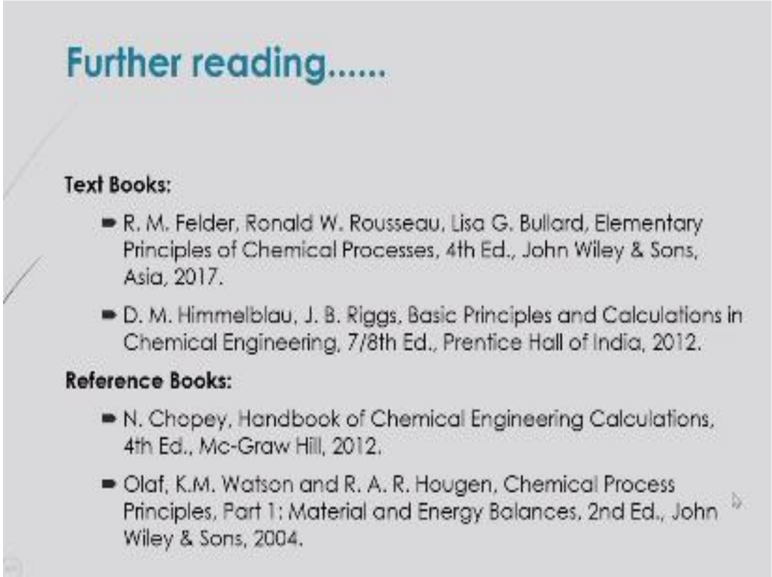

Further reading......

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 here from this lecture, we understood that what is the heat of formation, how heat of formation can be you know calculated based on the heat of reaction which is obtained experimentally and also from this heat of formation how to calculate that heat of reaction, whether it is single reaction or here multiple reaction.

Now for the multiple reaction by Hess law, you can manipulate these reactions along with that heat of reactions just by manipulating according to your you know problem and also convenience and then finally, you can get that total heat of you know reaction based on this you know heat of formation at a particular condition. In this lecture, we have described only at standard condition.

In the next lecture onward we will try to give some other examples, which are actually not in standard condition. There will be a you know that heat of reaction at a certain condition where you can get that there will be a change of you know enthalpy because of that temperature change as well as you will see that there will be a enthalpy change because of Hess change.

And based on that enthalpy change due to that temperature effect and also Hess transformation, how that heat of reaction can be calculated at a particular operating conditions. So we will be discussing all those things in the next lecture. Thank you.