Rate Processes

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Module No. # 01

Lecture No. # 03

Effect of Temperature on Reaction Rate

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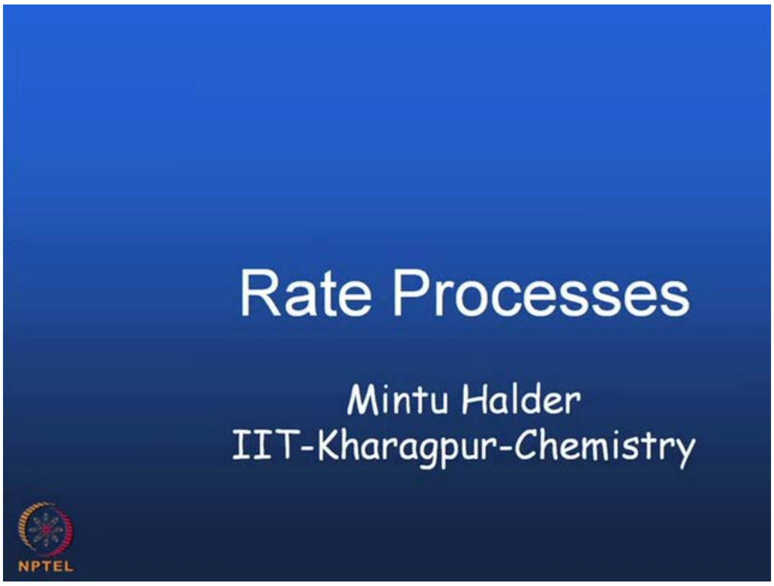

Rate Processes

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A very good morning to all of you. So, last day I talked about, I gave a very brief introduction of this effect of temperature on chemical reactions. So, today we will try to learn a little more on that.

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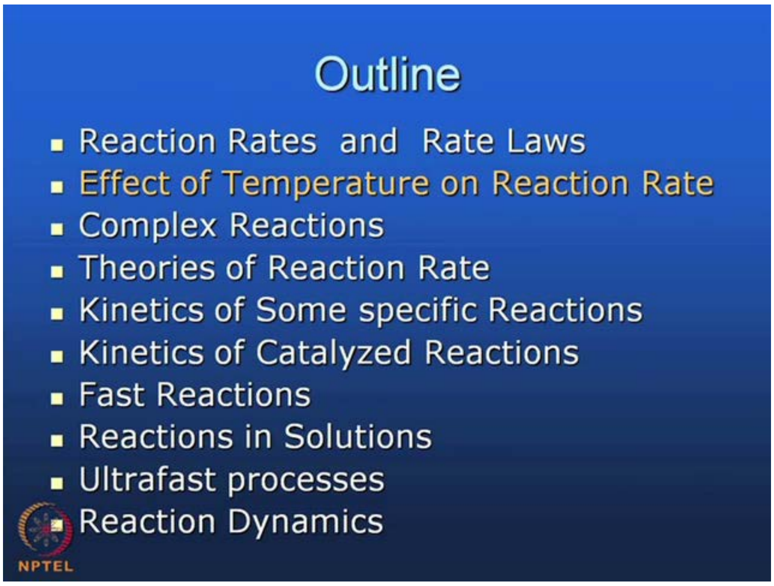

Outline

- Reaction Rates and Rate Laws
- Effect of Temperature on Reaction Rate
- Complex Reactions
- Theories of Reaction Rate
- Kinetics of Some specific Reactions
- Kinetics of Catalyzed Reactions
- Fast Reactions
- Reactions in Solutions
- Ultrafast processes
- Reaction Dynamics

So, let us again go back to the outline. So, we have just ended this reaction rates and rate laws. So, we will move onto the effect of temperature on chemical reaction rate.

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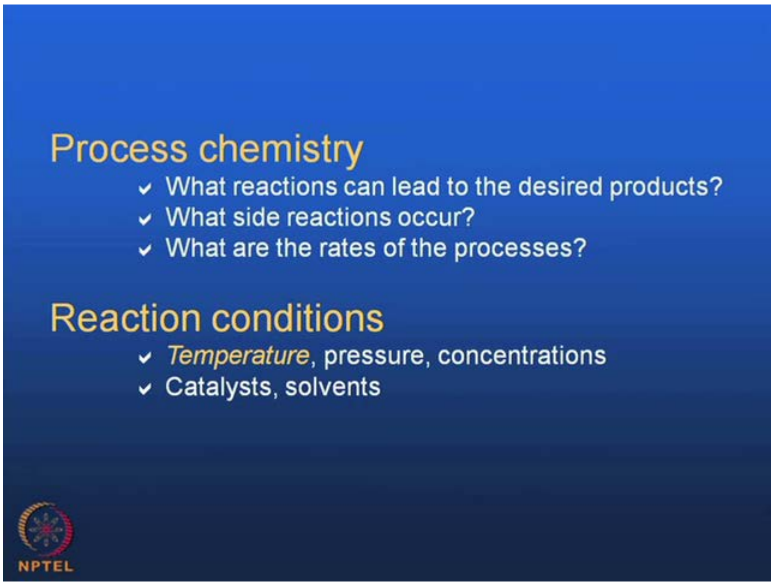

Process chemistry

- ✓ What reactions can lead to the desired products?
- ✓ What side reactions occur?
- ✓ What are the rates of the processes?

Reaction conditions

- ✓ *Temperature*, pressure, concentrations
- ✓ Catalysts, solvents

So, as I have mentioned in the earlier lectures that it is important to learn chemical kinetics in process chemistry and the reaction conditions in which temperature pressure and concentrations are very important thing. So, temperature is a very important parameter for this studying chemical kinetics or rate processes involving chemical substances.

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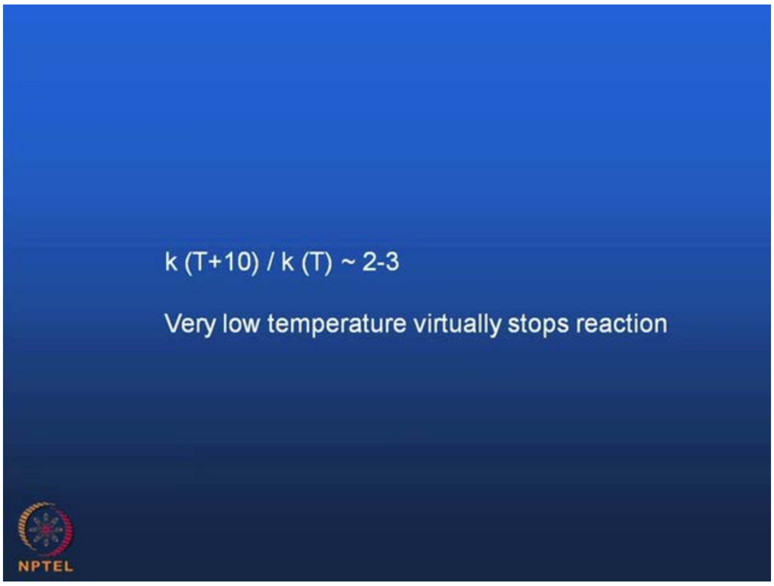

k (T+10) / k (T) ~ 2-3

Very low temperature virtually stops reaction

So, it is a general experience that when you study some chemical reaction say, at a temperature T and you increase the temperature say by, T to T plus ten degree.

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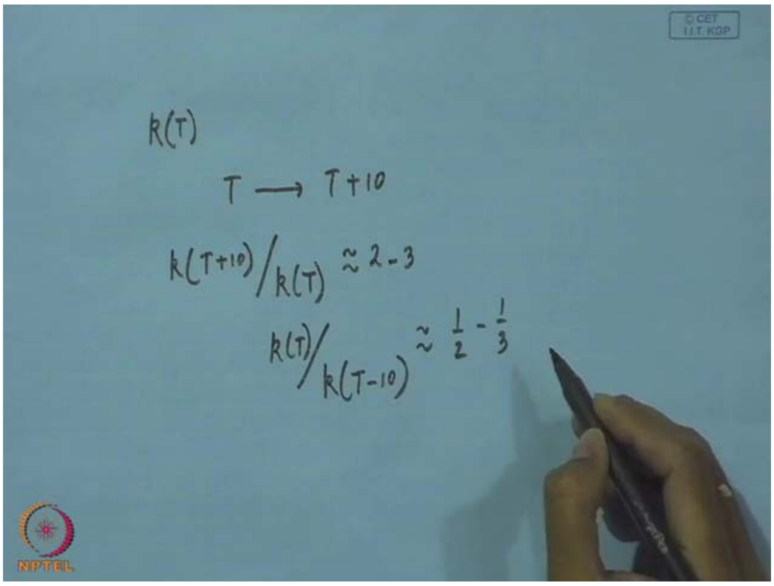

$k(T)$

$T \longrightarrow T+10$

$k(T+10)/k(T) \approx 2-3$

$k(T)/k(T-10) \approx \frac{1}{2} - \frac{1}{3}$

So, suppose you study a reaction for which say, you have got the value of rate constant that is, at temperature T and now you have increased the temperature. So, temperature is now increased to T plus ten in kelvin unit. So, in that case it is found that the rate constant what you get at T plus ten is about two to three times more than your k T two to three. So, this rate constant is very much temperature dependent and you see that as you move onto T plus ten, whatever value you have obtained at T it is two to three times, it is an experience. So, in the same way if you reduce the temperature by ten degree then it will be reduced by two to three times, that is it will become half or maybe one-third, that is k T by k T minus ten, will be of the order of half or will be of the order of one-third.

And it is also an experience that if you reduce the temperature, that is very low temperature, if you go to like subzero, that is much lower than zero degree centigrade. So, in that case it is found that virtually reaction stops. So, reaction does not at all proceed or even if it proceeds it is very slow. So, that is very low temperature virtually stops chemical reaction.

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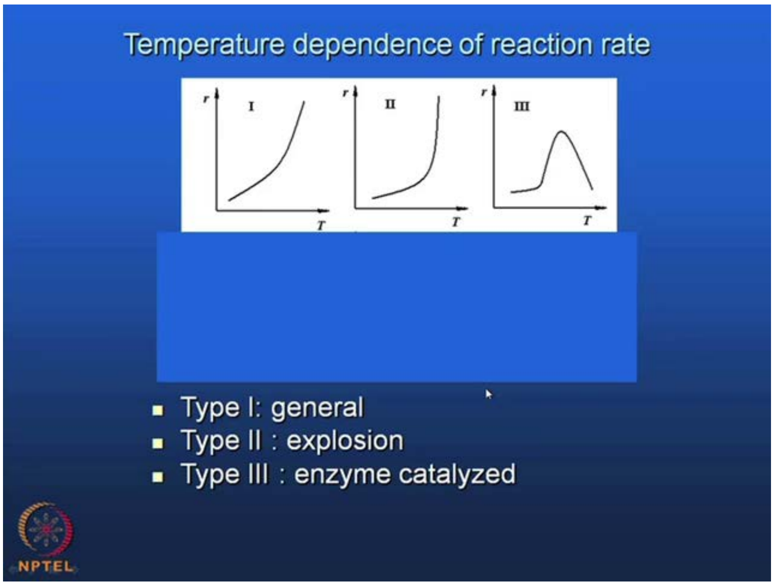

Temperature dependence of reaction rate

- Type I: general
- Type II : explosion
- Type III : enzyme catalyzed

So, let us have a look into various plots that is, rate versus temperature for various type of chemical reactions. So, this is type one, it is a general chemical reaction, type one where you see that as you increase the temperature so your rate is increasing, maybe in an exponential fashion close to an exponential fashion. So, it is the general chemical reactions which are generally carried out in laboratories.

Next type, type two where you see that this rate is not increasing very large; whatever value is here it is increasing to not to that extent. It is slowly increasing but, suddenly if you reach a temperature where you see that the reaction rate is increased to an enormous extent. So, this type of reactions are generally observed when explosion happens. So, it is an explosion kind of reaction.

And the third kind which is called the enzyme catalyze reaction; I will come to what is meant by catalysis; catalysts are basically, in case enzyme these are biocatalysts. So, these are present in the reaction mixture to a very little extent and it is constantly being used up and then regenerated like that. So, it does something that it is not taking part in the chemical reaction but, it expedites the chemical process that is, reaction rate is modified; it becomes, process become becomes facile. So, in that case you see that as you have increased the temperature for your enzyme catalyzed reactions you see not much change in reaction rate up to this and then it goes up, it reaches a maximum and then again it reduces. So, it is a kind of bell shaped curve or maybe inverted parabola like this. So, you see that in case of enzyme catalyzed reaction, basically, it is the optimum temperature; this temperature when the reaction rate is maximum is called the optimum temperature. So, optimum temperature, at this optimum temperature the reaction rate is maximum. So, it is called the optimum temperature. So, it goes up goes to a maximum and then it reduces on further increase of temperature.

So, type one is general, type two is explosion and type three is enzyme catalyzed. These are broad classification.

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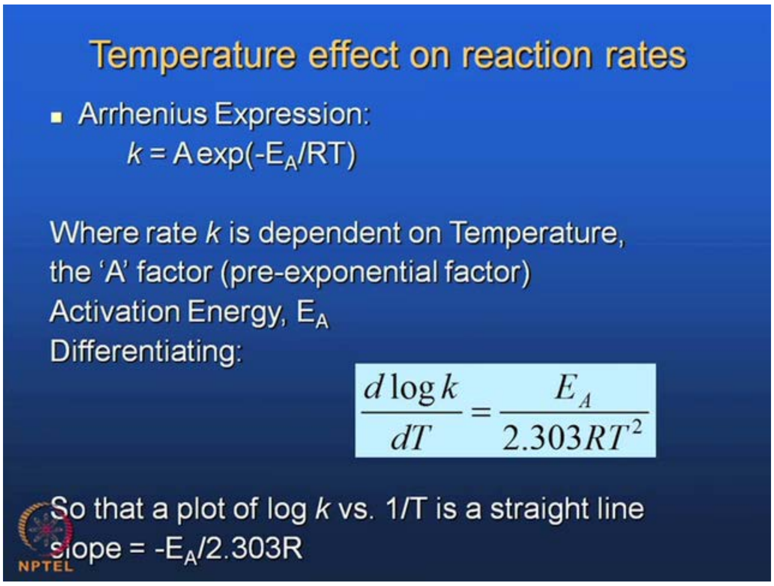

Temperature effect on reaction rates

- Arrhenius Expression:
  $k = A\exp(-E_A/RT)$

Where rate k is dependent on Temperature,
the 'A' factor (pre-exponential factor)
Activation Energy, E_A
Differentiating:

$$\frac{d\log k}{dT} = \frac{E_A}{2.303RT^2}$$

So that a plot of log k vs. 1/T is a straight line
slope = $-E_A/2.303R$

Now, let us move onto the effect of temperature on chemical reaction rate. So, there is a famous and very old expression which relates this chemical reaction rate constant with temperature which is nothing but, k is equal to A into exponential to the power, so it is exponential to the power minus E A by RT.

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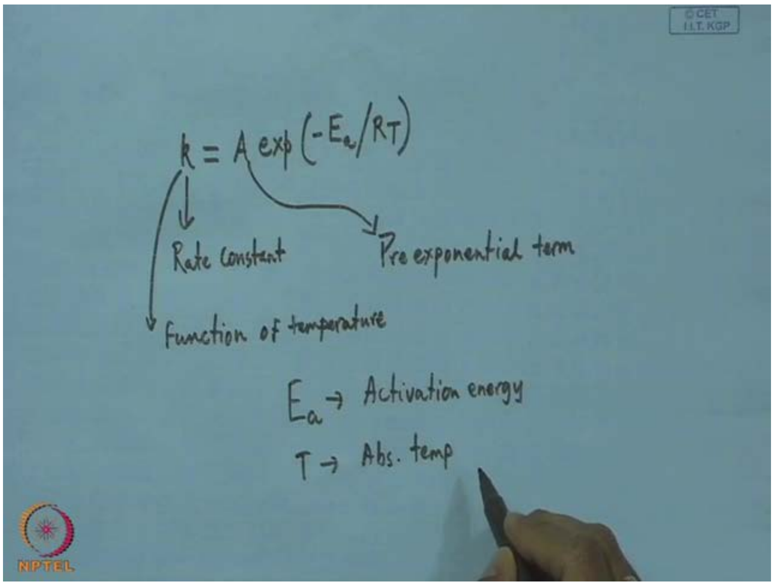

So, k is the reaction rate constant, is equal to A into exponential to the power minus E A by R T. So, this is your rate constant. It is a function of temperature. Exact functional form is difficult to determine, but it is known that rate constant is generally a function of temperature that is, it depends on temperature. This A is called the pre exponential term. Now, this E A is termed as; this is an energy term which is called the activation energy. I will come to what is meant by activation energy later on. T is temperature in absolute scale and of course, R is molar gas constant.

So, you see that this k increases exponentially with increase of temperature because this T is in denominator. So, as T is increased this term is decreased with a constant value of E A, this term is decreased, the whole term is decreased.

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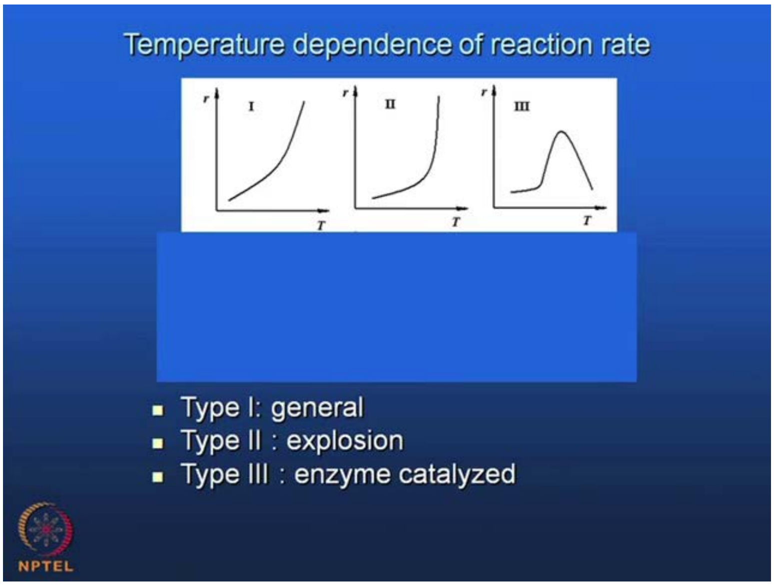
Temperature dependence of reaction rate

- Type I: general
- Type II : explosion
- Type III : enzyme catalyzed

So, decreased with a negative sign means there is a net rise. So, if you go back to the earlier slide that is, the type one pattern; that is, this R or rate versus this temperature, you see it rises. So, in the same way here also you see that rate increases and as also with temperature and here k is also increasing with temperature. So, it is basically an exponential rise with temperature.

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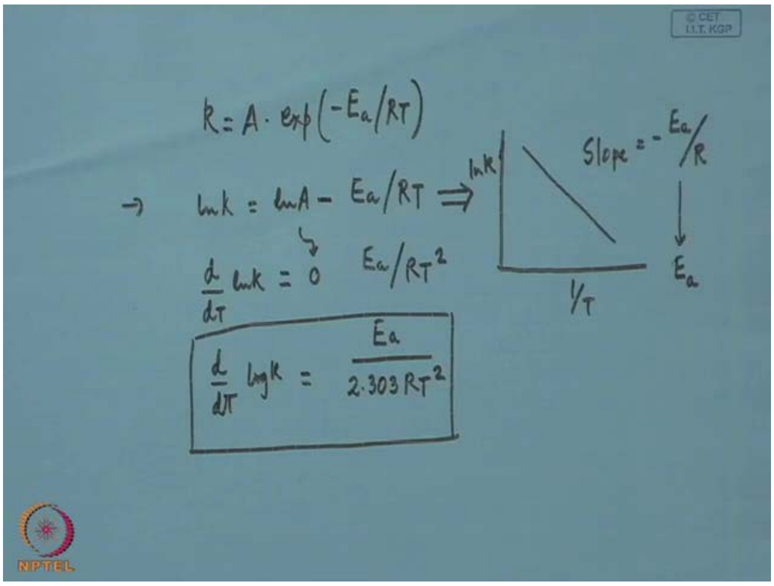
$$k = A \cdot \exp(-E_a/RT)$$

$$\rightarrow \ln k = \ln A - E_a/RT \Rightarrow$$

$$\frac{d}{dT} \ln k = 0 \quad E_a/RT^2$$

$$\boxed{\frac{d}{dT} \log k = \frac{E_a}{2.303\,RT^2}}$$

Now, next is if we differentiate with respect to temperature, absolute temperature then we will be getting this, we are having k is equal to A into exponential to the power minus

E A by R T. You take logarithm on both the sides. So, ln k is equal to ln A minus E A by R T.

Now, you differentiate with respect to T. So, d dT of ln k and that will be equal to, this will be equal to zero and with a minus and then T square. So, it will become E A by R T square and if you, this is in natural logarithm. So, log base ten will become d dT log k is equal to E A by two point 303 R T square. So, this is one expression that relates log k with temperature. So, now if we plot this one, I mean if we have a plot for this, either log k or ln k as a function of one by T. So, if we plot like this ln k or maybe log k because it is a factor by two point 303. So, ln k versus one upon T. So, it will have it will be a straight line like this and of course,, since there is a negative sign,. So, that is why it is with a negative slope and the slope will be equal to minus E A by R.

So, from slope if we have a plot like this, suppose we have got an experiment, we are doing an experiment and we are doing in such a way that, you know, we are finding out k and taking their logarithm and we are plotting against one upon T; that is ,the temperature at which this k is determined.

So, if we plot this ln k as a function of temperature we should be getting a curve like this; I mean a plot like this and from the plot we have got a slope. So, slope will be giving you E A by R T. So, that means, it is a way of finding out the term E A, the activation energy.

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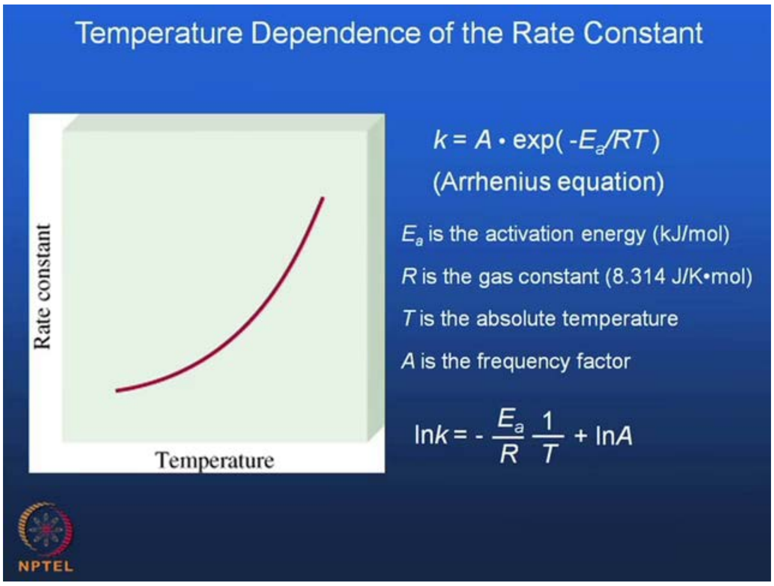

Temperature Dependence of the Rate Constant

$k = A \cdot \exp(-E_a/RT)$

(Arrhenius equation)

E_a is the activation energy (kJ/mol)

R is the gas constant (8.314 J/K•mol)

T is the absolute temperature

A is the frequency factor

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A$$

So, now let us move onto next slide. That, in this case it is plotted like rate constant versus temperature. So, it is basically, you see rate constant versus temperature, it is an exponential rise. It is an exponential rise with temperature and it happens always. There is no, nothing like you increase the temperature and rate constant is decreasing, it never happens.

So, here as I mentioned that E A is the activation energy, it is calculated generally in kilojoule per mole and gas constant has the value 8 point 314 joule per kelvin mole. T is absolute temperature and A it is a pre exponential term I mentioned earlier, but it is actually termed as frequency factor. So, it is related to some frequency quantity, I will come to that in some later classes. So, you see that ln k is equal to minus E A by R by T ln A. So, you have got the same thing but the only point to mention is that rate constant versus temperature is an exponentially rising function and this one is called the Arrhenius equation, this is a famous Arrhenius equation.

Now, let us again concentrate onto various reactions or maybe physical processes and since it is a question of physical process or maybe a chemical process. So, these processes require some activation energy. Now, what is activation energy; activation energy is the minimum amount of energy that is required to initiate the process; that is, it is a kind of just crossing the barrier.

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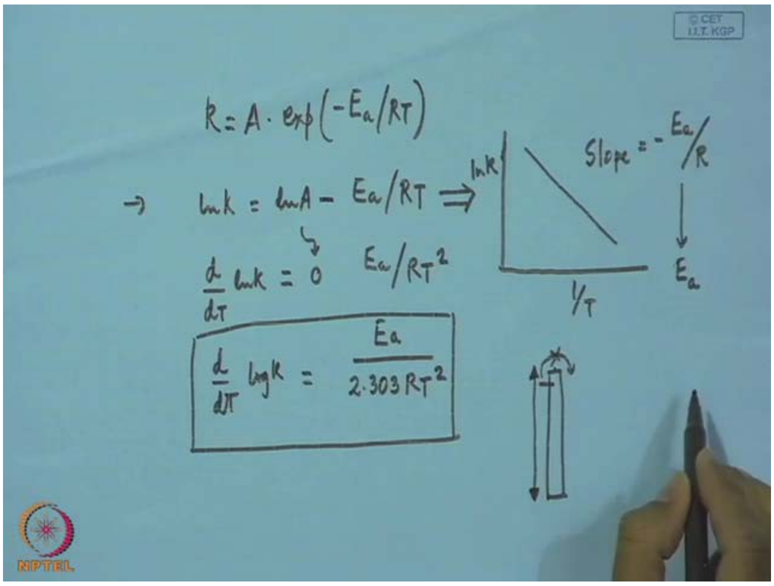

$$k = A \cdot \exp(-E_a/RT)$$

$$\rightarrow \quad \ln k = \ln A - E_a/RT \Rightarrow$$

$$\frac{d}{dT} \ln k = 0 \quad E_a/RT^2$$

$$\boxed{\frac{d}{dT} \log k = \frac{E_a}{2.303\,RT^2}}$$

Suppose we have got a barrier like this and we want to cross this barrier. So, that means, in order to cross this barrier we have to climb up to this and then we can pass. Suppose we have got energy which corresponds to; say going up to this level then we won’t be able to cross this barrier; no it is not possible. So, in that case, what we have to have is we have to still increase the energy to this much of extent. So, that we can go to the top and then we can move to the right hand side. So, this is the actually this is the minimum amount that is the threshold amount of energy that is required to initiate this transfer from left hand side to right hand side. So, that may be termed as the activation energy.

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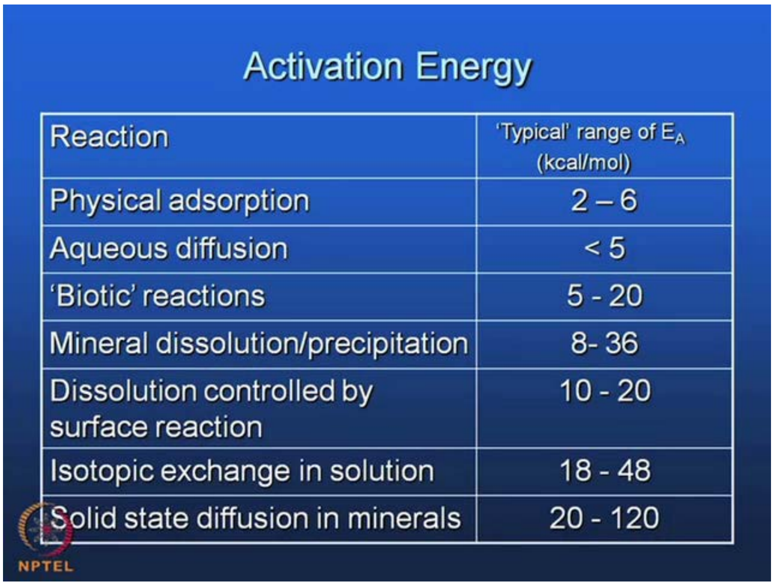

Activation Energy

Reaction	‘Typical’ range of E_A (kcal/mol)
Physical adsorption	2 – 6
Aqueous diffusion	< 5
‘Biotic’ reactions	5 - 20
Mineral dissolution/precipitation	8- 36
Dissolution controlled by surface reaction	10 - 20
Isotopic exchange in solution	18 - 48
Solid state diffusion in minerals	20 - 120

So, let us look at this slide that in the left column it is reaction type ;it may be physical process; it may be some chemical process and typical range of activation energy in kilocalorie although ,it is written it ;generally calculated in kilojoule, but it is here shown as a kilocalorie per mole. So, you can easily transfer to kilojoule because, four point two joules per calorie. So, one calorie is four point two joule. So, with that conversion factor you can convert it. So, you see that if it is a physical adsorption process; adsorption process means it is a surface phenomenon; suppose you have got a surface and molecules are preferred onto the surface rather than into the bulk, then we will call that it is an adsorption process rather than an absorption process. So, physical adsorption process requires of the order of two to six kilocalorie per mole.

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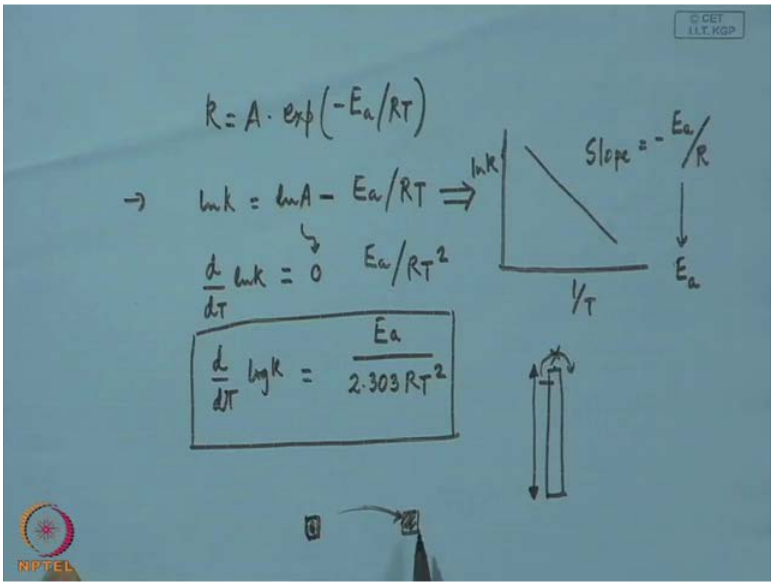

$k = A \cdot \exp(-E_a/RT)$

$\rightarrow \ln k = \ln A - E_a/RT \Rightarrow$

$\frac{d}{dT} \ln k = 0 \quad E_a/RT^2$

$$\boxed{\frac{d}{dT} \log k = \frac{E_a}{2.303 RT^2}}$$

Next comes aqueous diffusion; that is, in aqueous medium if something is diffusing then it will also require some amount of energy from being diffused, for being diffused from one position to the other because, diffusion is a process that, suppose you are here or the particle is here say and it wants to move from here to here. So, if there is no vacant position this particle cannot move from here to here. So, in order to move the particle from here to here, you need to create a vacuum over here or a free space. So, in order to create that free space you need to put in some amount of energy. And that amount of energy may be termed as the corresponding activation, that is you need to activate it; that is similar to activation energy..

So, aqueous diffusion requires of the order of less than five kilocalorie per mole. Then comes biotic reaction where it is of the order of five to twenty mineral dissolution process or precipitation process that requires about eight to thirty six. Dissolution of this (…) dissolution controlled by surface reaction it is about ten to twenty. So, dissolution controlled by surface reaction means; suppose you have got a lump of some substance. So, in order to get it dissolved. So, the solvent molecules should attack from the surface. So, that it why it is surface reaction; basically, it happens from the surface of the lump. So, dissolution controlled by surface reaction, if a surface reaction happens and as a result of which dissolution occurs. So, it is called dissolution controlled by surface reaction; it is about ten to twenty.

Isotopic exchange in solution, say you have got alcohol that is ROH and if you want to convert it to ROD; that is, deuterium hydrogen exchange reaction that requires about eighteen to forty-eight kilocalorie. Solid state diffusion in mineral it is twenty to one twenty, because it happens in solid phase. So, it requires a higher amount of energy. So, these are the typical values that you can have an idea about the kind of processes that are occurring. So, you can just classify different kind of processes in terms of their typical range of activation energies

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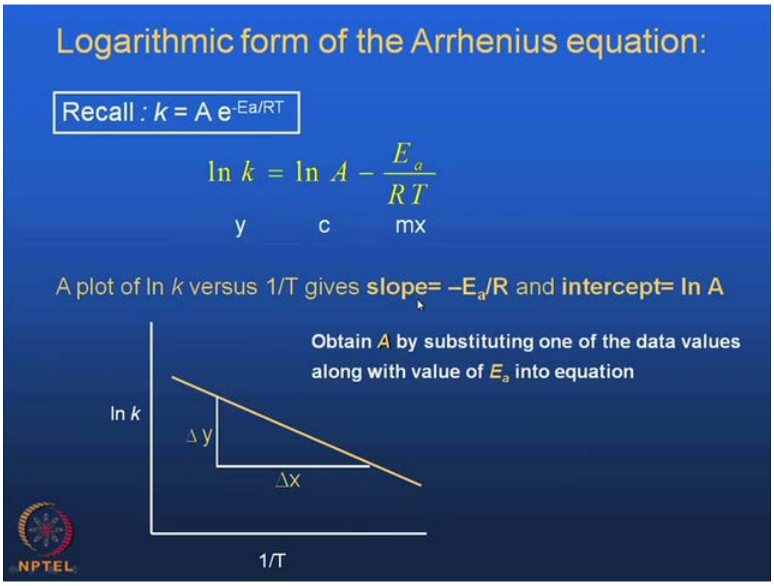

Logarithmic form of the Arrhenius equation:

Recall : $k = A\,e^{-Ea/RT}$

$$\ln k = \ln A - \frac{E_a}{RT}$$

y c mx

A plot of ln k versus 1/T gives **slope= $-E_a/R$** and **intercept= ln A**

Obtain A by substituting one of the data values along with value of E_a into equation

Now, let us move onto again onto logarithmic Arrhenius equation. So, again recall k is equal to A into e to the power minus E a by R T this is our starting equation. Take ln So, ln A Ea by RT. So, it is y this is c and this is m x. M x means it is, m is slope; a plot of k versus one upon T gives you slope; that is a Ea by R at an intercept.

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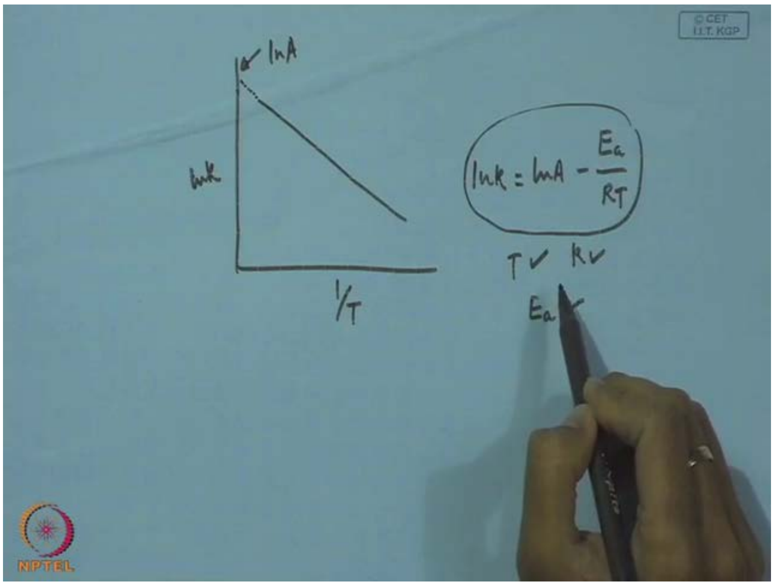

So, this intercept let us again look into it look at it that, this is your plot one upon T and this is lnk. So, this is your intercept. So, one upon T 0 means it is a very high temperature situation. So, that is why maybe we can go up to certain temperature, we cannot go to a very high value or infinitely high value. That is why your curve may be starting from somewhere over here not exactly it is touching, but you can extrapolate it to one upon T equal to 0 and that will give you ln A.

So, that is the logarithm of the frequency factor or maybe it is also called as the pre exponential term or maybe you can do, you can obtain A by substituting one of the data values along with the value of Ea into the equation.

That is you have got, means in that case you have to take, means take help of the equation itself that is lnk is equal to lnA minus Ea by RT. Suppose we know temperature, suppose it is known, suppose at that temperature k and also you have been able to find out Ea. So, Ea is known. So, you plug in all these three information into this expression and that will entail you in finding out this A. So, in this way you can find this pre exponential term as well maybe it is a it can be a graphical way or may be it can be just putting your these numbers into this equation to find out the value of A.

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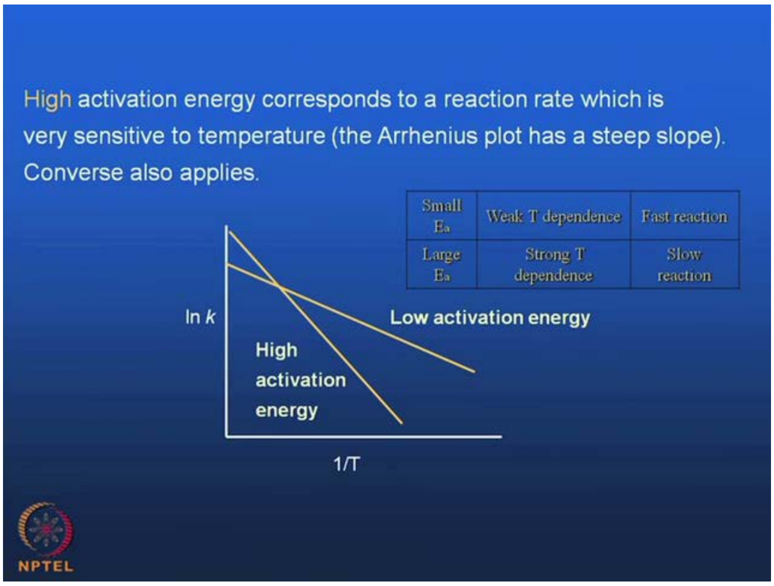

High activation energy corresponds to a reaction rate which is very sensitive to temperature (the Arrhenius plot has a steep slope). Converse also applies.

Small E_a	Weak T dependence	Fast reaction
Large E_a	Strong T dependence	Slow reaction

So, let us move onto next slide that is the significance of activation energy .What is the significance of activation ? As I told you that it is the minimum amount of energy that is required to cross the barrier cross the; means maybe minimum amount of energy needed to get transferred from the reactant side to the product side. So, high activation energy; what is the significance of a high activation energy? It corresponds to a reaction rate which is very sensitive to temperature. So, that means, it is a reaction if you change the temperature the reaction rate as also the rate constant is very much affected, means it is affected to a large extent.

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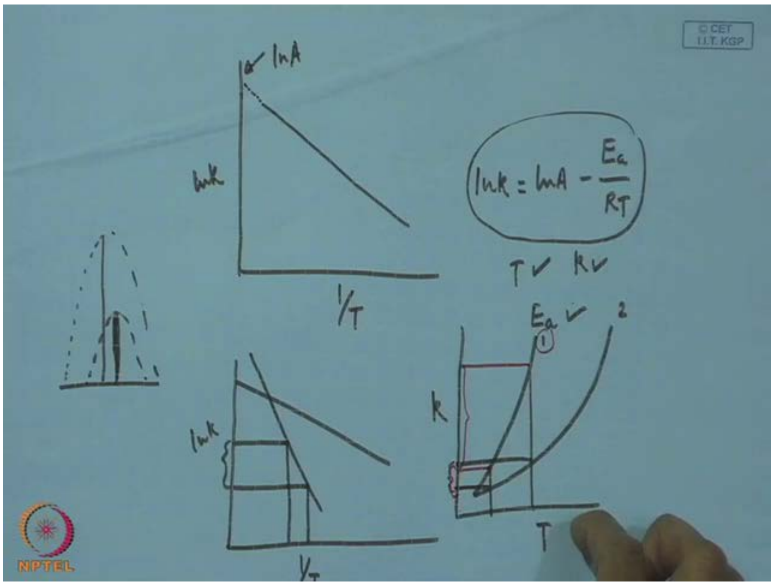

So, that is why high activation energy corresponds to a reaction rate which is very sensitive to temperature. So, in that case the corresponding Arrhenius plot has a very steep slope; that means, it is like this ; may be something like this or maybe even steeper. So, lnk versus one upon T is the very steep one. So, if you change a little value in this allows you to have a huge change in lnk or maybe you can have like a direct plot lnk, not lnk, if you have just k versus T plot then maybe in one case the plot is like this, in other case maybe plot is like this. So, you see if you have a change of temperature say from this value say to this value. You see that for this graph the second one, say this is graph number two and say this is graph number one. So, like if you go from here to here for graph two, you see the change of k is this much. And in another case for graph two; I mean for this one. So, if you change the temperature you see the same amount of change of temperature gives you a very high amount of change in the value of k you see previously it was like this; I mean this much and here it is huge. So, that is why the higher activation energy means the reaction rate and the reaction is very much sensitive to temperature. So, this one can be regarded as an example of higher activation energy corresponding to this..

So, you see that Ea high means slope is huge, it is a steeper one. So, and the other one you see, that for the second graph, you see if you change the temperature, change of k is not that much. So, in that case your slope, in the other case it is like this , if the slope is like this. So, it is not changing a lot because change of temperature does not lead to the same amount of change as it happened in case of the steeper one. So, higher activation corresponds to a reaction rate which is very sensitive temperature. So, temperature, very much temperature dependent. So, we can have a table like this, that small activation energy that is weak temperature dependence,,, but the reaction is fast.

Reaction is fast; that means, as I told you here that if the activation energy small although, the temperature dependence of k is not that much, but the reaction is found to be faster. Why faster ? Again it can be stated in the same way that, in that case this barrier height is less for your case when small activation energy,, but when it is activation energy is high although, it corresponds to a reaction which is very sensitive to temperature,, but it the reaction is slow because this barrier height in high activation energy case is high. So, it requires high amount of energy to cross this barrier,, but here it requires less amount of energy to cross the barrier.

So; that means, small activation energy with temperature dependence weak or less temperature dependence and the reaction is fast. So, fastness is related to the barrier height and steepness of your lnk versus one upon T or your k versus T is dependent on the amount of activation energy involved in the process. And large activation energy is strong temperature dependence. So, temperature, I mean a little increase of temperature will lead to a huge amount of change in k, but the reaction is slow for your large activation energy case.

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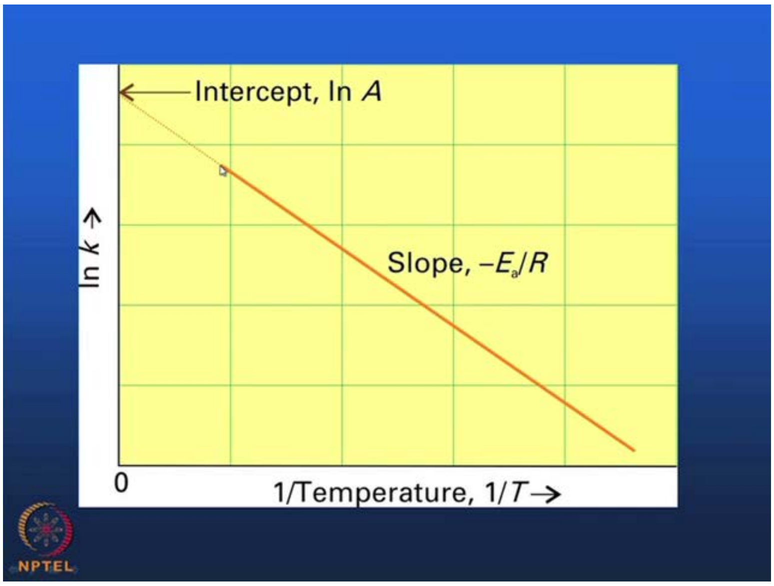

Again, we are looking into that same graph as I told you that the plot can be, this side is low temperature side; this side is high temperature side. So, that is why this orange graph you see, orange line is may, is shown up to this means, it is the temperature up to which one can do the experiment, beyond that it is the huge temperature. So, we cannot go maybe to that high value,, but you can extrapolate. So, this value gives you lnA and slope gives you activation, idea of activation energy because slope is nothing,, but minus E a by R.

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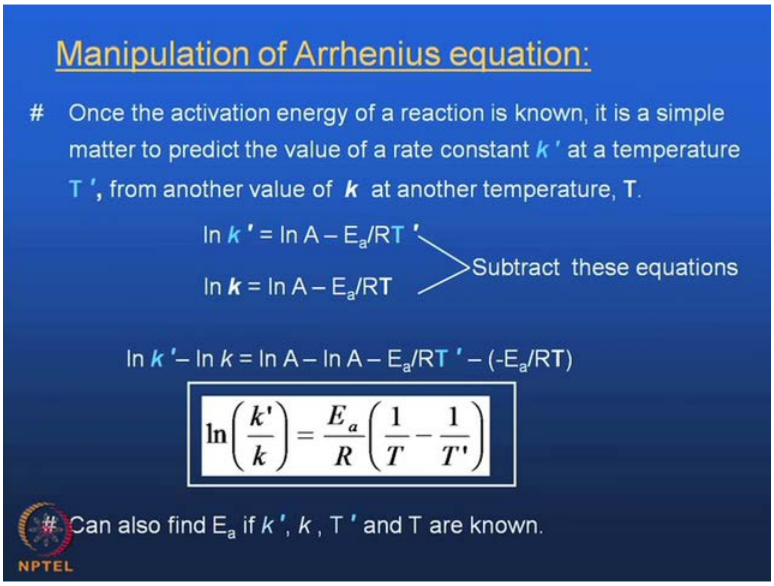

Manipulation of Arrhenius equation:

\# Once the activation energy of a reaction is known, it is a simple matter to predict the value of a rate constant k' at a temperature T', from another value of k at another temperature, T.

$\ln k' = \ln A - E_a/RT'$

$\ln k = \ln A - E_a/RT$

Subtract these equations

$\ln k' - \ln k = \ln A - \ln A - E_a/RT' - (-E_a/RT)$

$$\boxed{\ln\left(\frac{k'}{k}\right) = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)}$$

\# Can also find E_a if k', k, T' and T are known.

Now, manipulation of Arrhenius equation. So, means how to use it. Now, suppose we find out the activation energy of a reaction. In what way we can find out ? It is very simple.

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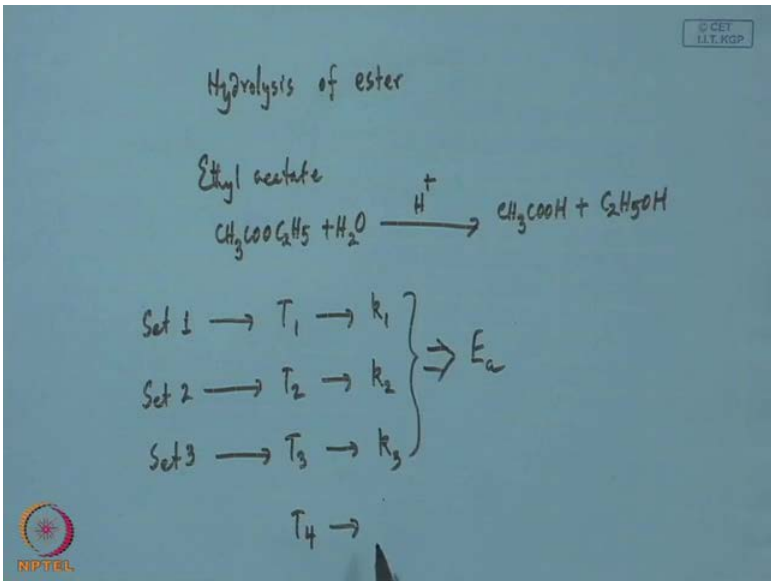

Hydrolysis of ester

Ethyl acetate

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

$$\left.\begin{array}{l} \text{Set 1} \longrightarrow T_1 \longrightarrow k_1 \\ \text{Set 2} \longrightarrow T_2 \longrightarrow k_2 \\ \text{Set 3} \longrightarrow T_3 \longrightarrow k_3 \end{array}\right\} \Rightarrow E_a$$

$T_4 \rightarrow$

Suppose we have got a very simple example, that hydrolysis of ester of say ethyl acetate, CH three COO C two H five plus water giving you acetic acid plus ethyl alcohol.

So, it may be, hydrolysis maybe catalyzed by H plus or maybe by O H minus. So, what you do? You have to have, say three sets of reaction mixture. So, set one, you have to carry out the reaction, say at temperature T one, absolute temperature T one. Set two maybe T two, set three maybe T three. Then find out corresponding k ; k one, k two, k three. For different sets you are getting k one k two k three; that means, different set corresponds to different temperature. So, that is why once the activation energy of a reaction is known, it is a simple method to predict the value of rate constant k primed at a temperature T primed, from another value of k at another temperature; that means, you can predict maybe if this active, from this you will be finding out the activation energy; from this will give you activation energy Ea.

Once Ea is known, suppose I ask you a question that, what will be the value; even if you do not do set four, what can be the value of k at temperature T four? So, you can make use of this Arrhenius equation and you have to manipulate a little bit to find out k four. Since Ea is known from these three, you can find out k four; So, that means, you have got this expression lnk primed which is unknown to you T primed is that corresponding temperature. So, lnk primed is equal to lnA minus Ea by RT primed. Ea is known because I as I told you that you have to be able to know the value of Ea and this you have got lnK which is known. LnA you may not need to know, Ea by RT is also known.

So, then you subtract these two; that means, this minus this is equal to this minus that. So, in that case lnA will just cancel each other. So, right hand side will become Ea by RT primed minus I mean this is minus E A by RT primed plus Ea by RT. So, that means, from this you can simplify to lnk primed by k is equal to Ea by R into one by T minus one by T primed where T primed is the higher temperature. I mean maybe higher temperature or may be low; it is the different temperature that is unknown temperature and this is the known temperature. And you can also find Ea if in the reverse way suppose you this value these two values and also this temperature you can reverse in and then you can find the value of Ea.

So, this expression has got an immense applicability. That if you know Ea, activation energy, you will be able, you should be able to find out the value of rate constant at a given, at a different temperature from another rate constant which is known at another temperature; that means, in that case if this is your unknown if k primed is unknown and if all other things are known like Ea k T and T primed then you should be able to find out the activation energy.

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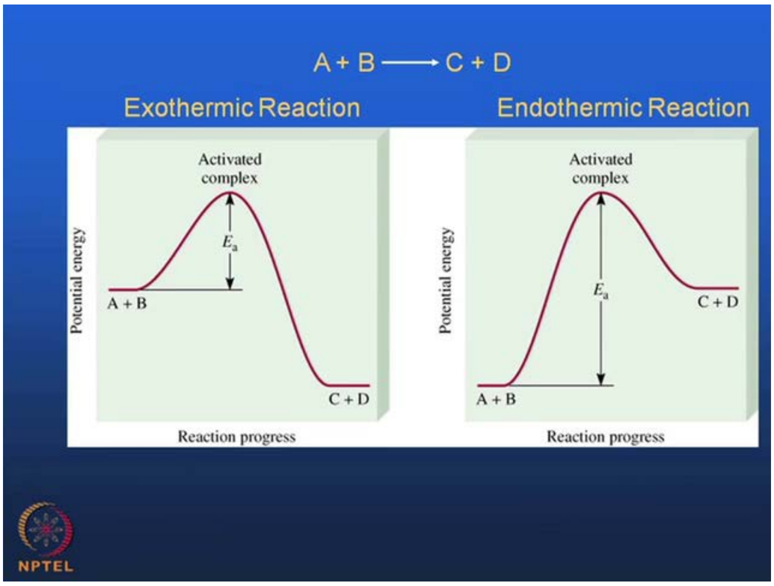

A + B → C + D

Exothermic Reaction

Endothermic Reaction

Now, let us look at this diagram; that the first diagram is for the exothermic process and the second diagram is for the endothermic process. Exothermic process means the process which gives out heat and endothermic process which takes up heat and the system becomes cooled down. And for exothermic case the system becomes hotter.

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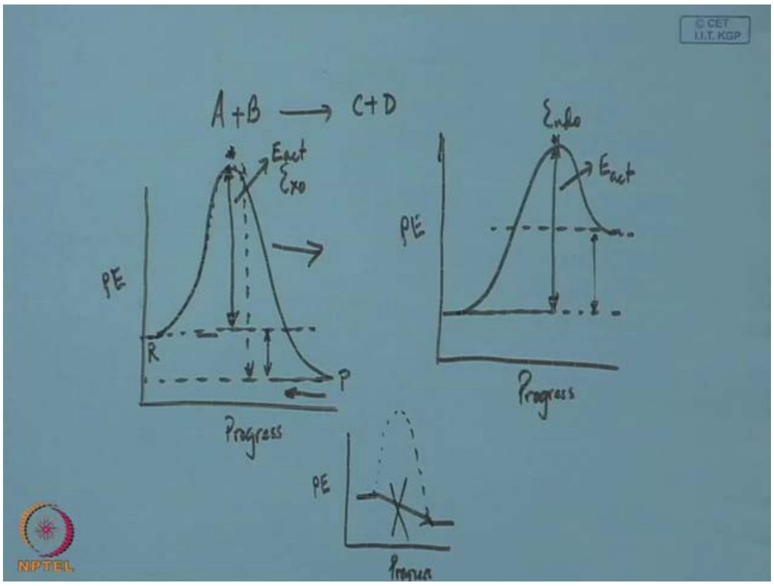

So, basically you are starting from A plus B and you are ending to C plus D. So, the process may be exothermic process may be endothermic

So, in terms of activation energy. So, maybe you can draw a energy diagram energy level diagram that this is your potential energy of the system, that your reactant and this is your product. So, reactant state is located here and the product state is located here. So, you see that the product is lower in energy that is why it is an exothermic process. So, it is giving this excess amount of energy. So, you started with a high energy system and you are ending up to a low energy one that is why this gap is, I mean because of this gap it is giving you this heat. And in case of your endothermic process, it is something like this potential energy, your reactant side is here and the product side is here.

So, that means, you have started with a lower energy, this is your progress of reaction and here you are ending up to a higher energy state; that means, you need to put in this extra amount of energy and that will be taken from your system. So, system will be cooled down. So, this is an endothermic one and this is an exothermic one. And in both the cases you see I have drawn a diagram; I mean two diagrams, where the as it the reaction progresses you see the energy is rising up then it reaches a top and then again it falls down. But no reaction cannot ever be, I mean any reaction you cannot depict a reaction directly in this way like this; that you have got this reactant,. So, this is your product. You cannot draw like this. This is a wrong way of drawing. PE versus progress, it should always pass through a barrier. And this barrier height is called the activation energy. And this activation energy should always be calculated from your reactant side.

If the process happens in this direction; that is, from left to right, then you should calculate this from this side. And if the process is in this direction then your corresponding activation energy will be this. Or, maybe here also activation energy is this.

So, this is the minimum amount of energy that is required this is the minimum amount of energy by the system barrier. So, this is your activation energy. Again this is your also activation energy. So, that is why activation energy is very important, that you will always need to consider the importance of activation energy; because, each process occurs via the formation of some activated complex; activated it may be an activated complex or may be a state of high energy; like here or maybe here.

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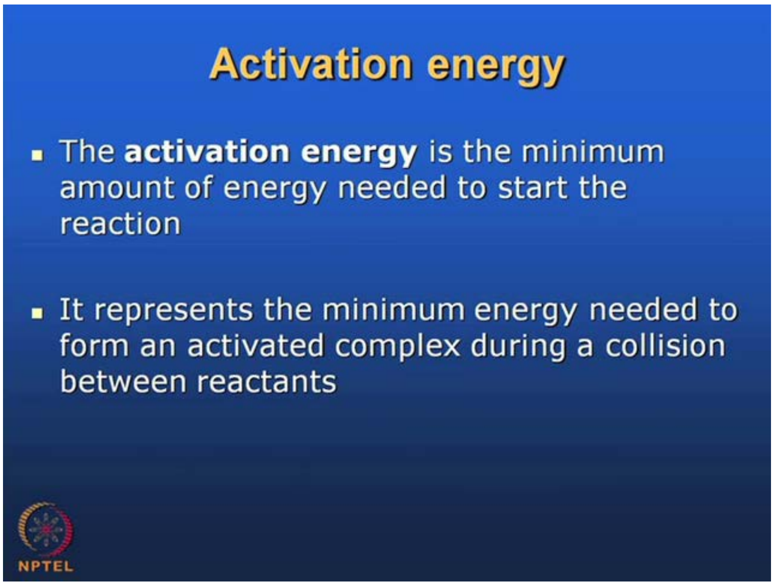

Activation energy

- The **activation energy** is the minimum amount of energy needed to start the reaction
- It represents the minimum energy needed to form an activated complex during a collision between reactants

So, let us move onto the next slide. So, then what we have learnt from these two diagrams; that is, about activation energy. That activation energy is the minimum amount of energy needed to start the reaction. I should refer to this or this particular thing; that it is the minimum amount of energy needed to cross the barrier from say left hand side to right hand side; like I depicted a diagram like this.

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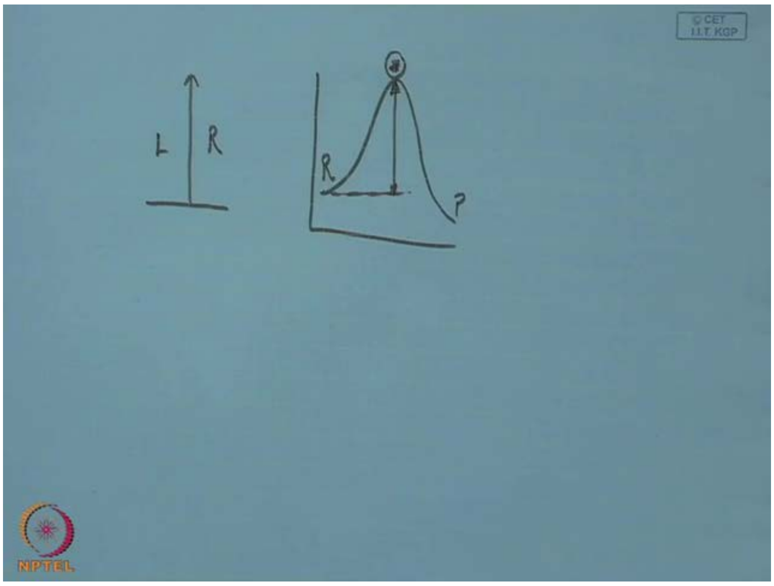

So, this is the minimum amount of energy needed to cross the barrier. So, this particular position it may be energetically high some species or maybe which is also called as activated complex or maybe it you can call this as activated state. So, all the chemical processes which we are dealing with here should occur via this activated state. And in order to form this activated state, you need some minimum amount of energy which is called the activation energy. That means activated state is a must for the transformation from your reactant side to your product side and it represents the minimum energy needed to form an activated complex during a collision between the reactants. So, I will come to why I am referring to collision; I will come to later on when I will discuss the theory of reaction rates.

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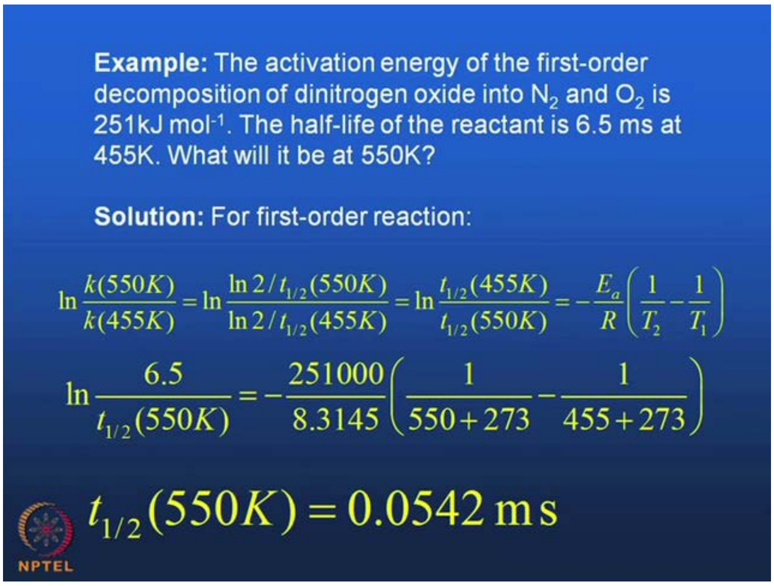

Example: The activation energy of the first-order decomposition of dinitrogen oxide into N_2 and O_2 is 251kJ mol^{-1}. The half-life of the reactant is 6.5 ms at 455K. What will it be at 550K?

Solution: For first-order reaction:

$$\ln\frac{k(550K)}{k(455K)} = \ln\frac{\ln 2/t_{1/2}(550K)}{\ln 2/t_{1/2}(455K)} = \ln\frac{t_{1/2}(455K)}{t_{1/2}(550K)} = -\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\ln\frac{6.5}{t_{1/2}(550K)} = -\frac{251000}{8.3145}\left(\frac{1}{550+273}-\frac{1}{455+273}\right)$$

$$t_{1/2}(550K) = 0.0542\ \mathrm{ms}$$

Let us have an example, that the activation energy of the first order decomposition of dinitrogen oxide into N two and O two is 251 kilojoule mole inverse and the half-life of the reaction, I mean the reactant; reactant means your dinitrogen oxide is 6.5 millisecond at 455k, 455 kelvin. So, what it will be at 550 kelvin ? So; that means, we would like to know the T half value at 550 kelvin. So, clearly since we are increasing the temperature; that means, the substance that is the dinitrogen oxide will require less time; I mean time less than 6.5 milliseconds to get decomposed to nitrogen and oxygen. So, and it is a first order reaction.

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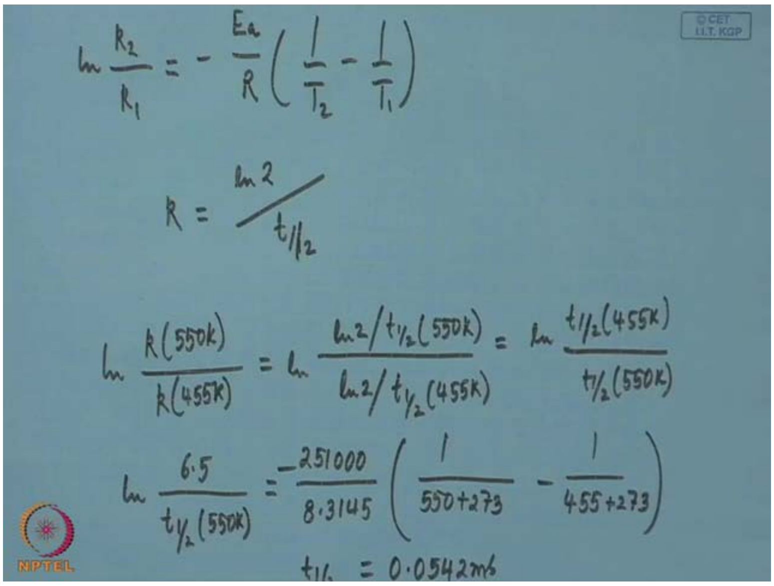

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$k = \frac{\ln 2}{t_{1/2}}$$

$$\ln \frac{k(550K)}{k(455K)} = \ln \frac{\ln 2 / t_{1/2}(550K)}{\ln 2 / t_{1/2}(455K)} = \ln \frac{t_{1/2}(455K)}{t_{1/2}(550K)}$$

$$\ln \frac{6.5}{t_{1/2}(550K)} = \frac{-251000}{8.3145}\left(\frac{1}{550+273} - \frac{1}{455+273}\right)$$

$$t_{1/2} = 0.0542\,ms$$

So, let us try to see how can we solve this. So, again we should refer to this Arrhenius equation, lnk two, k two means temperature two, by k one is equal to minus Ea by R into one by T two minus one by T one and for your first order reaction k is equal to ln two divided by T half.

So; that means, we can just plug in this information over here so; that means, we should write ln k550 kelvin divided by k 455 kelvin is equal to ln, ln two by T half 550 kelvin divided by ln two by T half 455 kelvin which is equal to ln T half 455 kelvin divided by T half 550 kelvin. So, now these two are identical, these two are identical and we know the activation energy is also known so; that means, we can write ln; this is 6.5 in milliseconds. So, 6.5 divided by T half 550 kelvin is equal to minus 251000 since it is kilojoule divided by 8.3145 into T two; this is T two. So, one by it is a negative sign; one by 550 plus 273 minus one by 455 plus 273; because here 273 means we are converting the temperature that is degrees centigrade; I mean basically it should be 273 since we are adding. Here actually in the question it should be 455 naught kelvin it should be 455 degrees centigrade otherwise we should not have added 273. So, anyway. So, 550 degrees centigrade I should write it 550 degrees centigrade. So, it should be it is a typographical mistake anyway.

So, if you do this calculation then T half is equal to is coming out to be equal to 0.0542 milliseconds. So, in that case there is a typo that this 455 degrees centigrade, if it is 455 then you should add 273, if it is kelvin you can do also this simple correction. If you make it 455 kelvin then you do not need to add this 273. So, it should be centigrade. So, here it should also be centigrade anyway. So, this is the way you can manipulate this number that is to find out this T half at a different temperature, when T half of one temperature is known and of course, it is a first order direction. This will be very important; otherwise we should not use this expression for first order, only you can use this, this particular relation.

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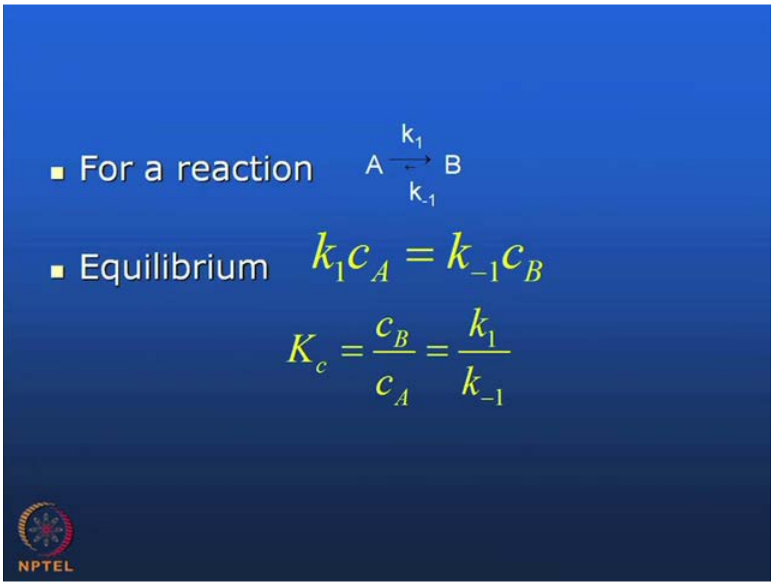

- For a reaction $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$
- Equilibrium $k_1 c_A = k_{-1} c_B$

$$K_c = \frac{c_B}{c_A} = \frac{k_1}{k_{-1}}$$

Now, let us move onto our next slide; that is, application of Arrhenius equation in a reaction where chemical equilibrium is established.

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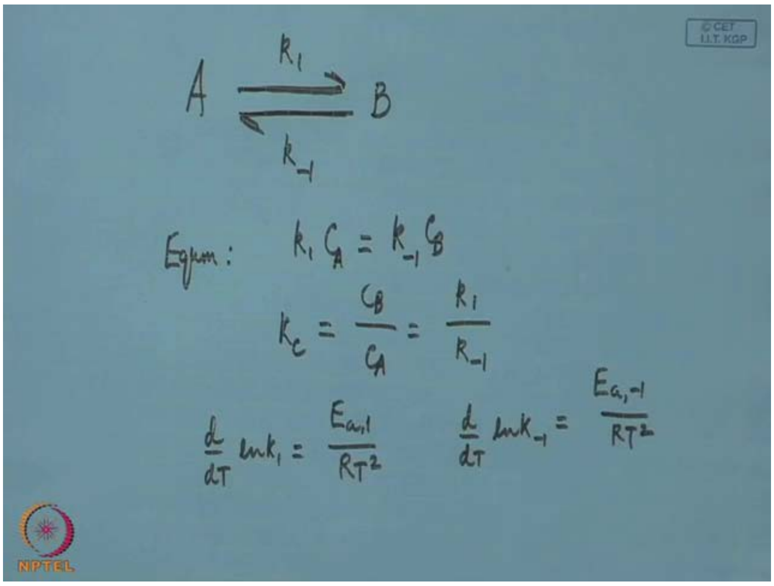

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

Eqlm: $k_1 C_A = k_{-1} C_B$

$$K_c = \frac{C_B}{C_A} = \frac{k_1}{k_{-1}}$$

$$\frac{d}{dT} \ln k_1 = \frac{E_{a,1}}{RT^2} \qquad \frac{d}{dT} \ln k_{-1} = \frac{E_{a,-1}}{RT^2}$$

So, let us start with a reaction say A to B. Forward reaction rate constant is k one and backward reverse is k minus one. So, when it is equilibrium and consider that in both direction, it is first order process. So, at equilibrium k one C A is equal to k minus one C B. So, k C; that is, concentration equilibrium constant. It is not the rate constant, it is the concentration equilibrium constant which is nothing, but C B by C A which is equal to k one by k minus one. Now, let us use Arrhenius equation for these two processes in two directions. So, d dT of ln k one; k one means it is rate constant; it is equal to Ea one by RT square. Ea means activation energy for the forward process. In the same way d dT, of it is the derivative form of Arrhenius equation, lnK minus one is equal to E a minus one by RT square.

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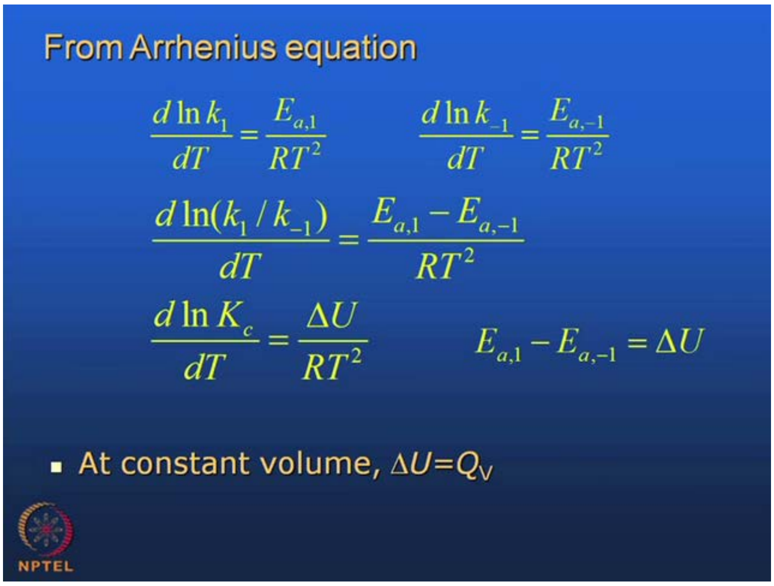

From Arrhenius equation

$$\frac{d\ln k_1}{dT} = \frac{E_{a,1}}{RT^2} \qquad \frac{d\ln k_{-1}}{dT} = \frac{E_{a,-1}}{RT^2}$$

$$\frac{d\ln(k_1/k_{-1})}{dT} = \frac{E_{a,1} - E_{a,-1}}{RT^2}$$

$$\frac{d\ln K_c}{dT} = \frac{\Delta U}{RT^2} \qquad E_{a,1} - E_{a,-1} = \Delta U$$

- At constant volume, $\Delta U = Q_V$

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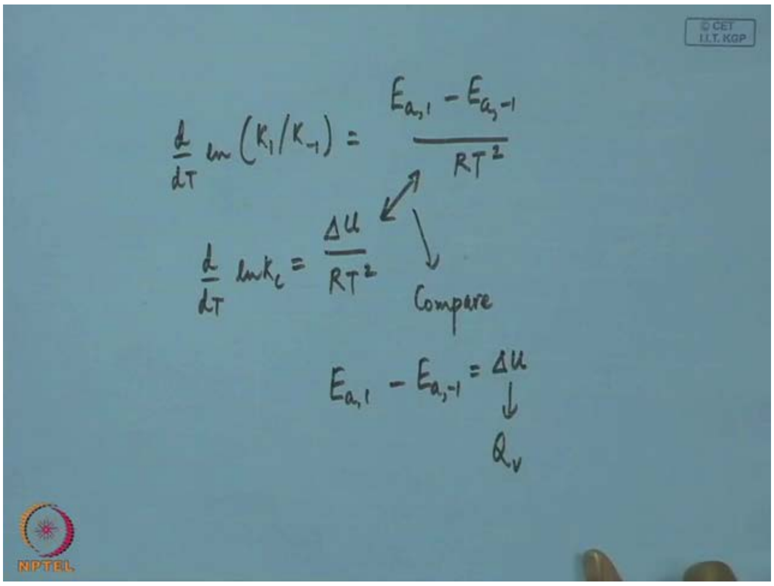

$$\frac{d}{dT}\ln(k_1/k_{-1}) = \frac{E_{a,1} - E_{a,-1}}{RT^2}$$

$$\frac{d}{dT}\ln k_c = \frac{\Delta u}{RT^2}$$

Compare

$$E_{a,1} - E_{a,-1} = \Delta u$$

$$\downarrow$$

$$Q_v$$

So, if you subtract this from this. So, what will you be getting that d dT of lnK one by k minus one is equal to Ea one minus Ea minus one by RT square and we know from chemical equilibrium; that is, concentration equilibrium constant, you can relate to temperature by this relation, d dT of lnk C it is another Van't Hoff’s equation delta u by RT square. So, now if you compare these two you can write if you compare these two you can write activation energy one minus activation energy minus one is equal to delta u. So, delta u is nothing, but Q V, heat exchange at constant volume. So, in this way you can relate your rate constant with some thermodynamic quantities like delta u.

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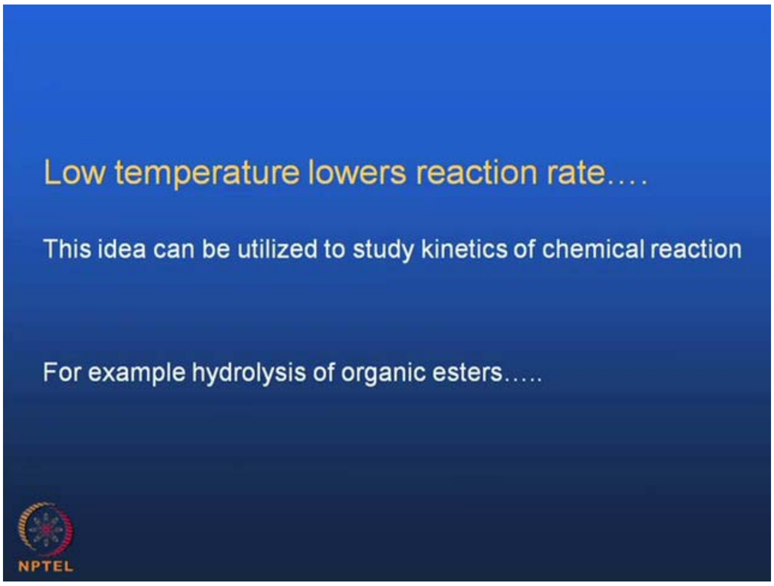

Low temperature lowers reaction rate….

This idea can be utilized to study kinetics of chemical reaction

For example hydrolysis of organic esters…..

Let us move onto some other experiences. What is the utility of this temperature variation, that idea is that if you reduce the temperature your rate will be reduced a lot. So, as I mentioned that when doing study of kinetics of hydrolysis of ester that you can find out this k.

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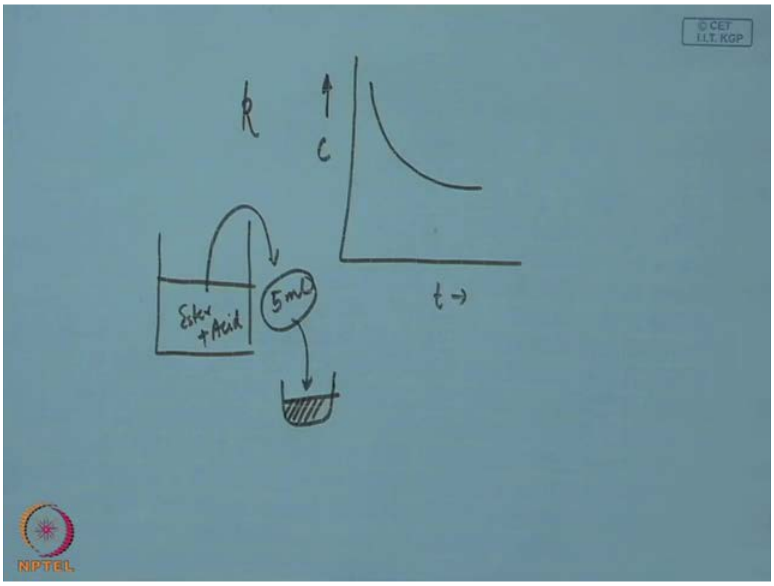

So, you have to, when you have to find out k means you have to plot something say concentration as a function of time concentration of ester remaining, but the thing is that as you have started the reaction there is no way to stop the reaction. So, what you can do you have got your reaction mixture where you have ester plus acid and the reaction continues. What you have to do you take out some; say from here say 5 ml, and then pour this 5 ml, onto a container, onto a conical flask containing ice cold water. So, you put it over here. So, that since the temperature is reduced. So, the reaction is enormously reduced. So, and if you quickly titrate the amount of ester remaining or maybe amount of acid produced then you can find out the momentary concentration of ester in the mixture. So, in that case you can plot C versus t maybe in maybe this way and then you can find out k.

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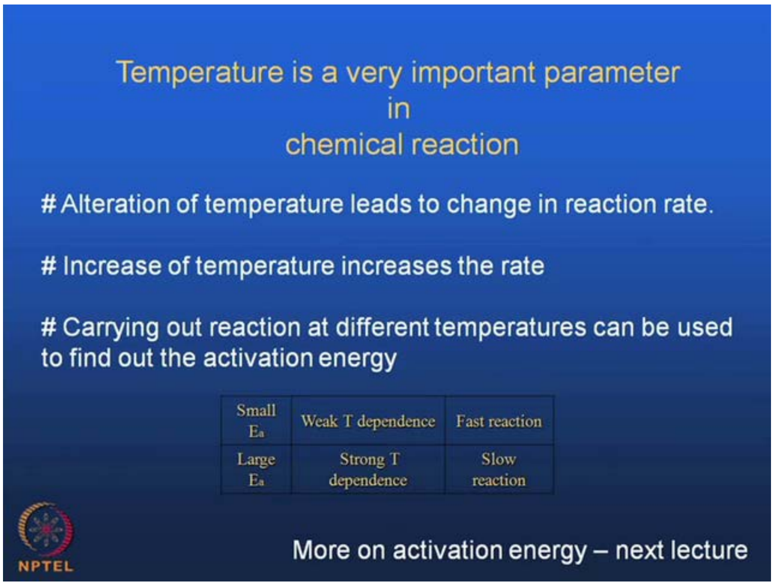

Temperature is a very important parameter
in
chemical reaction

Alteration of temperature leads to change in reaction rate.

Increase of temperature increases the rate

Carrying out reaction at different temperatures can be used to find out the activation energy

Small E_a	Weak T dependence	Fast reaction
Large E_a	Strong T dependence	Slow reaction

More on activation energy – next lecture

So, that is why low temperature lowers the reaction and utilizing that you can find out you can find out the rate constant or maybe you can follow the kinetics. So, what we have learnt in this lecture, that temperature is a very important parameter in chemical reaction. Remember I have started with this, that temperature in chemical reaction or may be any chemical process or maybe in physical chemistry, temperature is a very important thing. Because, you will be finding that temperature changes many things; many means most of the thermodynamic parameters. So, alteration of temperature leads to change in reaction rate and rate constant. Increase of temperature increases the rate.

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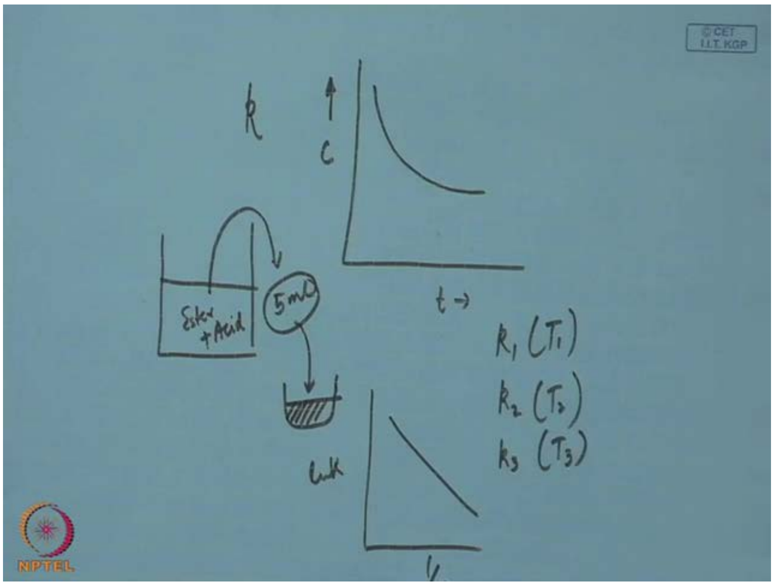

Now, carrying out reaction at different temperatures can be utilized to find out the activation energy; that is, you have got as I mentioned that say k one, k two, k three, k one T one, T two, T three that is three different temperatures you have got it.

So, you have got these k values and you can now plot ln k versus one upon T to find out this slope and from this slope you can find out the activation energy and significance of activation energy is that, it is the minimum amount of energy required to carry out the chemical process, to start the reaction and small activation energy means a weak temperature dependence and the reaction is first. I mean first means very quickly it happens. And large activation energy means there is a strong temperature dependence; means little change of temperature enables you to have a huge change in rate constant and the reaction is very slow.

So, in our next lecture we will learn more on activation energy. So, in the next lecture we will have that and then we will move onto other topics. So, till then have a nice time. Thank you.