Rate Processes

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Module No # 01
Lecture No # 04

Effect of Temperature on Reaction Rate (Contd.)

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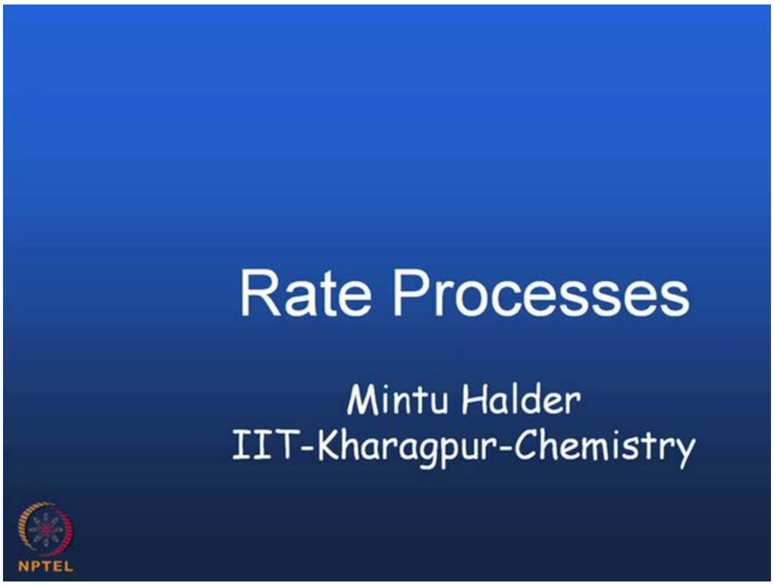

Rate Processes

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Hi, Good morning everybody. So, today we have come to our fourth lecture on rate processes.

So, we were discussing the effect of temperature on reaction rates. So, we will continue to this that is we will give a little detailed account on this. So, let us start.

So, with respect to reaction condition, temperature is a very important factor that controls the chemical reaction.

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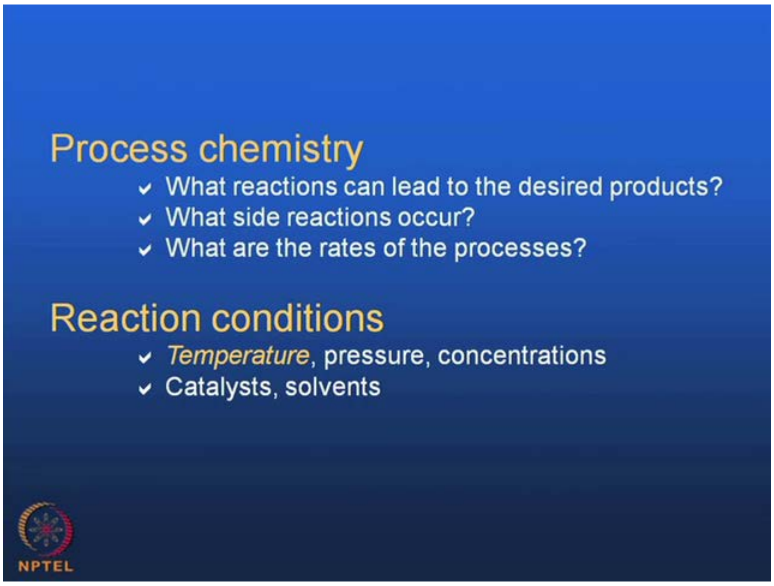

Process chemistry

- 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

Apart from temperature, pressure, concentration, catalyst, solvent; these are also important, but temperature is also a very important parameter and that if we change temperature, reaction rate is found to get affected and if you increase the temperature generally what is what happens is reaction rate increases you do not ever find that direction rate is decreased.

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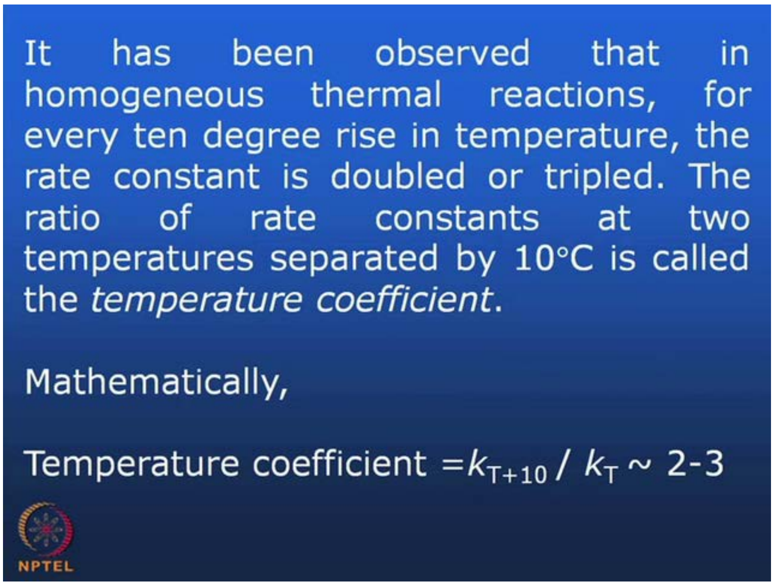

It has been observed that in homogeneous thermal reactions, for every ten degree rise in temperature, the rate constant is doubled or tripled. The ratio of rate constants at two temperatures separated by 10°C is called the *temperature coefficient*.

Mathematically,

Temperature coefficient $= k_{T+10} / k_T \sim 2\text{-}3$

So, it has been observed that in means it is basically a recapitulation of some parts we already have talked about; it has been observed that in homogeneous thermal reactions, thermal reaction means the reactions which occur just by applying heat from outside homogeneous means it happens in one phase, not in two phases or multi phases.

Homogeneous thermal reactions for every 10 degree rise in temperature the rate constant is doubled or even tripled; the ratio of rate constants at two different temperatures separated by 10 degree centigrade is called the temperature coefficient of the reaction and mathematically this temperature coefficient is nothing but, k at T plus 10 by k T and this is found to be of the means close to 2 to 3 and this is for homogeneous thermal reactions homogeneous thermal reactions in other cases something else may happen with respect to k T plus 10 by k T.

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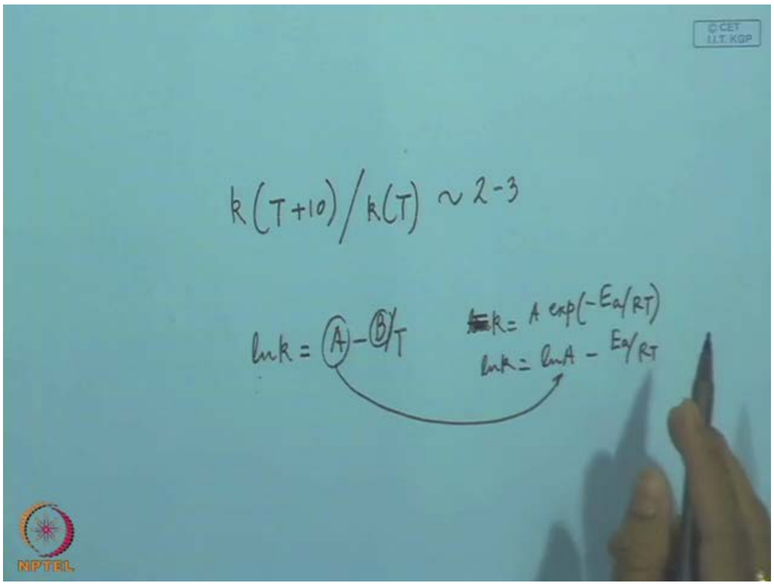

$$k(T+10)/k(T) \sim 2\text{-}3$$

$$\ln k = \textcircled{A} - \textcircled{B}/T$$

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

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

So, the first mathematical relation between rate constant and absolute temperature was given by hood in 1878 as follows that is ln k is equal to A minus B by T; you see, that it is an empirical relation that says that if you plot as I told you as I talked about in previous lecture that ln k versus 1 upon T will be giving you a linear slope. So, here also is a similar relation and it is prior to it is before Arrhenius proposed his equation, his famous equation.

So, A and B these are constant quantities for a reaction system the values of A and B these may be obtained by plotting ln k versus 1 upon T, that is from slope you will be getting B and from intercept you will be getting A.

Now, this hoods equation; this equation was based on the experimental result that is from the experience; that means, whatever data or whatever results people have gathered out of various chemical processes that is found to fit in this equation.

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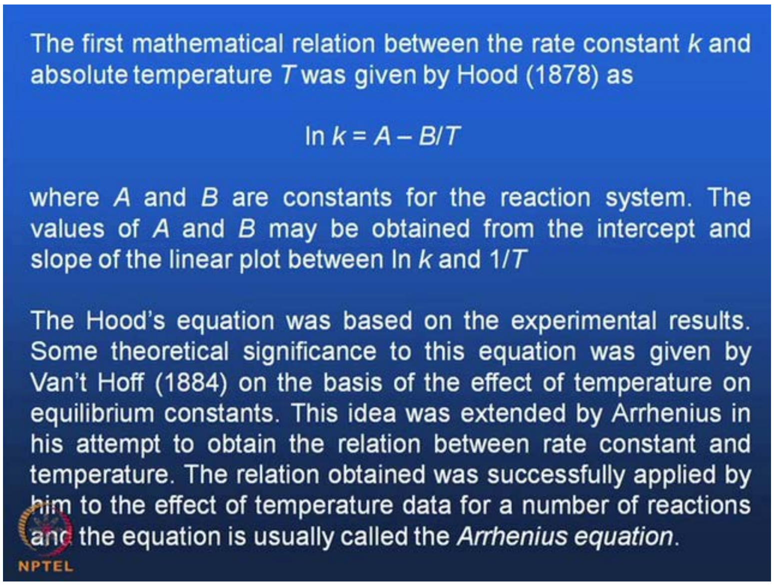

The first mathematical relation between the rate constant k and absolute temperature T was given by Hood (1878) as

$$\ln k = A - B/T$$

where A and B are constants for the reaction system. The values of A and B may be obtained from the intercept and slope of the linear plot between $\ln k$ and $1/T$

The Hood's equation was based on the experimental results. Some theoretical significance to this equation was given by Van't Hoff (1884) on the basis of the effect of temperature on equilibrium constants. This idea was extended by Arrhenius in his attempt to obtain the relation between rate constant and temperature. The relation obtained was successfully applied by him to the effect of temperature data for a number of reactions and the equation is usually called the *Arrhenius equation*.

So, it is basically based on experimental results, that is based on experience some theoretical significance to this equation was given by Van't Hoff in 1884 on the basis of the effect of temperature on equilibrium constant. So, Van't Hoff tried to give some idea why this happens.

On the basis of, effect of temperature on chemical equilibrium constant. So, in equilibrium constants are very sensitive to the temperature. So, if you change the temperature equilibrium constant will also change. So, based on that since equilibrium constants are affected; so, he tried to explain on the basis of this observation; this idea was further extended by Arrhenius in his attempt to obtain the relation between rate constant and temperature.

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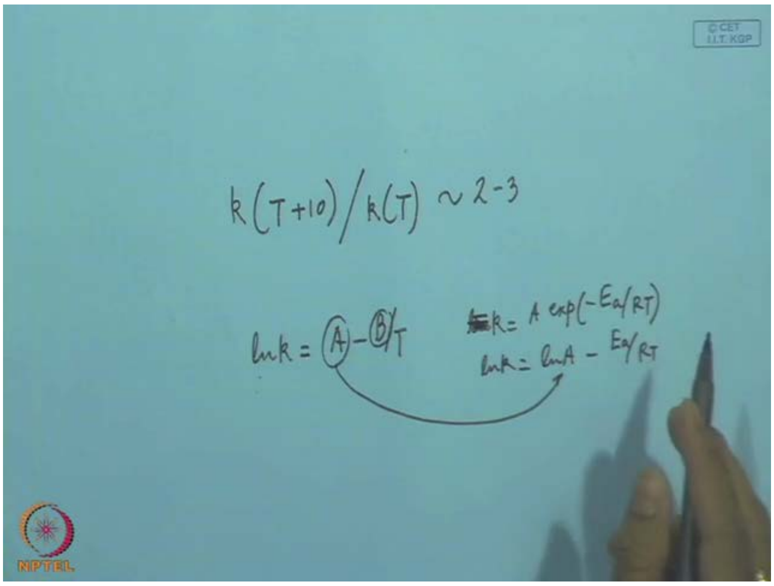

The relation obtained was then successfully applied by him to the effect of temperature data for a number of reactions, for a number of chemical processes and the equation is usually called the Arrhenius equation which is ln k is equal to A into, it is not ln k, k is equal to A into exponential minus E a by R T.

So, if you take ln k is equal to ln A minus E a by R T. So, these two are very similar. So, this A is similar to ln A and this one is similar to this.

So, actually Arrhenius from the idea of, for hoods equation he gave this new expression that is, k is equal to A into E to the power of minus x E a by R T and that has been found to fit very well with chemical systems, when temperature is modified.

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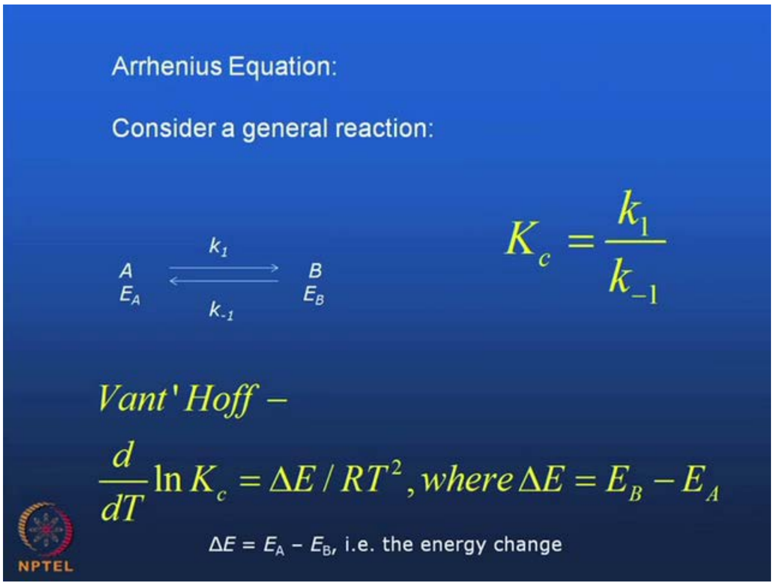

Arrhenius Equation:

Consider a general reaction:

$$\underset{E_A}{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{E_B}{B} \qquad K_c = \frac{k_1}{k_{-1}}$$

Vant' Hoff –

$$\frac{d}{dT}\ln K_c = \Delta E / RT^2, where\ \Delta E = E_B - E_A$$

$\Delta E = E_A - E_B$, i.e. the energy change

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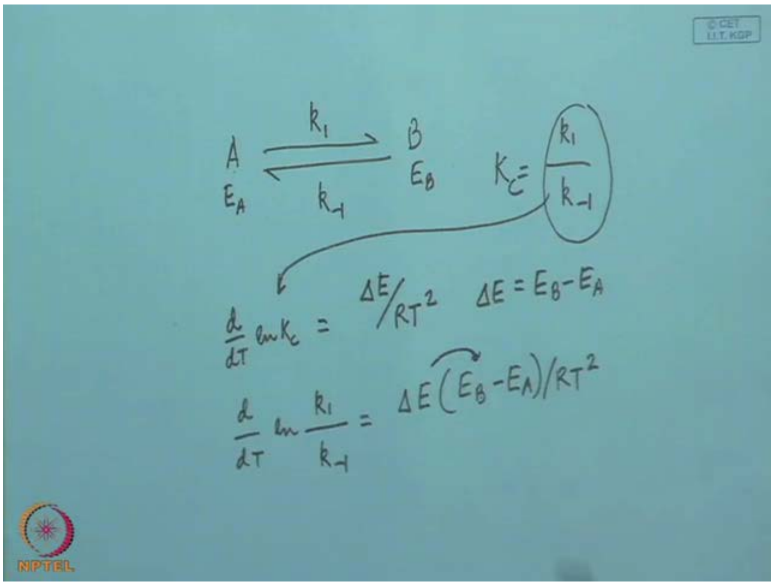

$$\underset{E_A}{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{E_B}{B} \qquad K_c = \frac{k_1}{k_{-1}}$$

$$\frac{d}{dT}\ln K_c = \Delta E / RT^2 \qquad \Delta E = E_B - E_A$$

$$\frac{d}{dT}\ln \frac{k_1}{k_{-1}} = \Delta E\,(E_B - E_A)/RT^2$$

So, Arrhenius equation consider a general reaction that A is converted to B and say energy of A is E A and energy of B is E B. So, like this A to B. So, it is k 1 reverse is k minus 1 and energy is E A, this is E B. So, concentration equilibrium constant which is k 1 by k minus 1.

So, what Van't Hoff tried to explain is like this based on his idea on effect of temperature on equilibrium constant, that d by dT of ln k c is equal to delta E by R T square where delta E is nothing but, E B minus E A that is final minus initial that is the energy change associated with this process of transformation from A to B. So, it is nearly the energy change associated with this chemical transformation.

So, he tried to use this expression and with the idea that A with EA B with E B. So, the difference in energy will be E B minus E A and then he has plugged in this value to this one, to this expression.

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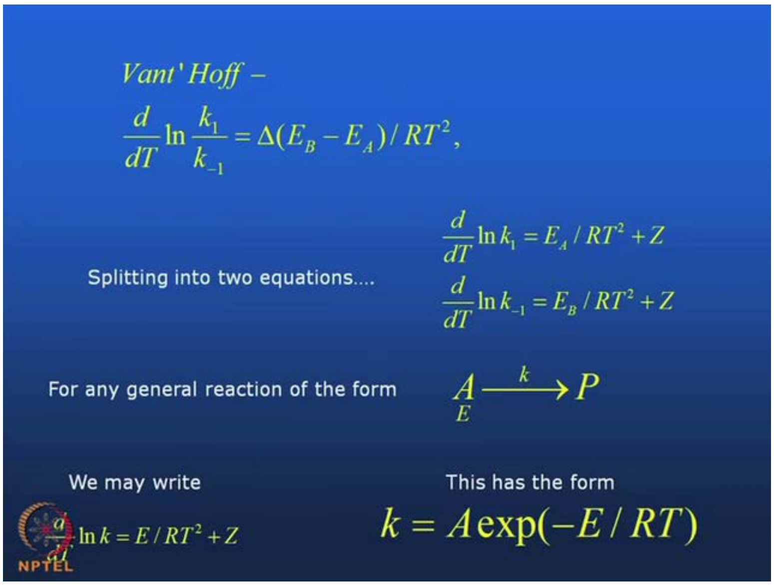

Vant' Hoff –

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

Splitting into two equations....

$$\frac{d}{dT}\ln k_1 = E_A/RT^2 + Z$$

$$\frac{d}{dT}\ln k_{-1} = E_B/RT^2 + Z$$

For any general reaction of the form

$$\underset{E}{A} \xrightarrow{k} P$$

We may write

$$\frac{d}{dT}\ln k = E/RT^2 + Z$$

This has the form

$$k = A\exp(-E/RT)$$

So, if we plug in this onto here then what do we get; d by dT of ln k 1 by k minus 1 which is equal to delta E, delta E means basically E B minus E A by R T square.

So, if we split this. So, basically delta E is nothing but, E B minus E A; either you can write delta E or may be E B minus E A in this way; I am just writing this together means this one is nothing but this one; delta E means this one.

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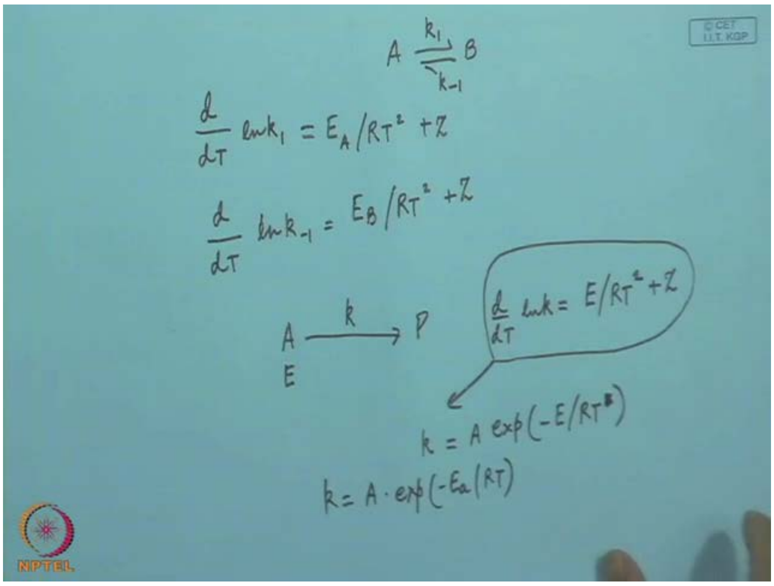

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$$\frac{d}{dT} \ln k_1 = E_A/RT^2 + Z$$

$$\frac{d}{dT} \ln k_{-1} = E_B/RT^2 + Z$$

$$\underset{E}{A} \xrightarrow{k} P$$

$$\boxed{\frac{d}{dT} \ln k = E/RT^2 + Z}$$

$$k = A \exp(-E/RT^2)$$

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

So, if we now split this expression into two equations then this will look like d by dT of ln k 1 that is rate constant for the forward process. So, basically we started with this A to B forward rate and backward rate. So, d by dT of ln k 1 is equal to E A by R T square plus some constant Z, is the first equation the second equation is d by dT of ln k minus 1 is equal to E B by R T square plus Z.

So, for any general reaction any general reaction what we get; suppose we have a general reaction like a to product with a rate constant k with energy E then, we write using this Arrhenius equation d by dT of ln k is equal to E by R T square plus Z.

So, basically this has the form this particularly in a general form. So, this has the form like k is equal to A into exponential minus E by R T square. This has the form not exactly the, this is not the exactly the energy of activation, but this has the form that rate constant has got some pre exponential term and within exponential there must be an energy term; this is R T. There must be an energy term within this exponential. So, this way this Arrhenius equation arrived into.

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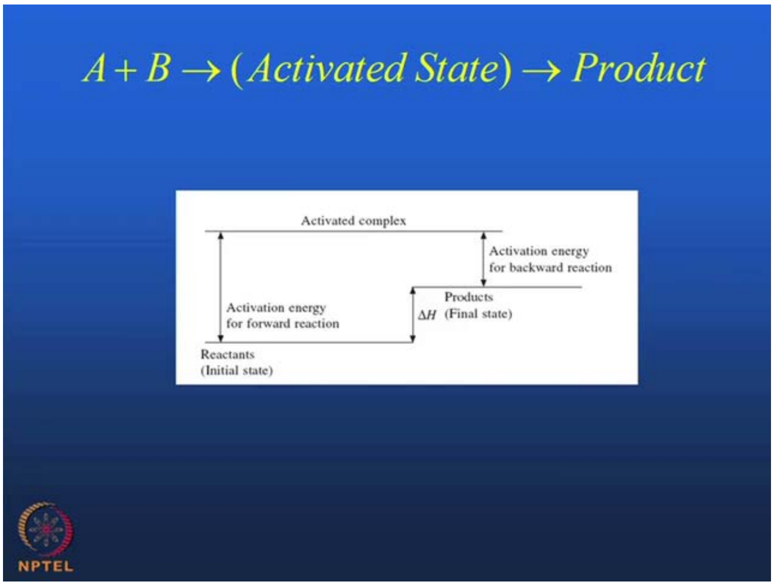

$$A + B \rightarrow (Activated\ State) \rightarrow Product$$

Activated complex

Activation energy
for backward reaction

Products
(Final state)

ΔH

Activation energy
for forward reaction

Reactants
(Initial state)

Then, again what is this E R for your Arrhenius equation k is equal to A into exponential to the power minus E a by R T. So, what is this E a; let us refer to this slide that this is the slide let us look into that this is your reactant initial state it is the starting port point of your reaction.

Then what happens an activated state is formed which may be called as an activated complex and then this activated complex or activated state is transformed to product. So, it is now then transformed to this product.

So, the difference in energy state between the reactant that is the initial state and the activated complex is called the activation energy for the forward process.

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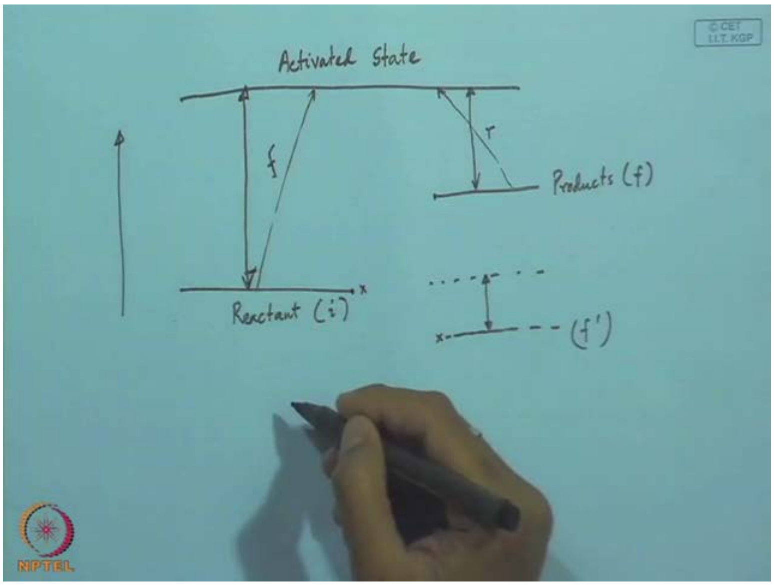

So, this is your reactant; or initial state; this is your activated state; and say this is your product state, say this is your products; that is your final. So, difference in energy of these two, difference in energy of these two, it is called the activation energy for transformation from reactant to activated state

So, like this. So, it is the forward process forward activation energy; in the same way this difference is the difference between the activated state and the product state and basically if you draw an arrow like this. So, it is for the backward or reverse process.

So, it is called the activation energy for the reverse process. So, this is forward activation process, I mean forward activation energy and this is your reverse activation energy and you see here we I have drawn the reactant state and the product state in such a way that product is above reactant state.

So, that means, that means what is happening that moving from here to here your energy state of the I mean whole energy of the system is increasing. So, that means, that means, it is energy extracting that is energy is taken up from outside. So, it is not energy generating. It is not an exothermic process.

Suppose if your product state is here, then your it is lower in energy. So, it is f primed it is lower in energy compared to a reactant. So, that means, that means, this much of energy would have been released; therefore, this process would have been an exothermic process. So, difference between these two, either this or maybe these two pairs, it is called the heat of reaction that is the energy I mean enthalpy difference between this and that.

So, it is higher heat H value this is lower H. So, that means, energy to be taken up and this is lower H, this is higher H. So, energy will be released.

So, that means, that means, reactant activated state then product and then their relative position in energy scale will determine whether the reaction will be exothermic or the reaction will be endothermic in nature.

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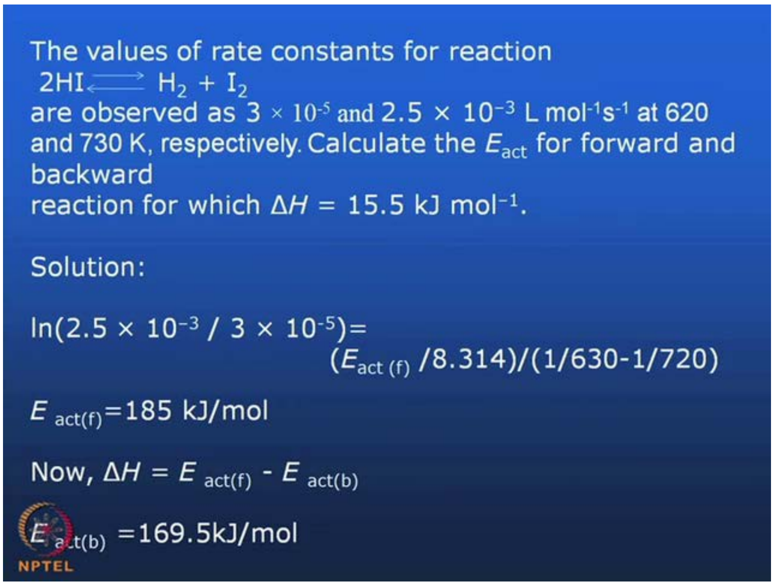

The values of rate constants for reaction
$2HI \rightleftharpoons H_2 + I_2$
are observed as 3×10^{-5} and 2.5×10^{-3} L $mol^{-1}s^{-1}$ at 620 and 730 K, respectively. Calculate the E_{act} for forward and backward
reaction for which ΔH = 15.5 kJ mol^{-1}.

Solution:

$\ln(2.5 \times 10^{-3} / 3 \times 10^{-5}) = (E_{act\ (f)} /8.314)/(1/630-1/720)$

$E_{act(f)}$=185 kJ/mol

Now, $\Delta H = E_{act(f)} - E_{act(b)}$

$E_{act(b)}$ =169.5kJ/mol

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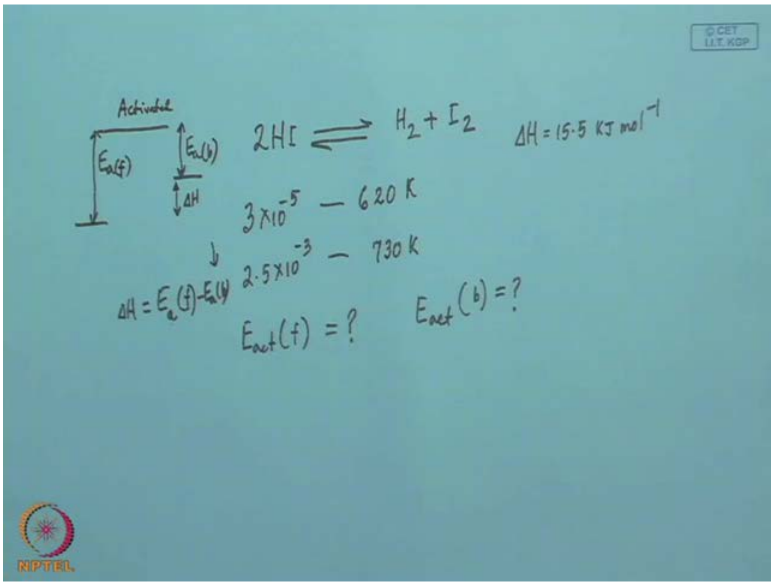

$2HI \rightleftharpoons H_2 + I_2$ $\Delta H = 15.5\ KJ\ mol^{-1}$

3×10^{-5} — 620 K

2.5×10^{-3} — 730 K

$\Delta H = E_a(f) - E_a(b)$

$E_{act}(f) = ?$ $E_{act}(b) = ?$

Now, let us move onto one example that dissociation of H I; at two different temperatures. So, let us look into this; this process 2 H I giving rise to H 2 plus I 2 in gas phase.

So, rate constants are given to be 3 into 10 to the power of minus 5, another is 2.5 into 10 to the power of minus 3 that is it is increasing; this is at 620 kelvin and this is at 730 kelvin.

Remember that, as you increase the temperature rate constant is increased like that thumb rule; that for every ten degree rise of temperature the rate constant is increased by two to three times, of course, that is for homogeneous thermal reactions; and given that delta H for this process H for this process is 15.5 kilojoule mole inverse.

So, we have to find out the activation energy for forward and backward reactions. So, E act forward and also E act activation or E a whatever you say backward is how much that we have to find out.

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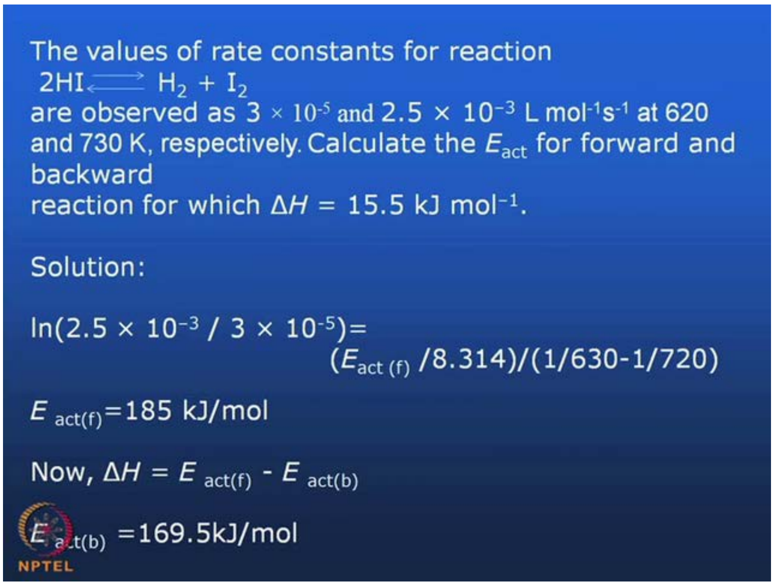

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Solution:

$\ln(2.5 \times 10^{-3} / 3 \times 10^{-5}) = (E_{act\ (f)} /8.314)/(1/630-1/720)$

$E_{act(f)} = 185$ kJ/mol

Now, $\Delta H = E_{act(f)} - E_{act(b)}$

$E_{act(b)} = 169.5$kJ/mol

So, how to do that; now first we have to use since we are means this rate constants are given for the forward processes. So, we have to make use of this Arrhenius equation to find out the activation energy of the forward process and then with the help of that diagram that I already have shown that this is your activated state; say this is your forward activation energy. So, E a f say and say this is your backward reaction activation energy E a b and this much is your delta H.

So, basically delta H is equal to E a forward minus E a backward. So, we have to make use of this equation to find out this backward activation energy, I mean activation energy for the back reaction.

So, let us first find out the forward activation energy. So, it is given like this; that ln k 1 by k 2 or k 2 by k 1 is activation energy by 8.314 into 1 by 2 different temperatures; one this is your initial temperature this is your final temperature.

So, upon calculation if you simplify then activation energy for the forward process will be coming out to be 185 kilojoule per mole.

So, just making use of your, this Arrhenius equation; you can find out the forward activation energy and then you use make use of this equation, that delta H is equal to E activation forward minus E activation backward since you know E activation forward.

So, backward activation I mean activation energy for the back process will be found from this one and this comes out to be this. So, backward activation energy is less. So, it is an endothermic process you see the sign is plus it is an endothermic process.

So, this way you can find out activation energy for the backward I mean back reaction and the forward reaction provided you are given delta H of reaction.

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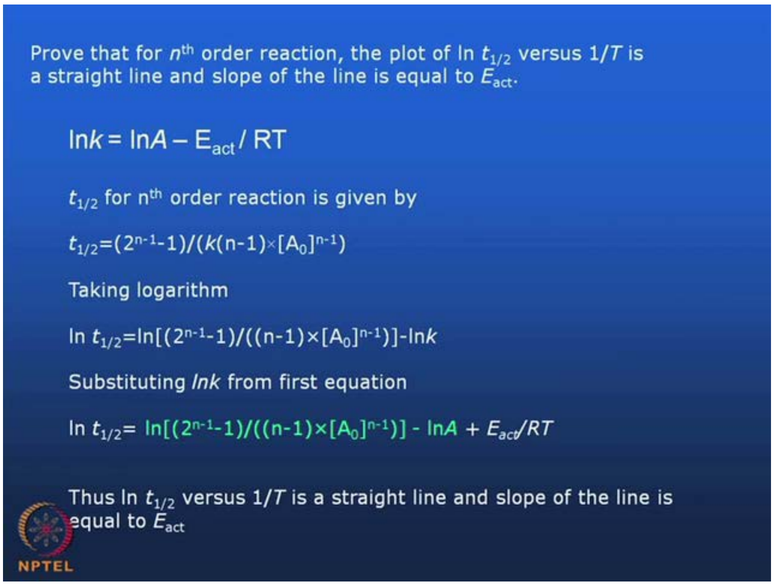

Prove that for n^{th} order reaction, the plot of ln $t_{1/2}$ versus $1/T$ is a straight line and slope of the line is equal to E_{act}.

$$\ln k = \ln A - E_{act} / RT$$

$t_{1/2}$ for n^{th} order reaction is given by

$t_{1/2}=(2^{n-1}-1)/(k(n-1)\times[A_0]^{n-1})$

Taking logarithm

$\ln t_{1/2}=\ln[(2^{n-1}-1)/((n-1)\times[A_0]^{n-1})]-\ln k$

Substituting $\ln k$ from first equation

$\ln t_{1/2}= \ln[(2^{n-1}-1)/((n-1)\times[A_0]^{n-1})] - \ln A + E_{act}/RT$

Thus ln $t_{1/2}$ versus $1/T$ is a straight line and slope of the line is equal to E_{act}

Next another problem; prove that the that for an for an nth order reaction the plot of T half versus 1 upon T is a straight line and the slope of the line is equal to activation energy.

So, we know ln k versus 1 upon T if we do a plot which is typical Arrhenius using Arrhenius equation then slope will be giving you activation energy; I mean E a by R, but here for an nth order reaction you have to prove that ln T half versus 1 upon T is a straight line its slope equal to E act.

So, we have to start with this one that ln k is equal to ln A minus E a by R T this is your Arrhenius equation and T half for the nth order reaction is given by this; this is your initial concentration.

So, this is I already have talked about the expression for T half for nth order reaction in this case n must not be equal to one that you have to remember.

So, if you take logarithm that is natural logarithm ln both the sides then you will be getting this expression; then what you have to do you have to plug in; I mean you have to replace ln k by this; ln k is equal to ln A minus E a by R T.

So, you write this in place of ln k ln A plus E a by R T. So, this is a constant quantity you see the ln A is a constant as long as temperature is fixed and the reaction I mean we are talking about a particular reaction. So, this is a constant.

So, you see that ln T half is equal to E a by R T. So, slope basically E a by R. So, slope is nothing but, from slope you will be getting E a.

So, for a typical nth order reaction n is not equal to 1 you can prove that that T half versus 1 upon T will be giving you activation energy.

So, this way you can show this one and this is a straight line because you see ln T half is equal to constant plus E a by R T. So, T half versus 1 upon T is a straight line.

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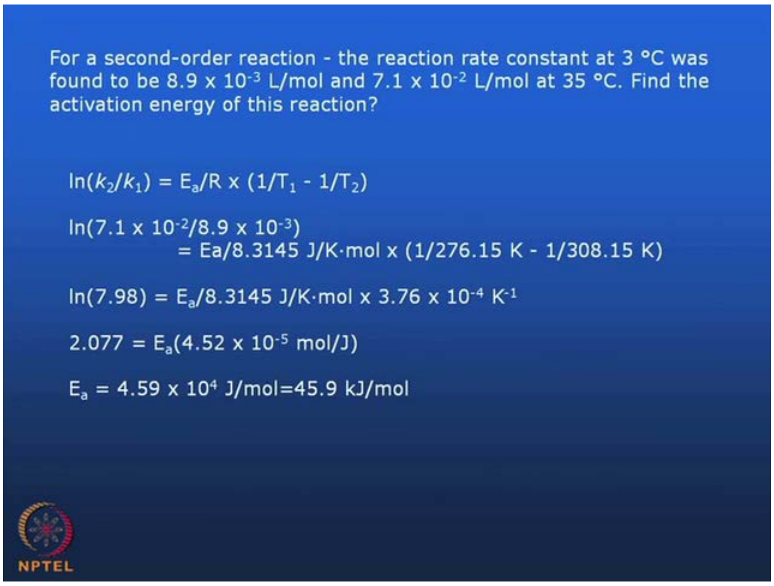

For a second-order reaction - the reaction rate constant at 3 °C was found to be 8.9×10^{-3} L/mol and 7.1×10^{-2} L/mol at 35 °C. Find the activation energy of this reaction?

$\ln(k_2/k_1) = E_a/R \times (1/T_1 - 1/T_2)$

$\ln(7.1 \times 10^{-2}/8.9 \times 10^{-3})$
$= Ea/8.3145\ \mathrm{J/K{\cdot}mol} \times (1/276.15\ \mathrm{K} - 1/308.15\ \mathrm{K})$

$\ln(7.98) = E_a/8.3145\ \mathrm{J/K{\cdot}mol} \times 3.76 \times 10^{-4}\ \mathrm{K}^{-1}$

$2.077 = E_a(4.52 \times 10^{-5}\ \mathrm{mol/J})$

$E_a = 4.59 \times 10^{4}\ \mathrm{J/mol} = 45.9\ \mathrm{kJ/mol}$

Another example, for a second order reaction the reaction rate constant at 3 degrees Celsius was found to be 8.9 into 10 to the power minus 3 liter mole inverse and 7.1 into 10 to the power minus 2 liter mole inverse at 35 degrees centigrade. So, find the activation energy.

So, it is a straight forward basically we use this expression ln k 2 by k 1 is E a by R into this one and upon plug in the respective numbers, you will be getting E a which is equal to 45.9 kilojoule mole inverse.

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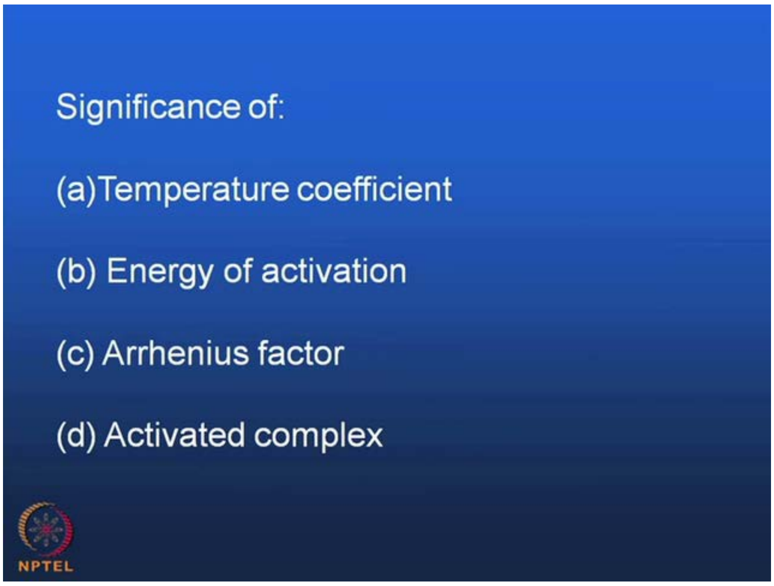

Significance of:

(a)Temperature coefficient

(b) Energy of activation

(c) Arrhenius factor

(d) Activated complex

So, what is the significance of temperature coefficient. So, temperature coefficient significance means T I mean k T plus 10 divided by k T which is equal to 2 to 3 means as you increase the temperature reaction rate increases rate constant is getting raised from a particular value.

So, that is the significance that is the typical signature of a chemical reaction that you if you increase the temperature your reaction rate is enhanced.

Next is energy of activation. What is energy of activation now as I told you that in order to form an activated state some energy is needed; and next is why activated complex is needed because you need to cross a barrier otherwise you cannot reach your product state.

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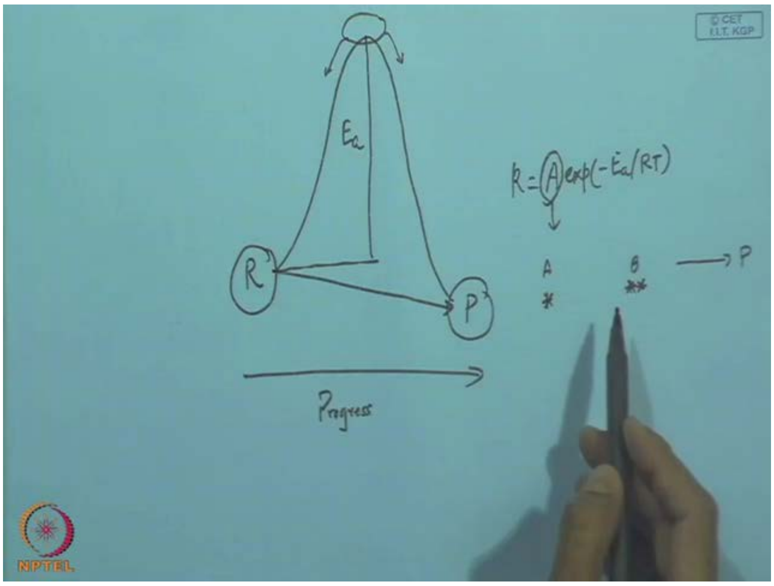

If you are now in a reactant state say this is your reactant state say this is your product state you cannot directly move from here to here there is a there is a barrier like this you must cross it otherwise you cannot go directly.

So, this barrier is called the activation barrier that you must cross. So, this is E a you must cross the barrier and this is the progress of reaction, progress of reaction or maybe called as reaction coordinate.

So, you must cross the barrier. So, this much of energy must be supplied from outside in order that the reactant is crossing can cross the barrier. So, this much of energy must be supplied, must be needed otherwise reaction will not will not take place. Arrhenius factor that is k is equal to A exponential minus E a by R T. So, this is your Arrhenius factor it is also called as a as the frequency factor. So, this is called the Arrhenius factor and this is your exponential term.

What is an activated complex? Activated complex is basically a state or activated state which is here, it is high in energy. High in energy means either reactant and or product these two are lower in energy compared to this activated state.

So, this is high in energy compared to reactant state or product state now this activated complex is formed in various ways it may be formed in various ways.

Now, the point is according to latest theories of reaction rates which we will discuss later time that suppose, if it is a homogeneous gas phase reaction then you have got reactant say reactant a and say another reactant B. So, what is needed is that. So, A and B should come close to each other.

Otherwise suppose there is required an atom transfer from say A to B to give your product P. So, that means, that means, they must be close to each other or they must be in vicinity of each other. So, that this atom transfer can take place; that means, only possibility in gas phase is that if there is a collision then they can come close to each other.

So, basically by means of collision they can form a momentary complex which may be regarded as an activated complex, then this activated complex one it is once it is formed then it has got the option, either it can go in this direction which explains the back reaction or maybe it can cross the barrier in the and go to the right hand side which explains the product formation this explains your again back reaction. So, that means this activated complex formation is a very important thing and it needs to be further discussed.

So, we will discuss this point later on means what is activated complex, how does it look and what are the factors, that you know that can affect the relative energy state of this activated complex that we will discuss and what is the effect of temperature and how temperature alters this activated complex formation whether it is expediting or something else we will talk about maybe later time.

So, A plus B producing products. So, it is a simple gas phase reaction it is a kind of collision. So, it is a collision reaction may be reaction all reactions are not gas phase reactions. So, in solution phase something else may happen.

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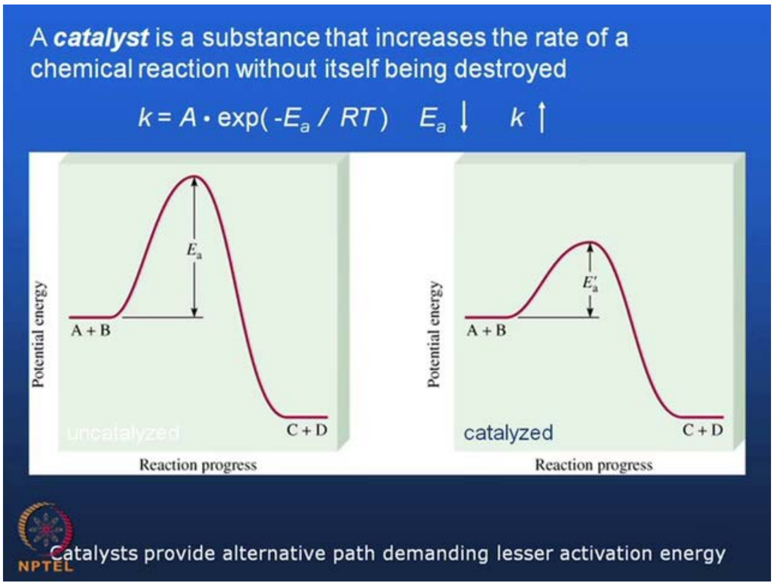

A ***catalyst*** is a substance that increases the rate of a chemical reaction without itself being destroyed

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

Catalysts provide alternative path demanding lesser activation energy

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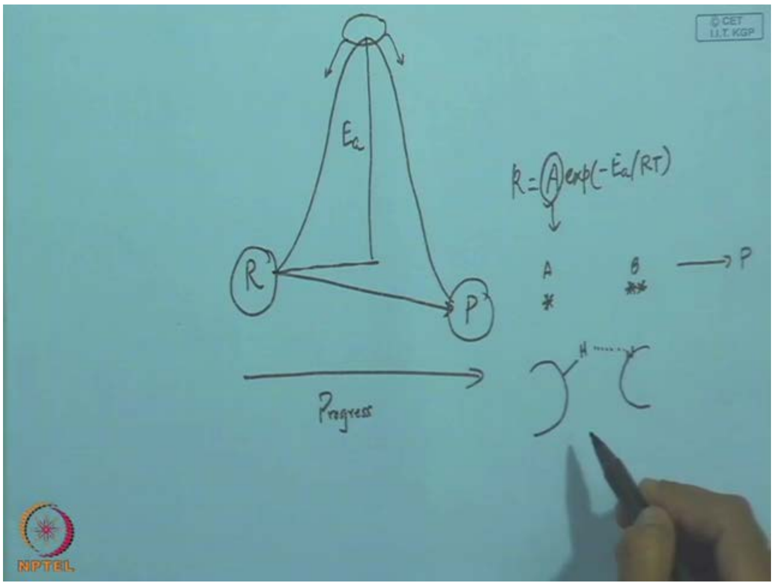

We must talk a little about catalyst what is a catalyst now because since I started to talk about I know although in brief, but I started to talk about this activated complex and a possible geometry of the activated complex, possible geometry may be say may be by means of a hydrogen bond formation; say, we have got one entity and there is a hydrogen which is just projected out and there is another entity suppose there is nitrogen.

So, in the gas phase there is a possibility of hydrogen bond formation. So, this hydrogen bonded complex sometime, can be an activated complex and then later on after you know after if we give more time, then this hydrogen will may be transferred from here to here, producing your product. So, that will come later on, but the thing is there is a definitive role of catalyst in speeding of the reaction.

Now, what is a catalyst? Catalyst is a substance that increases the rate of a chemical reaction without itself being destroyed or used up in this particular discussion we are not taking up catalyst in detail, but basic understanding what does a catalyst do for a chemical reaction, we just try to understand that.

So, you have this Arrhenius equation k is equal to A exponential minus E a by R T, where E a is the activation energy and this is your absolute temperature; and so, A plus B producing C plus D. So, this is your activation energy E a. Suppose an E a; so, if E a is more the barrier crossing rate will be less.

So, as I told you in earlier lecture that if activation energy is more, then reaction is generally slowed down; I mean slow reaction it is a result is a slow reaction although temperature effect is more, but it is a slow reaction when activation energy is less then reaction is fast.

So, suppose by a specific means or by some means, if we can reduce if we can reduce this E a maybe by introduction of a third component in the reaction mixture or maybe by some other means maybe if we raise the energy state by some means or maybe if we reduce the activated state by some means, then this separation will be reduced this separation will be reduced.

So, if this separation will be reduced then possibility of barrier crossing from here to here producing your product, that is the progress of reaction will be more; that means, lowering of activation energy will lead to an increase in rate constant.

So, if this is an uncatalyzed reaction and suppose in presence of catalyst if, this happens like your activation energy is reduced then your rate will be further increased.

So, then what is the role of a catalyst. So, basically catalyst provides an alternative path that demands lesser activation energy you see, this is a path this is also a path producing A plus B to C plus D giving from A plus B to C plus D, but it is an alternative path why I am saying alternative path because it demands less of activation energy E a primed where E a primed is less than Ea. So, it offers an alternate path with less of activation energy.

So, that means, rate of a catalyzed reaction will be more than the same reaction when it is under not catalyzed condition, uncatalyzed condition. So, in that case E a catalyzed is less than E a uncatalyzed.

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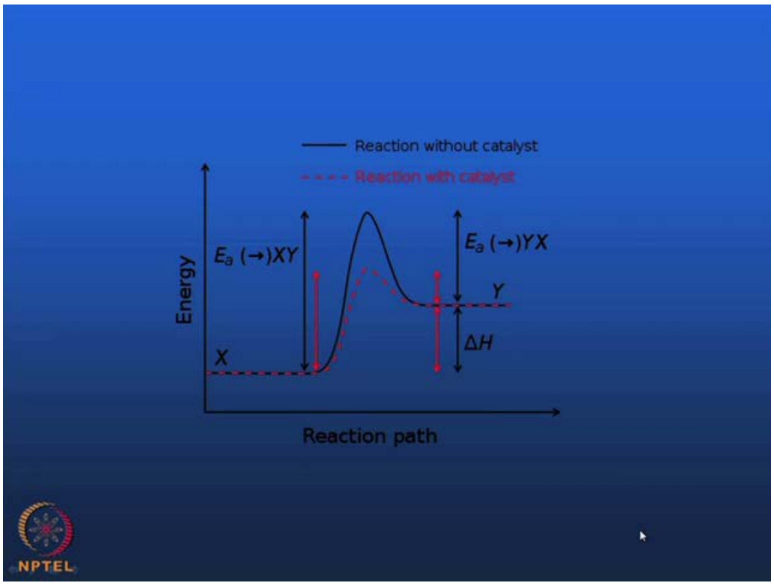

Next is, you see here this is the energy level diagram. So, activation energy is this is x y E a x y, x to y and this is activation energy for E a y to x. So, you see that the black one, the black line. So, it is having higher activation energy you see, E a x to y it is a normal reaction uncatalyzed higher activation energy and also for the backward process it is higher; this one is higher.

But the red one is the catalyzed one in presence of catalyst you see, the forward activation energy E a primed x y; you may call this as E a primed x y, or E a catalyzed x y it is less; and also E a catalyzed y x it is also less.

So, you see that in both the direction for both the direction forward or backward in both the direction your activation energy is reduced; that means, lower activation energy means your faster reaction. So, faster in both the direction.

Faster in both the direction means equilibrium is reached quickly compared to uncatalyzed reaction, although you see delta is in H, but the process is not altered, but only thing is that it provides that is catalyst provides an alternative path demanding less activation energy for both the direction. So, that is why catalyzed reactions are faster, because it demands less activation energy and this is your reaction path in this direction.

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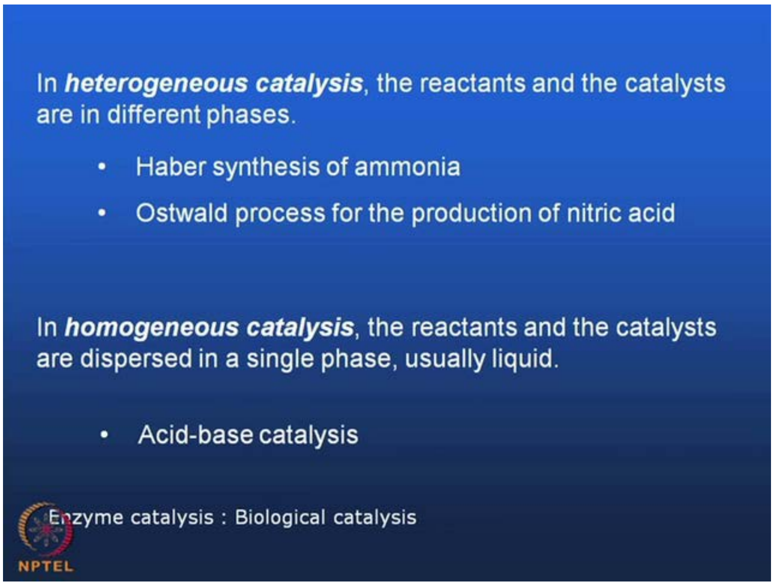

In ***heterogeneous catalysis***, the reactants and the catalysts are in different phases.

- Haber synthesis of ammonia
- Ostwald process for the production of nitric acid

In ***homogeneous catalysis***, the reactants and the catalysts are dispersed in a single phase, usually liquid.

- Acid-base catalysis

Enzyme catalysis : Biological catalysis

So, in heterogeneous catalysis, catalyst can be homogeneous; Catalyst can be heterogeneous. So, in homogenous case catalyst and your reactant both are in single phase or same phase; and in heterogeneous catalysis what is happening that the reactant and the catalyst are in different phases, maybe one is in liquid phase another is in solid phase or maybe one is in solid phase another is in gas phase.

So, typical example is Haber synthesis of ammonia. N 2 plus 3 H 2 is equal to 2 N H 3, it is a Haber synthesis of ammonia. So, here the catalysis occurs in a heterogeneous fashion also Ostwald process production of nitric acid, here also this is an, it is an example of heterogeneous catalysis.

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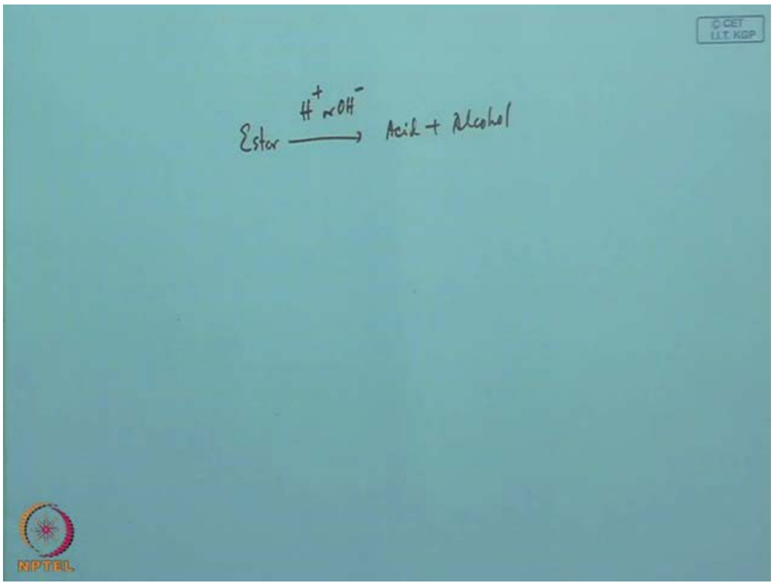

Ester $\xrightarrow{H^+ \text{ or } OH^-}$ Acid + Alcohol

Homogeneous catalysis there is in this case reactant and catalyst are in dispersed are dispersed in single phase usually liquid and typical example is acid base catalysis like say, ester hydrolysis say ester producing acid plus alcohol. It may be catalyzed by H plus or O H minus.

So, maybe you add a little amount of say H c l or maybe little amount of N a o H. So, ester will be organic ester will be hydrolyzed to produce acid and alcohol in presence of O H minus acid will be corresponding salt. So, it is the case of homogeneous catalysis.

So, if you don’t add H plus or O H minus the reaction happens, but it is a very slow reaction.

Now, enzyme catalysis is another example, it is a biological catalysis. I talked about heterogeneous catalysis or homogeneous catalysis. All these are non-biological processes, but for biological cases, it has got a different name which is called the enzyme catalysis.

Enzymes are small proteins or polypeptides. So, they tend to form a complex, like which is called the enzyme substrate complex with the substrate and then this substrate will proceed and proceed to this enzyme substrate complex will proceed towards the forward direction, giving rise to the product and then what happens this enzyme is retained back.

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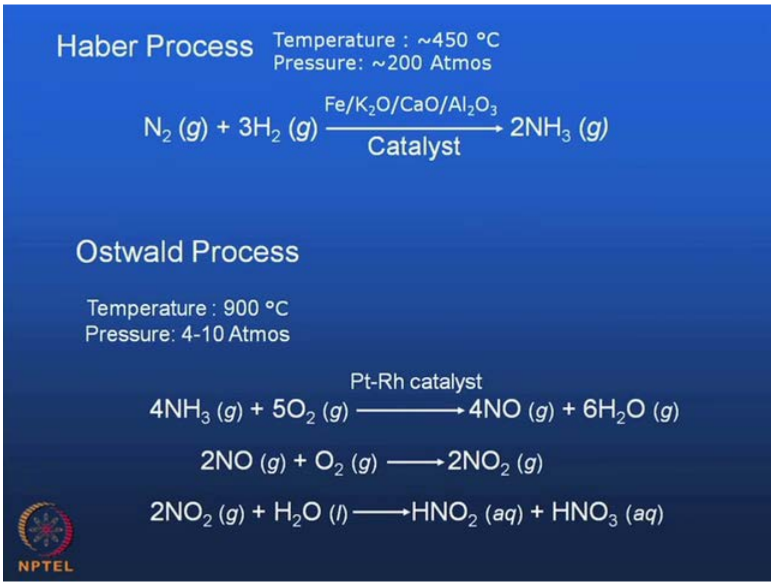

Haber Process Temperature : ~450 °C
Pressure: ~200 Atmos

$$N_2\,(g) + 3H_2\,(g) \xrightarrow[\text{Catalyst}]{Fe/K_2O/CaO/Al_2O_3} 2NH_3\,(g)$$

Ostwald Process

Temperature : 900 °C
Pressure: 4-10 Atmos

$$4NH_3\,(g) + 5O_2\,(g) \xrightarrow{\text{Pt-Rh catalyst}} 4NO\,(g) + 6H_2O\,(g)$$

$$2NO\,(g) + O_2\,(g) \longrightarrow 2NO_2\,(g)$$

$$2NO_2\,(g) + H_2O\,(l) \longrightarrow HNO_2\,(aq) + HNO_3\,(aq)$$

So, it is a typical biological catalysis. So, this biological catalysis part will be taken up in appropriate section, I mean appropriate lecture. So, let us have a look at this Haber ammonia synthesis. So, it happens normally since nitrogen is having a triple bond N plus H 2.

So, this is very unreactive we have plenty of nitrogen in atmosphere, but they are not reactive and this nitrogen. So, unreactive nitrogen undergoes this reaction N 2 plus 3 H 2 producing 2 N H 3 ammonia production and it requires catalyst iron catalyst and in presence of these are called promoters.

So, in presence of promoter iron catalyst and it is a huge temperature 450 degree centigrade and about 200 atmospheric pressure. So, it is a very high pressure and of course, high temperature. So, at elevated temperature and pressure condition what is happening that this nitrogen hydrogen combines to form 2 N H 3. So, this iron in k 2 O calcium oxide and A l 2 O 3 these are in solid phase.

And at a very high temperature and this nitrogen and hydration they are reacted at a high pressure high atmosphere I mean external pressure is very high. So, it is a case of heterogeneous catalyst catalysis.

Because if you don’t put these conditions then the reaction does not occur and this has got a tremendous industrial application, that just you have got this nitrogen enormous amount of nitrogen you can get from atmosphere there is no virtually no expenditure, just you have to supply hydrogen and then this is regenerated since it is a catalyst it is regenerated. So, it is regenerated means recycled after one complete cycle it is recycled back to your reaction chamber and then, again this process occurs to give you ammonia. So, and in presence of this catalyst this reaction at this temperature pressure condition it is, it gets facilitated.

So, catalyst has got an immense role in industrial preparation. There is another example Ostwald process for the preparation of nitric acid. So, it is at 900 degrees centigrade and pressure is 4 to 10 atmosphere; it is also a bit high pressure.

So, in presence of platinum rhodium catalyst this ammonia, combines with oxygen to produce nitric oxide then nitric oxide again, in presence of oxygen produces nitrogen dioxide then nitrogen dioxide, reacts with I mean dissolves in water to produce H N O 2 and H N O 3.

So, equated form of your nitric acid and then this nitric acid is further processed, to give you the further processed to get you nitric acid; this H N O 3 aqueous because it is a dilute situation. So, you have to concentrate it.

So, you see that 900 degree centigrade 4 to 10 atmosphere in presence of platinum rhodium catalyst if you do not give it, again it is a problem you do not get this one. So, this in presence of catalyst this reaction means under this condition, this reaction occurs to produce nitric oxide and further reactions. So, catalysts are having tremendous importance in chemical processes.

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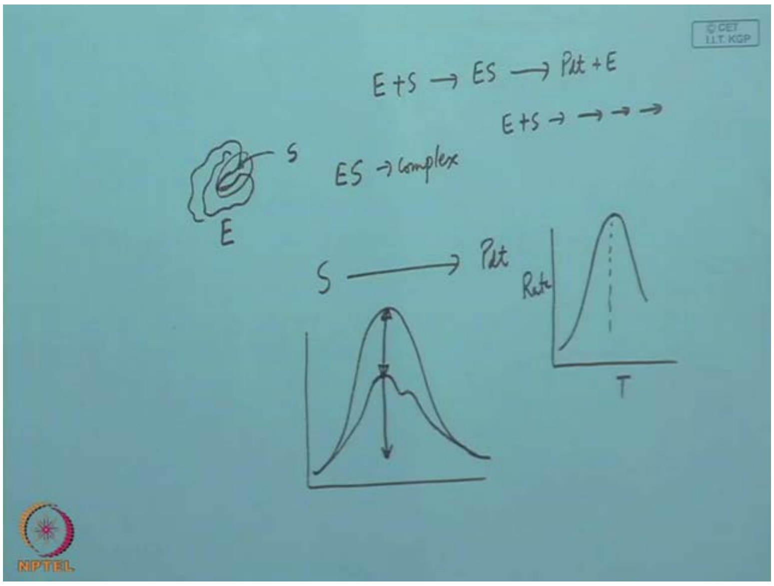

Now, next is let us have a very simplistic description of enzyme catalysis. So, enzyme is a macromolecule like this and it has got certain pockets. And in this pocket, the substrate forms. So, this is your enzyme say this is your substrate say it binds to produce an enzyme substrate complex, ES complex. Normally substrate giving rise to product.

So, it requires may be like this. This much of energy of activation, but the moment enzyme comes into picture then maybe. So, this is your enzyme substrate complex then enzyme substrate complex may be with is it is giving rise to like this.

So, enzyme substrate complex then another state maybe is there after enzyme substrate it is further converted to another spaces and then it gives rise to a product.

So, why this is like this I will come to that point later on, but I am just trying to give him, give you some idea. So, you see this much of gain in activation energy.

So, activation energy has been reduced this much therefore, therefore, reaction is faster and also another important point is that, the enzyme catalyzed reaction has got some if you plot rate versus temperature you will be seeing that it has got some optimum temperature.

Below this temperature, this process is not very much facile and also above this temperature when temperature is high, this is also reduced.

Because of the fact that this bio molecules, these are very temperature sensitive. So, at an elevated temperature, they are specific structure which is responsible for such enzyme substrate complex session is lost because of high temperature or increase of temperature this coiled structure because protein has got coiled structure in a three dimensional sense it has got a coiled structure.

So, it has it has got a folded structure; it is a long polymeric system; I mean it has got amino acid residue many amino acid residues and they form a coiled structure or maybe it is a folded structure.

So, if we increase the temperature maybe this portion the active side which is called the active side is mis-folded or maybe unfolded. So, that, this enzyme substrate complex session is no longer facile and as a result of which this lowering in enzyme substrate this activation energy is not there and as a result of which, the reaction rate is reduced.

So, enzyme substrate reaction is a special case of, special case where it is also called as bio catalysis. So, I will talk to this bio catalysis in more detail maybe in appropriate class, but I just have given you an idea what is this bio catalysis. So, basically the role of this enzyme is that it is regenerated.

So, enzyme then plus substrate producing enzyme substrate complex, then it is producing product plus enzyme back; then again this enzyme is recycled I mean then again next substrate molecule producing the same thing.

So, it is recycled. The small molecule small maybe it is a typical maybe 100 or 50 amino acid residue containing protein molecule. So, it will be regenerated after the reaction.

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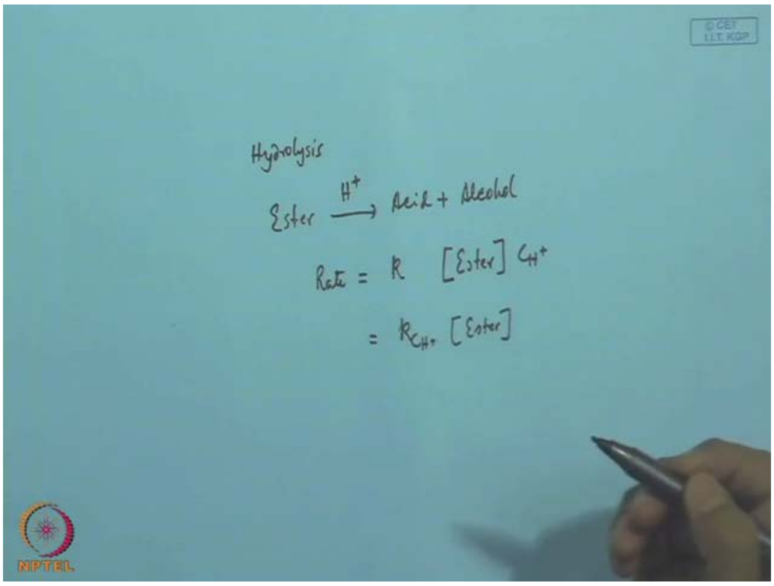

Hydrolysis

$$\text{Ester} \xrightarrow{H^+} \text{Acid} + \text{Alcohol}$$

$$\text{Rate} = k \quad [\text{Ester}]\, C_{H^+}$$

$$= k_{C_{H^+}} [\text{Ester}]$$

So, this is enzyme substrate I mean enzyme catalyzed reaction and I just told you this heterogeneous catalysis and also I gave you the idea of this homogeneous catalysis. And homogeneous catalysis has some more features which I will talk about like features means say if you have, say suppose you have got hydrolysis reaction. Acid catalyzed hydrolysis reaction that is your ester producing your acid plus alcohol. So, rate will be suppose if it is a first order reaction then rate is equal to k into your concentration of ester and C H plus is there.

C H plus is there means, if hydrogen ion concentration is double, then your rate is double it is a simple one to one correspondence. So, basically this C H plus including this is producing giving you k C H plus into ester. So, if you increase your C H plus concentration to double then your rate will be doubled.

So, if you just divide the old rate with the new rate, then you can find out the how many fold you have, how many fold increase of H plus has been made. So, this is basically called your C H plus is called the catalytic coefficient.

So, there is a one to one correspondence between this. So, that is why it is called the homogeneous catalysis; that is if you increase your catalyst concentration by a factor of two, your rate will be increased by a factor of two. So, this part maybe in a separate lecture where I will talk about this catalysis. So, these aspects will be taken up.

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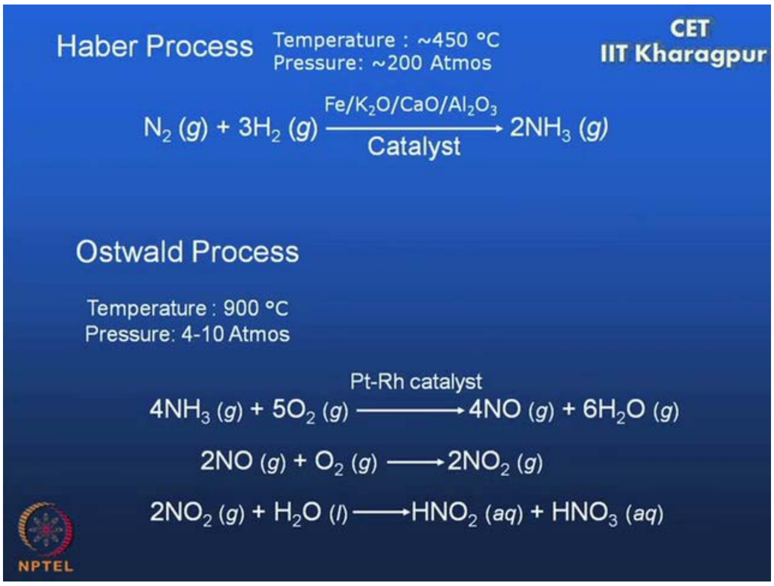

Haber Process Temperature : ~450 °C
Pressure: ~200 Atmos

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$$N_2\,(g) + 3H_2\,(g) \xrightarrow[\text{Catalyst}]{Fe/K_2O/CaO/Al_2O_3} 2NH_3\,(g)$$

Ostwald Process

Temperature : 900 °C
Pressure: 4-10 Atmos

$$4NH_3\,(g) + 5O_2\,(g) \xrightarrow{\text{Pt-Rh catalyst}} 4NO\,(g) + 6H_2O\,(g)$$

$$2NO\,(g) + O_2\,(g) \longrightarrow 2NO_2\,(g)$$

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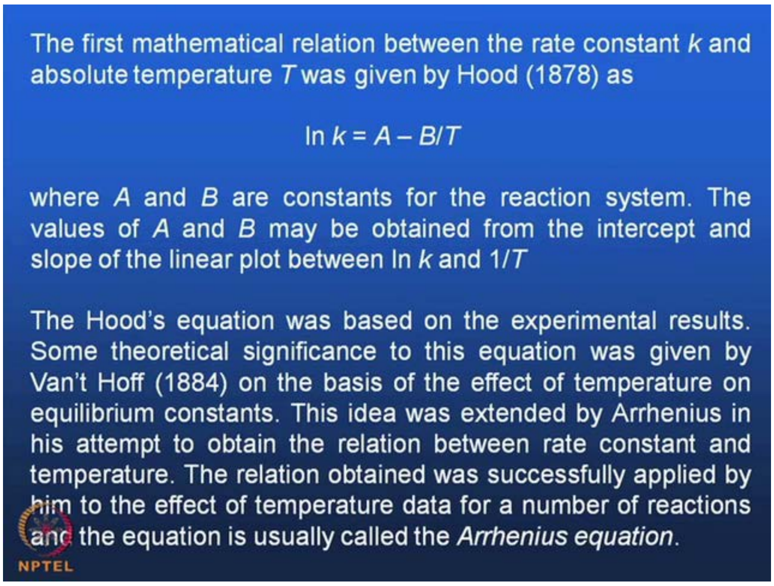

The first mathematical relation between the rate constant k and absolute temperature T was given by Hood (1878) as

$$\ln k = A - B/T$$

where A and B are constants for the reaction system. The values of A and B may be obtained from the intercept and slope of the linear plot between $\ln k$ and $1/T$

The Hood's equation was based on the experimental results. Some theoretical significance to this equation was given by Van't Hoff (1884) on the basis of the effect of temperature on equilibrium constants. This idea was extended by Arrhenius in his attempt to obtain the relation between rate constant and temperature. The relation obtained was successfully applied by him to the effect of temperature data for a number of reactions and the equation is usually called the *Arrhenius equation*.

So, what we have learnt in this concluding section of effect of temperature on chemical reaction that, this the hood was the person in 1878 gave the idea that ln k has got an inverse temperature dependence.

So, that is ln k is equal to A minus B by T and from that, using the idea of Van't Hoff Arrhenius put forward this, his famous equation; and his famous equation from his famous equation I mean Arrhenius equation we can find out the activation energy for the chemical reaction by doing some temperature variation experiment I already talked about it in last class, that how to do this how to find out activation energy that is you have to carry out the reaction at different temperatures maybe at three different temperatures.

And then in this three different temperatures you find out rate constant. You find out the rate constant and then plot logarithm of that found rate constant as a function of 1 upon T and from slope and intercept you find out the respective quantities like E activation that is activation energy and frequency factor.

And we have done a number of certain examples and then we also have talked about the significance of temperature coefficient, energy of activation which is very important parameter, which is a very important factor, Arrhenius factor and also the what is grossly meant by the term activated complex.

Activated complex means it is basically an activated step and it is a kind of complex formation in the activation activated state that is it is a higher energy state and that higher energy state would eventually be transformed to either the product side or maybe to the to the reactant side.

So, if it is crossing the barrier and if it goes to the right hand side means a product formation and if it comes back means, it is back reaction that is I talked about reversible reaction. So, it explains reversibility also.

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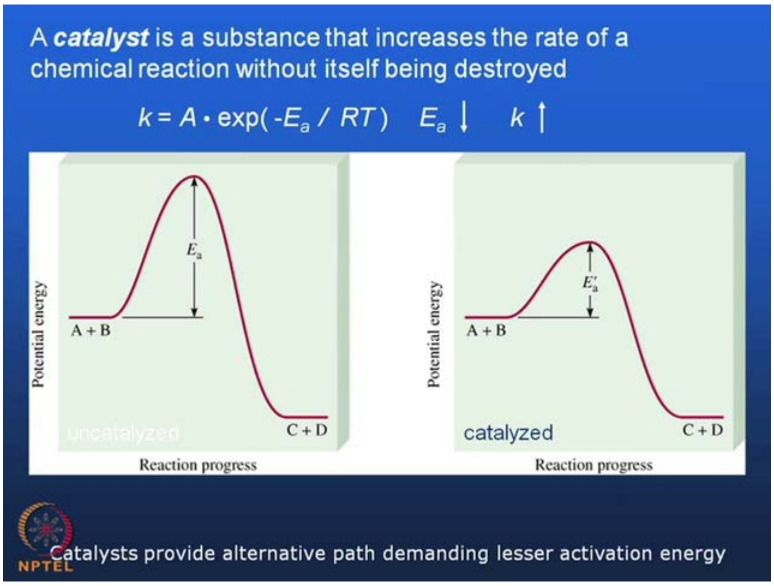

A ***catalyst*** is a substance that increases the rate of a chemical reaction without itself being destroyed

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

Catalysts provide alternative path demanding lesser activation energy

Then, I gave you a very short introduction of catalyst what is a catalyst that catalyst is a is a substance which provides an alternate path that is the path which demands lower activation energy or you can say that it lowers the activation energy by providing an alternate path. And also we discussed with two examples, one is Haber synthesis of ammonia where these are the examples of heterogeneous catalysis that is, catalyst is in a different phase than your reactant and product.

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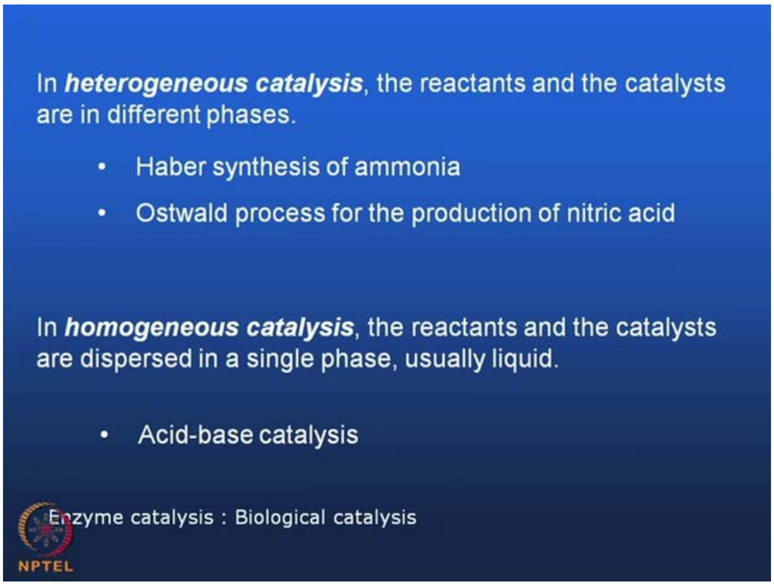

In ***heterogeneous catalysis***, the reactants and the catalysts are in different phases.

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- Ostwald process for the production of nitric acid

In ***homogeneous catalysis***, the reactants and the catalysts are dispersed in a single phase, usually liquid.

- Acid-base catalysis

Enzyme catalysis : Biological catalysis

And homogeneous catalysis, we also talked about that is catalysts reactants and products all these are in the same phase single phase that is why it is called the homogeneous catalysis. We also gave a very brief introduction of enzyme catalysis which is nothing but, a bio catalysis. So, in the next class what should we take up.

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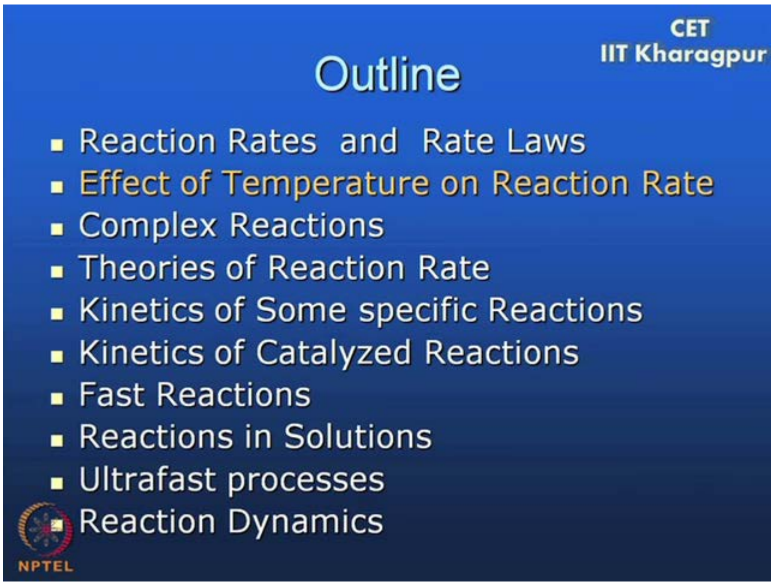

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Outline

- 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

Let us again go back to the maybe to the first slide that we will move onto complex reaction we just started with this back reaction, maybe parallel reaction, but we have not given a complete account of them.

So, in the next class in the next lecture, we will talk on complex reactions where, we will take up this parallel reaction, sequential reaction, reversible reaction and many other aspects.

So, till then have nice time thank you.