Material and Energy Balances
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Lecture - 56
Fundamentals for Energy Balances on Reactive Processes - Part 2

Hello everybody. Welcome back to the lectures for material and energy balances. Today we will continue with the fundamentals associated with reactions when we perform energy balances. In the last lecture, we looked at what heat of reaction was. So we looked at how enthalpy change happens when there is a reactive process. Today, we will start of with something called the internal energy of reaction.

So when there is change in enthalpy there can also be change in internal energy. So this change in internal energy would also have to be calculated and has to be used in energy balance calculations for close systems in constant volume. So for this reason, we need to know how we can calculate the internal energy of a reaction.

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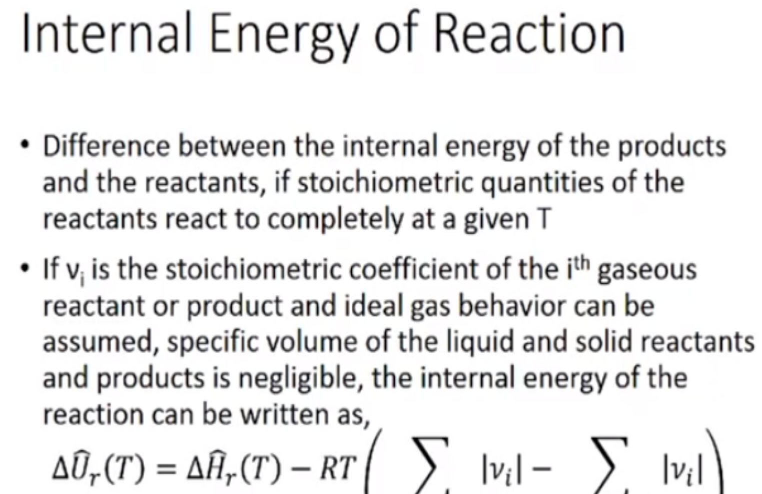

Internal Energy of Reaction

- Difference between the internal energy of the products and the reactants, if stoichiometric quantities of the reactants react to completely at a given T
- If v_i is the stoichiometric coefficient of the i^{th} gaseous reactant or product and ideal gas behavior can be assumed, specific volume of the liquid and solid reactants and products is negligible, the internal energy of the reaction can be written as,

$$\Delta\hat{U}_r(T) = \Delta\hat{H}_r(T) - RT\left(\sum_{\substack{\text{gaseous}\\\text{products}}} |\nu_i| - \sum_{\substack{\text{gaseous}\\\text{reactants}}} |\nu_i|\right)$$

So this is defined as the difference between the internal energy of the products and the reactants if stoichiometric quantities of the reactants react completely at a given temperature and pressure. So this would be the definition for internal energy of reaction. If nu i is the stoichiometric coefficient of the ith gaseous reactant or product and ideal gas behavior can be assumed, specific volume of the liquid and solid reactants and products are negligible then the internal energy of the reaction can be written as delta U r cap = delta H r cap - RT times the sigma of the stoichiometric coefficients of gaseous products minus the summation of the stoichiometric coefficients of gaseous reactants.

So this is how you would calculate the internal energy change associated with the reaction. So please note that this is valid because we are assuming ideal gas behavior for your all the gaseous components in the reaction and because the change in specific volume is very small for solids and liquids we can ignore that and therefore we get this equation.

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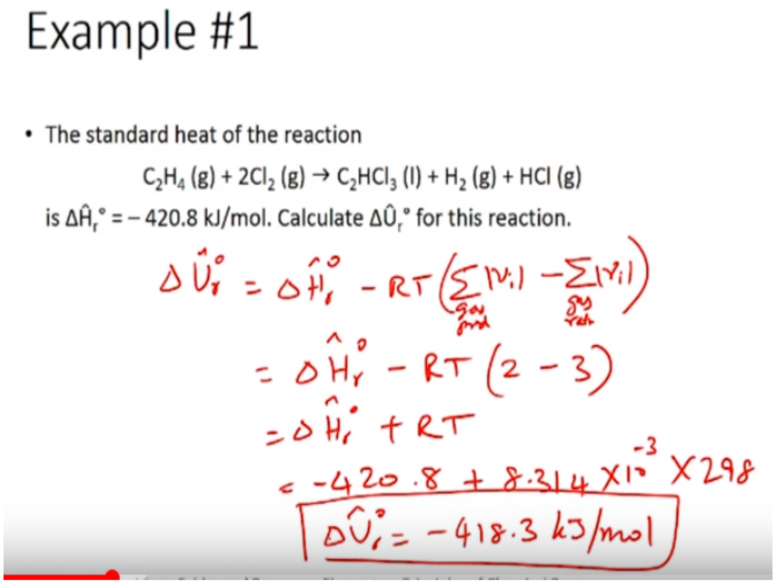

Example #1

- The standard heat of the reaction

$$C_2H_4\,(g) + 2Cl_2\,(g) \rightarrow C_2HCl_3\,(l) + H_2\,(g) + HCl\,(g)$$

is $\Delta\hat{H}_r^\circ = -420.8$ kJ/mol. Calculate $\Delta\hat{U}_r^\circ$ for this reaction.

$$\Delta\hat{U}_r^\circ = \Delta\hat{H}_r^\circ - RT\left(\sum_{\substack{\text{gas}\\\text{prod}}}|\nu_i| - \sum_{\substack{\text{gas}\\\text{react}}}|\nu_i|\right)$$

$$= \Delta\hat{H}_r^\circ - RT\,(2-3)$$

$$= \Delta\hat{H}_r^\circ + RT$$

$$= -420.8 + 8.314\times10^{-3}\times298$$

$$\boxed{\Delta\hat{U}_r^\circ = -418.3\ \text{kJ/mol}}$$

Here is a simple example problem which can be used to understand how to calculate the change in internal energy for a reaction based on the heat of reaction given. The standard heat of reaction for C2H4 gas reacting with 2Cl2 gas forming C2HCl3 + H2gas + HCl gas is given as delta H r = -420.8 kJ/mol. You are asked to calculate the delta U r cap for this reaction. How would we go about doing this calculation?

Based on the equation we had, delta U r cap would be equal to delta H r cap - RT times sigma of gaseous products stoichiometric coefficients minus the sigma of gaseous reactants stoichiometric coefficients. So here let us identify what are the gaseous products and reactants. You have C2H4, Cl2, H2 and HCl all as gases. Your C2HCl3 is in liquid phase. So we do not have to worry about this particular component.

So let us identify the stoichiometric coefficients of the reactants and the product gases. So the product gases are hydrogen and hydrochloride. So these have stoichiometric coefficients of 1. So the summation of these stoichiometric coefficients is 2. Similarly, you have the stoichiometric coefficients of 1 and 2 for the reactant gases. So the summation is 3. So the equation then becomes delta H r cap - RT (2 – 3).

So this becomes delta H r + RT and we have the H r value as -420.8 + R is 8.314 times 10 power -3 because we want it in kJ/mol Kelvin times your temperature. So the temperature for standard heat of reaction would be at 298 Kelvin. So using this we can calculate the change in internal energy for this reaction, the standard internal energy for this reaction as -418.3 kJ/mol. So this is how you would calculate the change in internal energy for a reaction.

And this value delta U r cap would have to be used for reactive processes happening in close systems at constant volume. So moving on to the next concept, how do we actually measure this H r cap? So we have been using the specific enthalpy value which is available from the tables. But how is this usually measured?

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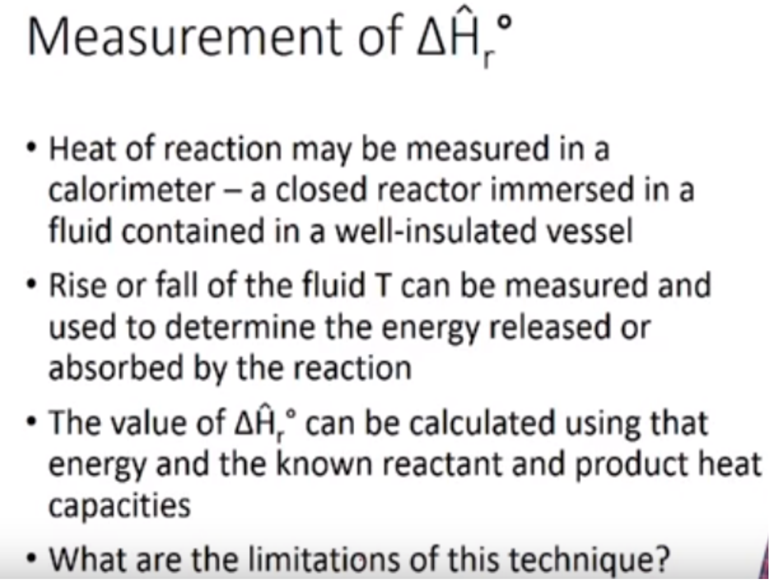

Measurement of $\Delta\hat{H}_r^\circ$

- Heat of reaction may be measured in a calorimeter – a closed reactor immersed in a fluid contained in a well-insulated vessel
- Rise or fall of the fluid T can be measured and used to determine the energy released or absorbed by the reaction
- The value of $\Delta\hat{H}_r^\circ$ can be calculated using that energy and the known reactant and product heat capacities
- What are the limitations of this technique?

So heat of reaction can be measured using a calorimeter which is a closed reactor which is immersed in a fluid contained in a well-insulated vessel. So you have a reactor which is surrounded by a fluid and this fluid is covered by a well-insulated system so that all the heat which is generated or lost during the reaction is transferred to the liquid or the fluid around it and nothing is lost to the surroundings outside of the fluid.

The rise or fall of the fluid temperature can be measured using a simple thermometer and this can be used to determine the energy released or absorbed by the reaction using simple energy balance calculations. So the value of delta H r cap can be calculated and for the known reactant and product heat capacities assuming that we have the reaction going to completion. So what are the limitations of this technique?

So I said that this is the experimental technique commonly used. So what could be the problem with this?

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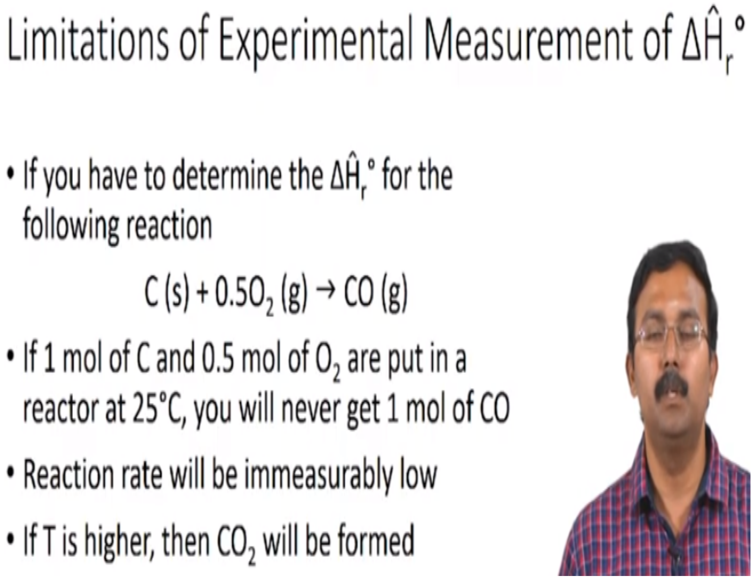

Limitations of Experimental Measurement of $\Delta\hat{H}_r^\circ$

- If you have to determine the $\Delta\hat{H}_r^\circ$ for the following reaction

$$C(s) + 0.5O_2(g) \rightarrow CO(g)$$

- If 1 mol of C and 0.5 mol of O_2 are put in a reactor at 25°C, you will never get 1 mol of CO
- Reaction rate will be immeasurably low
- If T is higher, then CO_2 will be formed

If you have to determine the reaction of this equation which is carbon plus half of oxygen forming carbon monoxide, it would be near impossible to perform this reaction without having any side reactions having because you will never be able to get 1 mole of carbon to react only with half a mole of oxygen to produce 1 mole of carbon monoxide.

There will always be carbon dioxide formed if the temperature is increased. If temperature is very low, the reaction rate will be too low and we would not be able to measure any change in temperature that can be used for measuring the heat of reaction.

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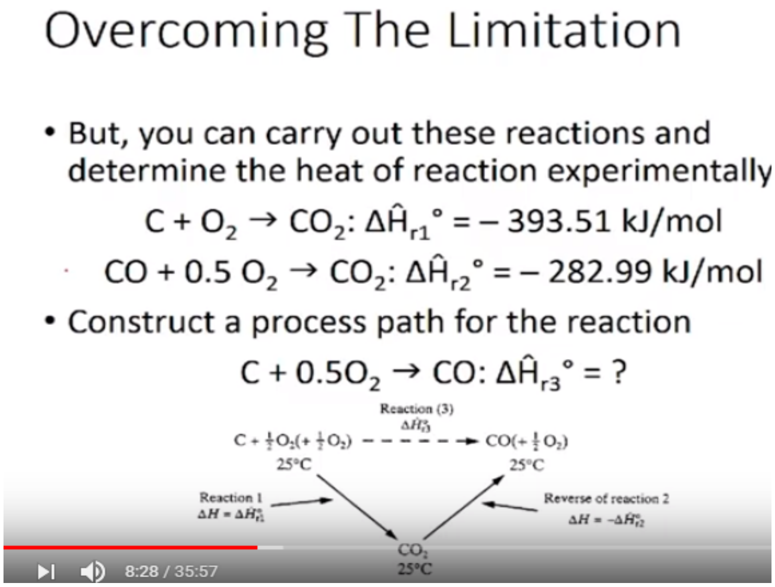

Overcoming The Limitation

- But, you can carry out these reactions and determine the heat of reaction experimentally

$$C + O_2 \rightarrow CO_2: \Delta\hat{H}_{r1}^{\circ} = -393.51 \text{ kJ/mol}$$

$$CO + 0.5\ O_2 \rightarrow CO_2: \Delta\hat{H}_{r2}^{\circ} = -282.99 \text{ kJ/mol}$$

- Construct a process path for the reaction

$$C + 0.5O_2 \rightarrow CO: \Delta\hat{H}_{r3}^{\circ} = ?$$

How do we overcome this limitation? What you can do is you can carry out the following reactions and determine the heat of reactions experimentally. The first reaction which you can carry out is carbon plus oxygen forming carbon dioxide. So this is just a simple combustion reaction of carbon and as long as the reaction is complete, complete combustion happens this reaction can be easily accomplished.

The other reaction is you take carbon monoxide and let it react with oxygen to form carbon dioxide. So again this reaction is also quite possible because once we have carbon monoxide we can easily let it react with oxygen to form carbon dioxide and the heat of reaction for these 2 things can be measured. So once we have this, we can build a process path for the reaction of interest. So our reaction of interest is carbon plus half oxygen gives carbon monoxide.

So this would mean the reaction which we have which is the reaction of interest is basically the first step where carbon plus oxygen forms carbon dioxide and from carbon dioxide you have carbon monoxide being formed with half of oxygen. So this is the first step is reaction 1 and the second step is the reverse of this first reaction. So using this, we can actually calculate the heat of reaction for the desired reaction.

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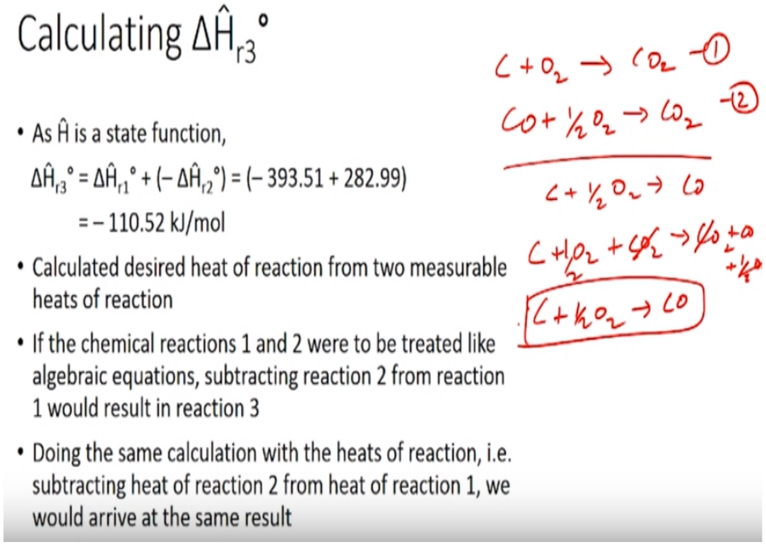

Calculating $\Delta\hat{H}_{r3}^{\circ}$

- As $\hat{H}$ is a state function,
  $\Delta\hat{H}_{r3}^{\circ} = \Delta\hat{H}_{r1}^{\circ} + (-\Delta\hat{H}_{r2}^{\circ}) = (-393.51 + 282.99)$
  $= -110.52$ kJ/mol
- Calculated desired heat of reaction from two measurable heats of reaction
- If the chemical reactions 1 and 2 were to be treated like algebraic equations, subtracting reaction 2 from reaction 1 would result in reaction 3
- Doing the same calculation with the heats of reaction, i.e. subtracting heat of reaction 2 from heat of reaction 1, we would arrive at the same result

$C + O_2 \rightarrow CO_2$ —①

$CO + \frac{1}{2}O_2 \rightarrow CO_2$ —②

$C + \frac{1}{2}O_2 \rightarrow CO$

$C + \frac{1}{2}O_2 + \cancel{CO_2} \rightarrow \cancel{CO_2} + CO + \frac{1}{2}O$

$\boxed{C + \frac{1}{2}O_2 \rightarrow CO}$

So we know that specific enthalpy is a state function. Using this parameter we can calculate the heat of reaction for the third reaction which is the reaction of interest as heat of reaction for the first reaction minus the heat of reaction for the second reaction thereby calculating delta H r 3 cap as - 110.52 kJ/mol. So this is doable and this is what people try to do when they calculate enthalpies and enthalpy changes for reactions that cannot be carried out directly.

So this is basically calculated, the desired heat of reaction has been calculated from 2 measurable heats of reactions. If chemical reactions 1 and 2 are technically treated like algebraic equations, all you did was subtract reaction 2 from reaction 1 to result in reaction 3. See that is what we have also done to the heat of reactions. So basically we have subtracted the second heat of reaction from the first heat of reaction to get the heat of reaction for the third reaction.

You can verify this with using the equations that we have. So equations we had were the first reaction was carbon plus oxygen forms carbon dioxide and the second reaction was carbon monoxide plus half oxygen forms carbon dioxide. And our equation of desire, the desired equation was carbon plus half oxygen gives carbon monoxide. How do we get this? So if we were to subtract reaction 1 and reaction 2, 1 - 2 would basically be C + O 2 + CO 2 gives CO 2 +

CO + 1/2 O 2. So CO 2 gets cancelled and this half O 2 will be subtracted from here giving you C + 1/2 O 2 gives CO. So this is the reaction of interest and we can do this.

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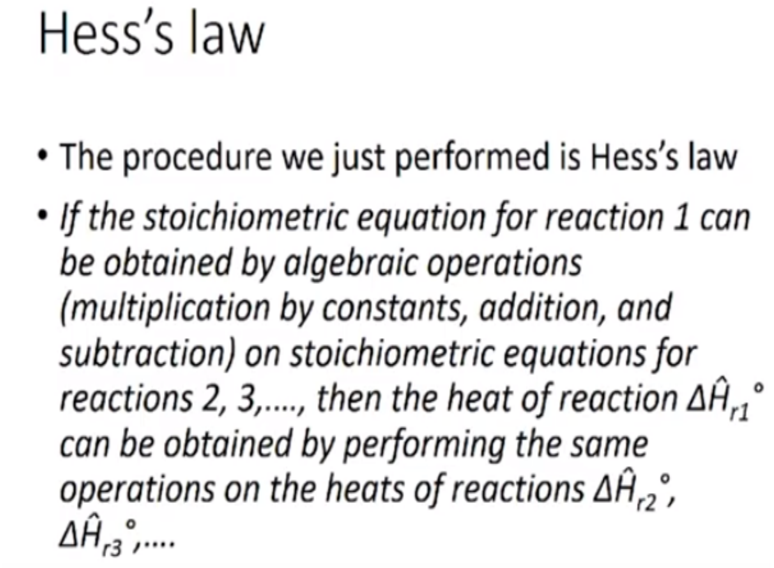

Hess's law

- The procedure we just performed is Hess's law
- *If the stoichiometric equation for reaction 1 can be obtained by algebraic operations (multiplication by constants, addition, and subtraction) on stoichiometric equations for reactions 2, 3,...., then the heat of reaction* $\Delta\hat{H}_{r1}^{\circ}$ *can be obtained by performing the same operations on the heats of reactions* $\Delta\hat{H}_{r2}^{\circ}$, $\Delta\hat{H}_{r3}^{\circ}$,....

What we did now is called as Hess's law. Hess's law is stated as if a stoichiometric equation for reaction 1 can be obtained by algebraic operations which could be multiplication by constants, addition and subtraction on stoichiometric equations for reactions 2, 3, 4 and so on then the heat of reaction for reaction 1 can be obtained by performing the same operations on the heats of reactions for reactions 2, 3, 4 and so on.

So this is the statement for Hess's law and this is what we just did and we can use this to calculate the heat of reaction for reactions that cannot be performed experimentally. So here is an example problem where we will try to use Hess's law and obtain the heat of reaction for a reaction which would not happen if you try to perform it experimentally.

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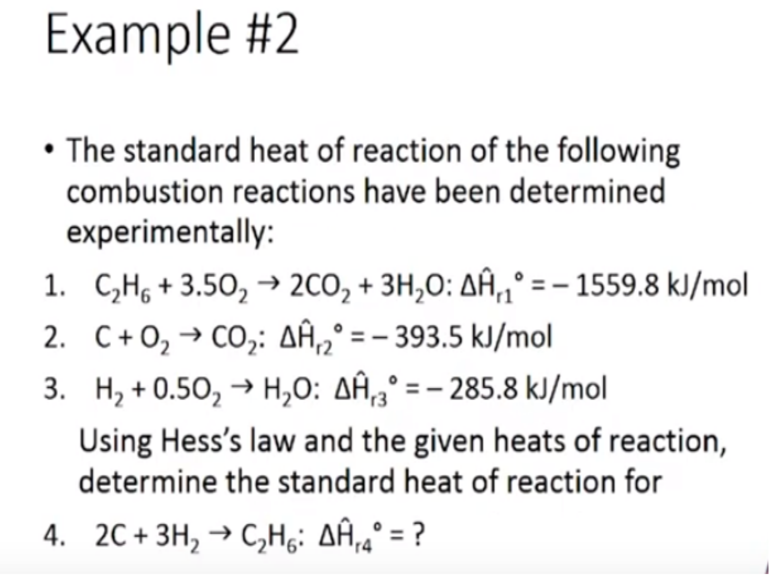

Example #2

- The standard heat of reaction of the following combustion reactions have been determined experimentally:

1. $C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$: $\Delta\hat{H}_{r1}^{\circ} = -1559.8$ kJ/mol
2. $C + O_2 \rightarrow CO_2$: $\Delta\hat{H}_{r2}^{\circ} = -393.5$ kJ/mol
3. $H_2 + 0.5O_2 \rightarrow H_2O$: $\Delta\hat{H}_{r3}^{\circ} = -285.8$ kJ/mol

Using Hess's law and the given heats of reaction, determine the standard heat of reaction for

4. $2C + 3H_2 \rightarrow C_2H_6$: $\Delta\hat{H}_{r4}^{\circ} = ?$

So the example states that standard heat of reaction of the following combustion reactions have been determined experimentally. C2H6 + 3.5O2 gives 2CO2 + 2H2O. C + O2 gives CO2. H2 + 0.5 O2 gives H2O. So all these are given. Now we need to calculate the heat of reaction for 2C + 3H2 gives C2H6 which is the fourth reaction. So this reaction would not happen in real life. Carbon and hydrogen directly reacting to form a hydrocarbon is not going to happen.

Though however the other reactions are all simple combustion reactions which could easily be carried out in a bomb calorimeter and you can measure the heat of reactions. So that is what has been done. Now our goal is to calculate the heat of reaction for the fourth reaction. How do we go about doing this?

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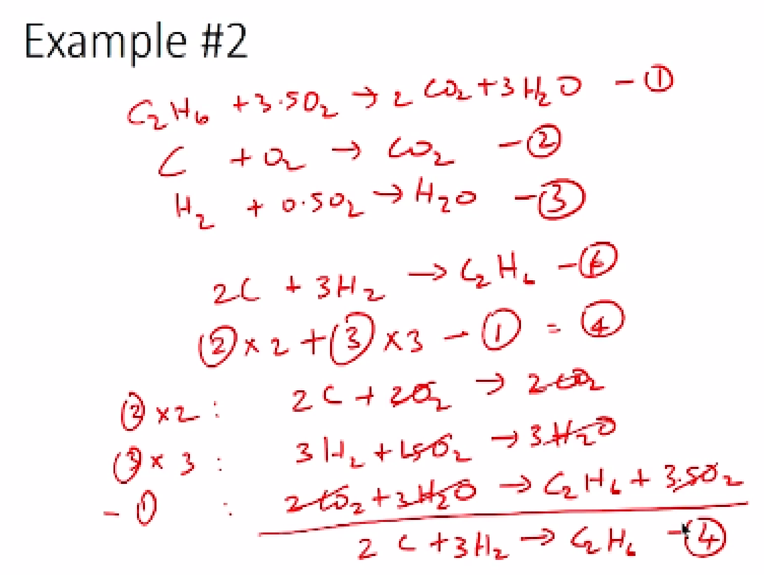

Example #2

$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$ − ①

$C + O_2 \rightarrow CO_2$ − ②

$H_2 + 0.5O_2 \rightarrow H_2O$ − ③

$2C + 3H_2 \rightarrow C_2H_6$ − ④

② × 2 + ③ × 3 − ① = ④

② × 2 : $2C + \cancel{2O_2} \rightarrow \cancel{2CO_2}$

③ × 3 : $3H_2 + \cancel{1.5O_2} \rightarrow \cancel{3H_2O}$

− ① : $\cancel{2CO_2} + \cancel{3H_2O} \rightarrow C_2H_6 + \cancel{3.5O_2}$

$2C + 3H_2 \rightarrow C_2H_6$ − ④

Let us look at the equations we had. The first equation we had was C2H6 + 3.5O2 gives 2 CO2 +3 H2O and the second equation is C + O2 gives CO2 and the third equation is H2 + 0.5 O2 gives H2O. So let us call this equation 1, 2, and 3. From here we have to get the fourth equation and the fourth equation is 2C + 3H2 gives C2H6. So from looking at the equations what we can see is C2H6 which is a reactant in the reaction one is a product in reaction 4.

So this means this has to be multiplied by -1 so that the reverse of the equation can be used and now what about the reactions 2 and 3. So in the reactions 2 you have 1 mole of carbon reacting. Whereas in your reaction 4 you have 2 moles of carbon reacting. So you can multiply reaction 2 with 2 to get 2 moles of carbon reacting on the in the fourth reaction. Similarly, for the third reaction you can multiply the reaction by 3 so that 3 moles of hydrogen reacts.

So let us do that. So if I were to do this particular algebraic operation which is reaction 2 times 2 + reaction 3 times 3 - reaction 1, I would get reaction 4. So let us see how that would look. So what you have would be when I do this operation 2 times 2 would basically look like 2C + 2O2 gives 2CO2 and 3 times 3 would basically look like 3H2 + 1.5 O2 gives 3H2O. Now reaction 1 I want to subtract it. So this would be changed.

So the reactants become the products and the products become the reactants. This becomes 2CO2 + 3H2O gives C2H6 + 3.5O2. So when I add all these what happens is these 3.5 oxygen molecules get cancelled and 2 moles of carbon dioxide gets cancelled and 3 moles of water gets cancelled and I end up with 2C + 3H2 gives C2H6 which is the reaction 4. So now that I have this equation, I know what algebraic operation has to be performed to the reactions 1, 2, and 3 to get the fourth reaction.

So I would be able to perform the same operations on the heat of reaction to get the heat of reaction for the fourth reaction.

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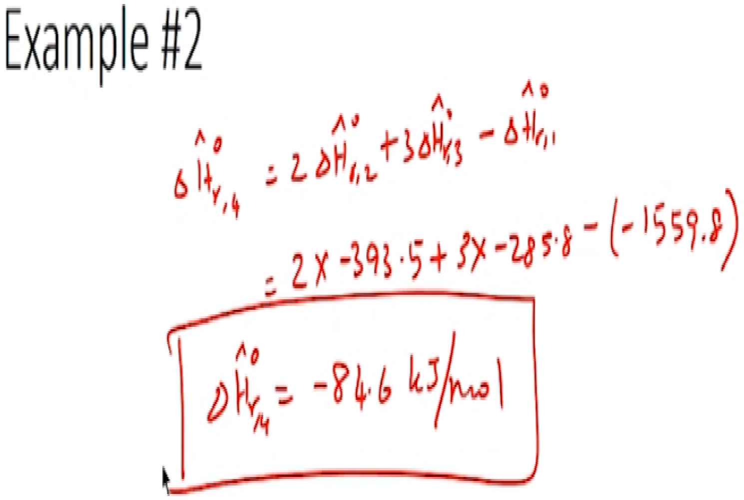

Example #2

$$\Delta \hat{H}^o_{r,4} = 2\Delta \hat{H}^o_{r,2} + 3\Delta \hat{H}^o_{r,3} - \Delta \hat{H}^o_{r,1}$$

$$= 2 \times -393.5 + 3 \times -285.8 - (-1559.8)$$

$$\boxed{\Delta \hat{H}^o_{r,4} = -84.6\ kJ/mol}$$

So the heat of reaction for the fourth reaction, standard rate of reaction for the fourth reaction would be equal to 2 delta H r 2 + 3 delta H r cap of reaction 3 - delta H r 1. So this would be 2 times -393.5 + 3 times -285.8 minus of -1559.8. So this is equal to -84.6 kJ/mol. So this would be the heat of reaction for the fourth reaction. Using Hess's law we have been able to calculate the heat of reaction for the fourth reaction using the 3 heats of reaction which we had.

All we had to identify was what algebraic operations had to be performed to actually get the fourth reaction from the first three reactions that were given. And then we performed the same algebraic operations on the heats of reactions as well. So now that we have an understanding of this let us move on to certain specific types of heats of reactions which can be used while we perform energy balance calculations.

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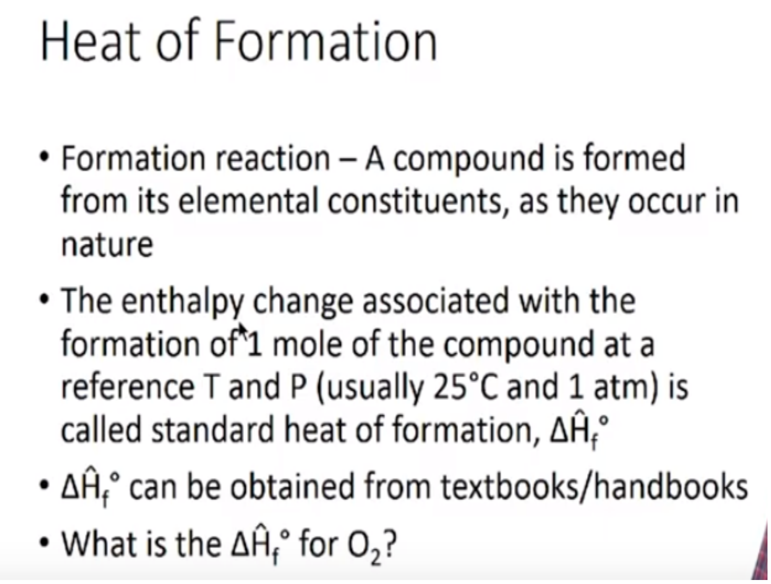

Heat of Formation

- Formation reaction – A compound is formed from its elemental constituents, as they occur in nature
- The enthalpy change associated with the formation of 1 mole of the compound at a reference T and P (usually 25°C and 1 atm) is called standard heat of formation, $\Delta\hat{H}_f^\circ$
- $\Delta\hat{H}_f^\circ$ can be obtained from textbooks/handbooks
- What is the $\Delta\hat{H}_f^\circ$ for O_2?

The first such reaction is a formation reaction. So the heat associated with the formation reaction is called as the heat of formation. So what is a formation reaction? A compound being formed from its elemental constituents as they occur in nature is called as the formation reaction.

So the enthalpy change which is associated with such a formation reaction where 1 mole of a compound is formed at a reference temperature and pressure which is usually 25 degree Celsius and 1 atmosphere is called as the standard heat of formation or it is given as delta H f cap and this value can be obtained from textbooks and handbooks. So if this is the case, then what would be the heat of formation, standard heat of formation for oxygen? It would be 0.

Because oxygen is an element in its native state. Oxygen gas would not have any heat of formation because that is what is present as nature. Whereas if you have a compound like carbon dioxide then you would have a heat of formation which would be carbon plus oxygen forming carbon dioxide.

In the previous example which we looked at for Hess's law the final equation which we had for C2H6 where you had 2C + 3H2 forming C2H6 is a type of formation reaction where ethane gas is formed assuming that all of them are existing in their native phases which was not explicitly listed but if we were to assume that then that reaction would be a heat of formation reaction.

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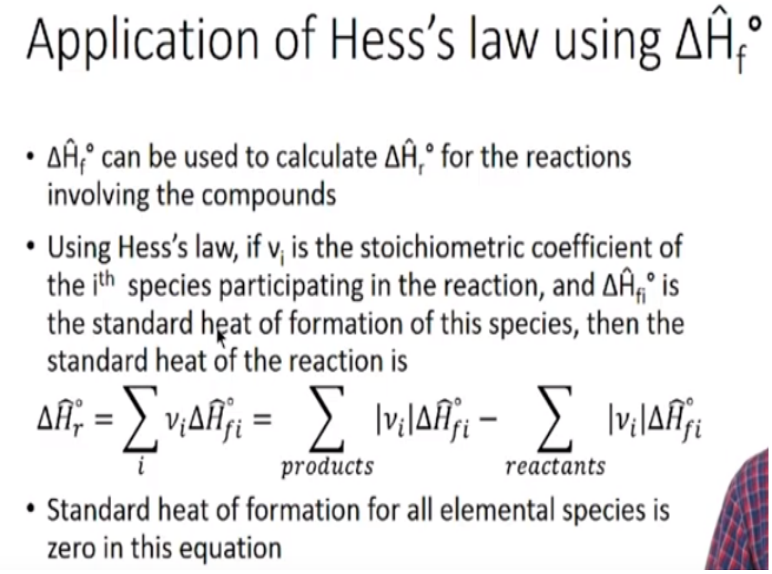

Application of Hess's law using $\Delta\hat{H}_f^\circ$

- $\Delta\hat{H}_f^\circ$ can be used to calculate $\Delta\hat{H}_r^\circ$ for the reactions involving the compounds
- Using Hess's law, if v_i is the stoichiometric coefficient of the i^{th} species participating in the reaction, and $\Delta\hat{H}_{fi}^\circ$ is the standard heat of formation of this species, then the standard heat of the reaction is

$$\Delta\hat{H}_r^\circ = \sum_i \nu_i \Delta\hat{H}_{fi}^\circ = \sum_{products} |\nu_i| \Delta\hat{H}_{fi}^\circ - \sum_{reactants} |\nu_i| \Delta\hat{H}_{fi}^\circ$$

- Standard heat of formation for all elemental species is zero in this equation

How do we apply Hess's law when we have heat of formation? Heat of formation can be used to calculate heat of reaction for any reaction which involves compounds. Using Hess's law if stoichiometric coefficient of an ith species can be given as nu i and the heat of formation, standard heat of formation of the species can be given as delta H cap f i then the standard heat of reaction can be calculated using this equation where standard heat of reaction is basically this.

First you find the sum of the stoichiometric coefficient times heat of formation of the products and subtract the sum of the stoichiometric coefficient times heat of formation of the reactants and you will finally get the heat of reaction. So we will verify how this works. We will look at an example problem that will help us understand and apply this principle correctly. So standard heat of formation for all elemental species will be 0 when you use this equation.

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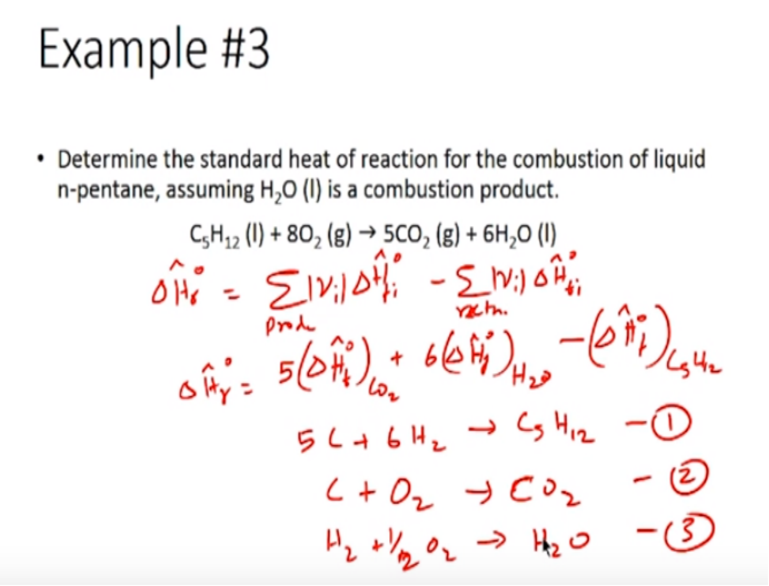

Example #3

- Determine the standard heat of reaction for the combustion of liquid n-pentane, assuming H_2O (l) is a combustion product.

$$C_5H_{12}\,(l) + 8O_2\,(g) \rightarrow 5CO_2\,(g) + 6H_2O\,(l)$$

$$\Delta\hat{H}_r^\circ = \sum_{prod} |\nu_i| \Delta\hat{H}_{fi}^\circ - \sum_{rctn.} |\nu_i| \Delta\hat{H}_{fi}^\circ$$

$$\Delta\hat{H}_r^\circ = 5(\Delta\hat{H}_f^\circ)_{CO_2} + 6(\Delta\hat{H}_f^\circ)_{H_2O} - (\Delta\hat{H}_f^\circ)_{C_5H_{12}}$$

$5C + 6H_2 \rightarrow C_5H_{12}$ −①

$C + O_2 \rightarrow CO_2$ −②

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ −③

So look at this example problem. So you are asked to determine the heat of reaction for combustion of liquid n-pentane assuming water liquid is a combustion product. So you might usually have water vapor as the combustion product. However, here they have given explicitly that water liquid is the combustion product so that we can find the standard heat of reaction for this reaction using the standard heats of formation.

So we need to know the heats of formation for n-pentane, carbon dioxide and water liquid and we can directly use these values and perform the calculations to identify the heat of reaction. While we do that we will verify if Hess's law is obeyed as we do the calculations. So based on the equation which you were given in the last slide, we would have delta H r cap as sigma (mu i) delta H f i cap - sigma (mu i) delta of H f i cap and the first one is for the products and the second one is for the reactants.

Now, this would mean that the equation would look like you have different components which are carbon dioxide and water liquid in the products. So the stoichiometric coefficients are 5 times (delta H f cap) carbon dioxide + 6 times (delta H f cap) water liquid and on the reactant side you only have pentane which is a compound. Oxygen is an element and we do not have to worry about that because the heat of formation for oxygen would be 0 and this would be 1 times (delta H f cap) pentane.

So once we have the heat of formation for these things we can actually calculate the heat of reaction. Now, before we perform these calculations let us verify if the equation we had is correct. So for that we will have to look at the Hess's law and for applying Hess's law we first need to use the formation reactions. We need to start with the formation reactions. Let us see if the formation reactions will follow the same equation to get the final equation of interest.

So the formation reaction for n-pentane would be 5 carbon + 6 Hydrogen gives C_5H_{12}. So this is the simple formation reaction for n-pentane. For carbon dioxide it would be $C + O_2$ gives CO_2. And for water it would be H_2SO_4 + 1/2 O_2 gives H_2O. So let us call these reactions 1, 2, and 3 and we will have to see if we can get the reaction of interest from these 3 equations and what operations we would have to do.

So the final reaction actually which is of interest actually has n-pentane being combusted. So n-pentane is in your reactant side. Here it is in the product side which means minus of reaction 1 has to be taken. So the reaction 1 has to be subtracted from the 2 and 3 reactions anyway. So the 2 and 3 you have again carbon dioxide as product and water as product in the reaction of interest and also in reactions 2 and 3.

However, we have 5 moles of carbon and 6 moles of water being produced. Here we have only 1 mole of carbon dioxide and 1 mole of water being produced. So we will have to multiply reaction 2 with 5 and reaction 3 with 6 to get the same number of moles of water and carbon dioxide as in the reaction of interest.

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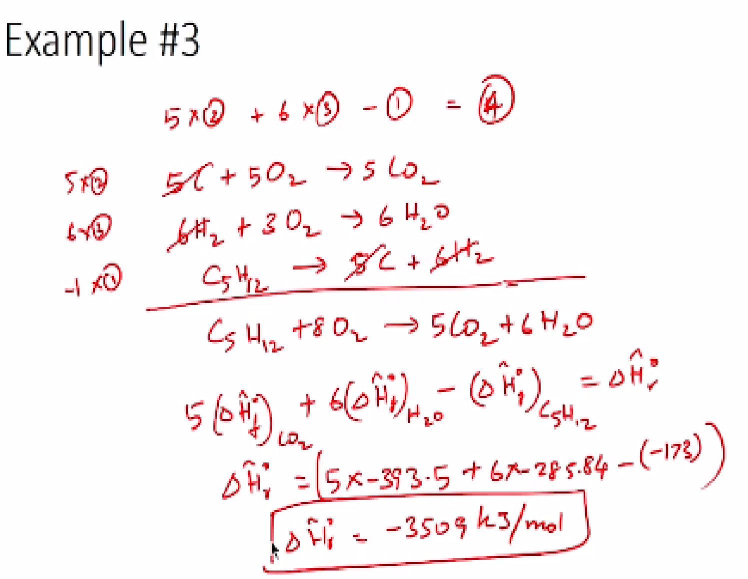

Example #3

$5\times② + 6\times③ - ① = ④$

$5\times②$ $\quad \cancel{5C} + 5O_2 \rightarrow 5CO_2$

$6\times③$ $\quad \cancel{6H_2} + 3O_2 \rightarrow 6H_2O$

$-1\times①$ $\quad C_5H_{12} \rightarrow \cancel{5C} + \cancel{6H_2}$

$C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$

$5(\Delta\hat{H}_f^\circ)_{CO_2} + 6(\Delta\hat{H}_f^\circ)_{H_2O} - (\Delta\hat{H}_f^\circ)_{C_5H_{12}} = \Delta\hat{H}_r^\circ$

$\Delta\hat{H}_r^\circ = (5\times-393.5 + 6\times-285.84 - (-173))$

$\boxed{\Delta\hat{H}_r^\circ = -3509\ kJ/mol}$

So let us do that. What we would have would be 5 times reaction 2 + 6 times reaction 3 - reaction 1 should give us reaction 4. So let us see what that would be. It would be 5C + 5O2 gives 5 CO2 and this next equation would be 6H2 + 6 times 1/2 this 3O2 gives 6H2O and the last equation because we are going to subtract it we will change the reactants and the product sides. So that would become C2H5 sorry C5H12 becomes 5C + 6H2, it is H12 okay.

Now, let us find the summation of these 3 reactions. So this is basically 5 times 2 that I have done, 6 times 3 that I have done and -1 times 1 that I have done. Adding all this, what we end up with is 5 carbon gets cancelled, 6 hydrogen gets cancelled and you have C5H12 + 8 oxygen gives 5CO2 + 6H2O.

So using Hess's law, what you have is 5 times the heat of reaction for reaction 2 which would be the heat of formation of carbon dioxide plus 6 times the heat of formation for water liquid minus the heat of formation for n-pentane which is exactly what we did based on the equation that was given. So if we were given the heat of formation for carbon dioxide, water, and n-pentane we can calculate the heat of reaction for the reaction of interest.

So knowing the heat of formation for carbon dioxide and water, we will plug them here. This can be obtained from your textbook or from any reference book. This would be 5 times -393.5 + 6 times -285.84 – (-173) and this value is delta H r cap = -3509 kJ/mol. So this is the heat of reaction for the combustion reaction where n-pentane liquid is burnt to produce carbon dioxide and water liquid.

So with this we have seen how we can use heat of formation for performing calculations using Hess's law and identifying the heat of reaction for any given reaction.

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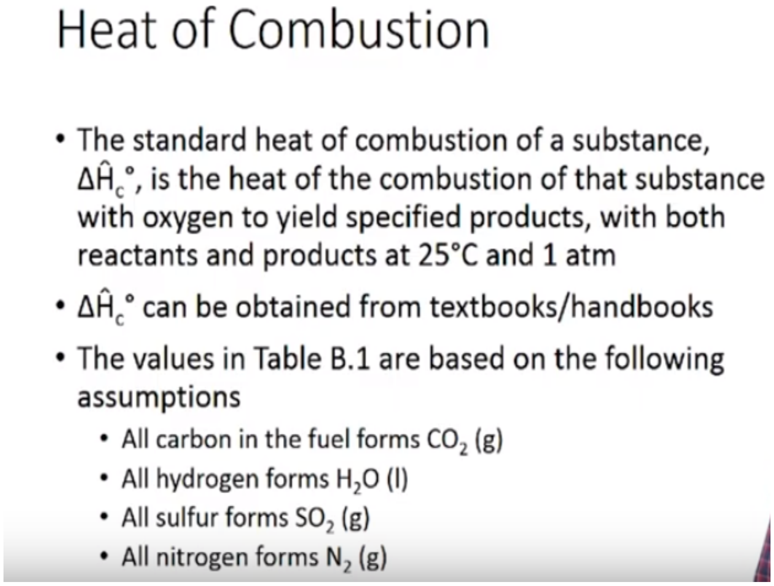

Heat of Combustion

- The standard heat of combustion of a substance, $\Delta\hat{H}_c^\circ$, is the heat of the combustion of that substance with oxygen to yield specified products, with both reactants and products at 25°C and 1 atm
- $\Delta\hat{H}_c^\circ$ can be obtained from textbooks/handbooks
- The values in Table B.1 are based on the following assumptions
  - All carbon in the fuel forms CO_2 (g)
  - All hydrogen forms H_2O (l)
  - All sulfur forms SO_2 (g)
  - All nitrogen forms N_2 (g)

Similar to heat of formation, there is also another type of reaction which is commonly used which is the combustion reaction. Heat of combustion also needs to be looked at carefully. The standard heat of combustion of a substance is the heat of combustion of that substance with oxygen to yield specified products with both reactants and products at 25 degree Celsius and 1 atmosphere.

This is the standard heat of combustion, so basically any component which you have when it is burnt will produce the combustion products. We have already looked at what is combustion and what complete combustion stands for when we discussed combustion reactions as part of material balances. Please go and look it up and refer back to understand what it is.

And when it yields these specific products and assuming the products and the reactants are at the same temperature, the change in enthalpy for this process, for this reaction is called as the standard heat of combustion. The standard heat of combustion can again be obtained from textbooks and handbooks.

And the values in table B.1 in the your textbook Felder Rousseau is based on the following assumptions, all carbon forms carbon dioxide which means the reaction goes to completion and all hydrogen forms water liquid and all sulphur forms sulphur dioxide gas and all nitrogen just remains as nitrogen. So based on this assumption, the heat of combustions have been listed in table B.1.

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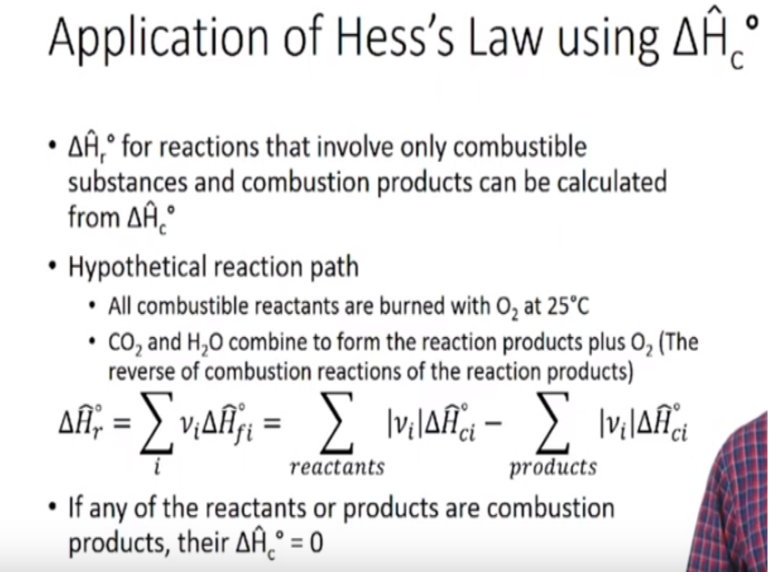

Application of Hess's Law using $\Delta\hat{H}_c^\circ$

- $\Delta\hat{H}_r^\circ$ for reactions that involve only combustible substances and combustion products can be calculated from $\Delta\hat{H}_c^\circ$
- Hypothetical reaction path
  - All combustible reactants are burned with O_2 at 25°C
  - CO_2 and H_2O combine to form the reaction products plus O_2 (The reverse of combustion reactions of the reaction products)

$$\Delta\hat{H}_r^\circ = \sum_i \nu_i \Delta\hat{H}_{fi}^\circ = \sum_{reactants} |\nu_i| \Delta\hat{H}_{ci}^\circ - \sum_{products} |\nu_i| \Delta\hat{H}_{ci}^\circ$$

- If any of the reactants or products are combustion products, their $\Delta\hat{H}_c^\circ = 0$

So just like how we did heat of formation and used Hess's law to calculate heat of reaction, we can use heat of combustion to calculate heat of reactions for reactions that involve only combustible substances and combustion products. So you can create a hypothetical path where all combustible reactants are burned with oxygen at 25 degree Celsius. Carbon dioxide and hydrogen combine to form the reaction products plus oxygen.

The reverse of combustion reactions of the reaction products and therefore using this assumption we can calculate the heat of reaction as first the summation of the stoichiometric coefficient times heat of combustion for the reactants minus the summation of the stoichiometric coefficients and the heat of combustion of the products. If any of the reactants or products are actually combustion products then you would use the heat of combustion as 0 for those things.

For example if you have carbon dioxide as part of the reaction then you would have the heat of combustion for carbon dioxide as 0.

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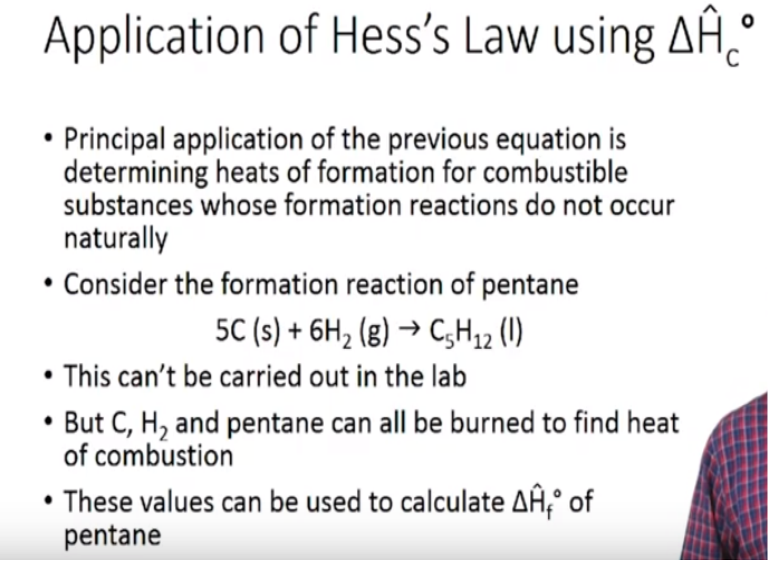

Application of Hess's Law using $\Delta\hat{H}_c^\circ$

- Principal application of the previous equation is determining heats of formation for combustible substances whose formation reactions do not occur naturally
- Consider the formation reaction of pentane

$$5C\ (s) + 6H_2\ (g) \rightarrow C_5H_{12}\ (l)$$

- This can't be carried out in the lab
- But C, H_2 and pentane can all be burned to find heat of combustion
- These values can be used to calculate $\Delta\hat{H}_f^\circ$ of pentane

So the principle application of this equation is to determine the heat of formation for combustible substances for which you cannot actually get the formation reactions occurring. So the example would be the example we used for Hess's law where we tried to calculate the heat of formation for ethane which is C2H6 and all we did was we had 3 different combustion reactions which we combined to get the reaction of interest.

So consider the formation of the reaction for pentane which is shown here. 5 carbon + 6 hydrogen giving C5H12. This reaction cannot be carried out in the lab. It will not happen. But carbon, hydrogen and pentane can all be burnt to find the heat of combustion. So then you can use these heat of combustions to get the heat of formation for n-pentane. So this is how Hess's law is applied for using heat of combustion to get the heat of formation of heat of reactions.

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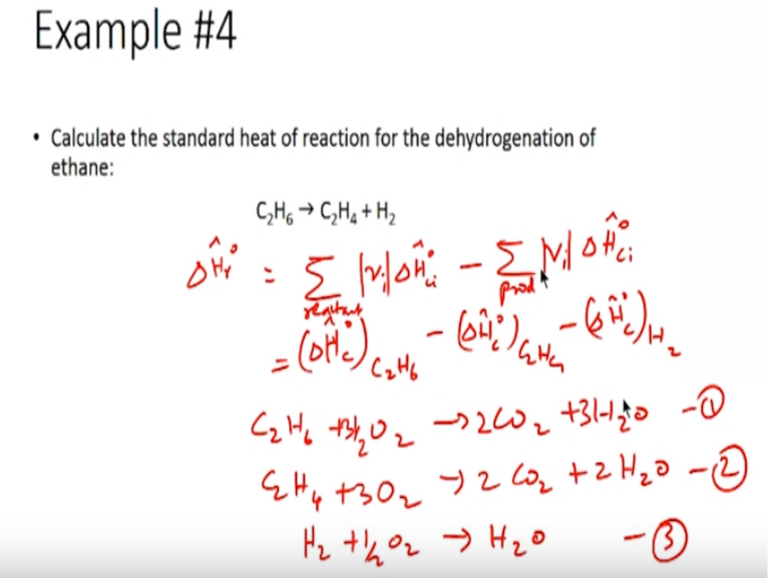

Example #4

- Calculate the standard heat of reaction for the dehydrogenation of ethane:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$$\Delta \hat{H}_r^\circ = \sum_{reactant} |\nu_i| \Delta \hat{H}_{c_i}^\circ - \sum_{prod} |\nu_i| \Delta \hat{H}_{c_i}^\circ$$

$$= (\Delta \hat{H}_c^\circ)_{C_2H_6} - (\Delta \hat{H}_c^\circ)_{C_2H_4} - (\Delta \hat{H}_c^\circ)_{H_2}$$

$$C_2H_6 + 3\tfrac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O \quad - ①$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad - ②$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \quad - ③$$

So here is one example problem where we have to calculate the heat of reaction for a dehydrogenation reaction. Ethane becomes ethylene and hydrogen and the heat of reaction for this has to be calculated using the heat of combustion for ethane, ethylene, and hydrogen. So combustion reactions can actually be used here. So let us see how it would be done. So we can use the equation directly and we will also verify if it obeys Hess's law.

So if we use the equation directly, the heat of reaction would be equal to sigma of reactants mu i delta H cap C i - sigma of products mu i delta of H cap C i. So this would be the heat of reaction. So we have reactants minus products. So reactants would be 1 times C2H6. So that is heat of combustion for C2H6 minus heat of combustion for C2H4 minus heat of combustion for hydrogen.

Now, let us look at the combustion reaction for the individual components and try to see if these values, the equation can be derived. So you have C2H6 + oxygen forming CO2 + H2O. So you would have 2CO2 and 3H2O being formed involving 3 1/2 moles of oxygen reacting so that you have 7 atoms, 4 + 3, 7 atoms of oxygen. And you have C2H4 + oxygen forming 2CO2 + 2H2O being formed. You will have 3 molecules of oxygen reacting for this.

And finally you would have hydrogen + 1/2 O2 reacting to form H2O. So now let us call these as equations 1, 2, and 3. So to get this final equation, we have C2H6 in the reactant side. So you can have the reaction 1 as such. The second equation we have the reactant C2H4 in the product side. So we multiply this by -1 and the other one we will again multiply it by -1 so that the hydrogen goes to the next side.

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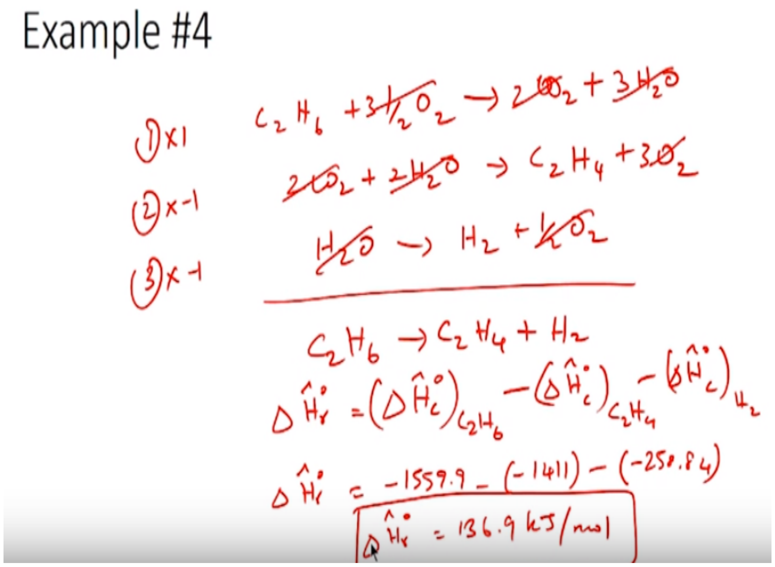

Example #4

① ×1 $C_2H_6 + \cancel{3\frac{1}{2}O_2} \rightarrow \cancel{2CO_2} + \cancel{3H_2O}$

② ×-1 $\cancel{2CO_2} + \cancel{2H_2O} \rightarrow C_2H_4 + \cancel{3O_2}$

③ ×-1 $\cancel{H_2O} \rightarrow H_2 + \cancel{\frac{1}{2}O_2}$

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$$\Delta\hat{H}_r^\circ = (\Delta\hat{H}_c^\circ)_{C_2H_6} - (\Delta\hat{H}_c^\circ)_{C_2H_4} - (\Delta\hat{H}_c^\circ)_{H_2}$$

$$\Delta\hat{H}_r^\circ = -1559.9 - (-1411) - (-250.84)$$

$$\boxed{\Delta\hat{H}_r^\circ = 136.9\ kJ/mol}$$

So what you would have is equation 1 times 1, equation 2 times -1 and equation 3 times -1 as the operations so that we get the combustion equations as C2H6 + 3 1/2 O2 gives 2CO2 + 3H2O and the next equation would be 2CO2 + 2H2O gives C2H4 + 3O2. So this is basically the reverse of the second reaction which we had. And similarly the reverse of the other reaction would be H2O gives H2SO4 + 1/2 O2.

So now, in this equation, when we add these equations, the 3 1/2 oxygen in the reactant side will get cancelled with the 3 1/2 oxygen in the product side. Carbon dioxide gets cancelled. Water gets cancelled. So leaving out C2H6 gives C2H4 + H2. So the operation we did was 1 times reaction 1 - 1 times reaction 2 - 1 times reaction 3 which means your delta H r cap would be equal to delta heat of combustion for C2H6 minus heat of combustion for C2H4 minus heat of combustion for hydrogen.

So this is the same as the equation which we have here which was obtained from the equation that was given earlier. So therefore, we can calculate the heat of reaction using the heat of combustions that can be obtained from any table. So the heat of combustions for these values are

-1559.9 for C2H6 – (-1411) for C2H4 and – (-258.84) for hydrogen giving the heat of reaction for the reaction of interest as 136.9 kJ/mol.

So this is how we can apply Hess's law for combustion reactions. With this we have looked at all the fundamentals that are required for performing energy balances in reactive processes. So in the next lecture we will perform more calculations to strengthen our fundamentals by performing a tutorial session on these concepts. Until then thank you and good bye.