Material and Energy Balances
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Lecture - 55
Fundamentals for Energy Balances on Reactive Processes - Part 1

Hello everybody. Welcome to today's lecture for the material energy balances course. So today, we will be talking about fundamentals associated with reactive processes that need to be understood so that we can apply them for energy balances. What are reactions?

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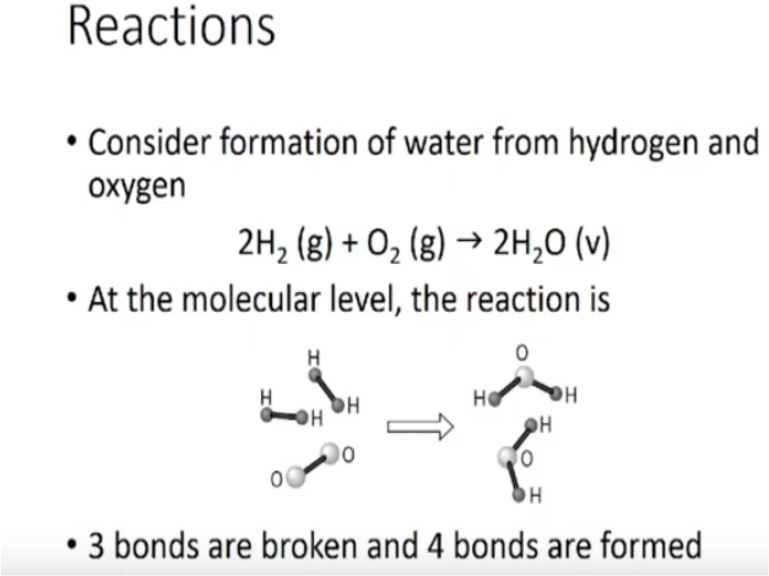

Reactions

- Consider formation of water from hydrogen and oxygen

$$2H_2\ (g) + O_2\ (g) \rightarrow 2H_2O\ (v)$$

- At the molecular level, the reaction is

- 3 bonds are broken and 4 bonds are formed

Consider this particular reaction. This is basically two reactants forming one product. You have water being produced from hydrogen and oxygen. So 2 moles of hydrogen gas and 1 mole of oxygen gas forms 2 moles of water vapor. So this is the reaction. So if you look at it from a molecular level what is happening. You have 2 molecules of hydrogen. So basically H H and another H H are actually reacting with O O to finally form H2O.

So the H2 has bonds which are there and O2 also has bonds holding the two atoms of hydrogen and two atoms of oxygen together. These bonds are broken and you have new bonds which are formed between the hydrogen and the oxygen atoms to form H2O. So this means 3 bonds are broken. 3 bonds in the reactants are actually broken and 4 bonds, 4 bonds in the product are actually formed. So this is the process of reaction.

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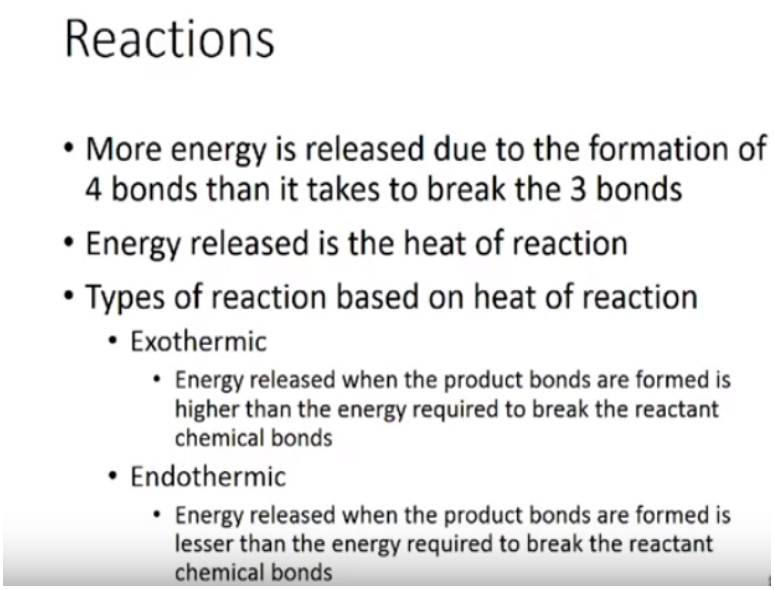

Reactions

- More energy is released due to the formation of 4 bonds than it takes to break the 3 bonds
- Energy released is the heat of reaction
- Types of reaction based on heat of reaction
  - Exothermic
    - Energy released when the product bonds are formed is higher than the energy required to break the reactant chemical bonds
  - Endothermic
    - Energy released when the product bonds are formed is lesser than the energy required to break the reactant chemical bonds

So why do we need to look at energy balances? What happens is when more energy is released due to the formation of 4 bonds than it takes to break 3 bonds you would have energy being released and this energy which is released is called the heat of the reaction. If it is the other way where the amount of energy required during the formation of 4 bonds is lesser than the amount of energy required to break the 3 bonds then energy will be absorbed.

And that would also be the heat of the reaction and this needs to be accounted for while you perform energy balance calculations. Consider a reactor. If you have a process where this kind of reactions are happening and you want to maintain temperatures and you want to understand how temperatures can be maintained, what needs to be supplied, all those things can be done only when you know the energy associated with such reaction.

Types of reactions based on heat of the reaction. So based on the heat of the reaction, you can classify the type of reaction. So this is the classification which all of us are familiar with. We have exothermic reactions where energy released when the product bonds are formed is higher than the energy required to break the chemical bonds for the reactants. So for this you have energy being released.

Heat is released usually and you also have endothermic reactions where the energy released when the product bonds are formed is lesser than the energy which is required to break the reactant chemical bonds. Now these are the 2 types of reactions which we would be looking at.

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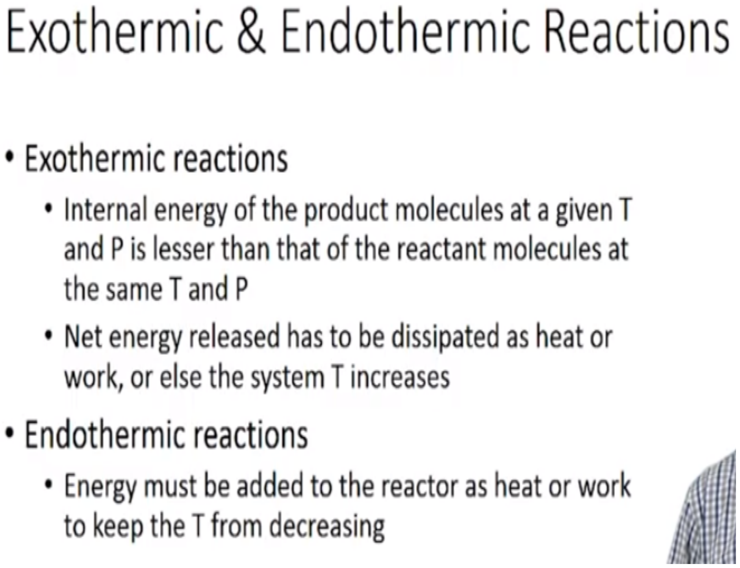

Exothermic & Endothermic Reactions

- Exothermic reactions
  - Internal energy of the product molecules at a given T and P is lesser than that of the reactant molecules at the same T and P
  - Net energy released has to be dissipated as heat or work, or else the system T increases
- Endothermic reactions
  - Energy must be added to the reactor as heat or work to keep the T from decreasing

What are exothermic and endothermic reactions from an energy balance perspective. Exothermic reactions are basically the reactions when internal energy of the product molecules at a given temperature and pressure is less than that of the reactant molecules at the same temperature and pressure. Net energy released has to be dissipated as heat or work, otherwise the system temperature will increase.

So you need to make sure that there is some way to cool down the system so that the temperature does not increase. If you want an isothermal process you would have to supply the, you have to remove heat by providing some kind of a cooling jacket or something across the reactor. If you have a process where you have endothermic reactions, energy must be added to the reactor as heat or work to keep the temperature from decreasing.

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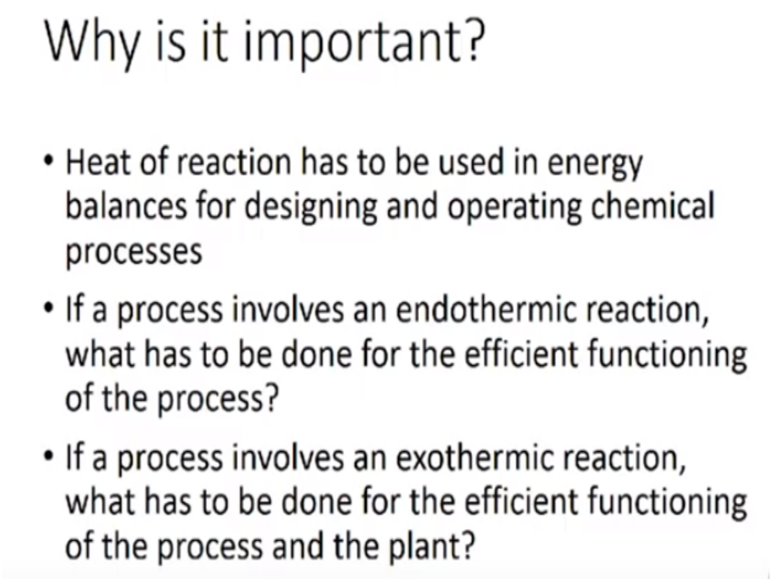

Why is it important?

- Heat of reaction has to be used in energy balances for designing and operating chemical processes
- If a process involves an endothermic reaction, what has to be done for the efficient functioning of the process?
- If a process involves an exothermic reaction, what has to be done for the efficient functioning of the process and the plant?

Why is this important? Why do we want to maintain the temperature within desirable levels. For an exothermic reaction if you do not cool it down, the temperature will keep increasing to a point where it can be a safety hazard or it can cause severe damage to the reactor and other equipment which is being used. So that is a problem. In an endothermic reaction, the temperature will keep dropping further and further so that the rate of the reaction will keep decreasing.

This would mean you will not be able to produce the desired product. So that would be a serious problem in an industry too. So for these reasons you want to maintain the temperature at certain desirable limits. For this we need to understand the energy associated with these reactions and perform calculations that can help us solve these energy balance problems.

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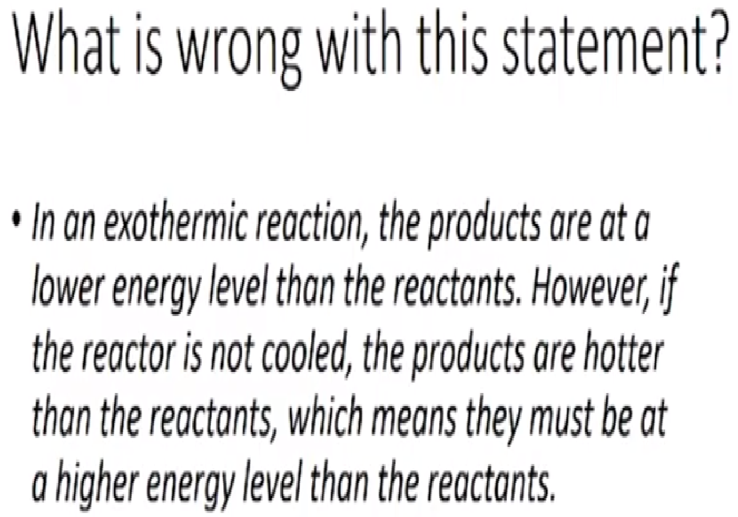

What is wrong with this statement?

- *In an exothermic reaction, the products are at a lower energy level than the reactants. However, if the reactor is not cooled, the products are hotter than the reactants, which means they must be at a higher energy level than the reactants.*

Okay, now let us look at this statement. So I am going to tell you that the statement is incorrect. I want you to identify what is wrong with the statement. The statement is, in an exothermic reaction, the products are at a lower energy level than the reactants. So that is why energy is being released. However, if the reactant is not cooled, the products are hotter than the reactants which means they must be at a higher energy level than the reactants.

Then how is it that we claim products are at a lower energy level. Please think about this. Please read this statement again. Think about the statement and see what is the information that is missing that is making you think this might be correct. If you remember when we discussed what this heat of reaction would be we talked about interval energy changes for exothermic reactions.

We said the internal energy of the product and the reactant has to be compared at the same temperature and pressure. Here we are not doing that. We are taking the reactant at an initial temperature and we are taking the product at a final temperature which is a much elevated temperature compared to the reactant. Because of this difference in temperature, obviously there is going to be a difference in internal energy. That is not what the heat of reaction talks about.

So just like how we have been looking at phase change or mixing, here also we need to account for only one component changing. In phase change we had only phase change happening at constant temperature and pressure. For mixing and solutions we assumed that the formation of the mixture or the solution happened at constant temperature and pressure from the pure components.

Similarly, here for understanding the heat of reaction, we have to assume that the products are formed from the reactants at a constant temperature and pressure and the change associated in enthalpy just because of this process happening is the heat of reaction.

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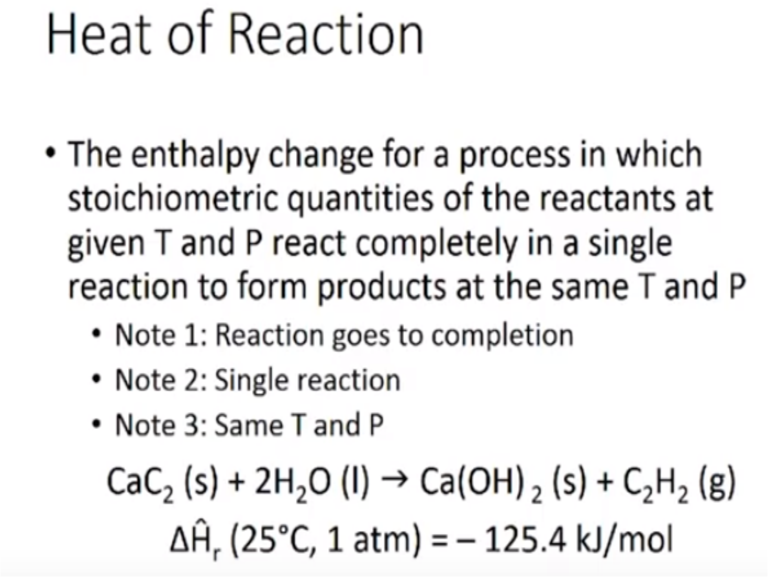

Heat of Reaction

- The enthalpy change for a process in which stoichiometric quantities of the reactants at given T and P react completely in a single reaction to form products at the same T and P
  - Note 1: Reaction goes to completion
  - Note 2: Single reaction
  - Note 3: Same T and P

$$CaC_2\ (s) + 2H_2O\ (l) \rightarrow Ca(OH)_2\ (s) + C_2H_2\ (g)$$

$$\Delta\hat{H}_r\ (25°C,\ 1\ atm) = -\ 125.4\ kJ/mol$$

What is the heat of reaction? Enthalpy change for a process in which stoichiometric quantities of the reactants at given temperature and pressure react completely in a single reaction to form products at the same temperature and pressure, okay? So just like how we had phase change at the same temperature and pressure, here we have product formation at same temperature and pressure. We will have to use it appropriately.

What do you need to note in this definition is the reaction goes to completion. That is the first thing. If the reaction is partially complete then the heat of reaction you calculate would reflect for that partially completed reaction. It will not be the standard heat of reaction for the stoichiometric equation which you would have written. Note 2. It is a single reaction. If there are multiple reactions that can happen. It is quite possible.

We looked at many cases where we have multiple reactions right? So you could either have reactions in parallel or in series or there could be completely different reactions happening because of the different components present. So if you are measuring this heat of reaction in an experimental setup it needs to be a single reaction that is happening. No side reactions should be happening along with the reaction of interest.

The third aspect which we need to look at is it should happen at the same temperature and pressure. Let us look at this equation. We have calcium carbide solid reacting with water liquid to form calcium hydroxide solid and C2H2 gas, acetylene gas. And the heat of reaction for this is given at 25 degree Celsius and 1 atmosphere as -125.4 kJ/mol.

So what this means is when this reaction goes to completion and this is the only reaction which is happening and if the reactants and the products are at the same temperature and pressure before and after the reaction and if that temperature is 25 degree Celsius and the pressure is at 1 atmosphere, then the heat of reaction you have is -125.4 kJ/mol.

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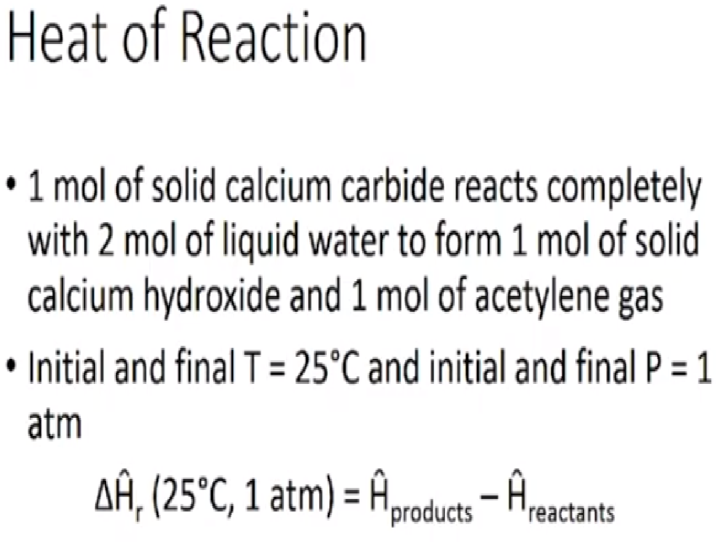

Heat of Reaction

- 1 mol of solid calcium carbide reacts completely with 2 mol of liquid water to form 1 mol of solid calcium hydroxide and 1 mol of acetylene gas
- Initial and final T = 25°C and initial and final P = 1 atm

$$\Delta\hat{H}_r\,(25°C,\ 1\ atm) = \hat{H}_{products} - \hat{H}_{reactants}$$

So this is basically 1 moles of calcium carbide solid reacting completely with 2 moles of water which is in liquid form to form 1 mole of solid calcium hydroxide and 1 mole of acetylene gas. So initial and final temperature has to be 25 degree Celsius and initial and final pressure has to be 1 atmosphere. Then what you have is the heat of reaction is the enthalpy of products minus enthalpy of the reactants which is basically the enthalpy of the final condition minus the enthalpy of the initial condition.

So since the reaction has gone to completion, the final condition will not have any reactants and assuming that only reactants are fed, you would not have any products at the initial condition. So this value is -125.4 kJ/mol.

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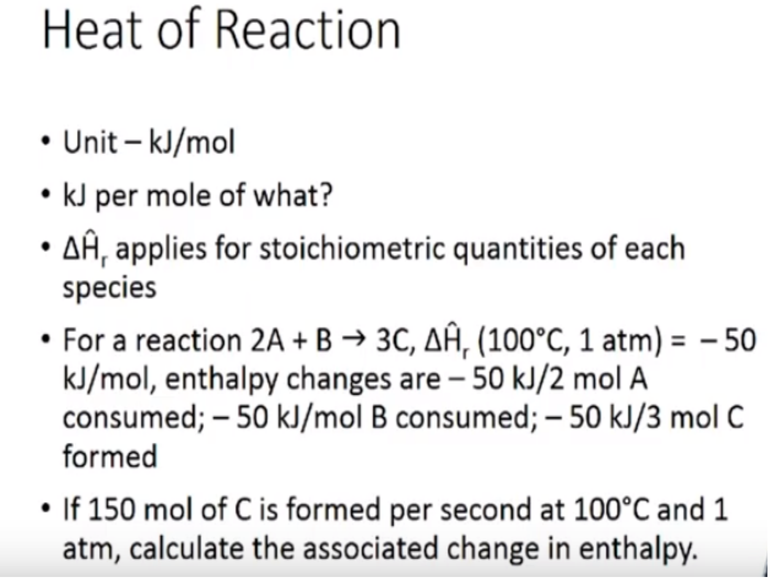

Heat of Reaction

- Unit – kJ/mol
- kJ per mole of what?
- $\Delta\hat{H}_r$ applies for stoichiometric quantities of each species
- For a reaction $2A + B \rightarrow 3C$, $\Delta\hat{H}_r$ (100°C, 1 atm) = – 50 kJ/mol, enthalpy changes are – 50 kJ/2 mol A consumed; – 50 kJ/mol B consumed; – 50 kJ/3 mol C formed
- If 150 mol of C is formed per second at 100°C and 1 atm, calculate the associated change in enthalpy.

So once we have this we should look at the units. So we have always been using the front units, right? So we have actually been building specific enthalpy tables and we fill the number of moles or masses of the components based on the units for the specific enthalpy or the internal energy. So here we have heat reaction. For heat of reaction, we have been given kilo joules per mol.

When we talk about enthalpy of phase change like heat of vaporization or something it is again given as kilo joules per mole or kilo joules per kilogram and we know which component we are talking about. If we are talking about the vaporization of water it is the number of moles of water which is being vaporized. So similarly here we have kilo joules per mole. So mole of what? So that is a question. So we know kilo joules per mole but kilo joules per mole of what?

That is an important question which we need to clearly understand if we want to use heat of reaction correctly. Heat of reaction applies for stoichiometric quantities of each species. By that what I mean is in the reaction we looked at we had 1 mole of calcium carbide reacting with 2 moles of water to form 1 mole of calcium hydroxide and 1 mole of acetylene gas.

So this would mean the heat of reaction accounts for 1 mole of calcium carbide being consumed and 2 moles of water being consumed and 1 mole of calcium hydroxide being produced and 1 mole of acetylene being produced. So in other words, let us look at this reaction where you have 2A + B forming 3C and if I tell you that the heat of reaction at 100 degree Celsius and 1 atmosphere is -50 kJ/mol the enthalpy changes associated are -50 kJ per 2 moles of A consumed and -50 kJ per 1 mole of B consumed and -50 kJ per 3 moles of C formed.

So depending on which component you are looking at you will have to identify the stoichiometric coefficient and use that appropriately while you are performing the calculations. If 150 moles of C is formed per second at 100 degree Celsius and 1 atmosphere can you calculate the associated change in enthalpy for this process. We know that -50 kJ is the change in enthalpy for 3 moles of C being formed.

Which means 150 moles of C is formed means you would have -50 times 50 as the change in enthalpy for this process which we are looking at. However, if it were 150 moles of B which is consumed then the change in enthalpy would actually be -50 kJ/mol times 150. So here what we do is we basically multiply the number of moles of a component with the heat of the reaction and divide it by the stoichiometric coefficient.

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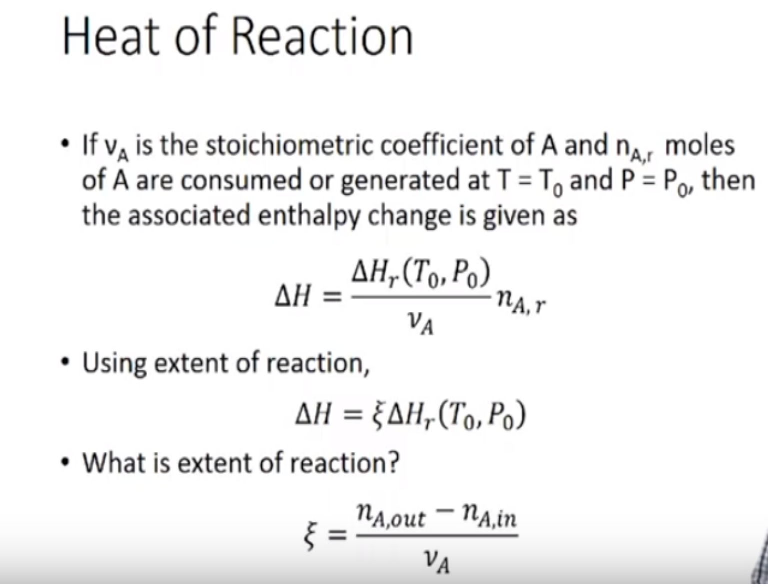

Heat of Reaction

- If v_A is the stoichiometric coefficient of A and $n_{A,r}$ moles of A are consumed or generated at $T = T_0$ and $P = P_0$, then the associated enthalpy change is given as

$$\Delta H = \frac{\Delta H_r(T_0, P_0)}{\nu_A} n_{A,r}$$

- Using extent of reaction,

$$\Delta H = \xi \Delta H_r(T_0, P_0)$$

- What is extent of reaction?

$$\xi = \frac{n_{A,out} - n_{A,in}}{\nu_A}$$

So what we do because of this is if mu A is the stoichiometric coefficient of A and n A r moles of A are consumed or generated at temperatures T naught and pressure P naught then the associated enthalpy change is given as delta H = delta H r times n A r divided by you A where mu is the stoichiometric coefficient and n A r is the change in the number of moles of a component and delta H r is the heat of the reaction. So the total enthalpy change can be calculated this way.

So if you remember a term named extent of reaction, we can use that here. So we discussed extent of reaction long time back when we talked about reactions during material balance. We talked about this term called extent of reaction. What is extent of reaction? Extent of reaction using this would actually be the change in enthalpy would be extent of reaction times heat of reaction. So what is extent of reaction? Do you remember the definition for it?

So extent of reaction is n A out - n A in divided by the stoichiometric coefficient. So this gives you the value which is basically the amount of a component consumed or generated divided by the stoichiometric coefficient. The stoichiometric coefficient would be positive for products and it will be negative for reactants. So because of this the extent of reaction will always be positive.

Reactants will have lesser number of moles in the outlet compared to the inlet which means the numerator would be negative. Since the stoichiometric coefficient for the reactant would also be taken as a negative you would end up with a extent of reaction which is positive. So for products it will be the other way. The number of moles in the outlet would be higher than the number of moles in the inlet which means the numerator would be positive and the stoichiometric coefficient would also be positive giving you an extent of reaction which would be positive.

So extent of reaction is always positive and this times the heat of reaction will give you the total change in enthalpy for the process. If we were to consider the previous example where we had 150 moles of C being formed per second, what we would have is the extent of reaction would be 150 moles in the numerator which is the number of moles of C which is generated divided by 3 which is the stoichiometric coefficient giving you 50 which is the extent of reaction.

And so the extent of reaction times the heat of reaction is what we would have done to identify the change in enthalpy.

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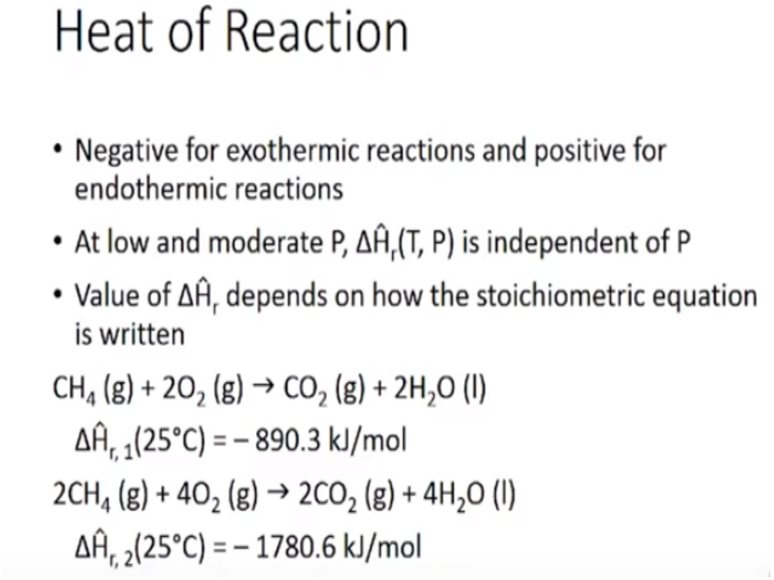

Heat of Reaction

- Negative for exothermic reactions and positive for endothermic reactions
- At low and moderate P, $\Delta\hat{H}_r(T, P)$ is independent of P
- Value of $\Delta\hat{H}_r$ depends on how the stoichiometric equation is written

$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)$

$\Delta\hat{H}_{r,1}(25°C) = -890.3$ kJ/mol

$2CH_4\,(g) + 4O_2\,(g) \rightarrow 2CO_2\,(g) + 4H_2O\,(l)$

$\Delta\hat{H}_{r,2}(25°C) = -1780.6$ kJ/mol

So now you have to identify what these values are. These values can be positive and negative. The heat of reaction can be positive or negative. So it is negative for exothermic reactions and positive for endothermic reactions. This is obvious, right? We said that the enthalpy of the products is lower than the enthalpy of the reactants for an exothermic process and it is the vice versa for endothermic process.

So this would mean enthalpy of products minus enthalpy of reactants for exothermic reactions would be negative and enthalpy of products minus enthalpy of reactants for endothermic processes reactions would be positive. At low and moderate pressures you have enthalpy of reaction independent of pressure. So in many cases you do not have to worry about effect of pressure unless the reaction happens at very high pressures.

Value of delta H r cap depends on how the stoichiometric equation is written also. So if you have a stoichiometric equation which is given here you have 1 mole of methane reacting with 2 moles of oxygen forming 1 mole of carbon dioxide and 2 moles of water liquid. So the heat of reaction is given as -890.3 kJ/mol. However, if I have this equation reaction written slightly differently with 2 moles of methane reacting then what happens is you have 2 moles of methane reacting with 4 moles of oxygen to form 2 moles of carbon dioxide and 4 moles of water.

So finally your heat of reaction would also be double because now what has happened is the heat of reaction for the first reaction is -890.3 kJ for 1 mole of methane reacting or 2 moles of oxygen reacting or 1 mole of carbon dioxide forming or 2 moles of water forming. Whereas in the second reaction, you have the denominator as 2 moles of methane forming or 4 moles of sorry 2 moles of methane reacting or 4 moles of oxygen reacting or 2 moles of carbon dioxide being formed or 4 moles of water being formed.

Because you have double the number of moles reacting or forming the heat of reaction would also become double.

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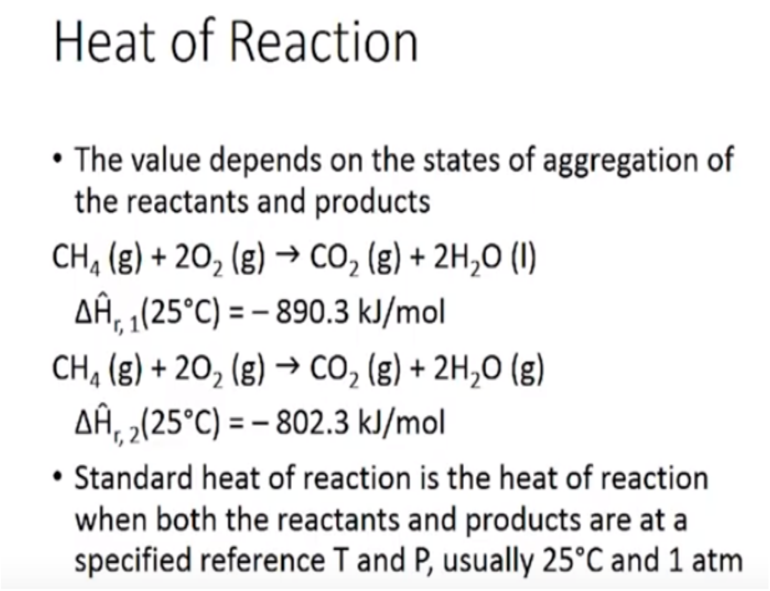

Heat of Reaction

- The value depends on the states of aggregation of the reactants and products

$CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l)$

$\Delta\hat{H}_{r,1}(25°C) = -\ 890.3\ kJ/mol$

$CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (g)$

$\Delta\hat{H}_{r,2}(25°C) = -\ 802.3\ kJ/mol$

- Standard heat of reaction is the heat of reaction when both the reactants and products are at a specified reference T and P, usually 25°C and 1 atm

Similar to this you also have the effect due to the state of aggregation of the reactants and products. So if your state of aggregation of one of the components changes then your heat of reaction will also change. If you have methane gas plus oxygen gas forming carbon dioxide gas and water liquid you would have the heat of reaction as -890.3 kJ/mol.

However, if you have methane gas reacting with oxygen gas to form carbon dioxide gas and water gas or water vapor instead of water liquid you would have the heat of reaction as -802.3 kJ/mol. So the heat of vaporization of water would have to be accounted for while we perform the calculations. What happens here is the enthalpy of the products minus enthalpy of the reactants.

So the enthalpy of the products is now different because you have water vapor instead of water liquid. So the heat of vaporization has to be accounted for. So that brings in the value. So since you have 2 moles of water which is present in the product, so two times the heat of vaporization which is 88. So heat of vaporization is 44, two times 44 is 88 is the difference between the two. That is why you see the difference in heat of reaction.

Standard heat of reaction for both the reactants and the products, see standard heat of reaction is the heat of reaction when both the reactants and the products are at a specified reference temperature and pressure. The temperature and pressure which is usually used is 25 degree Celsius and 1 atmosphere.

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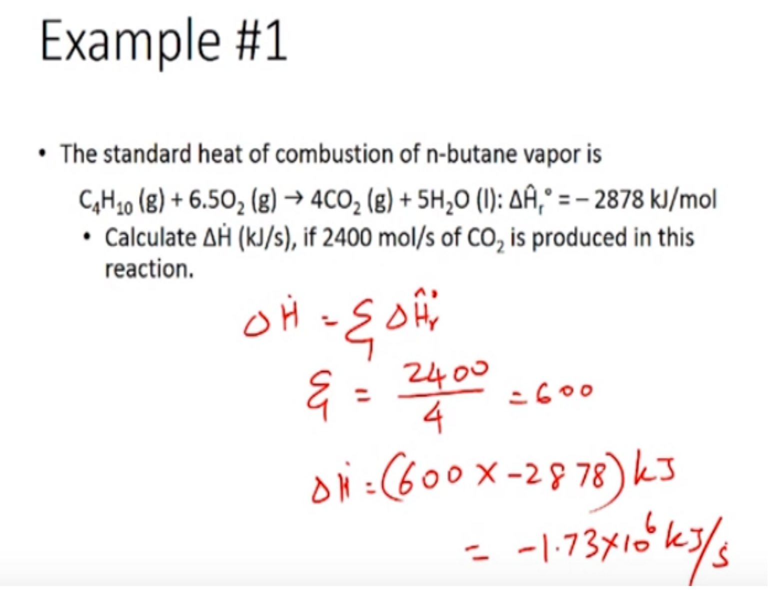

Example #1

- The standard heat of combustion of n-butane vapor is

  $C_4H_{10}\,(g) + 6.5O_2\,(g) \rightarrow 4CO_2\,(g) + 5H_2O\,(l)$: $\Delta\hat{H}_r^\circ = -2878$ kJ/mol

  - Calculate $\Delta\dot{H}$ (kJ/s), if 2400 mol/s of CO_2 is produced in this reaction.

$$\Delta\dot{H} = \xi\,\Delta\dot{\hat{H}}_r$$

$$\xi = \frac{2400}{4} = 600$$

$$\Delta\dot{H} = (600 \times -2878)\,\text{kJ}$$

$$= -1.73\times10^{6}\ \text{kJ/s}$$

So here is a simple example problem. We will look at a few things which will help us understand the concepts which we looked at. The standard heat of combustion of n-butane vapor is given here. 1 mole of butane reacts with 6.5 moles of oxygen to form 4 moles of carbon dioxide and 5 moles of water liquid. So this heat of reaction for this process is given as -2878 kJ/mol.

You are asked to calculate delta H dot in terms of kJ/s if 2400 mol/s of carbon dioxide is produced in this reaction. So what we have to find is 2400 mol/s of carbon dioxide being produced. So we need to calculate delta H dot. So delta H dot would be equal to your extent of reaction psi times delta H r cap. So we need to calculate the extent of reaction. So the number of moles of carbon dioxide produced is 2400 divided by the stoichiometric coefficient which is 4.

So this would be 600 and would be the extent of reaction. So now that we have 600 as the extent of reaction, the delta H dot would be equal to 600 times -2878 kJ. So that is the total change in enthalpy associated with this process. So the numerical value for this would be -1.73 times 10 power 6 kJ/s.

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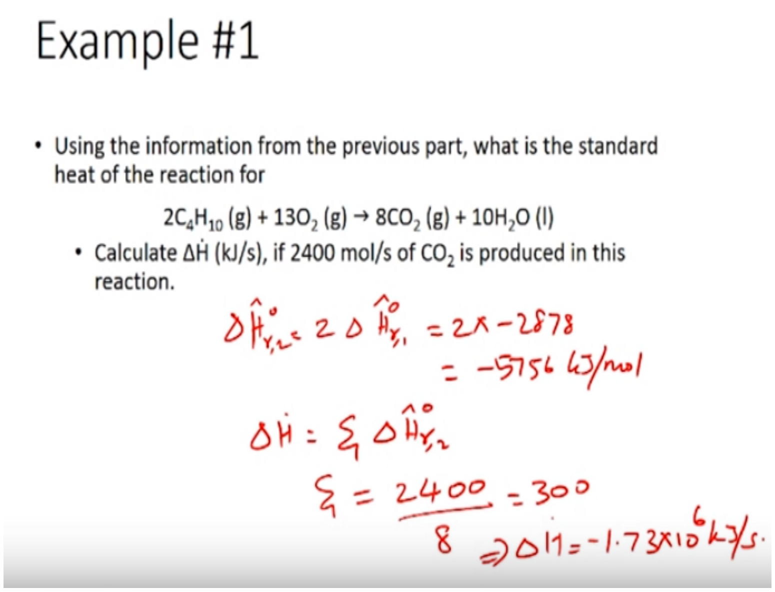

Example #1

- Using the information from the previous part, what is the standard heat of the reaction for

$$2C_4H_{10}\,(g) + 13O_2\,(g) \rightarrow 8CO_2\,(g) + 10H_2O\,(l)$$

  - Calculate $\Delta\dot{H}$ (kJ/s), if 2400 mol/s of CO_2 is produced in this reaction.

$$\Delta\hat{H}^{o}_{r,2} = 2\,\Delta\hat{H}^{o}_{r,1} = 2\times -2878$$
$$= -5756\ kJ/mol$$
$$\Delta\dot{H} = \xi\,\Delta\hat{H}^{o}_{r,2}$$
$$\xi = \frac{2400}{8} = 300$$
$$\Rightarrow \Delta\dot{H} = -1.73\times10^{6}\ kJ/s.$$

So now let us look at a slightly different equation. So the same thing has there. Now instead of having 1 mole of butane reacting we have 2 moles of butane reacting. So the equation has actually been modified. We first have to calculate the heat of reaction for this reaction and then again calculate the change in enthalpy. So the heat of reaction for the second reaction would be equal to two times the heat of reaction for the first reaction.

Because you have 2 moles of butane reacting instead of 1 mole of butane reacting which means the heat of reaction for this would be two times -2878 giving you a value of -5756 kJ/mol and delta H dot = psi times delta H r. So here we would again use the second heat of reaction. So the value we have for the extent of reaction would be 2400 moles of carbon dioxide produced divided by the stoichiometric coefficient which is 8 giving us the extent of reaction as 300.

Therefore your delta H dot would not change from the previous value which is -1.73 times 10 power 6 kJ/s. So the extent of reaction has changed in a way that your delta H dot does not have to change.

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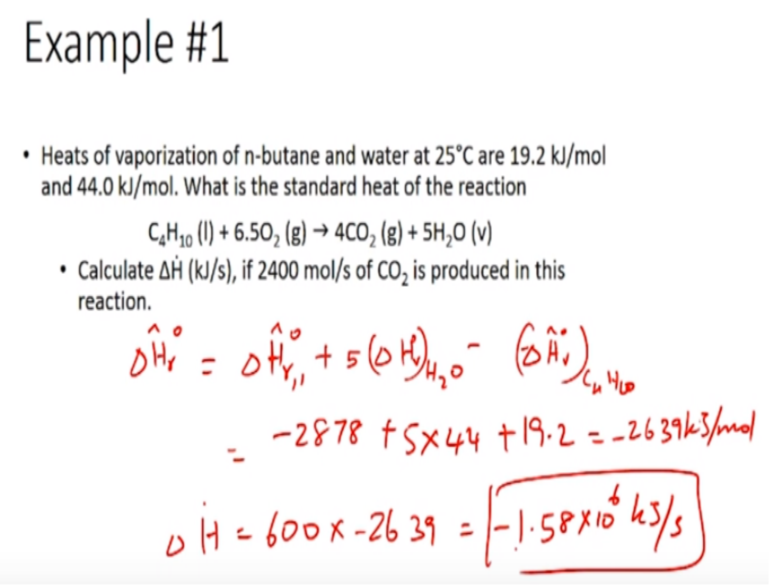

Example #1

- Heats of vaporization of n-butane and water at 25°C are 19.2 kJ/mol and 44.0 kJ/mol. What is the standard heat of the reaction

$$C_4H_{10}\,(l) + 6.5O_2\,(g) \rightarrow 4CO_2\,(g) + 5H_2O\,(v)$$

  - Calculate $\Delta\dot{H}$ (kJ/s), if 2400 mol/s of CO_2 is produced in this reaction.

$$\Delta\hat{H}_r^o = \Delta\hat{H}_{r,1}^o + 5(\Delta\hat{H}_v)_{H_2O} - (\Delta\hat{H}_v^o)_{C_4H_{10}}$$

$$= -2878 + 5\times 44 + 19.2 = -2639\,kJ/mol$$

$$\Delta\dot{H} = 600\times -2639 = \boxed{-1.58\times 10^6\,kJ/s}$$

So the last aspect for this problem is we have the phase change happening. So you have butane liquid reacting with oxygen gas forming carbon dioxide gas and water vapor. So initially we had butane gas and water liquid. So here we have flipped it. So now we need to calculate the heat of reaction, standard heat of reaction for this reaction. So what we have is, we need to know the heat of vaporization for butane and water which is given.

Heat of vaporization for butane is given as 19.2 kJ/mol and heat of vaporization for water is given as 44 kJ/mol. So trying to accommodate that your heat of reaction for this new reaction would be equal to heat of reaction for the first reaction which we had + 5 times the heat of vaporization for water minus of negative heat of vaporization for butane. So how did I get this? So what I have done here is you have the first step where water is being vaporized.

In the first reaction, it was water liquid. Now here it is water vapor. So liquid goes to vapor. So you have this term 5 moles is being vaporized. So you need to add the heat of vaporization to the product side so which means it is added to the heat of reaction and you have condensation of butane gas to liquid.

So the negative of heat of vaporization which is the heat of condensation needs to be added to the reactant side which means it needs to be subtracted from the heat of reaction so giving you this equation. So your new heat of reaction would actually be -2878 + 5 times 44 + 19.2 giving you a value roughly -2639 kJ/mol. So now for the same 2400 moles of carbon dioxide to be formed, the enthalpy change will be different.

Delta H dot would be equal to 600 which is the extent of reaction times the new heat of reaction for this third reaction which is -2639 giving you a total change in enthalpy of 1.58 times 10 power 6 kJ/s. So with this we have looked at some basic principles associated with heat of reaction. So in the next lecture we will continue with the fundamentals associated with reactive processes and then perform some more tutorial problems and apply these principles to perform energy balance calculations. Thank you.