Material and Energy Balance Computations

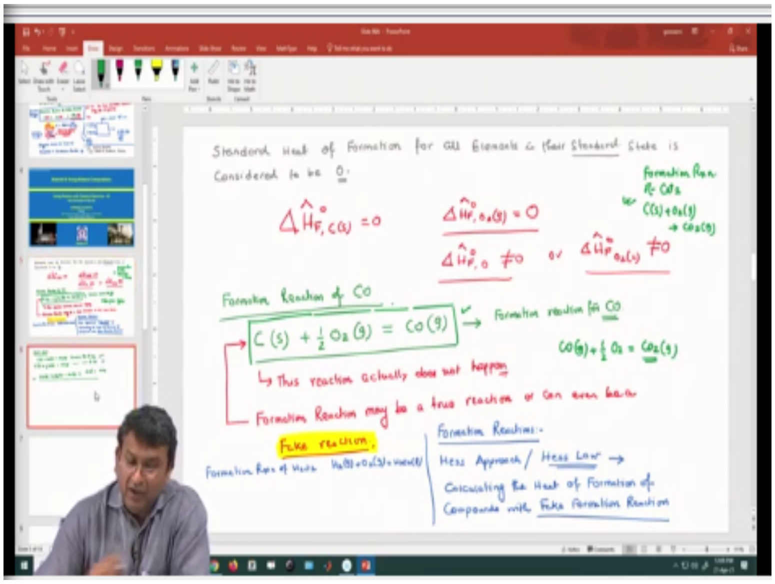
Prof. Rabibrata Mukherjee
Department of Chemical Engineering
Indian Institute of Technology-Kharagpur

Lecture-52
Energy Balance with Chemical Reactions-II

Welcome back, we will continue our discussion on energy balance with chemical reactions which we just started in the previous class. This class now knows what is heat of formation and therefore that gives us a formalism for calculating the heat of reaction. So, we all know about heat of reactions, we had all known about it for long time from our school days about endothermic and exothermic reactions. And we also realized that in exothermic reactions the total enthalpy of the products is actually lower than that of the reactants and therefore some energy gets released.

But how do you sort of quantify the total enthalpy of the products? So, the total enthalpy of the products or the change in the enthalpy of the reactants and products can be quantified in terms of heat of reaction and what about the individual components? So, that is related to what is known as the heat of formation. So, we have talked about heat of formation and we have also learnt about the formation reaction and we learnt something very interesting. That a formation reaction can be a true reaction, or it can be a fake reaction also.

(Refer Slide Time: 01:26)



Standard Heat of Formation for All Elements in their Standard State is Considered to be 0.

$\Delta \hat{H}^\circ_{F,C(s)} = 0$

$\Delta \hat{H}^\circ_{F,O_2(g)} = 0$

$\Delta \hat{H}^\circ_{F,O} \neq 0$ or $\Delta \hat{H}^\circ_{F,O_2(l)} \neq 0$

Formation Rxn for CO_2: $C(s) + O_2(g) \rightarrow CO_2(g)$

Formation Reaction of CO

$\boxed{C(s) + \frac{1}{2} O_2(g) = CO(g)} \rightarrow$ Formation reaction for CO

$CO(g) + \frac{1}{2} O_2 = CO_2(g)$

This reaction actually does not happen

Formation Reaction may be a true reaction or can even be a Fake reaction.

Formation Rxn of Water $H_2(g) + O_2(g) = Water(l)$

Formation Reactions:-

Hess Approach / Hess Law →

Calculating the Heat of Formation of Compounds with Fake Formation Reaction

So, therefore when we talk about let us say the formation reaction of carbon dioxide there is absolutely no problem, because formation reaction of carbon dioxide for example. So, formation reaction you must mention the states because all the products or the reactants must be in their natural state. So, this is a true formation reaction,

$$C\ (S) + O_2\ (g) = CO_2\ (g);\ \Delta H_{F,\,CO2}^{0}$$ cap = -393.51 kilo joule per gram mole of carbon

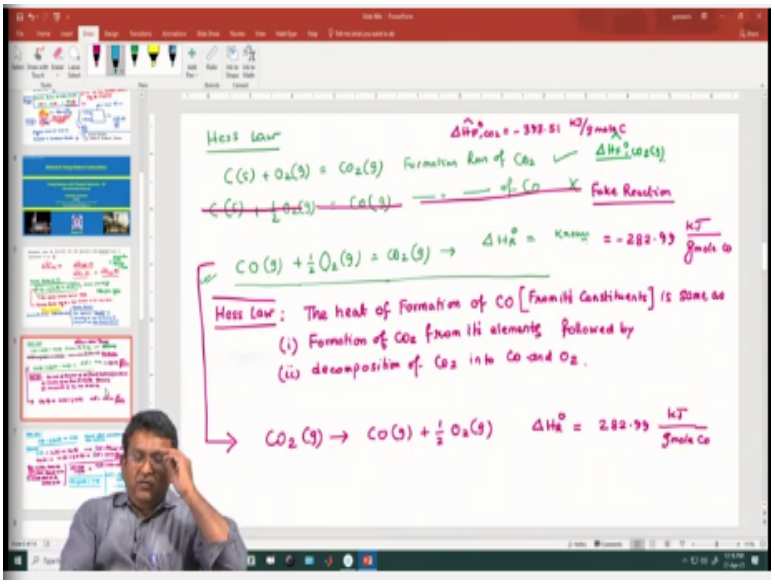
But let us say when we talk about carbon monoxide, we can certainly write the formation reaction.

$$C\ (S) + 1/2O_2\ (g) = CO\ (g).$$

So, you take stoichiometrically half amount of oxygen in principle and you should get carbon monoxide but that does not happen. What happens is we had discussed in the previous class that if you have less amount of oxygen than the stoichiometric requirement of carbon what will happen is some part of 50% of the carbon will get converted to carbon dioxide and remaining 50% of the carbon will remain unreacted. But then how do you calculate the heat of formation of something like carbon monoxide?

Because or any product, so the question essentially emerges is how essentially do you calculate the heat of formation of all compounds which have fake formation reaction? So, this is the question we were looking into and then we realized that though this reaction is fake, oxidation of carbon monoxide into carbon dioxide is highly possible. This is a reaction which is possible and then the moment a reaction is possible using some instrument maybe a calorimeter, you can actually measure the heat; or the thermal effects associated with heat or the change of energy associated with the particular reaction.

(Refer Slide Time: 03:40)



Hess law

$\Delta \hat{H}^0_{F,CO_2} = -393.51$ kJ/gmole C

$C(s) + O_2(g) = CO_2(g)$ Formation Rxn of CO_2 ✓ $\Delta H^0_{F,CO_2(g)}$

~~$C(s) + \frac{1}{2}O_2(g) = CO(g)$ — — of CO~~ ✗ Fake Reaction

$CO(g) + \frac{1}{2}O_2(g) = CO_2(g) \rightarrow$ $\Delta H^0_R =$ Known $= -282.99 \frac{kJ}{gmole\ CO}$

Hess Law: The heat of Formation of CO [From its Constituents] is same as

(i) Formation of CO_2 from its elements followed by

(ii) decomposition of CO_2 into CO and O_2.

$CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g)$ $\Delta H^0_R = 282.99 \frac{kJ}{gmole\ CO}$

So, here is the situation, what we have is the, we know the formation reaction of CO_2 or we know this ΔH_F^0 for CO_2. And for formation of CO, this is not available. But nonetheless though it is a fake reaction for CO, this is the formation reaction and the heat of reaction for this particular reaction is known.

So, here comes a very important concept of what is known as the Hess law which essentially has two basic meaning which is very simple actually.

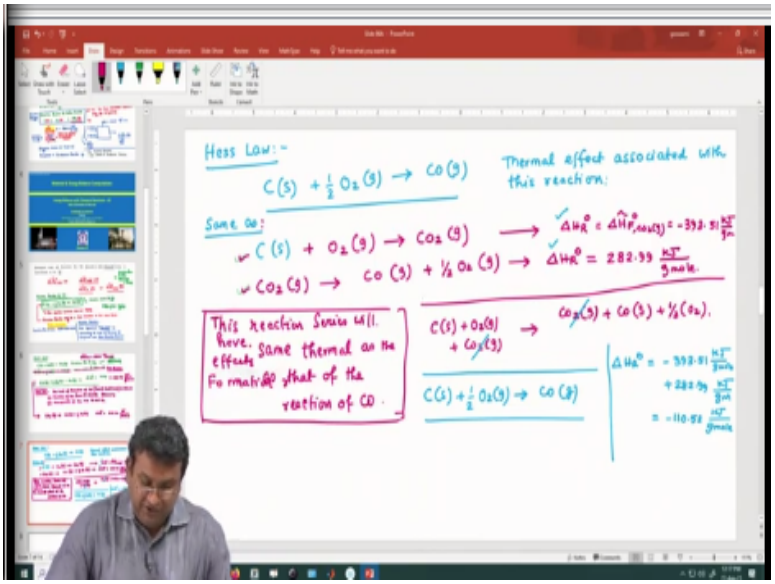
For CO (g)+ ½ O_2 = CO_2 (g), $\Delta H_R^0 = -282.99$ kJ/gmol of CO.

So, now according to the 'Hess law' which is a very important formalism, the heat of formation I am writing it down for the benefit of all. The moment we say heat of formation of carbon monoxide it means that from it is constituents in their standard state etcetera**.** So, the heat of formation of carbon monoxide is (1) Formation of CO_2 from its elements in their standard form; (2) Decomposition of CO_2 into carbon monoxide (CO) and oxygen (O_2).

So, what exactly does it mean?

The inner implication of this statement is that if this is the heat of reaction of the forward reaction, the heat of reaction of the backward reaction will be exactly the same but the magnitude will be negative of whatever is the heat of reaction for the forward reaction. So, now let us try to find out what Hess law says? So, what Hess law says is as follows.

(Refer Slide Time: 07:30)



Hess Law:-

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

Thermal effect associated with this reaction:

Same as:

✓ $C(s) + O_2(g) \rightarrow CO_2(g) \longrightarrow$ ✓ $\Delta H_R^0 = \Delta \hat{H}^0_{f,CO_2(g)} = -393.51 \frac{kJ}{gm}$

✓ $CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g) \rightarrow$ ✓ $\Delta H_R^0 = 282.99 \frac{kJ}{gmole}$

This reaction Series will have same thermal effects as the Formation that of the reaction of CO.

$C(s) + O_2(g) + \cancel{CO_2}(g) \rightarrow \cancel{CO_2}(g) + CO(g) + \frac{1}{2}(O_2)$

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

$\Delta H_R^0 = -393.51 \frac{kJ}{gmole} + 282.99 \frac{kJ}{gm} = -110.52 \frac{kJ}{gmole}$

So, the consequence of Hess law is the thermal effect associated with this reaction is same as followed by dissociation of carbon dioxide into carbon monoxide and oxygen. This is the implication of Hess law; this is what Hess law says. So, this reaction series will have same thermal effects as that of the formation reaction of CO. So, this is what Hess law says.

The heat of formation of gaseous carbon dioxide, the energy is associated is -393.51 kilo joule per gram mole. And this one the heat of reaction, now for the backward reaction CO_2 (g)→ CO (g)+ ½ O_2 is 282.99 kilo joule per gram mole. And for oxidation reaction of carbon monoxide, the heat of reaction will be -282.99 kilo joule per gram mole.

So, theoretically if there is a dissociation, there is another important question whether this dissociation actually happens or not? And it is not that easy to happen, carbon dioxide is a very, very stable compound and it does not dissociate. But, so therefore this can again be a fake reaction. But what we are considering that if the thermal effect or the heat of reaction for the forward reaction is known to us then the heat of reaction of the reverse reaction or the backward reaction will be exactly it is opposite.

The number of the value will be same, and the sign will simply change. So, if that be the case, now what we do? We treat these two chemical reactions simply like two algebraic equations. So, just add the left side and the right side and what you get is

C (S) + O_2 (g) + CO_2 (g) → CO_2(g) + CO (g) + ½ O_2. And you can also add these heat of reaction values, so the net heat of reaction according to Hess law is going to be -393.51 kilo joule per gram mole + 282.99 kilo joule per gram mole = -110.52 kilo joule per gram mole.

And if you now look into these equations, what you have obtained after adding? You see that there is carbon dioxide on both sides, so it gets cancelled out and here you have 1 O 2 and here you have half O 2. So, essentially what you have on the left-hand side after you remove this is carbon + half O 2 leading to carbon monoxide in gaseous form. So, this is what is Hess law, and this is a very, very powerful technique. So, what you have seen after a little bit of hustle not exactly hustle a little bit of understanding.

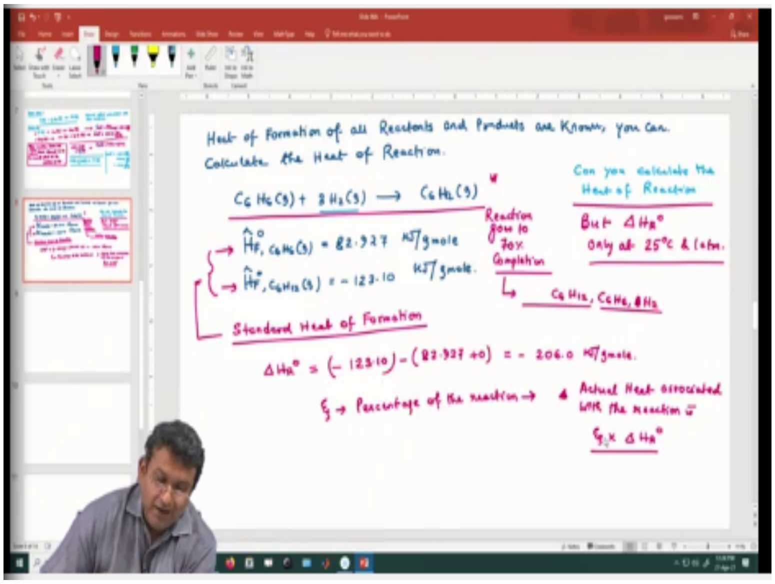
We have actually very nicely utilized the concept of Hess law, in the sense that, so essentially the formation of carbon monoxide from it is constituent elements the energy associated with the formation of carbon monoxide from it is constituent elements is essentially the same as obtaining carbon dioxide. And then if you consider that carbon dioxide gets dissociated into carbon monoxide and oxygen.

And in the process, you have just taken one more we learnt another important thing that whether a reaction happens or not, chemically happens or not? That is a different question. But what you can write is that if you know the heat of reaction of the forward reaction, the heat of reaction of the backward reaction is exactly it is opposite value, the negative of the same value. And if you write those and all you have to do is essentially according to Hess law you write these 2 equations and then you simply add them up over here.

As if these 2 are like algebraic equations here, that is a rule of thumb I am telling you, do not say all these things but this is how you proceed. And so essentially after that you also add up the heat of reactions and do a cancellation of the similar terms and do the basic algebra over here. Like you have one O_2 on the left-hand side and half O_2 on the right-hand side, so it is essentially it is as similar to having net half O_2 on the left-hand side.

So, what you get is $C(s) + 1/2\ O_2 = CO$ and therefore you can calculate the heat of formation of carbon monoxide using Hess law and some feasible actual reactions that take place for a particular compound which may have a fake formation reaction. So, this is the important concept, what I thought, I should teach you.

(Refer Slide Time: 16:10)



Heat of Formation of all Reactants and Products are Known, you can Calculate the Heat of Reaction.

$C_6H_6(g) + 3H_2(g) \longrightarrow C_6H_{12}(g)$

$\hat{H}^0_{F, C_6H_6(g)} = 82.927$ KJ/gmole

$\hat{H}^0_{F, C_6H_{12}(g)} = -123.10$ KJ/gmole.

Standard Heat of Formation

Reaction goes to 70% Completion → C_6H_{12}, C_6H_6, $3H_2$

Can you calculate the Heat of Reaction

But ΔH_R^0 Only at 25°C & 1 atm.

$\Delta H_R^0 = (-123.10) - (82.927 + 0) = -206.0$ KJ/gmole.

$\xi \rightarrow$ Percentage of the reaction → Actual Heat associated with the reaction is $\xi \times \Delta H_R^0$

Once the heat of formation of all reactants and products are known, you can calculate the heat of reaction that is easy. For example, we have this particular reaction taking place

$$C_6H_6\ (g) + 3H_2\ (g) = C_6H_{12}\ (g).$$

And what is known is heat of formation of C_6H_6 (g) is 82.927 kilo joule per gram mole. And heat of formation for C_6H_{12} is -123.10 kilo joule per gram mole. So, if I now ask you to calculate the heat of reaction. So, can you calculate the heat of reaction? The answer is everybody will say, we can calculate because see this is an element and therefore it is heat of formation is 0. But here comes the real rider, your real understanding. Your answer should be ‘yes’, we can calculate the heat of reaction but we can calculate this value only at 25 degree centigrade and 1 atmospheric pressure or in other words if this reaction proceeds at 25 degree centigrade and 1 atmospheric pressure, then only we can calculate the heat of reaction values. Why? because these are all standard heat of formation data. So, whatever is provided though we loosely say this is heat of formation, this is actually standard heat of formation. So, this standard heat of formation is valid only at 25 degree centigrade and 1 atmospheric pressure.

So, therefore if I ask you and if somebody is very, very careful about pedagogy and if I say can you calculate the heat of reaction? I have not mentioned that I am specifying the temperature and pressure. So, please do not fall into the trap that you can, with this data calculate if this reaction let us say is happening at let us say 100 degree centigrade and 1 atmosphere or 5 atmospheric pressure, you cannot calculate.

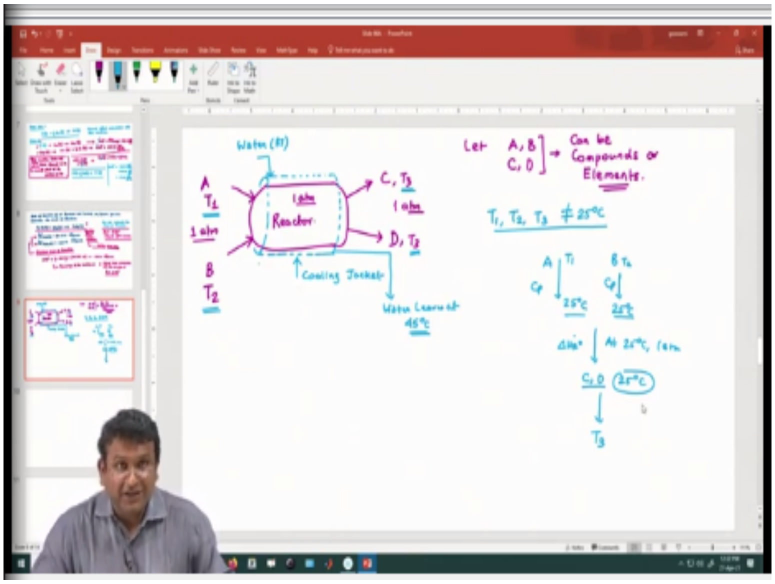
So, we can calculate the heat of reaction for this particular equation and standard heat of reaction at under standard condition which will turn out to be the heat of formation of the product - the heat of formation of the reactants = -206.0 kilo joule per gram mole, so this you can calculate. Now think of a situation there are several very small, small issues associated with it, which I can explain very nicely.

We can develop a very nice understanding. So, one of them can be let us say this reaction goes to 70% completion, so what does it mean? 70% of the reactants have reacted to form some product, so what is the final product? Had the reaction gone to complete 100% completion? Then the final product stream would have contained only C_6H_{12}. But now it says that the reaction has progressed only up to 70% let us say. So, what will be the composition of the final product?

Final product will be 70% will be C_6H_{12} and remaining part, so 30% here does not mean anything because this is a molar fraction or whatever. But the final product will comprise of C_6H_{12}, you understand it very well because you have learnt about incomplete combustion in the other part. So, it will contain and some hydrogen also, this will be the product, that is perfectly fine, that the number of moles you can find out considering a basis understanding of your mass balance, that is not a problem.

But the question is, if the reaction has gone up to the level of 70% what is the amount of heat associated with the reaction? And it is very easy, you calculate. So, if the reaction has taken place at 1 atmospheric pressure and 25 degree centigrade and you know the percentage conversion or whatever, it is very easy. Whatever is the heat of reaction you get; you simply multiply it with the eta for an incomplete reaction. So, if eta is the percentage of the reaction, then the total actual heat, so associated with the reaction is eta into whatever is the standard heat of reaction. And in this particular case it is going to be 70, so that is 0.7 into 206 that is very, very simple.

(Refer Slide Time: 23:15)



Now I have a question. So, let us say you have this reactor, you have a reactor and let us say 2 reactants, this can be elements or compounds let us say these are compounds. Let A and B be C, D all be compounds or can some can be elements also. What is the only difference? If you have a compound versus an element, if you have compounds you will have non-zero heat of formation values, if you have elements the heat of formation values will be 0.

So, they can be compounds or elements or whatever. And let us say I say that this one enters at temperature T_1. For the simplicity let us assume everything is at 1 atmospheric pressure, the B enters at a temperature T_2. It is not very wise to write that C and D to just to make the problem more complicated, it is not very logical to write that C and D leaves at two different temperatures. Because after all they are coming out as the reactor product and probably for, they will have the same temperature as that of the reactor.

So, let us say C and D, so I hope all of you understood what I meant that in principle the two raw materials or the feeds can enter the system at two different temperatures. But the products typically even if there are two products which are let us say one is a gaseous product and one is a liquid product which leaves separately. It is very difficult to imagine a situation that the two products leave at two different temperatures probably they will leave at the same temperature.

And what we write is T_1, T_2, T_3 are none of them are equal to 25 degree centigrade, let us say they are all above 25 degree centigrade. So, what exactly do you do, can you calculate the heat change associated with it? So, let us say you have been told that this is a, so why do you need this data for example? What exactly are you going to do with the heat of reaction data other than just calculating and getting some marks in this course?

So, it is like if you have an exothermic reaction you know that heat will get generated. So, if heat gets generated what will progressively happen? The reactor temperature will go up. Now which you do not want? You may want there are many effects which you will learn your reaction kinetics later, the reaction may become slower with time or if there is continuous generation of heat the reactor becomes too hot and there can be potential material failure.

If the reactor becomes hot, there are issues associated with insulation, some rubber lining may go bad and all these things can happen. So, it is generally lot of reactors actually work under isothermal conditions, so you have to maintain the temperature. So, how does this calculation help? So, based on this calculation, now from the heat of reaction data you now know how much amount of heat is going to be generated.

And therefore, accordingly around the reactor you might actually having a cooling jacket. Where you might enter water let us say at room temperature and you modulate the flow of water in such a way that let us say water leaves at 45 degree centigrade or something like that. So, how does your heat of reaction data help? Heat of reaction data helps in the way that you now know how much is going to be the water flow rate.

Also please do not think that you would like to cool down a reactor and therefore you will take water at 0 degree centigrade, industrially it does not happen like that. Nobody at the site of the plant is going to run an additional chiller plant for producing cooling water, which is just an utility, which is not even taking participating in any reaction. Nobody is going to cool it down to 0 degree centigrade or 5 degree centigrade.

So, that you know lot of things, ok, so why do we take water, liquid? Let us take ice at 0 degree centigrade, then we can harvest the latent heat not the sensible heat only, nobody is going to give you all that. So, you will be given water at whatever is the temperature. So, these are actually design problems, that if you have a plant where there is seasonal fluctuation of temperature which is very common in a country like India.

How essentially do you handle your water supply system? And then again, I have written an outlet temperature of 45 degree centigrade. So, why 45 degree centigrade? Why not use less amount of water and go all the way up to let us say 100 degree centigrade? Because you have to consider that if you release water at 100 degree centigrade that can itself be a hazard for the operators or the people around.

So, everything has some limits, I mean this is not a design class, so I cannot go into all the detail. So, this is the utility of the heat of reaction. So, now we are running out of time, so what exactly do we do? We essentially have reactants entering at different temperatures, product living at different temperature. But we know, we can calculate the heat of reaction data only at 25 degree centigrade.

So, what we will consider is? As if whatever is the temperature of A, it is brought down from T_1 to 25 degree centigrade, B is brought down and how do you calculate? You know the mass of this A; you know the C_p values of this A. And then once as if they are down to 25 degree centigrade, now you can calculate the heat of reaction. And based on that at 25 degree centigrade and 1 atmospheric pressure, so you can very well calculate the heat of reaction data and you get C and D at 25 degree centigrade.

And then if they are living at a higher temperature, you can again consider what is the amount of heat that is required for heating up their temperature and from there you can calculate. So, it is like sometimes if you have to cross a deep gorge in a hilly road, you might have seen that you do not have a bridge at a very high level. You go down along the first hill, go to the base there is a bridge which crosses the river and then you go up again, it is something like that.

So, all this initial temperature you first bring it down to 25 degree centigrade, have the reaction out there and then again heat up to the final temperature, this is how you can do the calculations. So, I will write the mathematical expression associated with this in the next class and get started from here, thank you very much.