Material and Energy Balance Computations
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Lecture-54
Energy Balance with Chemical Reactions-IV

In this class we will continue with calculation of the heat of formation using the 'Hess law' and heat of combustion data. Now you may not always be interested in finding out the heat of formation data only there might be situations that you are dealing with compounds, all of which you know the heat of combustion data. We know that for a given reaction if heat of formation data of all compounds which are in the products and the reactants getting a element as the product is very rare; in most of the cases you get products straight away, you get compounds as products, but reactants might be elements or compounds. So, for any given chemical reaction if the heat of formation data of all compounds that are involved either in the form of product or maybe also as reactants.

If those are known the standard heat of reaction at 25°C you can find out and we also discussed about what happens if you have reactants and products at different temperature you essentially have to consider that the change in enthalpy. So, maybe I will just write it down, so for the sake of completeness because this I remember I did not write down the expression I just mentioned.

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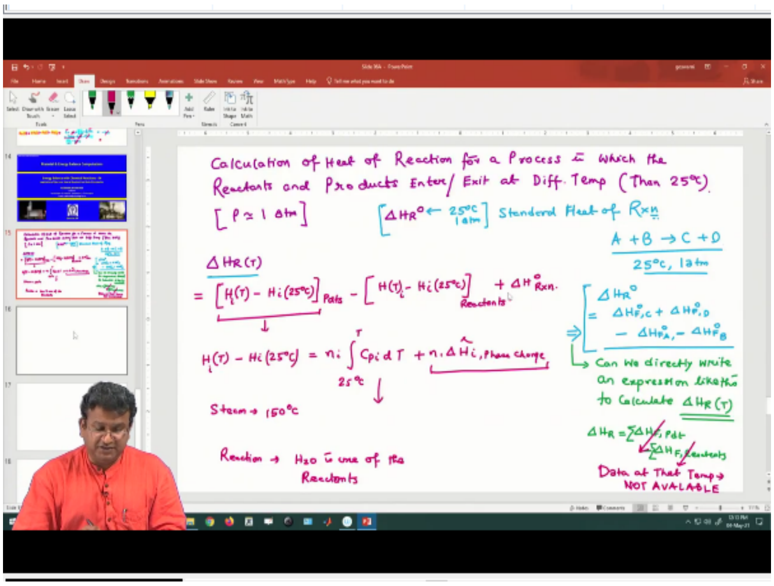

Calculation of Heat of Reaction for a Process in which the Reactants and Products Enter/ Exit at Diff. Temp (Than 25°C).

$[P \simeq 1\ \text{atm}]$ $\left[\Delta H_R^\circ \leftarrow \begin{smallmatrix}25^\circ C\\ 1\,atm\end{smallmatrix}\right]$ Standard Heat of Rxn

$A + B \rightarrow C + D$

25°C, 1 atm

$\Delta H_R(T)$

$$= \underbrace{\left[H_i(T) - H_i(25^\circ C)\right]_{Pdts}}_{\downarrow} - \left[H_i(T) - H_i(25^\circ C)\right]_{Reactants} + \Delta H^\circ_{Rxn}$$

$$\Rightarrow \left[\Delta H_R^\circ = \Delta H^\circ_{F,C} + \Delta H^\circ_{F,D} - \Delta H^\circ_{F,A} - \Delta H^\circ_{F,B}\right]$$

$$H_i(T) - H_i(25^\circ C) = n_i \int_{25^\circ C}^{T} C_{pi}\, dT + \underbrace{n_i \Delta \hat{H}_{i,\text{Phase change}}}$$

Steam → 150°C

Reaction → H_2O is one of the Reactants

→ Can we directly write an expression like this to Calculate $\Delta H_R(T)$

$\Delta H_R = \sum \Delta H_{F,Pdt} - \sum \Delta H_{F,Reactants}$

Data at That Temp → NOT AVALABLE

So, calculation of heat of reaction for a process in which the reactants and products enter or exit at different temperature than 25°C. As of now we are assuming pressure is constant at 1 atmosphere. So, what is the fundamental difference between standard heat of reaction (ΔH_R^0) and heat of reaction $\Delta H_{R(T)}$? Heat of reaction at any particular temperature, this temperature you need to specify, and the symbol is no longer this 0.

This 0 actually implies that your reaction is taking place at 25°C and 1 atm. So, this is the standard heat of reaction, however it is possible as I mentioned in the previous class it is possible to calculate or have heat of reaction at any temperature. So, when you talk about heat of reaction at any temperature. So, what exactly do you do? Because the problem is as follows.

So, suppose if you have a reaction where let us say $A + B \rightarrow C + D$. Now if the reaction is taking place at 25°C and 1 atm and A, B, C, D can be elements or compounds. So, what I was trying to emphasize that C and D since they are products of a chemical reaction in most cases, they are compounds, that there are certain reactions where elements get generated.

For example, synthesis reactions of oxygen. So, A, B, C, D can be elements or compounds. Now you know that if reaction is progressing at 25°C and 1 atm, the standard heat of reaction you can straight away find out from the standard heat of formation the calculating the standard heat of formations as follows

$$\Delta H_R^0 = \Delta H_{P,\,C}^0 + \Delta H_{P,\,D}^0 - \Delta H_{P,\,A}^0 - \Delta H_{P,\,B}^0$$

Now, can we directly write an expression like this to calculate $\Delta H_{R(T)}$ at any temperature?

The answer is theoretically yes provided you know the heat of formation data for all these participating reactants and products at that temperature. But unfortunately heat of formation you typically would not find a table which gives heat of formation at different temperatures. Heat of formation is available only under the standard condition because that is why it is called the standard heat of formation.

So, even if you write an expression like this and you say that $\Delta H_R = \sum \Delta H_{F,\,pdt} - \sum \Delta H_{F,\,reactants}$

It is a very practical problem and you need to understand the practicality these data are not available at that temperature.

So, what is the way out? The way out is very simple you essentially need to think that as if your reactants are first brought down to a temperature of 25°C, then the reaction takes place over there and then the products are heated up back to whatever is the exit temperature. The reactants and the products can be at the same temperature. So, your expression for heat of reaction at any particular temperature now reduces to,

$\Delta H_{R(T)} = [H_i(T) - H_i(25°C)]_{pdts} - [H_i(T) - H_i(25°C)]_{reactants} + \Delta H_R^0$

Where $[H_i(T) - H_i(25°C)]$ is the enthalpy change for i^{th} component and how do you calculate it? So, these are very simple actually.

So, $[H_i(T) - H_i(25°C)] = n_i \int_{25°C}^{T} C_{Pi}\, dT + n.\Delta H_{i,\text{ phase change}}$ cap

Where n_i is number of moles present. The 2^{nd} term is required when there are any phase changes. So, if there is some phase change associated then even for the first term, it might get more complicated. Then we have to first calculate the enthalpy change up to the phase change temperature let us say up to the boiling point. So, it can be very simple example suppose you have steam entering into a reaction chamber as a reactant not being used as a cooling medium or heating medium. So, what does it mean? Let us say steam enters the chamber at 150 degree centigrade and then you have a reaction where water is one of the reactants. So, what does it mean? What you have to do? You have to assume as if this steam let us say it is at 1 atmospheric pressure let us complicate the complication associated with pressure.

So, you have to assume that this steam is reduced to a temperature from vapour phase to the liquid phase; from vapour phase 150 degree centigrade at vapour phase to liquid phase at 25 degree centigrade. So, what happens to this particular term? You actually have the sensible heat part to be calculated based on the C p value of steam from 150 degree centigrade to 100 degree centigrade.

Then there is a phase change at 100 degree centigrade and then you have to consider the C p value or the calculate the sensible heat for liquid water from 100 degree centigrade to 25 degree centigrade, it goes like this. So, essentially this is how you calculate the heat of reaction if your reactants and products are at different a temperature which is not at 25 degree centigrade. I am not talking about the pressure effects right now. So, anyway this is sort of a side discussion which probably is little bit of left over from one of our previous classes.

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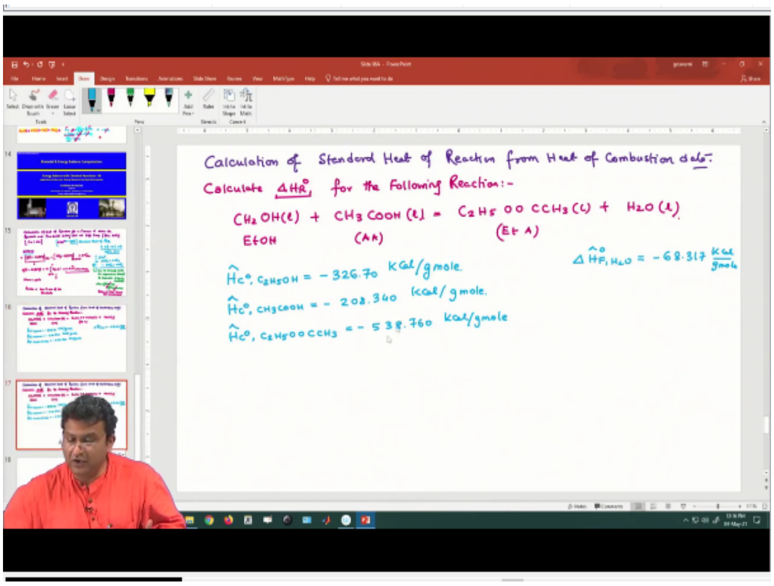

Calculation of Standard Heat of Reaction from Heat of Combustion data:

Calculate $\underline{\Delta H_R^0}$ for the Following Reaction:-

$CH_2OH(l) + CH_3COOH(l) = C_2H_5OOCCH_3(l) + H_2O(l)$

EtOH (AA) (EtA)

$\hat{H}_{c,C_2H_5OH}^0 = -326.70$ KCal/gmole

$\hat{H}_{c,CH_3COOH}^0 = -208.340$ KCal/gmole.

$\hat{H}_{c,C_2H_5OOCCH_3}^0 = -538.760$ KCal/gmole

$\Delta \hat{H}_{F,H_2O}^0 = -68.317 \frac{KCal}{gmole}$

So, right now for this lecture we were continuing with the application of Hess law and essentially, we are going to pick up another example of calculation of standard heat of reaction from heat of combustion data. So, this is how it goes and for this let us pick up one example. So, let us say calculate the standard heat of reaction (ΔH_R^0). Here '0' represents that it is standard heat of reaction. And if it is simply ΔH_R then immediately you must ask for the temperature and pressure? Because ΔH_R^0 is specified at 25 degree centigrade and 1 atmospheric pressure. So, calculate ΔH_R for the following reaction and this is the beginning of some very interesting discussion.

$$C_2H_5OH\ (l) + CH_3COOH\ (l) = C_2H_5OOCCH_3\ (l) + H_2O\ (l)$$

(Ethyl Alcohol) + (Acetic Acid) = (Ethyl Acetate) + (Water)

If one is told to calculate the heat of reaction for this and if you know the heat of formation of water, ethyl acetate, acetic acid and ethyl alcohol; you can straight away do that. But instead of these 3 'heat of combustion' data {$H_{C,\ C2H5OH}^0$ cap = -326.70 KCal/gmole; $H_{C,\ CH3COOH}^0$ cap = -208.340 KCal/gmole; $H_{C,\ C2H5OOCCH3}^0$ cap = -538.760 KCal/gmole} along with the heat of formation data of water i.e. $\Delta H_{F,\ H2O}^0$ cap = -68.317 Kcal/gmole are provided to you. So, how do we go about this whole stuff?

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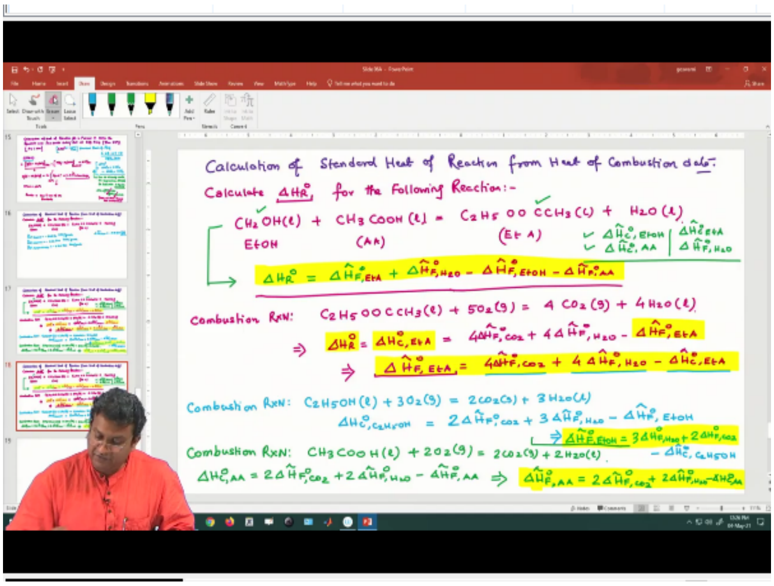

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EtOH (AA) (EtA)

✓ $\Delta\hat{H}^0_{C,EtOH}$ | $\Delta\hat{H}^0_{C,EtA}$

✓ $\Delta\hat{H}^0_{C,AA}$ | $\Delta\hat{H}^0_{F,H_2O}$

$$\Delta H_R^0 = \Delta\hat{H}^0_{F,EtA} + \Delta\hat{H}^0_{F,H_2O} - \Delta\hat{H}^0_{F,EtOH} - \Delta\hat{H}^0_{F,AA}$$

Combustion RxN: $C_2H_5OOCCH_3(l) + 5O_2(g) = 4CO_2(g) + 4H_2O(l)$

$$\Rightarrow \Delta H_R^0 = \Delta\hat{H}^0_{C,EtA} = 4\Delta\hat{H}^0_{F,CO_2} + 4\Delta\hat{H}^0_{F,H_2O} - \Delta\hat{H}^0_{F,EtA}$$

$$\Rightarrow \Delta\hat{H}^0_{F,EtA} = 4\Delta\hat{H}^0_{F,CO_2} + 4\Delta\hat{H}^0_{F,H_2O} - \Delta\hat{H}^0_{C,EtA}$$

Combustion RxN: $C_2H_5OH(l) + 3O_2(g) = 2CO_2(g) + 3H_2O(l)$

$$\Delta H^0_{C,C_2H_5OH} = 2\Delta\hat{H}^0_{F,CO_2} + 3\Delta\hat{H}^0_{F,H_2O} - \Delta\hat{H}^0_{F,EtOH}$$

$$\Rightarrow \Delta\hat{H}^0_{F,EtOH} = 3\Delta\hat{H}^0_{F,H_2O} + 2\Delta\hat{H}^0_{F,CO_2} - \Delta\hat{H}^0_{C,C_2H_5OH}$$

Combustion RxN: $CH_3COOH(l) + 2O_2(g) = 2CO_2(g) + 2H_2O(l)$

$$\Delta H^0_{C,AA} = 2\Delta\hat{H}^0_{F,CO_2} + 2\Delta\hat{H}^0_{F,H_2O} - \Delta\hat{H}^0_{F,AA} \Rightarrow \Delta\hat{H}^0_{F,AA} = 2\Delta\hat{H}^0_{F,CO_2} + 2\Delta\hat{H}^0_{F,H_2O} - \Delta H^0_{C,AA}$$

So, to calculate the standard heat of reaction for this equation we know that the expression is going to be

$$\Delta H_R{}^0 = \Delta H_{F,\,EtA}{}^0 \text{ cap} + \Delta H_{F,\,H2O}{}^0 \text{ cap} - \Delta H_{F,\,EtOH}{}^0 \text{ cap} - \Delta H_{F,\,AA}{}^0 \text{ cap}$$

So, this is the final expression that you will be needing under any circumstances. So, what exactly is the challenge here? Challenge here is heat of combustion data for all these compounds are given. So, now we need to look into the heat of combustion reactions for each one of them. So, for example the combustion reaction for ethyl acetate for example C 2 H 5 OOCCH 3 and this is in the liquid form if you stoichiometrically write it as follows

$$C_2H_5OOCCH_3\ (l) + 5O_2\ (g) = 4CO_2\ (g) + 4H_2O\ (l)$$

So, in other words what we have is

Heat of reaction of this particular reaction = (Heat of combustion for ethyl acetate) = 4×(Heat of formation of CO_2) + 4×(Heat of formation of water) – (Heat of formation of ethyl acetate).

Of course, as we know heat of formation of oxygen is going to be 0. So, from here we actually now get an expression for

Heat of formation of ethyl acetate = 4×(Heat of formation of CO_2) + 4×(Heat of formation of H2O) – (Heat of combustion of ethyl acetate).

I hope it is clear to all of you. So, what are we doing? We now know in order to calculate the heat of reaction we actually have to use this expression. So, what we are doing is we are looking at the combustion reactions, so we know the expression of these combustion reactions. So, essentially the heat of combustion is nothing but the heat of reaction and which involves the expression of the heat of combustion or the heat of formation of ethyl acetate.

So, all we are doing is we are now rearranging the expression in such a way that we now have an equation for heat of formation of ethyl acetate and that we are getting it in terms of heat of formation of carbon dioxide, heat of formation of water and heat of combustion of ethyl acetate. I hope it is clear. So, you can start guessing what next. What next is that we need to look into the combustion reaction for C_2H_5OH and which turns out to be

$$C_2H_5OH\ (l) + 3O_2 = 2CO_2\ (g) + 3H_2O\ (l)$$

So, the heat of combustion of C_2H_5OH which is the heat of reaction = 2×(Heat of formation of carbon dioxide) + 3×(Heat of formation of water) – (Heat of formation oxygen) (which of course gets cancelled away) – (Heat of formation of EtOH).

So, from here we will get an expression for heat of formation of EtOH = 3×(Heat of formation of water) + 2×(Heat of formation of CO_2) – (Heat of combustion of C_2H_5OH).

So, here we have looked into the combustion reaction of ethyl acetate, the combustion reaction of ethyl alcohol. So, next we need to look into the combustion reaction of Acetic Acid (CH_3COOH).

$$CH_3COOH\ (l) + 2O_2\ (g) = 2CO_2\ (g) + 2H_2O\ (l)$$

So, from here one can write for the heat of combustion for acetic acid = 2× (Heat of formation CO_2) + 2× (Heat of formation of H_2O) – (Heat of combustion of Acidic Acid). This is what we get and what is important for us is these 3 expressions as highlighted in yellow in the following slide.

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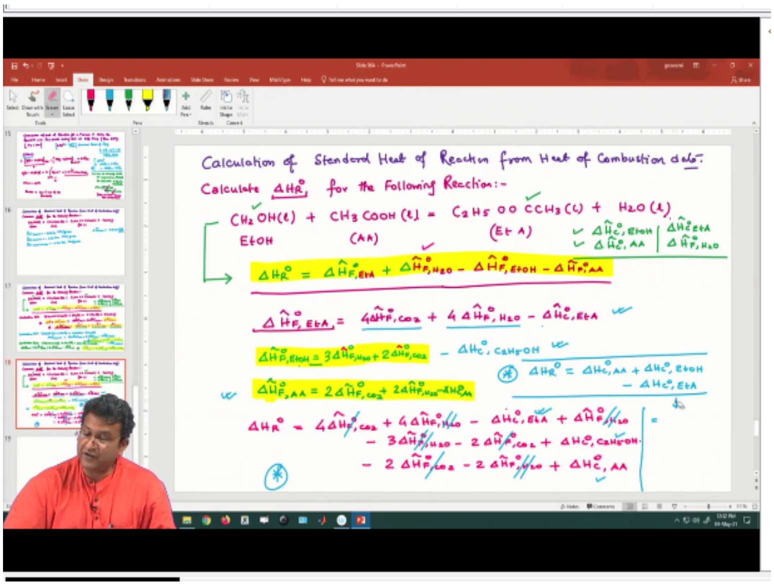

Calculation of Standard Heat of Reaction from Heat of Combustion data:

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EtOH (AA) (Et A)

✓ $\Delta\hat{H}^\circ_{c,EtOH}$ | $\Delta\hat{H}^\circ_{c,EtA}$

✓ $\Delta\hat{H}^\circ_{c,AA}$ | $\Delta\hat{H}^\circ_{F,H_2O}$

$\Delta H_R^\circ = \Delta\hat{H}^\circ_{F,EtA} + \Delta\hat{H}^\circ_{F,H_2O} - \Delta\hat{H}^\circ_{F,EtOH} - \Delta\hat{H}^\circ_{F,AA}$

$\Delta\hat{H}^\circ_{F,EtA} = 4\Delta\hat{H}^\circ_{F,CO_2} + 4\Delta\hat{H}^\circ_{F,H_2O} - \Delta\hat{H}^\circ_{c,EtA}$

$\Delta\hat{H}^\circ_{F,EtOH} = 3\Delta\hat{H}^\circ_{F,H_2O} + 2\Delta\hat{H}^\circ_{F,CO_2} - \Delta H^\circ_{c,C_2H_5OH}$

$\Delta\hat{H}^\circ_{F,AA} = 2\Delta\hat{H}^\circ_{F,CO_2} + 2\Delta\hat{H}^\circ_{F,H_2O} - \Delta H^\circ_{c,AA}$

(*) $\Delta H_R^\circ = \Delta H^\circ_{c,AA} + \Delta H^\circ_{c,EtOH} - \Delta H^\circ_{c,EtA}$

$$\Delta H_R^\circ = 4\cancel{\Delta\hat{H}^\circ_{F,CO_2}} + 4\cancel{\Delta\hat{H}^\circ_{F,H_2O}} - \Delta H^\circ_{c,EtA} + \cancel{\Delta\hat{H}^\circ_{F,H_2O}} - 3\cancel{\Delta\hat{H}^\circ_{F,H_2O}} - 2\cancel{\Delta\hat{H}^\circ_{F,CO_2}} + \Delta H^\circ_{c,C_2H_5OH} - 2\cancel{\Delta\hat{H}^\circ_{F,CO_2}} - 2\cancel{\Delta\hat{H}^\circ_{F,H_2O}} + \Delta H^\circ_{c,AA}$$

(*)

So, now what we already have is the expressions for the 3 heat of formations as you need over here and calculate the heat of reaction as shown in the last of the above slide. So, what we get is a very neat and compact expression of heat of reaction is as follows

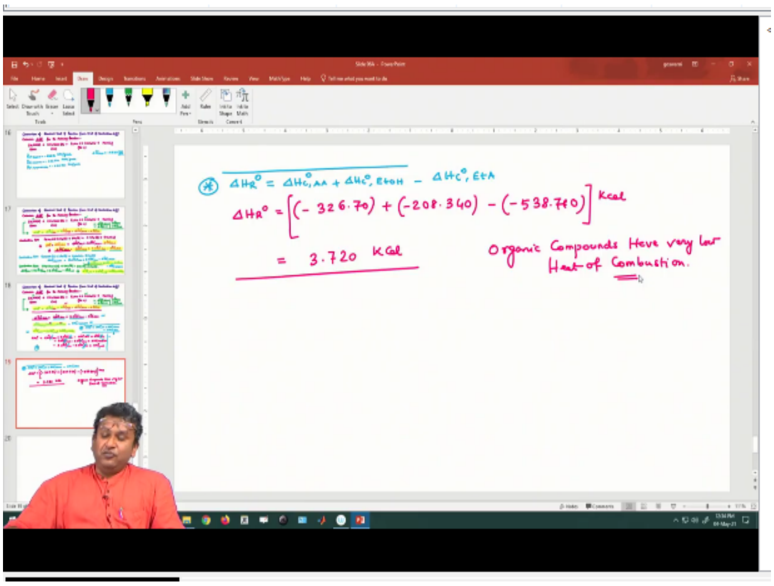
$$\Delta H_R^0 = \Delta H_{c,\,AA}^0 + \Delta H_{c,\,EtOH}^0 - \Delta H_{c,\,EtA}^0$$

So, it is interesting to note actually that here we know that the heat of reaction is of course you need to do this step to show that the carbon dioxide and water actually cancel out and you do not need those data.

So, that also if the equation is properly balanced this is going to happen. What is interesting to note is when you are writing the heat of reaction or the standard heat of reaction in terms of the heat of formation data it is actually the summation of the heat of formation of the products minus the heat of formation of the reactants, but what you see over here it is a very interesting relation and which you have essentially derived in front of your eyes.

That the standard heat of reaction turns out to be in the form of the summation of the heat of combustion of the reactants minus the heat of combustion of the products of course water is of course not present. So, this way there can be n number of such examples and I request you to look into Himmelblau's book and practice some. This way with heat of combustion data you may not waste your time in calculating the heat of formation values.

Of course, each of these reactions now can be used to calculate the heat of formation value of these organic compounds, you can actually quite easily find out straight away the heat of combustion data. So, that is how it goes and if you just for the sake of curiosity you would like to calculate the heat of reaction over here it will turn out to be minus or let me change slide at this point of time.



$$\Delta H_R^\circ = \Delta H^\circ_{c,AA} + \Delta H^\circ_{c,EtOH} - \Delta H^\circ_{c,EtA}$$

$$\Delta H_R^\circ = \left[(-326.70) + (-208.340) - (-538.760)\right] \text{Kcal}$$

$$= 3.720 \text{ KCal}$$

Organic Compounds Have very low Heat of Combustion.

So, standard heat of reaction turns out to be very small; it is 3.20 kilo calorie (as can be seen from the calculation in the above slide). So, typically organic compounds have very low heat of combustion.

So, I think that sort of brings us to the end of this particular class and in the next class what I am going to pick up we will continue our discussion on heat of reaction and we will look into some very interesting system particularly the neutralization reaction between acid and base, reaction between salts and then look into the heat the thermal effect associated with dilution, thank you very much.