Polymer Process Engineering
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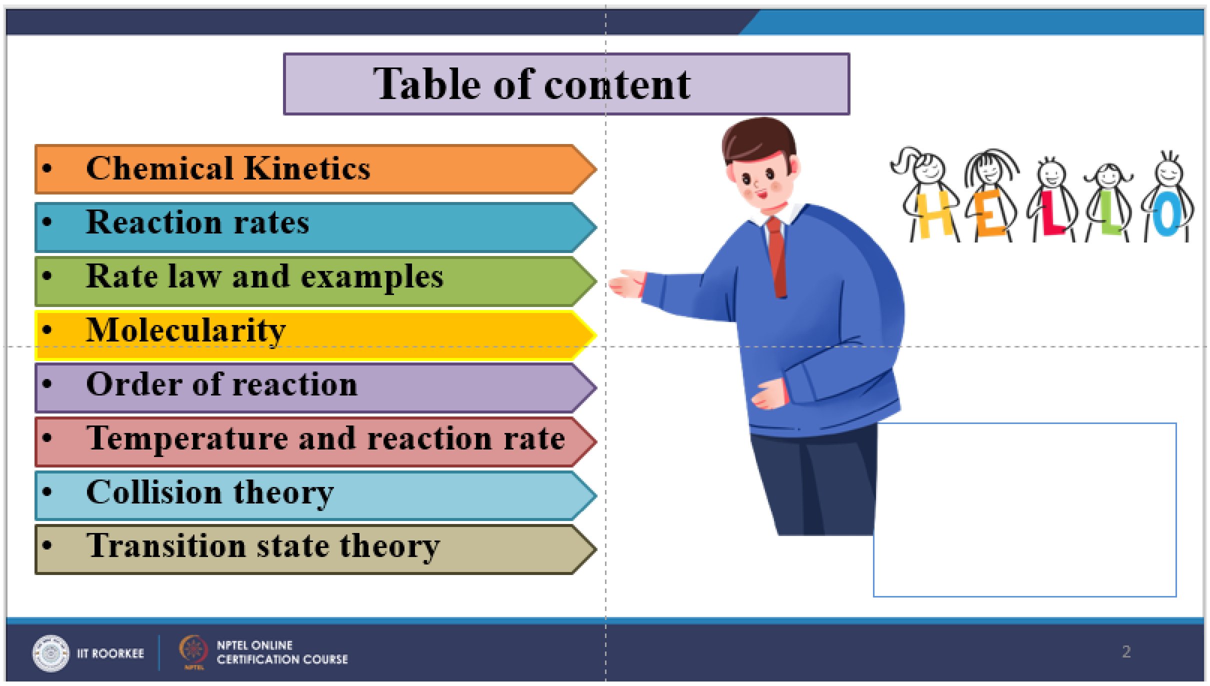
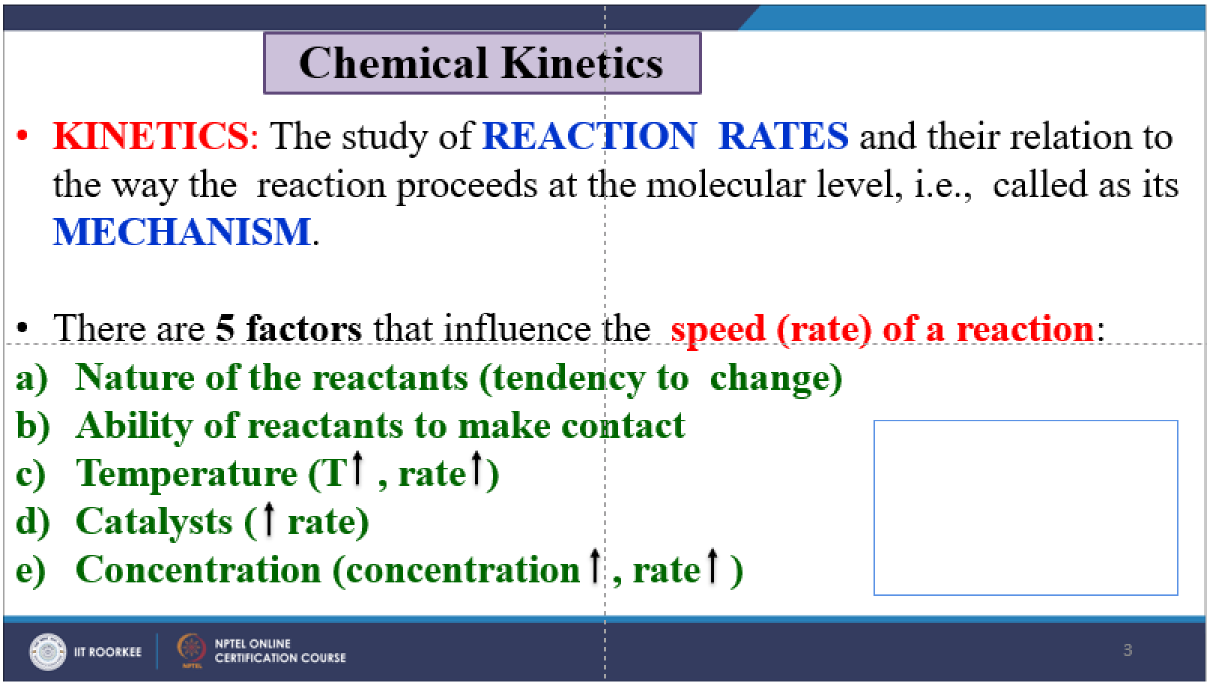
Lecture – 26
Chemical reaction engineering in polymers: Introduction

Hello friends, welcome to the Chemical Reaction Engineering aspect in polymers. As you know that the polymerize during the polymerization process, a lot of chemical reaction takes place and the pressure, temperature, all these things play a very vital role sometimes, because of the formation of the chains and formation of the bonds, etcetera, the reaction engineering play a very vital role. To learn this particular thing, we have introduced this particular segment under the edges of polymer process engineering.

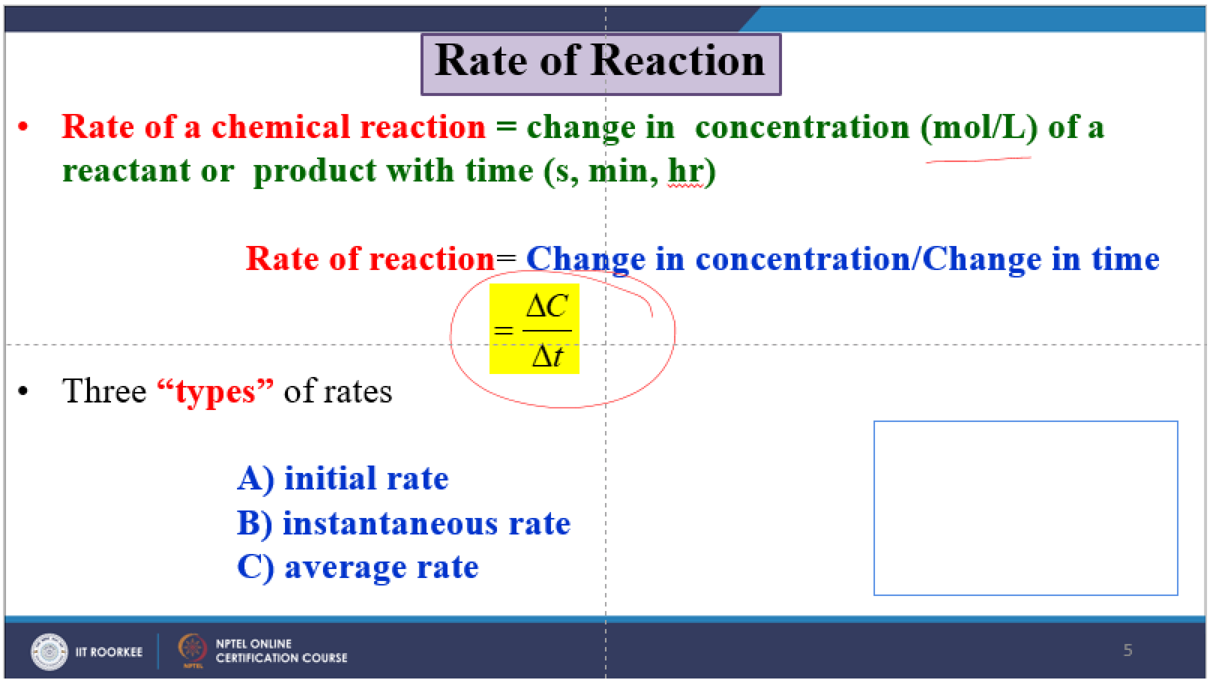


So, let us have an introductory section on chemical reaction engineering in polymers. So, in this particular segment, we are going to deal with chemical kinetics, reaction rates, rate law and examples, molecularity, order of reaction, temperature and reaction rate, collision theory, and transition state theory. Now, the first thing is to let us take up chemical kinetics.

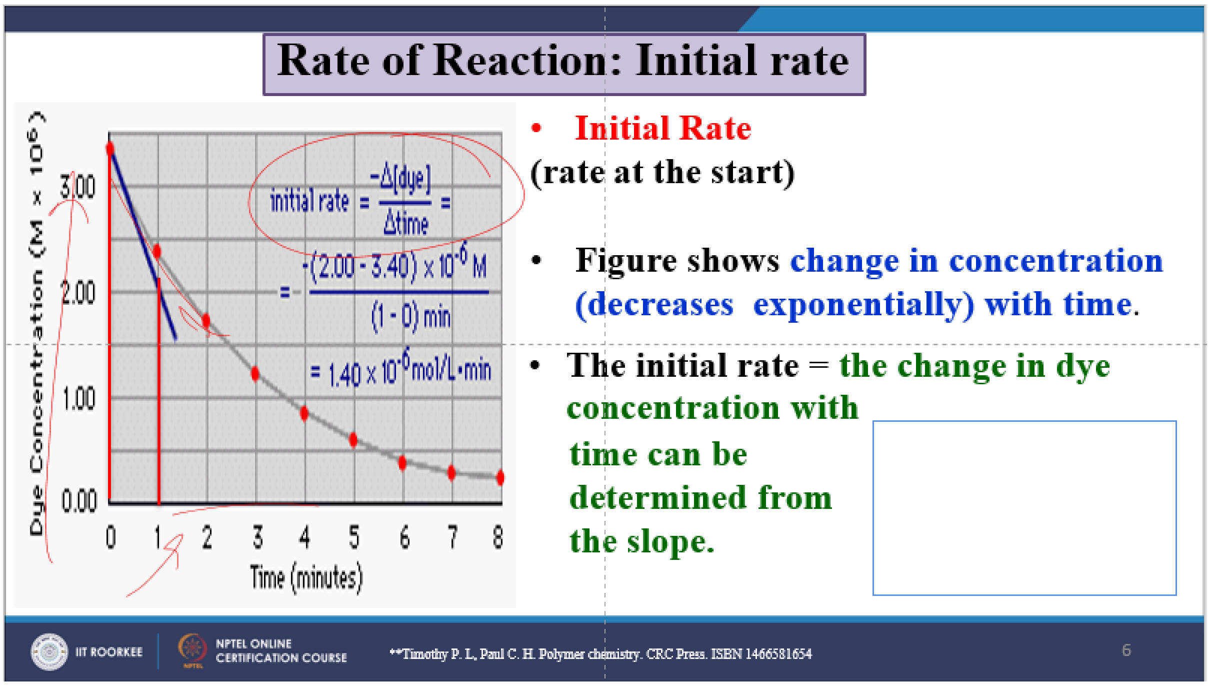


Now, what is kinetics? Kinetics is the study of the reaction rate and its relation to the way of reaction proceeds at the molecular level which is called a mechanism. So usually there are so many factors involved in this particular aspect. So, we are going to discuss the five factors that influence the speed or rate of reaction. One is the nature of reactants which is a tendency to change.

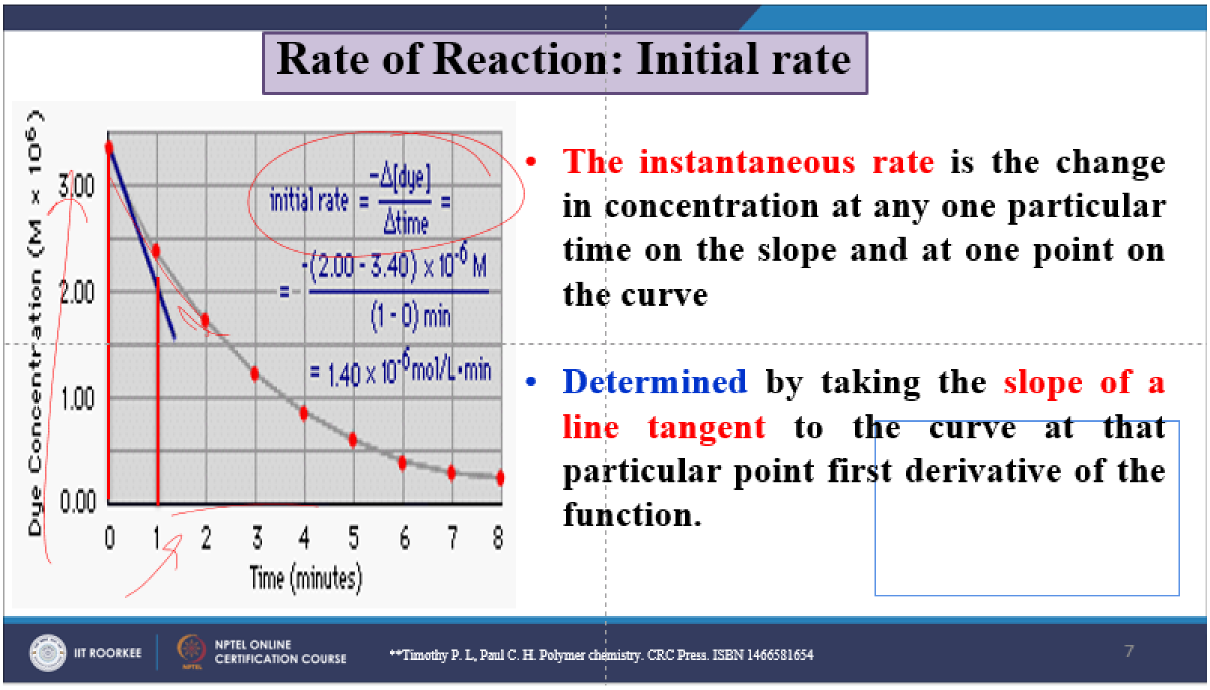
Second is the ability of reactant to make contact and the temperature, catalyst, concentration, all these things play a very vital role. Now, let us talk about the rate. The rate is how much quantity of changes occurs in a given period of time. This determines the rate at the speed of the car is driven as a rate that is the distance the car travels usually in kilometres or metres in a given period of time like say 1 hour or 10 minutes. So, the speed of the car is a unit of the kilometre per hour and it can be given as the rate is equal to speed that is the distance travelled divided by the time domain.



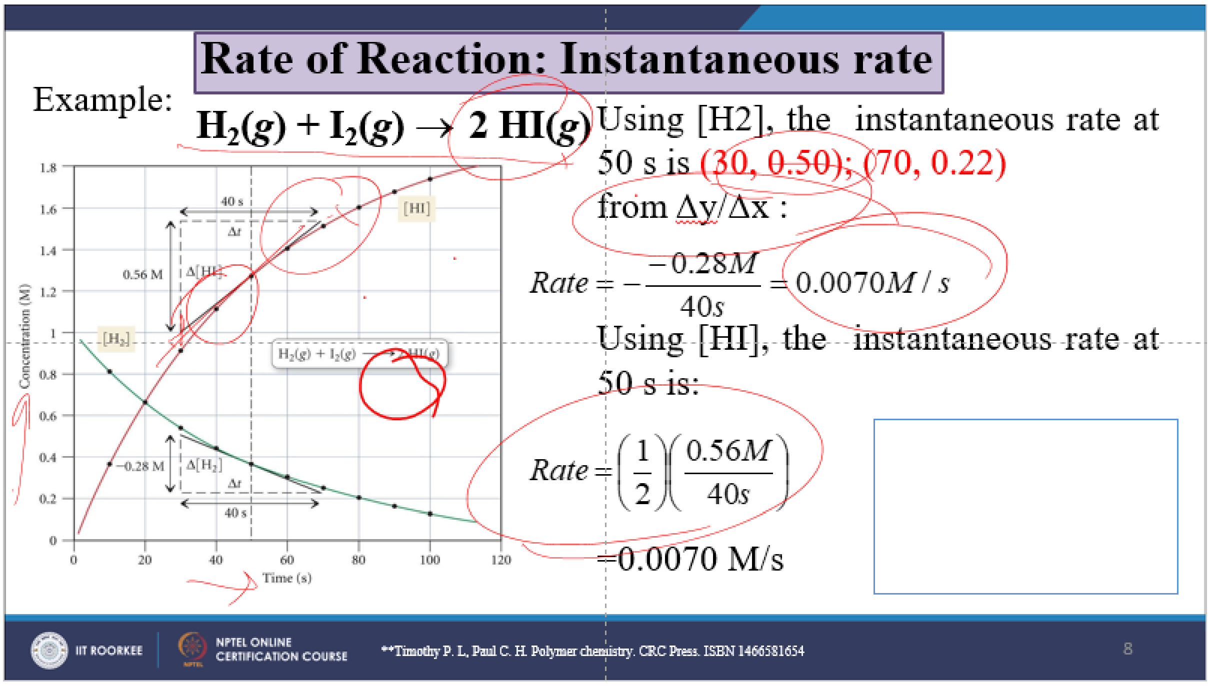
Then the rate of reaction, the rate of reaction, rate of chemical reaction, this is the change in the concentration usually depicted in moles per litre of a reactant or product with the time in second minute hour whatever that is the rate of reaction is equal to the change of the concentration over change in time that is delta C over delta T. Now, there are usually 3 types of rates, initial rate, instantaneous rate and average rate. Now here you see that let us talk about the initial rate, initial rate that is the rate at start. Now, this particular figure shows the change in the concentration versus with time. So, initial rate that is the change in dye concentration, let us take the example of a dye concentration with the time, this can be determined at the with the help of a slope like here.



Now, this is the initial rate that is how much dye is consumed in a particular dye solution and because minus sign depicts that the concentration or the dye is being consumed over the period of time versus time. So, in that case you can determine the rate.

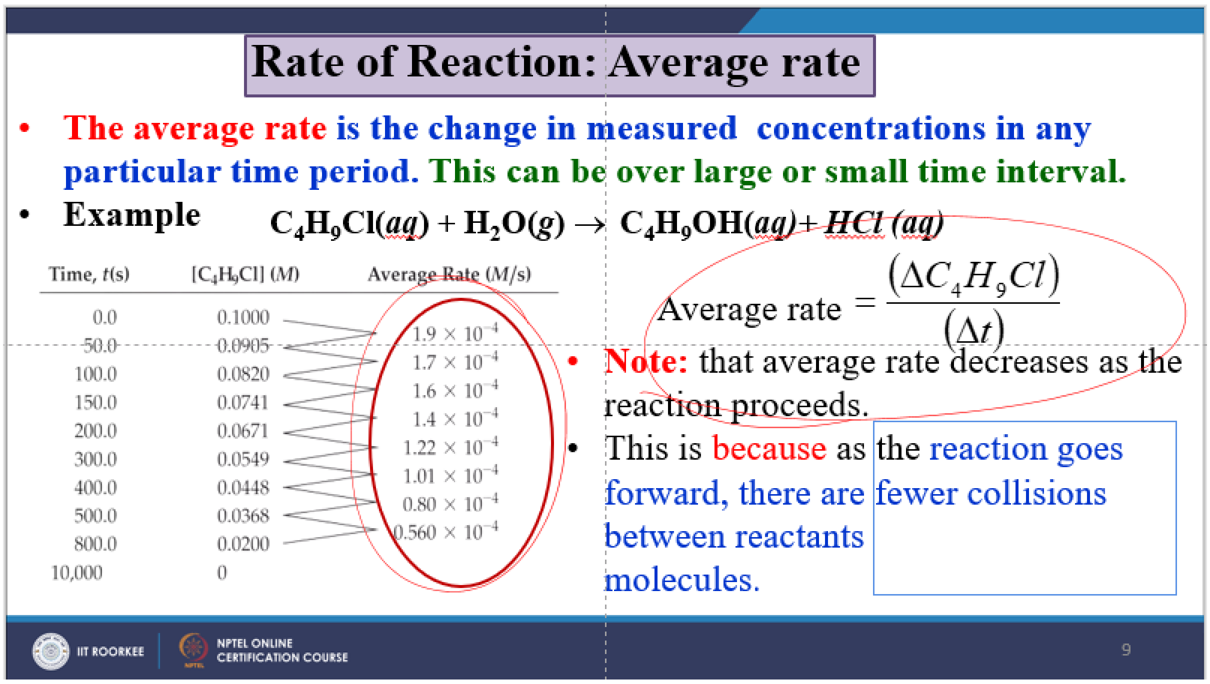


Now, next is the instantaneous rate, the instantaneous rate is the change in the concentration at any one particular time on the slope and at any point of time in the curve. This is determined by the taking the slope of a line or a tangent to the curve at that particular point first derivative of the function. Now here you see that if let us take a particular example that is h2 plus i2, this gives you 2 hi, this the instantaneous rate supposes if it is at 50 second.

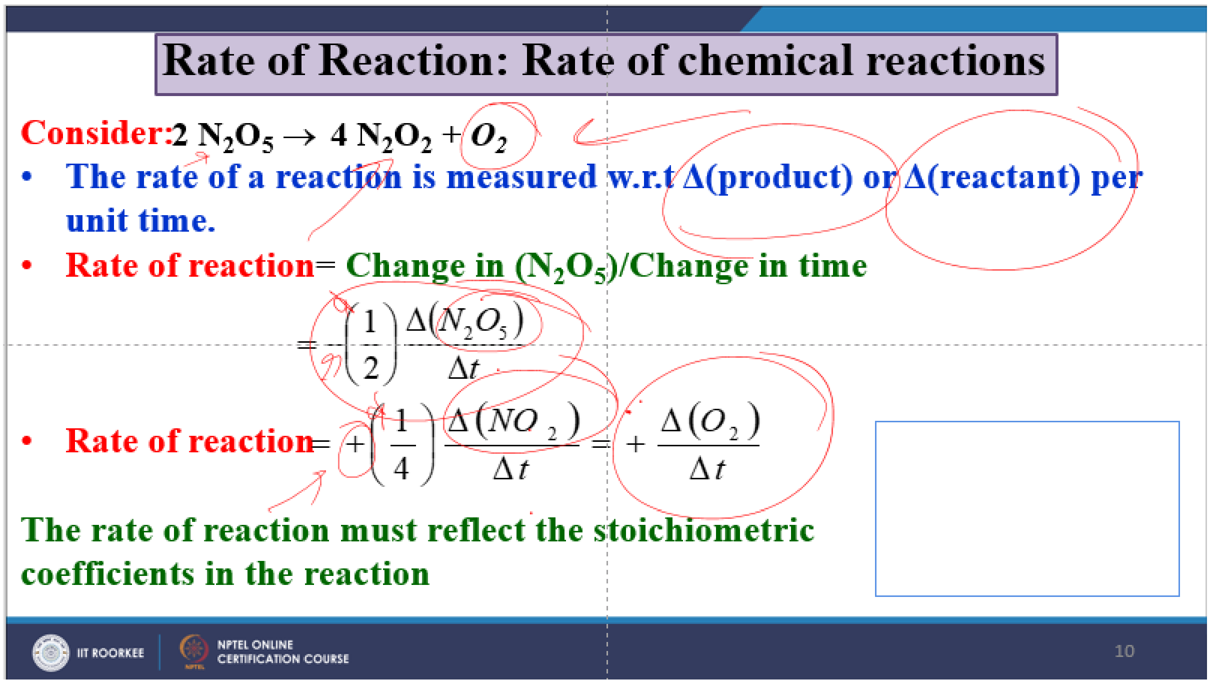


Now, let us take the example of this particular chemical reaction like h2 reacts with i2, this gives you 2 hi. Now, if we take if we plot the concentration versus time plot, here like the instantaneous rate suppose at 50 second that is given by the say the coordinates is 30 and 0.5 and 17 to 0.2. So, if we need to determine then we need to take the slope and that is the rate is equal to delta y over delta x.

Now, this is the concentration versus time. So, rate is given by 0.2 minus 0.28 over 40. So, this is this comes out to be 0.007 m. Now, if using this hydrogen iodide for instantaneous rate at 50 second the rate is given by rate is equal to half into 0.56 over 40 that is comes out to be 0.0070.

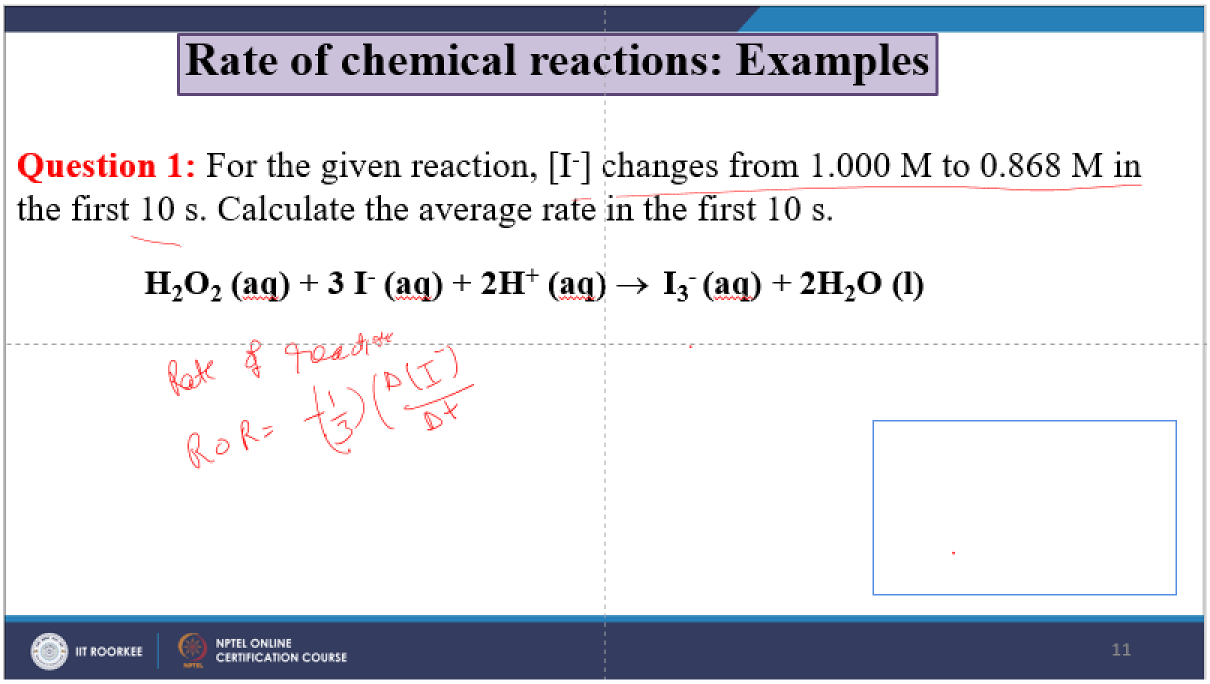


Now, average rate, the average rate is the change in measured concentration in any particular time period. This can be over a large or a small-time interval. So, let us take the example of C4H9Cl plus H2O this gives to you the C4H9OH plus HCl. So, if we need to determine the average rate, this is equal to the change in the concentration of C4H9Cl over delta t that is the time change. So, this is the average rate being calculated. Now, the average rate decreases as the reaction proceeds. Now, this is because as the reaction goes forward, there are fewer collisions between the reactant molecules.



Now, let us talk about the rate of chemical reaction. Let us take another example of this particular equation that is 2N2O5 this dissociates into 4N2 plus O2. The rate of reaction is measured with respect to the change in the product concentration or the change in the reactant concentration per unit of time. So, the rate of reaction that is the change in N2O2 over change in time and that comes out to be minus 1 upon 2 into delta N2O2 over delta t that is the change in the concentration of N2O2. Now, the rate of a reaction is given by 104 into the change in the concentration of NO2 over delta t.

Now, plus sign this designates that this NO2 being produced and N2O2 the negative sign bears because this N2O2 is being consumed over the period of time. So, the rate of reaction is given as delta and again because oxygen is again one of the products, so delta O2 over delta t. So, the rate of reaction must reflect the stoichiometric coefficient in the reaction. Now, this is the stoichiometric coefficient.



$$= -\left(\frac{1}{3}\right)\left(\frac{0.868M - 1.00M}{10s}\right)$$

$$= 4.40 \times 10^{-3}\ M/s$$

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Now, let us take an example that is for the given reaction the I change from 1 molar to 0.868 molar in a first 10 seconds. So, you need to calculate the average rate in first 10 seconds. The equation is given as H2O2 plus 3I plus 2H ion this gives us your I3 ion plus twice H2O. So, the rate of reaction ROR with respect to iodine concentration iodine ion concentration delta t. So, this comes out to be minus 1 by 3 into 0.868 which is given which is the final concentration required minus 1.0 over 10 second. This comes out to be 4.40 into 10 to the power minus 3 molar and that this is our answer. Now, another example if the rate of consumption that is the disappearance of one substance is known, the stoichiometric can be used to deduce the rate of formation of other participant in the reaction.

Rate of chemical reactions: Examples

- If the **rate of consumption (disappearance)** of one substance is known, **the stoichiometry** can be used to **deduce the rates of formation** of other participants in the **reaction**.

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Rate of chemical reactions: Examples

Question 2: In the given reaction, rate of disappearance of $H_2 = 4.5 \times 10^{-4}$ mol L^{-1} min^{-1}. Find:

Rate of consumption N_2 = ?

Rate of formation of NH_3= ?

Rate of Consumption of N_2

$\frac{1}{3}\frac{N_2}{H_2} \times 4.5 \times 10^{-4}$ mol/l m

$= 1.5 \times 10^{-4}$ mol/l m

Rate of formation of NH_3

$\frac{2 \text{ mol } NH_3}{3 \text{ mol } H_2} \times 4.5 \times 10^{-4}$ mol/l m $=$ 3.0×10^{-4} mol/l m

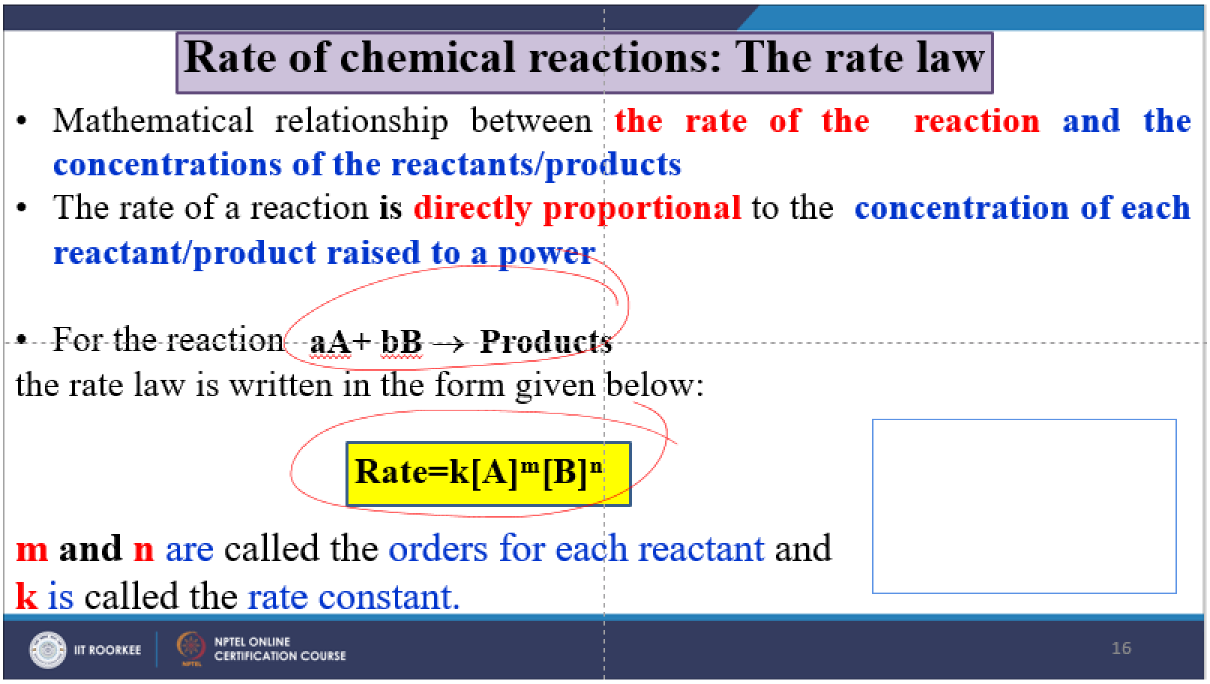
Solution 2: Rate of consumption of N_2

$$\frac{1molN_2}{3molH_2} \times 4.5 \times 10^{-4} molL^{-1}\, min^{-1} = 1.5 \times 10^{-4} molL^{-1}\, min^{-1}$$

Rate of formation of NH_3:

$$\frac{2molNH_3}{3molH_2} \times 4.5 \times 10^{-4} molL^{-1}\, min^{-1} = 3.0 \times 10^{-4} molL^{-1}\, min^{-1}$$

Let us take another example. Now, in a given reaction the rate of disappearance of say hydrogen is 4.5 into 10 to the power minus 4 moles per liter per minute. You need to find out the rate of consumption that is the nitrogen and the rate of formation for ammonia. Now, let us take the rate of consumption of N2 that is 1 by 3 N2 raise to into 4.5 which is given here 4.5 into 10 to the power minus 4 moles per liter minute and this is equal to 1.5 into 10 to the power minus 4 moles per liter minute. So, the rate of formation of NH3 which is equal to 2 moles of NH3 upon 3 moles of H2 multiplied by 4.5 into 10 to the power minus 4 moles per liter minute. This comes out to be 3.0 into 10 to the power minus 4 moles per liter minute. So, this is our answer.



Now, let us talk about the rate law, the mathematical relationship between the rate of the reaction and the concentration of the reactant or product. So, the rate of reaction is directly proportional to the concentration of each reactant or product raised to a power. Now, for a reaction like this is the generic reaction small a plus a plus bb is equal to product.

So, the rate law can be written as rate is proportional to a to the power m and b to the power n. Now, this is can be represented as rate is equal to k a to the power m b to the power n. Now, m and n call the order of the reactant and k is called the rate constants. Now, let us talk about the molecularity. Molecularity is the sum of the number of molecules of reactant involved in the balanced chemical equation.

Rate of chemical reactions: Molecularity

- **Molecularity** is the **sum of the number of molecules of reactants** involved in the balanced chemical equation.
- **Molecularity** of a reaction is derived from **the mechanism of the given reaction**. Molecularity **can not be greater** than **three** because more than three molecules may not mutually collide with each other.
- **Molecularity** of a reaction **can't be zero, negative or fractional**. **Order of a reaction** may be **zero, negative, positive or in fraction and greater than three**. Infinite and imaginary values are **not possible**.

Example :

So, the molecularity of the reaction usually is derived from the mechanism of the given reaction. Now, molecularity cannot be greater than 3 because more than 3 molecules may not mutually collide with each other. So, the molecularity of the reaction cannot be 0 or negative or fraction because order of a reaction may be 0, negative, positive or infraction and the greater than 3 infinite imaginary n values are not possible. Let us take an example. The example is like NH_4NO_2 this dissociates into N_2 plus twice H_2O that is the unimolecular.

$NH_4NO_2 \rightarrow N_2 + 2H_2O$ (Unimolecular)

$NO + O_3 \rightarrow NO_2 + O$ (Bimolecular)

$2NO + O_2 \rightarrow 2NO$ (Tri molecular)

NO plus O_3 NO_2 plus O and that is bimolecular. Twice NO plus O_2 this is equal to 2NO and this is the trimolecular.

Rate of chemical reactions: Reaction order

- **The order of a reaction** with respect to a reactant, **is the exponent of its concentration term in the rate expression**

$$\boxed{Rate = k[A]^m[B]^n}$$

m is the order w.r.t A and **n** is the order w.r.t B. Order can be **0, 1, 2 or fractions, negative**

- The total **reaction order** is the **sum of all exponents** on all concentration terms.

$$\boxed{Rate = k\,[A]^m[B]^n[C]^p}$$

$$\boxed{\text{Total order} = m + n + p}$$

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Now, the order of reaction with respect to a reactant is the exponent of its concentration in the rate expression. So, this is the rate is equal to k a to the power m b to the power n. m is the order with respect to a and n is the order with respect to b.

Rate of chemical reactions: Rate constant (k)

- **The rate constant (k)** is a **proportionality constant** that relates rate of reaction and concentration at a given temp.
- Rate constants have **units** consistent with the **units for other terms in the rate equation.**

$\boxed{\text{General: } M^{1-n}\ \text{time}^{-1}}$ **where M= mol/L**

0 order: $k = \text{mol/L} \cdot \text{time}$ $(M\ s^{-1})$

1 st order: $k = \text{time}^{-1}$ (s^{-1})

2 nd order: $k = \text{L/mol} \cdot \text{time}$ $(M^{-1}\ s^{-1})$

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So, this order can be 0, 1, 2 or fraction negative and the total reaction order is a sum of all exponents on all concentration terms and that is rate is equal to k a to the power m b to the power n c to the power let us say p. So, if we talk about the total order and that comes out to be m plus n plus p. The rate constant, the rate constant, is the proportionality constant that relates the rate of reaction and concentration at a given temperature. So, the rate constant have a unit consistent with the unit of other terms in rate equation and generally it is m to the power n minus 1 and time inverse where m is represented in with respect to mole per liter or 0 order the k is given as mole per liter time that is m over s. First order k is given as time inverse or second inverse or second order k is given as liter per mole time or mole inverse second inverse.

Rate of chemical reactions: Example

Question 3: Determine the rate law and rate constant for the reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$. The experimental data is given below

Expt. No.	Initial $[NO_2]$ (M)	Initial $[CO_2]$ (M)	Initial rate (M/s)
1.	0.10	0.10	0.0021
2.	0.20	0.10	0.0082
3.	0.20	0.20	0.0083

Let us take up another question. Now here you need to determine the rate law and the rate constant for the reaction which is given as NO_2 plus CO both are in the gaseous form NO plus CO_2. So, the experimental data which is given as the initial NO_2 concentration, initial CO_2 concentration, and initial rate which is supplied to you. So, 0.1, 0.2 initial NO2 concentration varies from 0.1 to 0.2 and then initial CO2 concentration again from 0.1 to 0.2. So, the initial rate is given.

$$Rate = k[NO_2]^n[CO]^n$$

Step 1 →

Step 2 → Determine by what factor the concentrations and rates change in these expt (1, 2)

The comparison of concentration & rate for these

$$\frac{[NO_2]_{exp2}}{[NO_2]_{exp1}} = \frac{0.20}{0.1} = 2$$

$$\frac{(Rate)_{exp2}}{(Rate)_{exp1}} = \frac{0.0082}{0.0021} = 4$$

$$\frac{(NO_2)_{exp\,t2}}{(NO_2)_{exp\,t1}} = \frac{0.20M}{0.10M} = 2$$

$$\frac{(Rate)_{exp\,t2}}{(Rate)_{exp\,t1}} = \frac{0.0082M/s}{0.0021M/s} = 4$$

$$\frac{(CO)_{exp\,t3}}{(CO)_{exp\,t2}} = \frac{0.20M}{0.10M} = 2$$
$$\frac{(Rate)_{exp\,t3}}{(Rate)_{exp\,t2}} = \frac{0.0083M/s}{0.0082M/s} = 1$$

Determine to what power the concentration factor must be raised to equal the rate factor

$\left[\frac{(NO_2)_{\exp t2}}{(NO_2)_{\exp t1}}\right]^n = \frac{(Rate)_{\exp t2}}{(Rate)_{\exp t1}} (2)^n = 4, n = 2$ *(Second order)*

$\left[\frac{(CO)_{\exp t3}}{(CO)_{\exp t2}}\right]^m = \frac{(Rate)_{\exp t3}}{(Rate)_{\exp t2}} (2)^m = 1, m = 0$ (Zero order)

Substitute the exponents into the general rate law to get the rate law for the reaction.

Rate= $k[NO_2]^n[CO]^m$

Rate= $k[NO_2]^2[CO]^0$

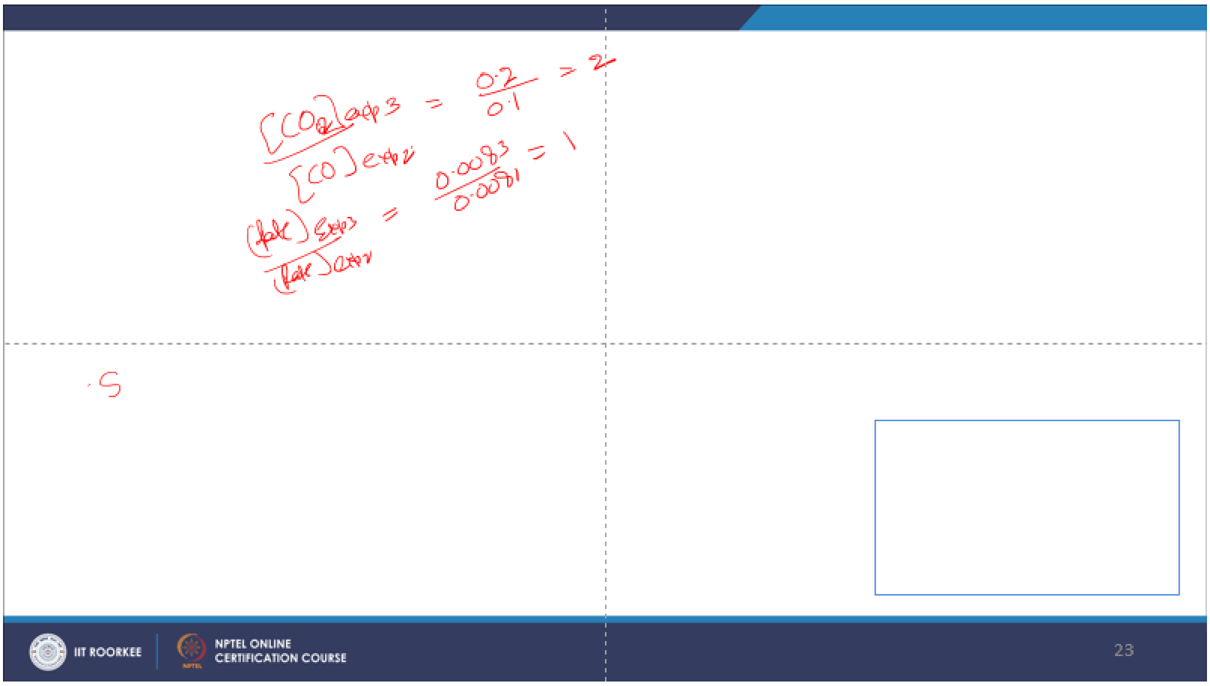
Rate= $k[NO_2\,]^2$

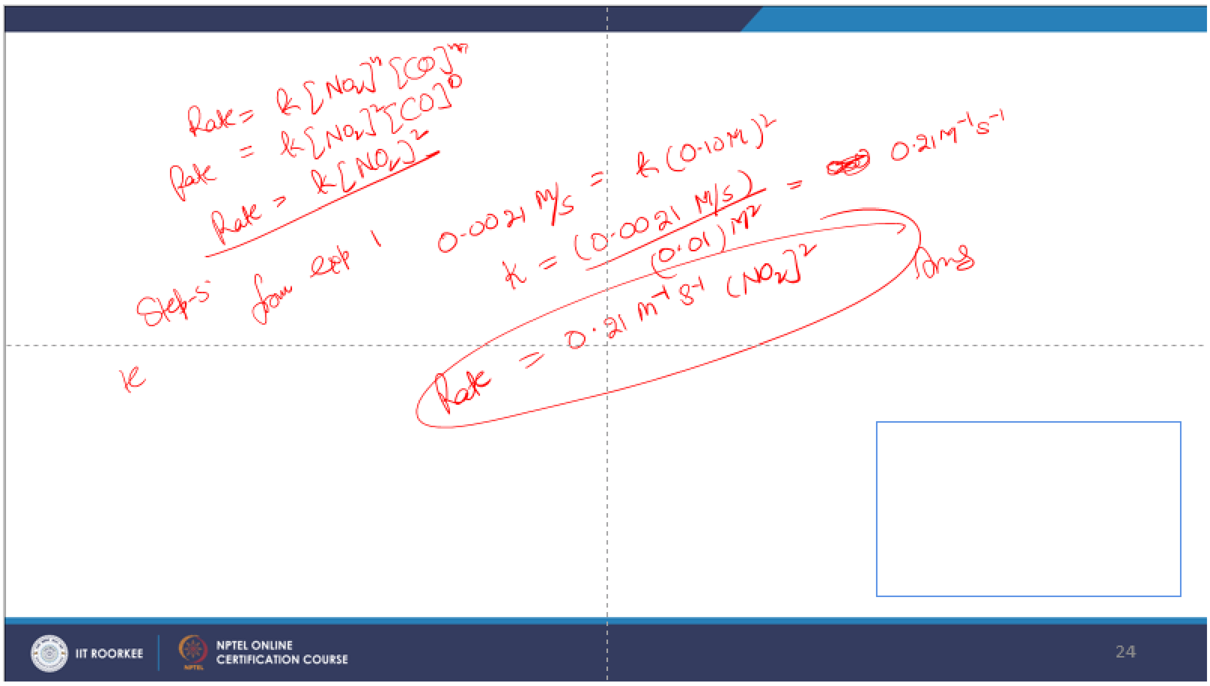
Substitute the concentrations and rate for any experiment into the rate law and solve for k

$$0.0021M/s = k(0.10M)^2 k = \frac{(0.0021M/s)}{(0.01)M^2} = 0.21M^{-1}s^{-1}$$

Rate=$0.21M^{-1}s^{-1}(NO_2)^2$

Now let us take up the solution. So, general law including all reactant is written as rate is equal to again go back to this reaction. Now step 1, let us this is this can be dealing with couple of steps. So, examine the data and find two experiments in which the concentration of one reactant changes but the other concentration are the same. So, therefore, comparing the experiment 1 and experiment 2 the NO_2 changes but CO does not.

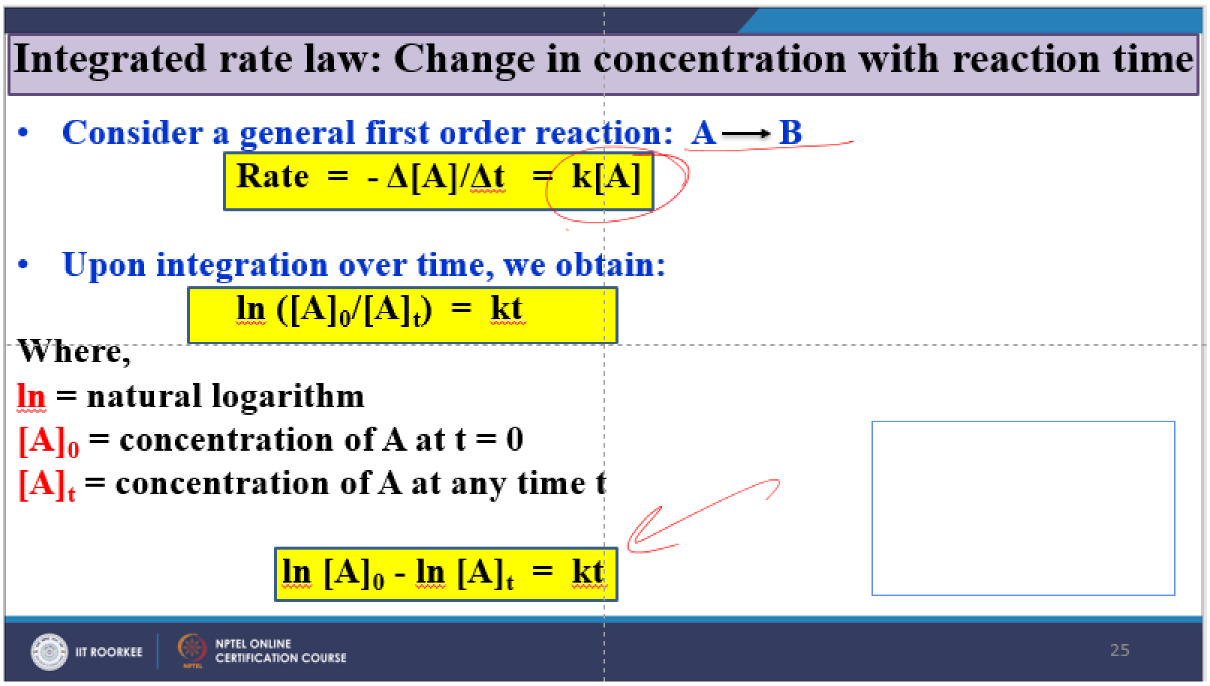




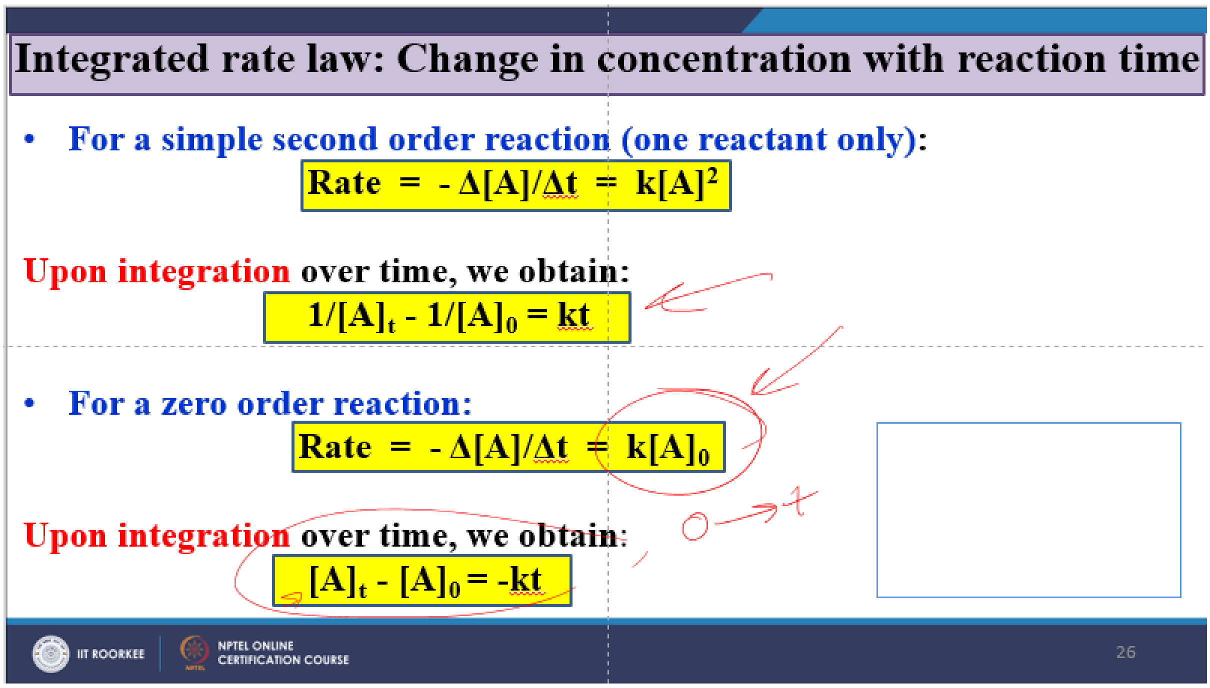
So, the rate of reaction also changes. Now another step to determine by what factor the concentration and rates change in these experiments may be experiment 1 and 2. Therefore, we will first compare the concentration of NO_2 in two experiments and then their rate So similarly, we will proceed with carbon monoxide in experiment 2 and experiment 3 like here. Here you see that these two concentrations are same and here these two concentrations are same. Then the comparison of concentration, the comparison of concentration and rate for NO_2 in experiment 1 and 2, this is the experiment 1 and 2 is can be written as, this is for the experiment 2 then NO2, this is for experiment 1, this comes out to be if you see that 0.20 and 0.1. So, this comes out to be 0.20 over 0.12. Similarly, the rate for experiment 2 over rate for experiment 1, this comes out to be 0.0082 over 0.0021 which comes out to be 4. So, the comparison of concentration and the rate of CO2 can be given in a similar fashion. Now, this is the CO2, sorry CO carbon monoxide experiment 3 and this is 0.2 over 0.1, this is coming out to be 2 and similarly the rate for experiment 3 over rate experiment 2, 0.0083 over 0.0081, this comes out to be 1. Let us take another step that is step 3, determine to what power the concentration factor must be raised to equal the rate factor of both NO2 and CO. So, in this case NO2 experiment 2 over NO2 experiment 1 rate experiment 1, this comes out to be 2 to the power n is equal to 4 and n is equal to 2. Similarly, the for CO2, for CO2 sorry carbon monoxide CO experiment 3 over experiment 2 to the power m which is equal to rate experiment 3 over experiment 2 which is 2 to the power m is equal to 1 or m is equal to 0. So, by this way we find out this the value of m and n. Now, in another step that is step 4, let us substitute the exponents into the general rate law to get the rate law for the reaction where the order of reactions are 2, n is equal to 2 and m is equal to 1.

So, the rate is equal to k NO2 to the power n CO to the power m which is equal to rate is equal to k NO2 to the power 2 CO to the power 0 which, because n and m value we have already determined. So, the rate is equal to k NO2 to the power 2. Now, step 5, you need to substitute the concentration and rate for any experiment into the rate law and solve for k.

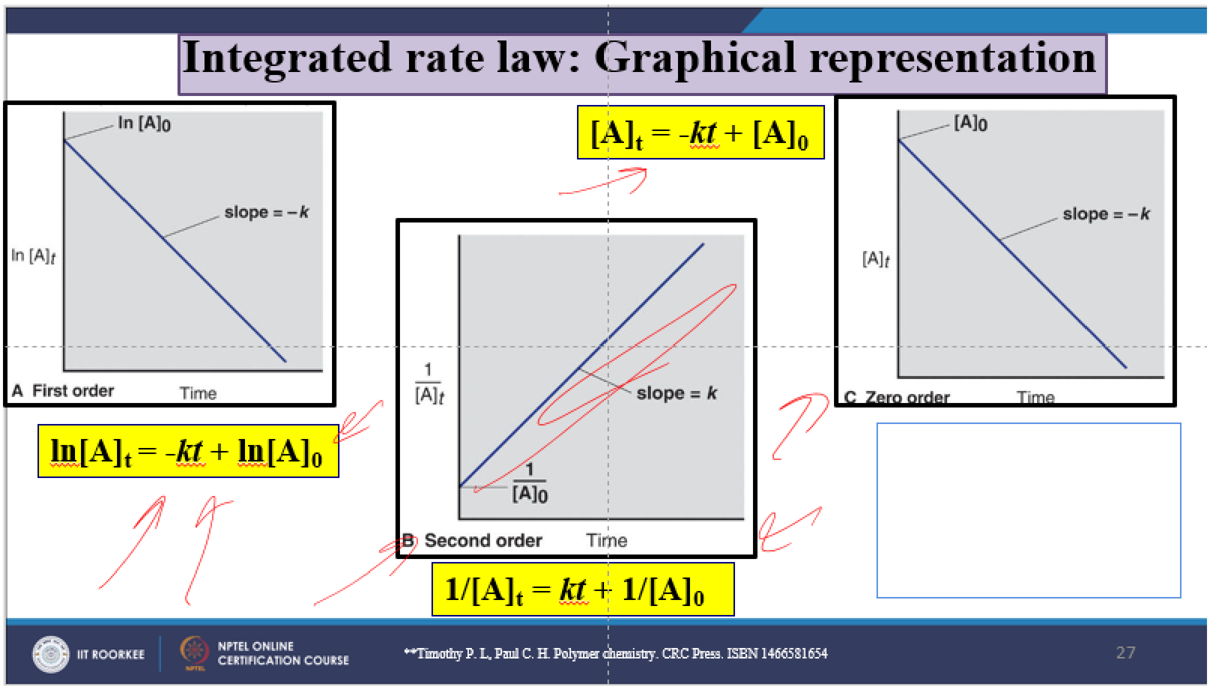
So, from experiment 1, 0.0021 is equal to k 0.10. Now, k is equal to 0.021 m to the power 2 and which is comes out to be 0.21 this one. So, the rate is given at last we find out the rate that is 0.21 mole inverse second inverse NO2 to the power 2 and that this is our answer.



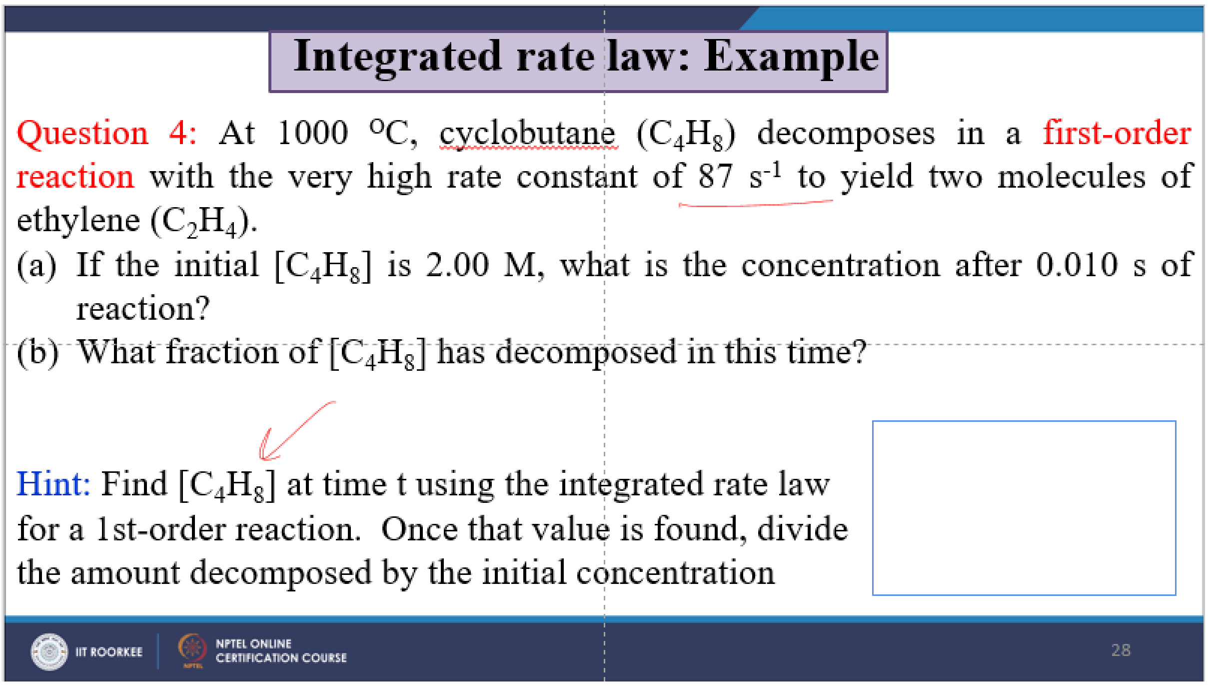
Now, let us talk about the integrated rate law that is the change in the concentration with reaction time. Now, consider a general first order reaction which is given as A is converting into B. So, the rate can be given as change in the concentration of A minus change in the concentration of A over delta t and that is given as k A. If we integrate this thing, then we can obtain that the ln A naught over A t is equal to k t, where ln is the natural logarithm, A naught is the initial concentration that is at time t is equal to 0 and A t is the concentration of A at any time which is given as t. So, ln A naught minus ln A t is equal to k t, this is the generic law.



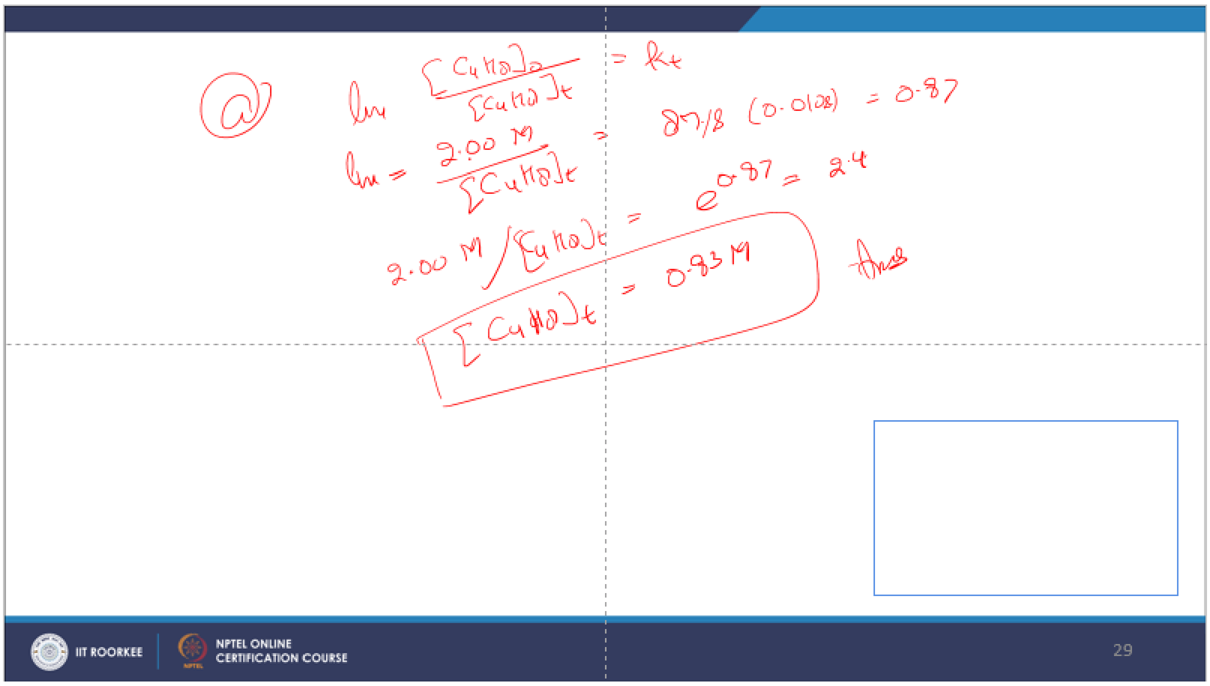
For simple second order reaction that is one reactant only that is given as rate is equal to minus delta A because minus is there because the concentration of A is depleted over the period of time t. So, minus delta A over delta t is equal to k A to the power 2. If we integrate, then it comes out to be 1 over A t minus 1 over A naught is equal to k t. So, for 0 order reaction if we talk about rate is equal to minus delta A over delta t and that is comes out to be k A naught. So, if we integrate, so it comes out to be for over a time from time t is equal to 0 to time t is equal to t.



So, A t concentration of A t minus A naught is equal to minus k t. Now, this can be represented as a graphical representation of all equations like this equation reflect this is the first order reaction, this is a 0-order reaction and this is the second order reaction. So, you can see the nature of the slopes like here ln A t is equal to minus k t plus ln A naught this is the basic equation for the first order and the second order this is 1 over A t is equal to k t plus 1 over A naught you can see the slope here and this is for the 0th order. The generic equation is A t is equal to minus k t plus A naught.



Now, another let us take another example and that is that at 100 degree Celsius the cyclobutane that is C4H8 decomposes in a first order reaction with a very high rate constant at 87 second inverse to yield to 2 molecules of ethylene C_2H_4.



Solution

$$\text{(a)} \quad \ln \frac{[C_4H_8]_0}{[C_4H_8]_t} = kt$$

$$\ln \frac{2.00\ M}{[C_4H_8]_t} = (87\ s^{-1})(0.010\ s)$$

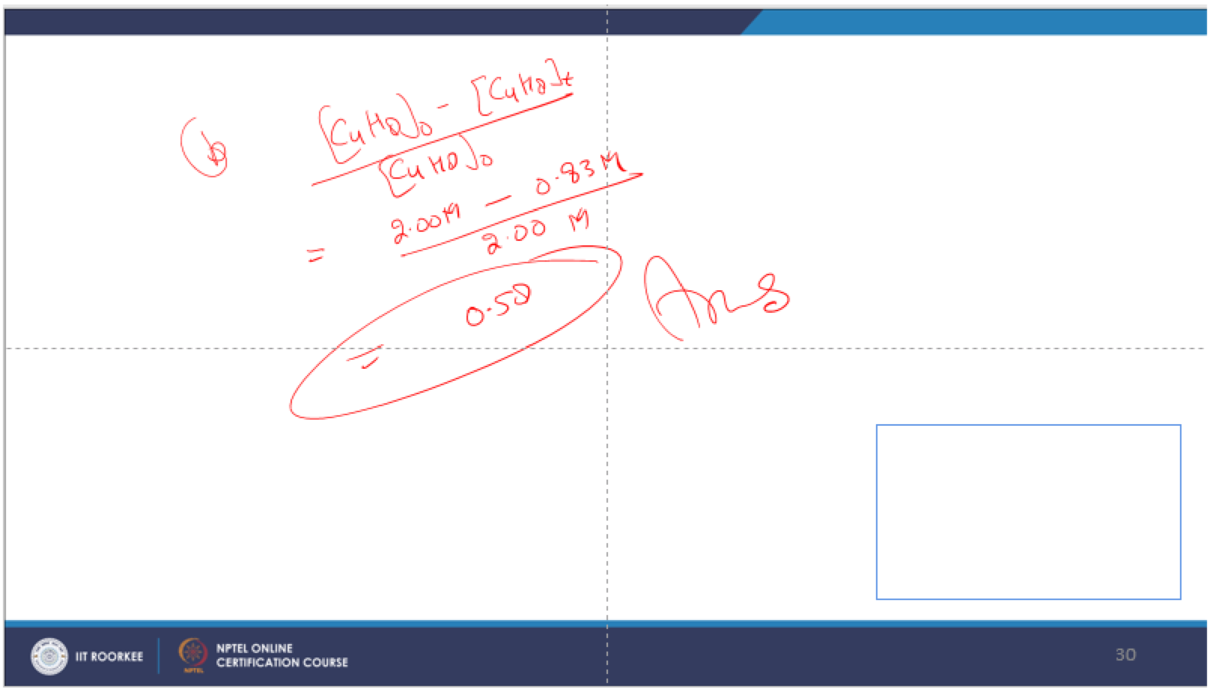
2.00 M / $[C_4H_8]_t$ = $e^{0.87}$ = 2.4

$[C_4H_8]_t$ = 0.83 M

(b) $$\frac{[C_4H_8]_0 - [C_4H_8]_t}{[C_4H_8]_0} = \frac{2.00\ M - 0.83\ M}{2.00\ M}$$

= 0.58

Now, if the initial concentration of C_4H_8 is 2 mole, what is the concentration after say 0.01 second of the reaction and second part is that what fraction of C4H8 has decomposed in time. We are giving one hint that we need to find out the concentration of C4H8 at time t using the integrated rate law which we have discussed here as a first law, first order reaction. Once that value is found that divide the amount decomposed by the initial concentration. So, let us try to solve this particular thing for A ln C4H8 at time t is equal to 0 over C4H8 at time t is equal to that is k t.



So, ln is equal to because these values are given to you concentration which is equal to 87 second per second into 0.01 that is 0.87. So, 2 concentration of C4H8 t that is e to the power 0.87 is equal to 2.4. So, the concentration of C4H8 t is given as 0.83 mole. This is the answer to the first segment. Now let us talk about the second segment. Now part B which says that what fraction of C4H8 has decomposed in this time. Now C4 concentration of C4H8 at time t is equal to 0 minus C4H8 at time t over C4H8 0. This is 2.0 minus 0.83 over 2.0 mole and this is equal to 0.58. This is our answer.

Temperature and reaction rate

Consider the rate law for a first order reaction: $A \longrightarrow B$

$$\boxed{\text{Rate} = k[A]}$$

Where is the temperature dependence?

Answer: It is embodied in the rate constant, k, that is, **k depends on the temperature at which the reaction is conducted.**

- **Arrhenius law**

This law suggests a formula **for the temperature dependency of reaction rates**

Rate constant (k) is the only term which is a **temperature dependent term in the rate law.**

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Now let us talk about the temperature and reaction rate. Now consider the rate law for a first order reaction which is again our basic equation remains same that is A is converting into B. So, rate is given as k concentration. Where is the temperature dependency? The answer is that it is embodied in the rate constant k and that is k and k depend on the temperature at which the reaction is conducted.

Temperature and reaction rate

According to Arrhenius law rate constant (k) can be described as:

$$k = k_0 e^{\frac{-E_a}{RT}}$$

Where,

✓ **k_0**- represent **the frequency factor** or pre-exponential factor having the same unit as a **rate constant k**. This equation is fitted experimentally over wide ranges of true temperature.

✓ **E_a**- activation energy (J/mol)

✓ **R**- universal gas constant (8.314 J/mol K)

✓ **T**- absolute temperature (K)

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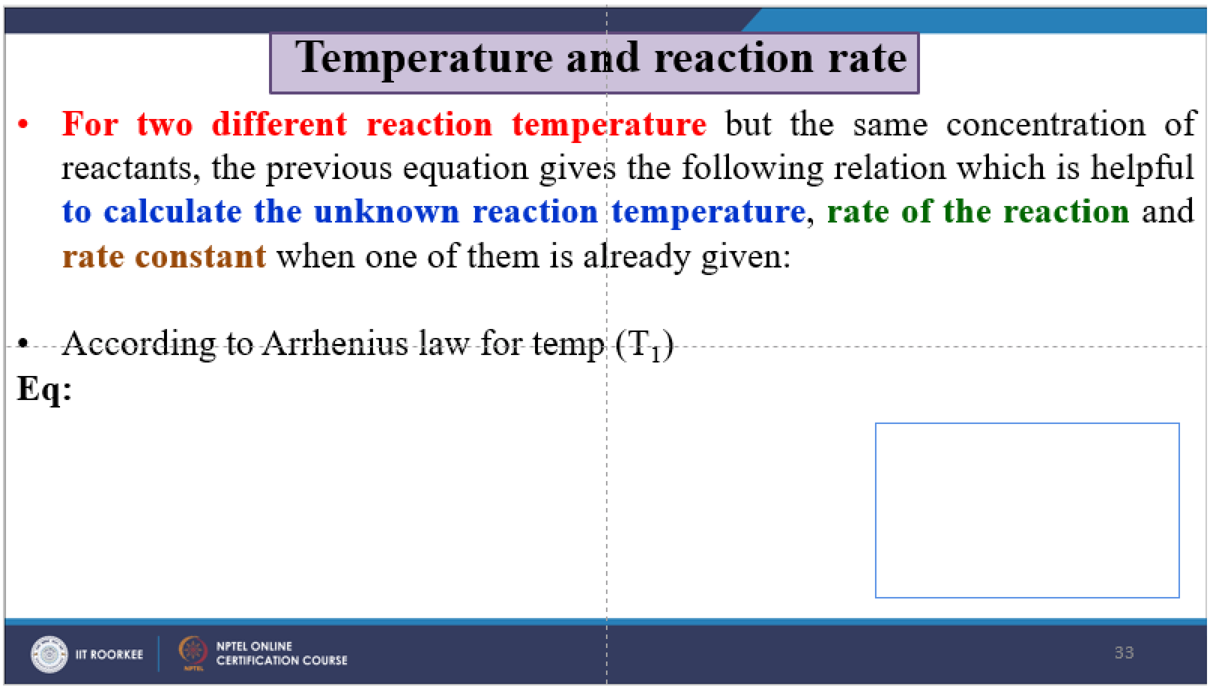
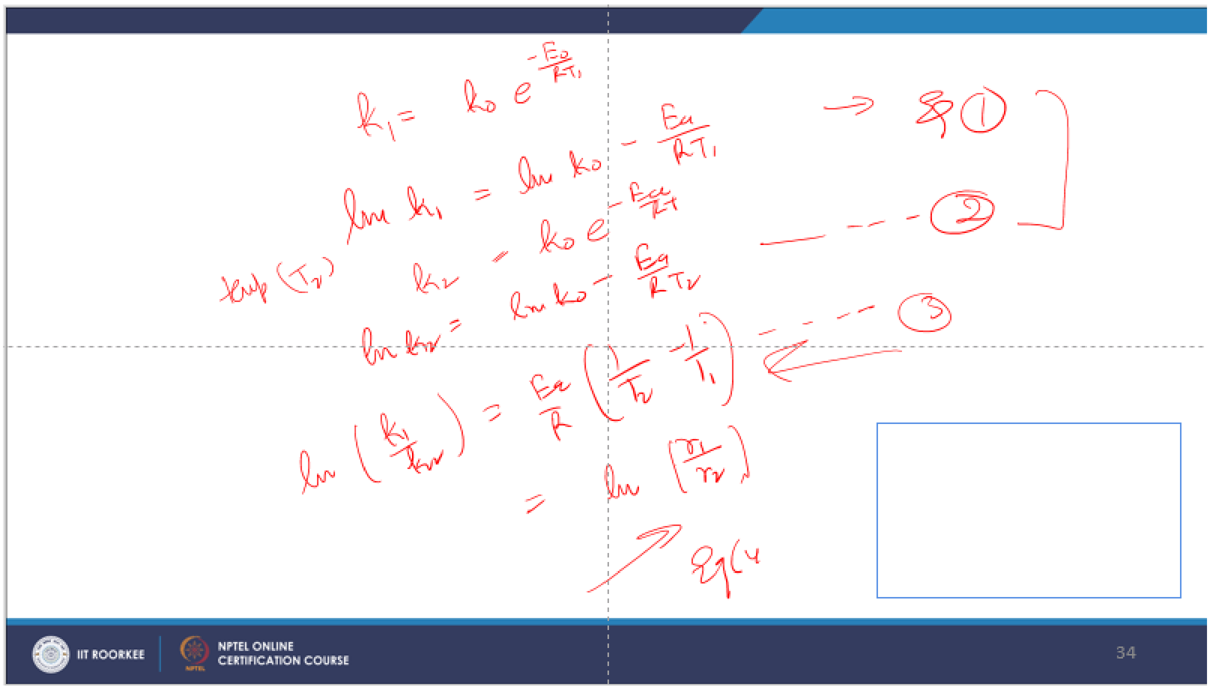
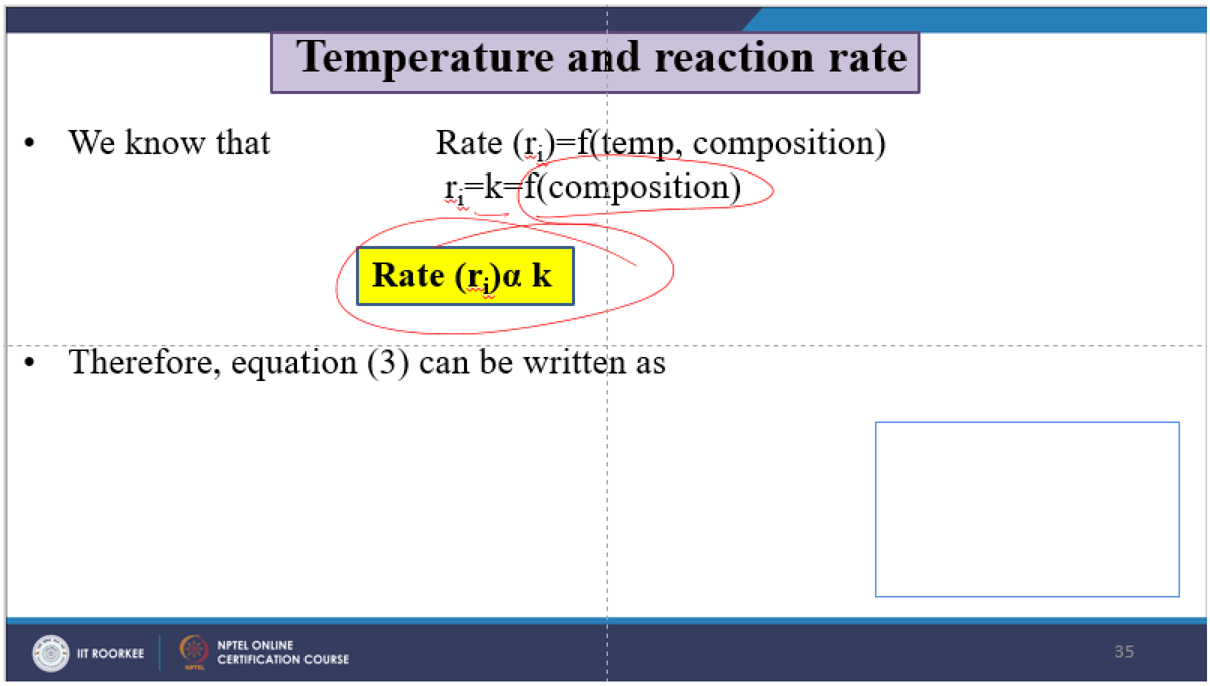
$$k = k_0 e^{\frac{-E_a}{RT}}$$

So, this is the basic question. Now let us talk about the Arrhenius law. This law suggests a formula for a component for a temperature dependency of a reaction rate. Now rate constant k is the only term which is temperature dependent term in the rate law. Now according to the Arrhenius law rate constant k can be described as k is equal to k naught e to the power minus E over RT where k naught this is this represents the frequency factor or 3 exponential factors having the same unit as a rate constant k. Now this equation is fitted experimentally over wide range of temperature.

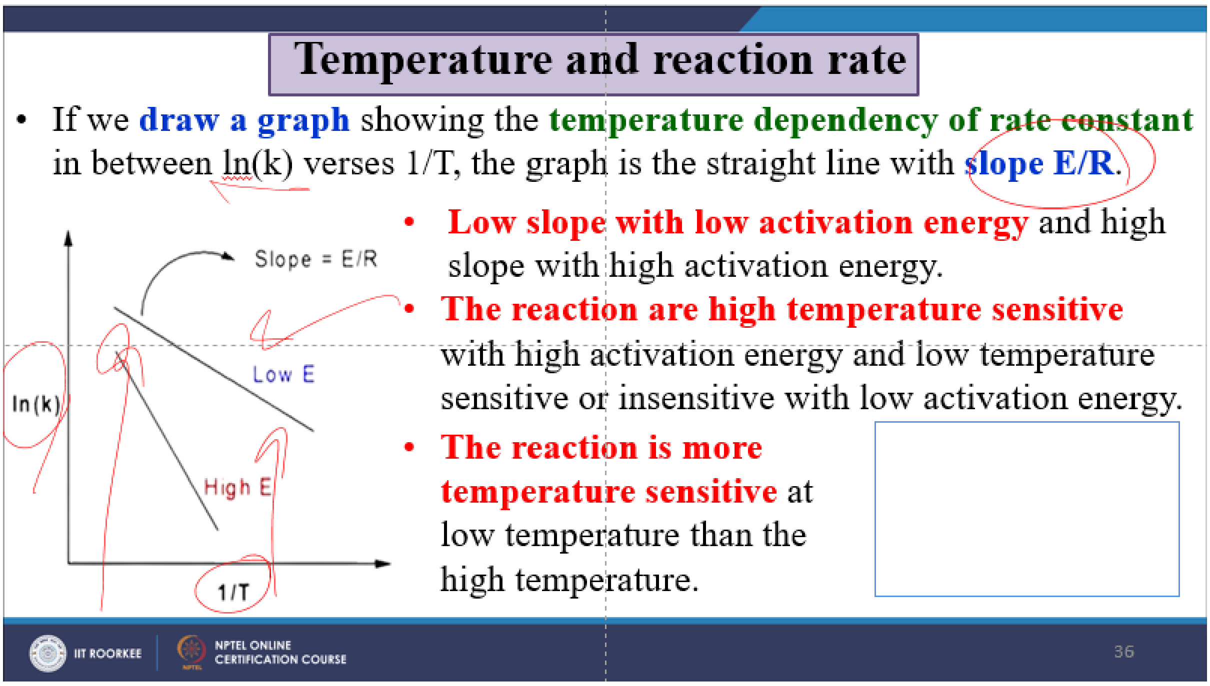




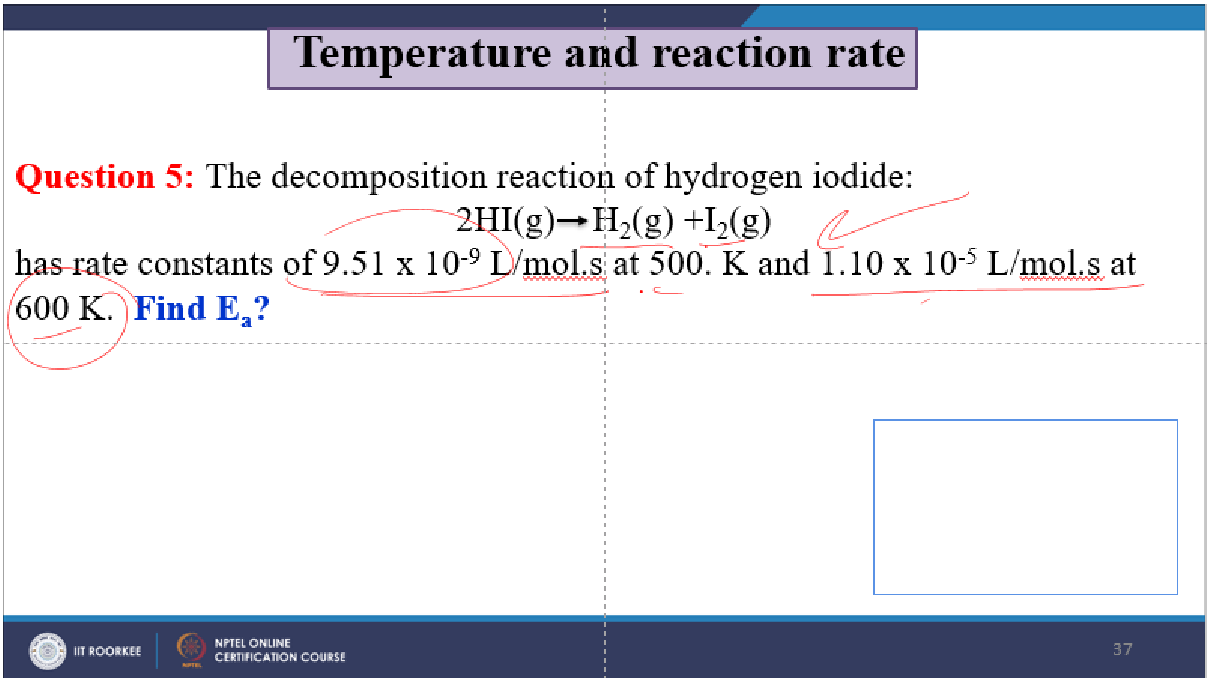
Now E naught is the activation energy which is usually represented as joule per mole. R is the universal gas constant and temperature T is given in the absolute temperature Kelvin. Now for two different reaction temperature but the same concentration of the reactant this particular equation this gives the different relations which are helpful for to calculate the unknown reaction temperature and rate of a reaction and a rate of constant for when usually one of them is already given. Now for according to Arrhenius law for temperature T1 the for temperature T1 the k1 can be k naught e to the power minus E naught over RT1 or ln k1 is equal to ln k naught minus EA upon RT1.

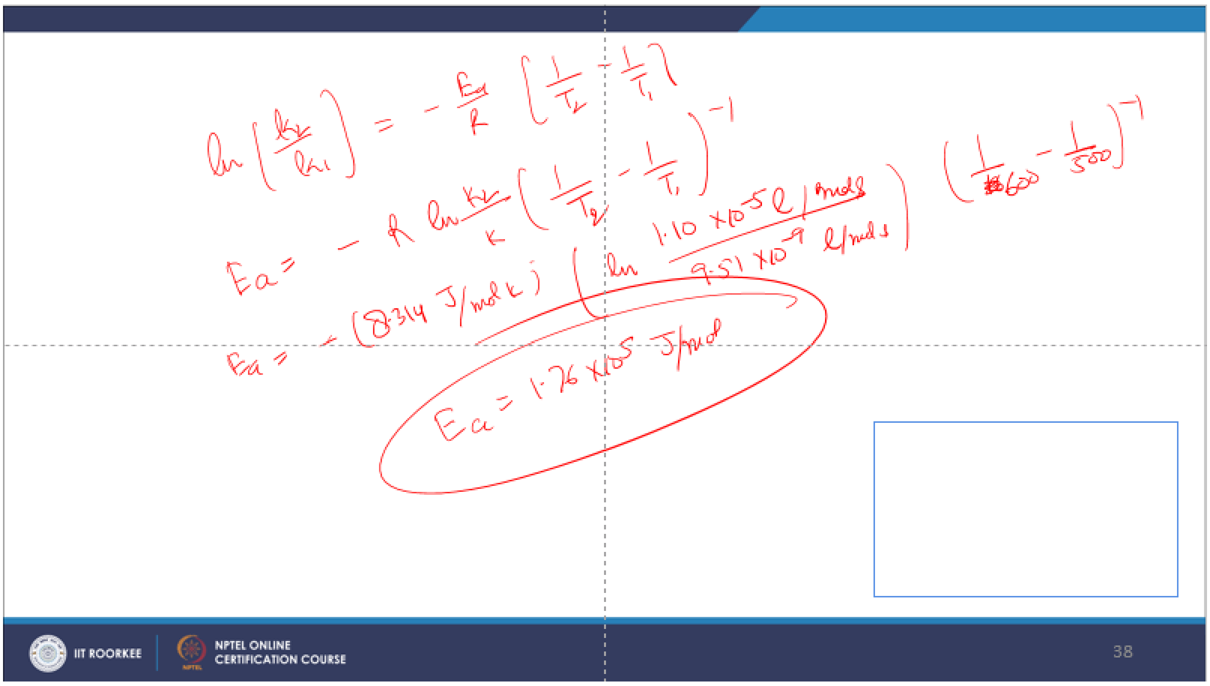


This is equation number 1 please remember this is the equation number 1. Now for if we take the temperature T2 k2 is equal to k naught e to the power minus EA over RT. Now ln k2 is equal to ln k naught minus EA upon RT2 this is equation number 2. Now if we combine both the equation and rearrange then it comes out to be ln k1 over k2 that is equal to EA upon R into 1 upon T2 minus 1 upon T1. This is equation number 3. Now another thing is that if we see that this particular equation this can be written as in another form if we take the rate is into consideration so this equation can be written as ln R1 over R2.



This is equation number 4. Now you know that because why we have written this particular equation because the rate initial rate is function of temperature and composition and this is equal to the k or f composition. So, rate is proportional to the k so we can write this particular equation in the previous form like this. Now if we draw a graph showing the temperature dependency of a rate constant in between the logarithmic of k versus 1 over T the graph is in the straight line and the slope is given as E over R. So, the low slope with the low activation energy and high slope with the high activation energy one aspect is here. The reaction are high temperature sensitive with high activation energy and the low temperature sensitive or insensitive with the low activation energy.

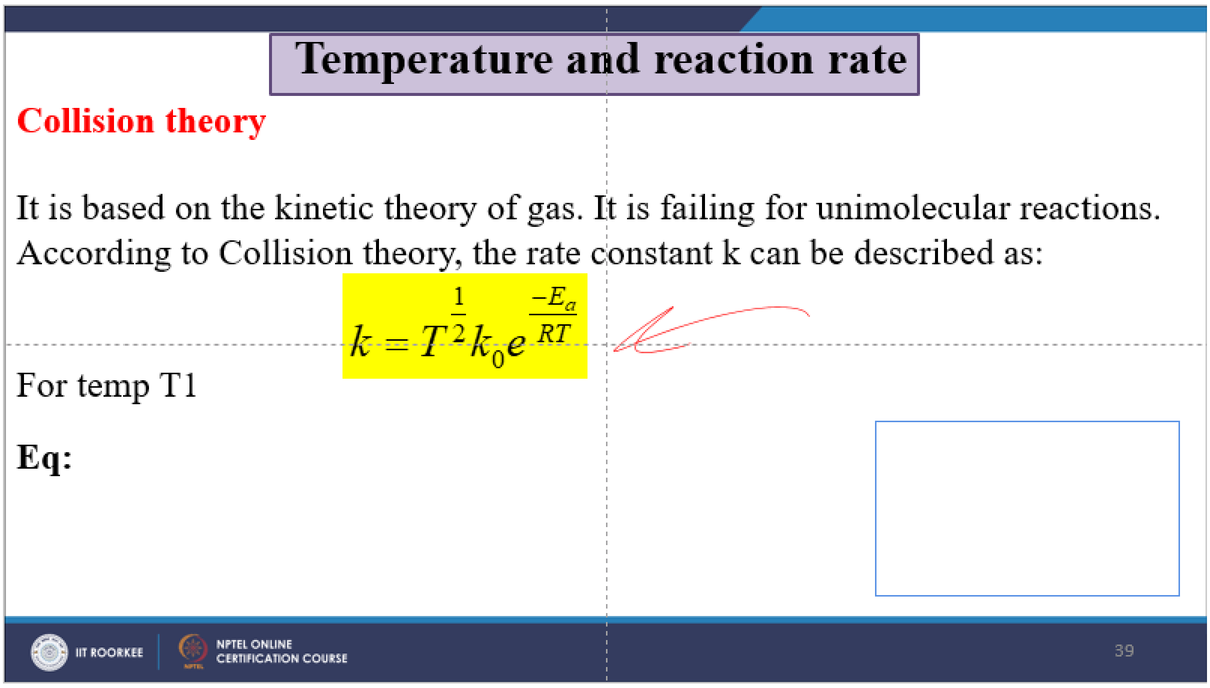




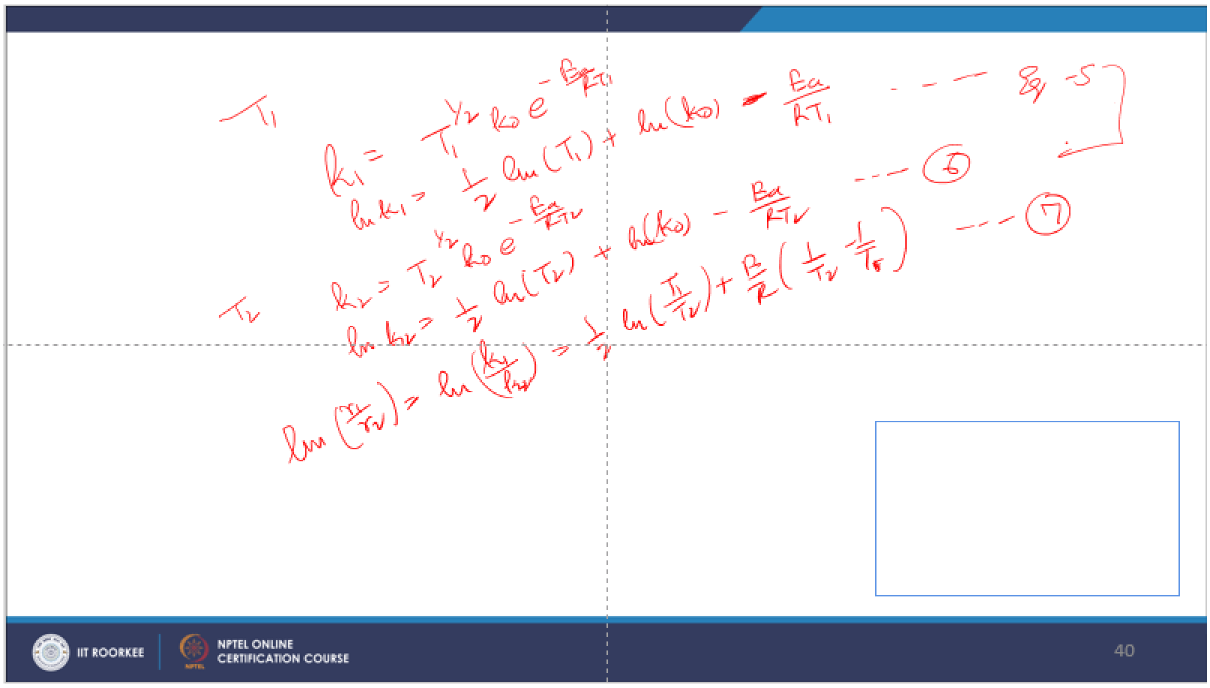
$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) E_a = -R\ln\frac{k_2}{k_1}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)^{-1}$$

$$E_a = -(8.314 J/mol.K)\left(\ln\frac{1.10\times10^{-5} L/mol.s}{9.51\times10^{-9} L/mol.s}\right)\left(\frac{1}{600K}-\frac{1}{500K}\right)^{-1} \quad E_a = 1.76\times10^{5} J/mol$$

Now the reaction is more temperature sensitive at low temperature if you see that the reaction is more temperature sensitive at low temperature then the high temperature. Let us talk about another example and that is the question number 5. The decomposition reaction of hydrogen iodide that is 2 Hi which is in the gaseous form is given as 2 Hi is equal to hydrogen H2 plus I2. This has the rate constant of 9.51 into 10 to the power minus 9 liter per mole second at 500 degree Celsius, 500-degree Kelvin and 1.10 into 10 to the power minus 5 liter per mole second at 600 Kelvin. You need to find out the Ea. Now how you will find out? The thing is that we are having ln k2 over k1 which is equal to minus Ea over R into 1 upon T2 minus 1 upon T1. Here T1, T2 they are given and you are having the rate constant. So, we can substitute the value after rearranging this equation ln k2 over k1 into 1 over T2 minus 1 over T1 minus 1 and this Ea is equal to minus 8.314 joule per mole Kelvin into ln 1.10 into 10 to the power minus 5 over 9.51 into 10 to the power minus 9 into 1 upon 600 minus 1 upon 500. This is in Kelvin. So Ea comes out to be 1.76 into 10 to the power 5 joule per mole. This is our answer.



$$k = T^{\frac{1}{2}} k_0 e^{\frac{-E_a}{RT}}$$



Now let us talk about the collision theory. It is based on the kinetic theory of a gas. It is failing to for a unimolecular reaction. Now according to collision theory, the rate constant k can be described as k is equal to T to the power half k naught e to the power minus Ea over RT. So, let us take for the for temperature say T1 the equation can be represented as k1 is equal to T1 to the power half k naught e to the power minus Ea over RT1 and ln k1 is equal to 1 upon 2 ln T1 plus ln k naught minus Ea upon RT1.

Let us say this is our equation number 5. Now for temperature this is for temperature T1 and let us take for temperature T2 that is k2 is equal to T2 to the power half k naught e to the power minus Ea over RT2 and this is ln k2 is equal to half ln T2 plus ln k naught minus Ea upon RT2. This is equation number 6. Now if we substitute and rearrange these equations 5 and 6 we get ln R1 over R2 which is equal to ln k1 over k2 1 upon 2 ln T1 over T2 plus Ea over R 1 upon T2 minus 1 upon T1. Let us say this is equation number 7. Now the transition state theory, this theory explains the reaction rate of elementary chemical reactions.

Temperature and reaction rate

Transition state theory

This theory explains **the reaction rates of elementary chemical reactions**. The theory assumes a special type of chemical equilibrium (quasi-equilibrium) between reactants and activated transition state complexes.

According to this theory specific rate constant have the relation

$$k = Tk_0 e^{\frac{-E_a}{RT}}$$

For temp T_1

Eq:

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T_1: $k_1 = T_1 k_0 e^{-\frac{E_a}{RT}}$ --- (8)

$\ln k_1 = \ln(T_1) + \ln(k_0) - \frac{E_a}{RT_1}$ --- (9)

T_2: $k_2 = T_2 k_0 e^{-\frac{E_a}{RT}}$

$\ln k_2 = \ln(T_2) + \ln(k_0) - \frac{E_a}{RT_2}$

$\ln\left(\frac{r_1}{r_2}\right) = \ln\left(\frac{k_1}{k_2}\right) = \ln\left(\frac{T_1}{T_2}\right) + \frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ --- (10)

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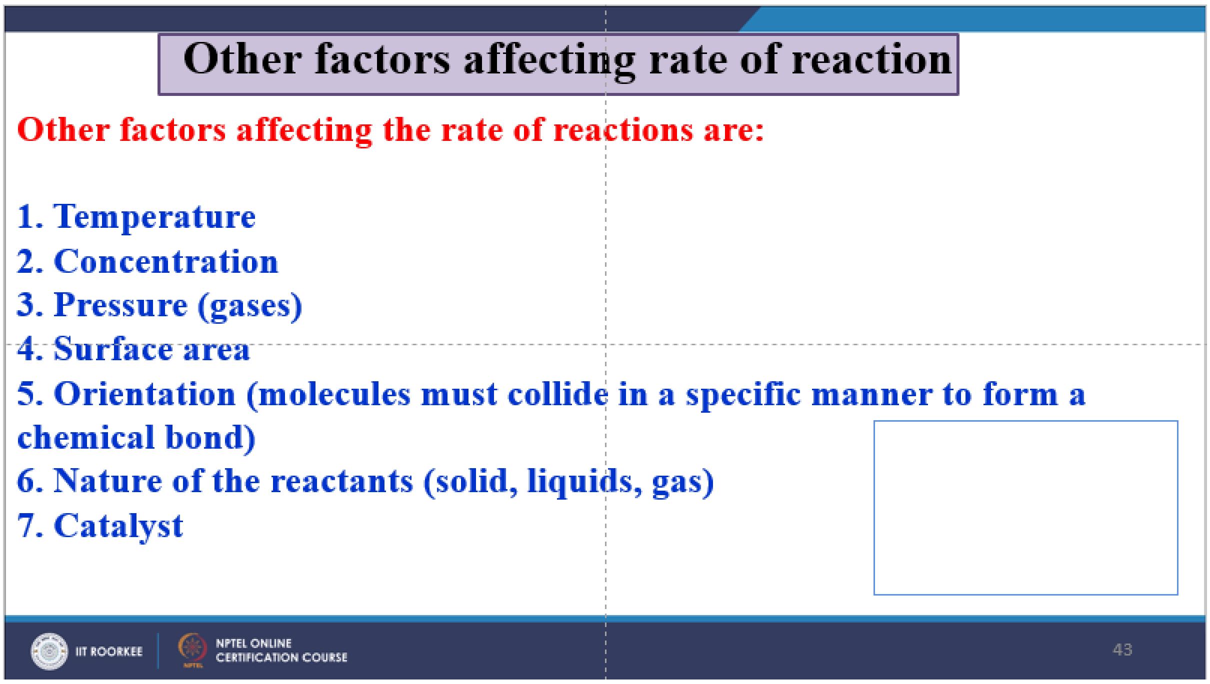
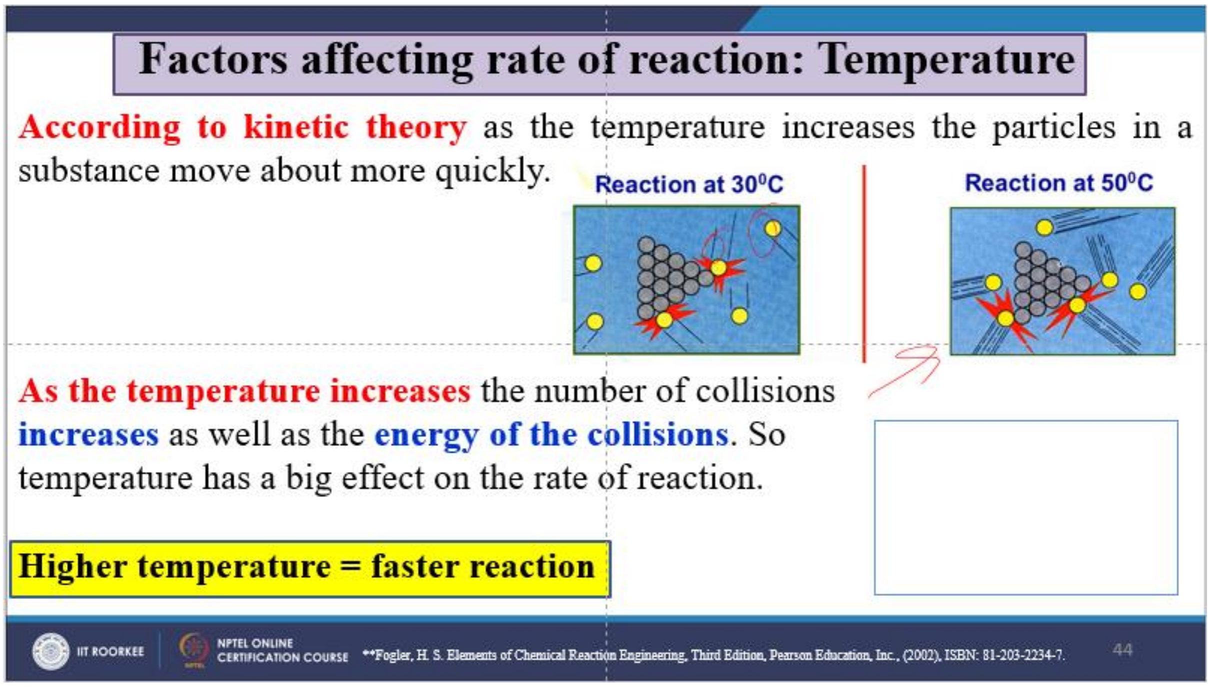
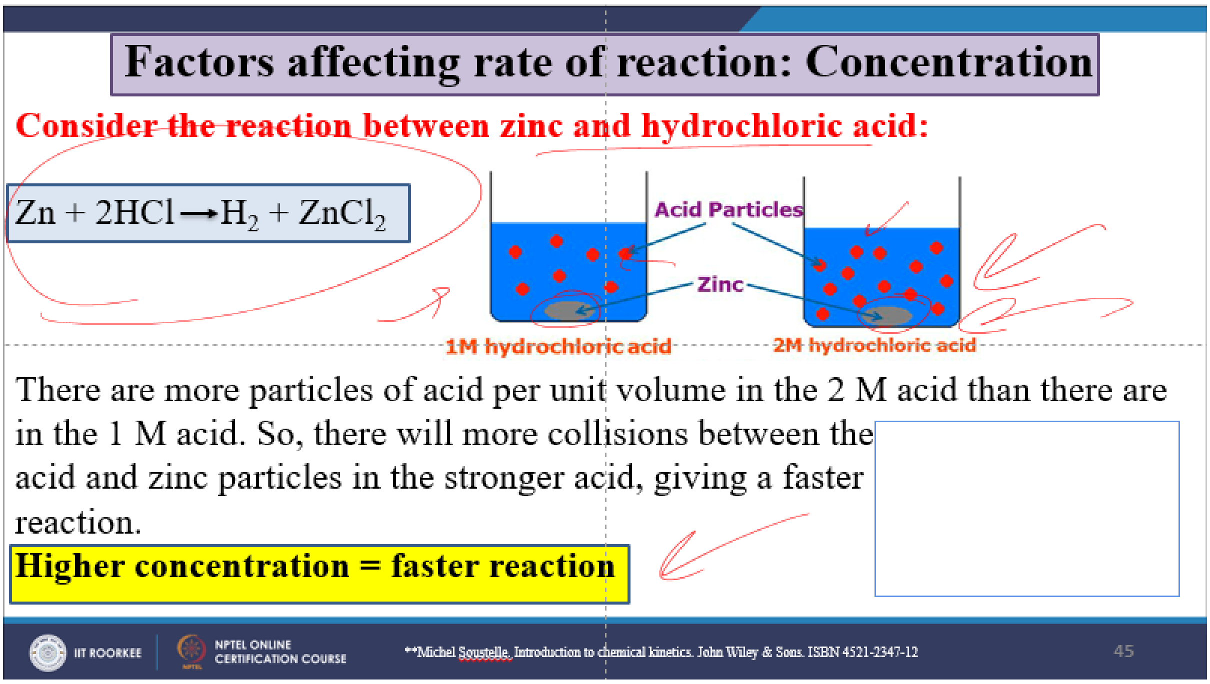
Now the theory assumes a special type of chemical equilibrium sometimes referred as a quasi-equilibrium between the reactant and activated transition state complexes. Now according to this particular theory, the specific rate constant, the mathematical representation for this is equal to k is equal to T k naught e to the power minus Ea over RT. Now let us take for the temperature T1, for temperature T1 the k1 is equal to T1 k naught e to the power minus Ea over RT and ln k1 is equal to ln T1 plus ln k naught minus Ea upon RT. This is equation number, let us say that this is our equation number 8. Now if we talk about the temperature T2, say this is T2, so k2 can be given as T2 k naught e to the power minus Ea upon RT and ln k2 is ln T2 plus ln k naught minus Ea upon RT2. Let us say this is equation number 9. So, if we substitute both the equation then ln R1 over R2 can be represented as ln k1 over k2 which is ln T1 over T2 plus E over R 1 upon T2 minus 1 upon T1. Now this is our equation number 10.



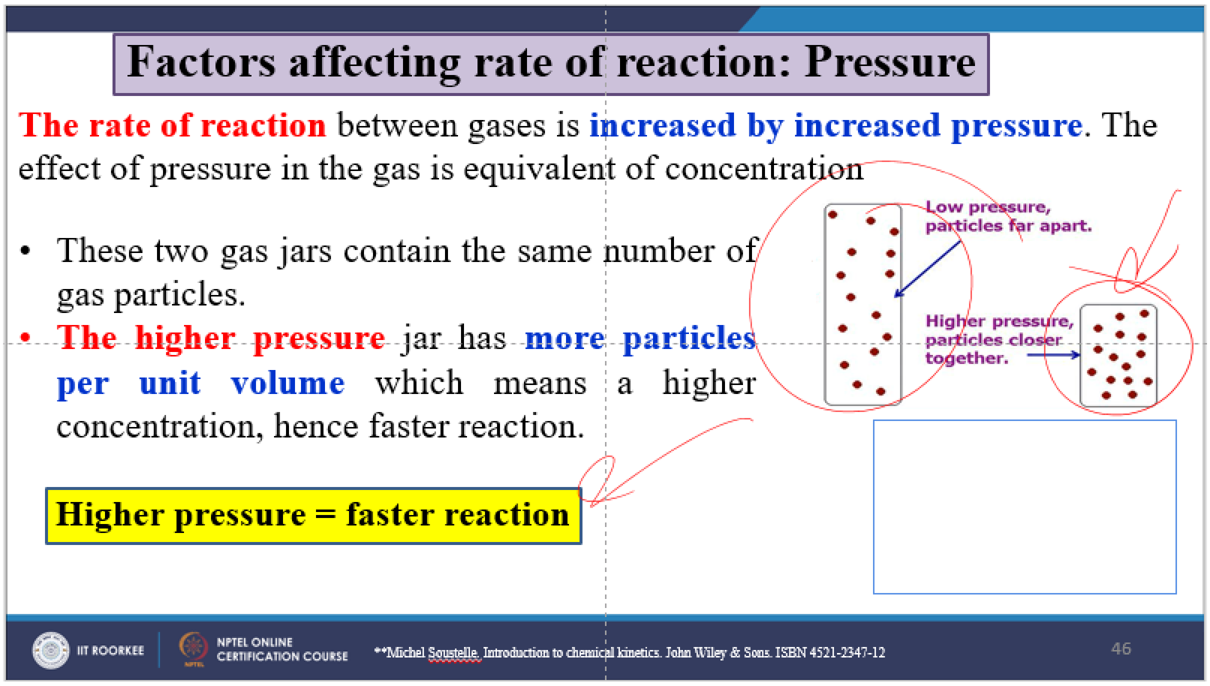
Now there are several other factors those who are affecting in the reaction, rate of reaction, these are like temperature, concentration, pressure of the gases, surface area, orientation that is molecule must collide in a specific manner to form a chemical bond and the nature of the reactants, solid, liquid or gas, catalyst all those things. Let us take about the temperature. Now as per the kinetic theory as the temperature increases the particle in the substance move about more quickly like here you see that we are having the temperature at 30 degree Celsius the particles are colliding each other.



Now as we increase the temperature, the number of collisions increases as well as the energy of collision. So, the temperature has a big effect on the rate of collision. Now the higher temperature you may have a faster reaction. Similarly, let us talk about the concentration.



Now consider the reaction between the zinc and hydrochloric acid. This is the basic formula Zn plus twice HCl is equal to H2 plus ZnCl2. Now here these are the acid particles, red dots are the acid particles and here you see that this is a zinc. Now there are more particles of acid per unit volume in these 2 molar acids then there are lesser number of particles at 1 molar solution. So, there will be more collision between the acid and zinc particles in the stronger acid and this is this may give the faster reaction.

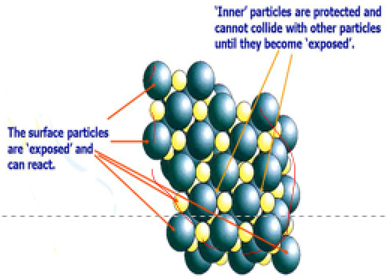


So, the higher concentration this gives the faster reaction. Then the pressure the rate of reaction between the gases this increased by the increased pressure. The effect of pressure in the gas is equivalent of concentration. So, these two there are two gas jars you see having the same number of gas particles. The higher pressure jar this one the more particles per unit volume that means the particles are more closer so which means the higher concentration hence the faster reaction.

So, the higher pressure equal to the faster reaction. Now surface area when solid takes part in a chemical reaction only the surface particles are exposed. Here you see these are the surface particles which are exposed. So, there are only one that can collide with the particles of other reactants. Now if we break up this lump into the smaller pieces the number of particles has not changed but there are more and more surface exposed particles.

Factors affecting rate of reaction: Surface area

- When solids take part in chemical reactions **only the surface particles are exposed** so they are the only ones that can collide with particles of other reactants.
- If we break up this **'lump'** into smaller pieces the number of particles has not changed but the there are now **more 'surface' particles**.
- There is now a greater surface area with more exposed particles so more collisions can occur, hence faster reaction



Large surface area=faster reactions

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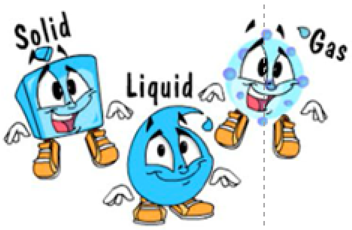
So, there is a greater surface area which is available for the reaction. So therefore, the larger surface area the faster reaction. Nature of reactant, the chemical reaction occurs faster if the reactants are in the same state. So, all gas particles they are homogeneous. Now the chemical reactions proceed more slowly if the reactants are in different states.

Factors affecting rate of reaction: Nature of reactant

- **Chemical Reactions occur faster if the reactants are in the same state**; example: **All are gases particle (homogeneous)**
- **Chemical Reactions proceed more slowly if the reactants are in different states**; example: **Solid and a liquid particles (heterogeneous)**



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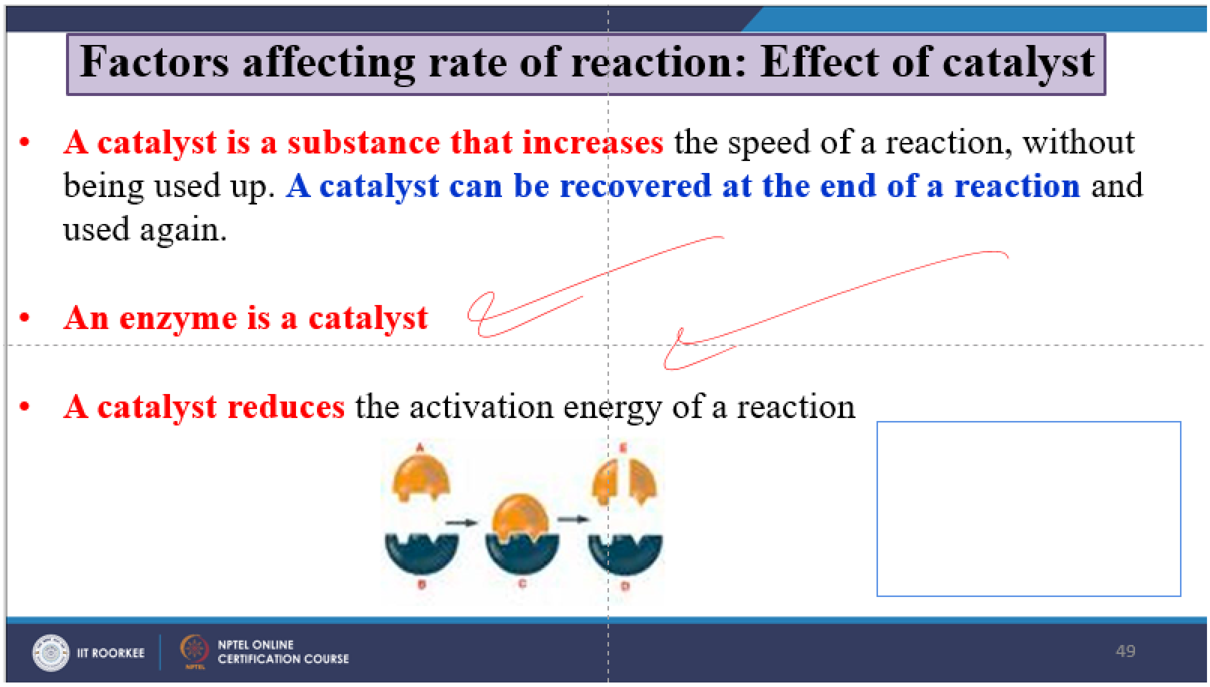
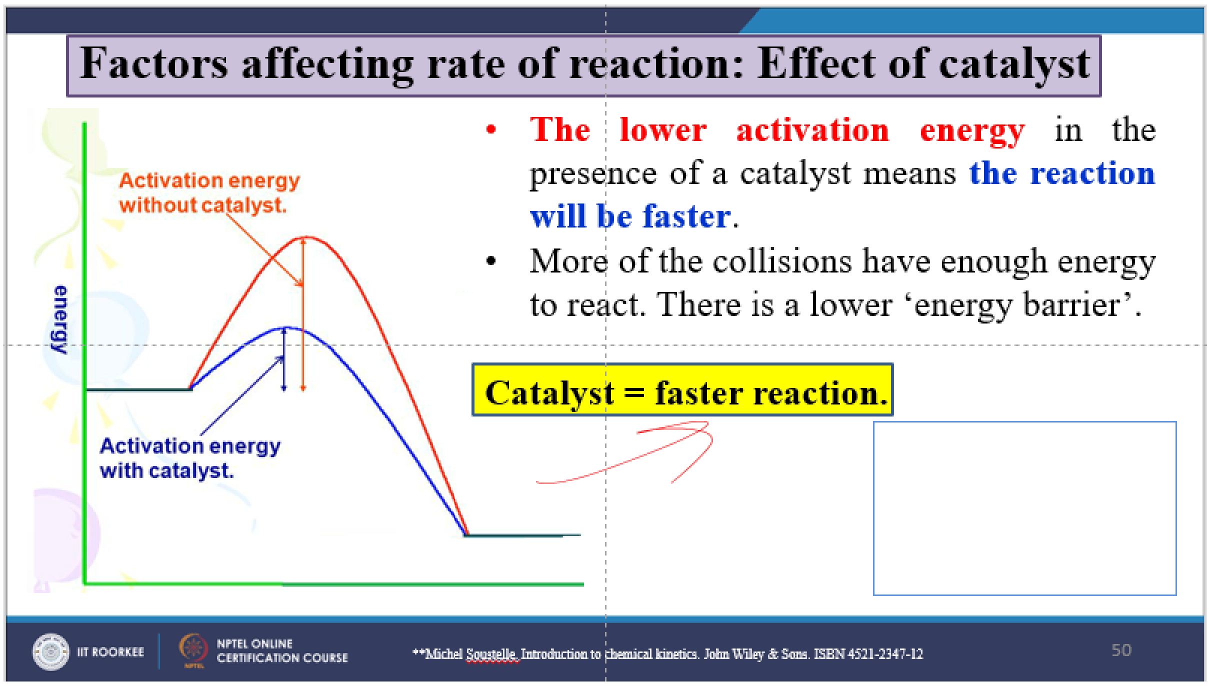
For example, solid and liquid particles, are heterogeneous. Effect of catalyst, a catalyst is a substance that increases the speed of reaction without being used up. Now a catalyst can be recovered at the end of a reaction and can be regenerated and used again. Now for example like enzyme is a catalyst and a catalyst reduce the activation energy of the reaction. So, the lower activation energy in the presence of a catalyst this means the reaction will be faster.





So more the collision has enough energy to react and there is a lower energy barrier. So, catalyst they must have a faster reaction. So dear friends in this particular segment the introductory segment of chemical reaction engineering we discussed various parameters those affect the rate of a reaction we discussed in detail with a couple of examples.

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For your convenience we have enlisted several references which you can use as per your requirement. Thank you very much.