

## UNIT – VII – CHEMICAL KINETICS | Mr. S.JOHNSON., M.Sc., M.Sc., B.Ed.,

## UNIT – 7 – CHEMICAL KINETICS

## II. Answer the following questions:

## 1. Define average rate and instantaneous rate.

## Average rate of chemical reaction:

The average rate is defined as the ratio of change in the final concentration of reactants and the initial concentration of reactants over the entire time period of reaction.

$$\text{Average rate} = \frac{(\text{Final concentration of reactants} - \text{Initial concentration of reactants})}{\text{Change in Time}}$$

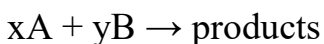
The rate of the reaction at a particular instant during the reaction is called the instantaneous rate.

## Average rate of chemical reaction:

It may be defined as the rate of a reaction of a particular instant. Instantaneous reaction rate  $\frac{d[l_2]}{dt}$  where,  $d(l_2)$  = small change in concentration.  $d+$  = small change in time.

## 2. Define Rate law and Rate constant.

Rate law: The expression in which reaction rate is given in terms of molar concentration of the reactants with each term raised to some power, which may or may not be same as the Stoichiometric coefficient of the reacting species in a balanced chemical equation.



$$\text{Rate} = k[\text{A}]^m[\text{B}]^n \quad k = \text{Rate constant}$$

Rate constant: For a reaction involving the reactants A and B, Reaction rate =  $k[\text{A}]^m[\text{B}]^n$ . The constant  $k$  is called rate constant of the reaction. If  $[\text{A}] = 1\text{M}$  and  $[\text{B}] = 1\text{M}$ ; Reaction rate =  $k$ . Thus, the rate constant ( $k$ ) of a reaction is equal to the rate of reaction when the concentration of each reactant is equal to 1 mol L<sup>-1</sup>. The change in the concentration of reactant or product per unit time under the condition of unit concentration of all the reactant.

3. Derive integrated rate law for a zero order reaction  $\text{A} \rightarrow \text{product}$ . [PTA6, QY-19, MAR-20, AUG-21, JUL-22]

A reaction in which the rate is independent of the concentration of the reactant over a wide range of concentrations is called as zero order reactions. Such reactions are rare. Let us consider the following hypothetical zero order reaction.

The rate law can be written as,

$$\text{Rate} = k [\text{A}]^0$$

$$\frac{-d[\text{A}]}{dt} = k(1)$$

$$(\because [\text{A}]^0 = 1)$$

$$-d[\text{A}] = kdt$$

Integrate the above eq. between the limits of  $[\text{A}]^0$  at zero time and  $[\text{A}]$  at some later time 't',

$$-\int_{[\text{A}_0]}^{[\text{A}]} d[\text{A}] = k \int_0^t dt$$

$$-([\text{A}])_{[\text{A}_0]}^{[\text{A}]} = k(t)'_0$$

$$[\text{A}_0] - [\text{A}] = kt$$

$$k = \frac{[\text{A}_0] - [\text{A}]}{t}$$

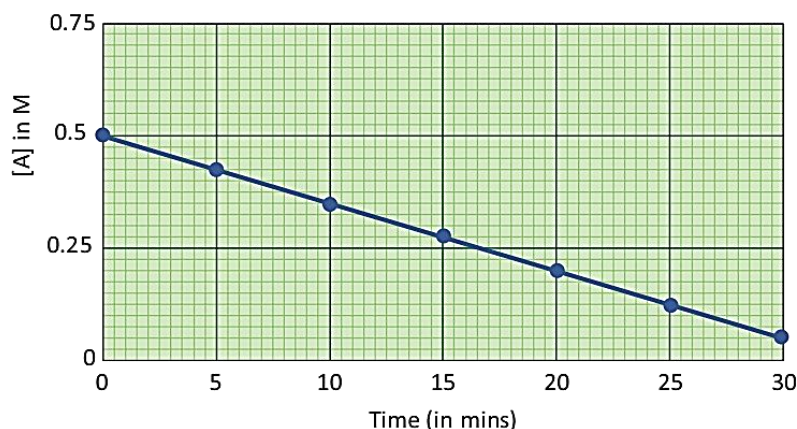
Equation (2) is in the form of a straight line

$$y = mx + c$$

$$\text{ie., } [\text{A}] = -kt + [\text{A}_0]$$

$$y = c + mx$$

A plot of  $[\text{A}]$  vs time gives a straight line with a slope of  $-k$  and  $y$ -intercept of  $[\text{A}_0]$



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✚ The half life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value.

✚ For a first order reaction, the half life is a constant i.e., it does not depend on the initial concentration. The rate constant for a first order reaction is given by

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

at  $t = t_{1/2}$  ;  $[A] = \frac{[A_0]}{2}$

$$k = \frac{2.303}{t_{1/2}} \log \frac{[A_0]}{[A_0]/2}$$

$$k = \frac{2.303}{t_{1/2}} \log 2$$

$$k = \frac{2.303 \times 0.3010}{t_{1/2}} = \frac{0.6932}{t_{1/2}}$$

$$t_{1/2} = \frac{0.6932}{k}$$

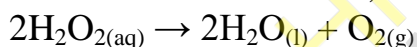
**5. What is an elementary reaction? Give the differences between order and molecularity of a reaction. [PTA-1, QY-19, QY, HY, JUL-22, QY-23, FRT-24]**

Each and every single step in a reaction mechanism is called an elementary reaction.

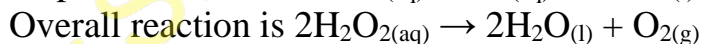
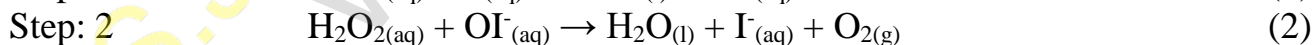
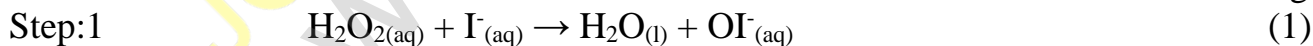
ORDER OF A REACTION	MOLECULARITY OF A REACTION
It is the sum of the powers of concentration terms involved in the experimentally determined rate law.	It is the total number of reactant species that are involved in an elementary step.
It can be zero (or) fractional (or) integer	It is always a whole number, cannot be zero or a fractional number.
It is assigned for a overall reaction.	It is assigned for each elementary step of mechanism.

**6. Explain the rate determining step with an example. [PTA-4, HY-23]**

Let us consider reaction, the decomposition of hydrogen peroxide catalysed by I<sup>-</sup>.



It is experimentally found that the reaction is first order with respect to both H<sub>2</sub>O<sub>2</sub> and I<sup>-</sup>, which indicates that I<sup>-</sup> is also involved in the reaction. The mechanism involves the following steps.

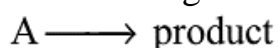


These two reactions are elementary reactions. Adding equ (1) and (2) gives the overall reaction.

Step 1 is the rate determining step, since it involves both H<sub>2</sub>O<sub>2</sub> and I<sup>-</sup>, the overall reaction is bimolecular.

**7. Describe the graphical representation of 1<sup>ST</sup> order reaction. [PTA-2, MAR-20, HY, JUL-22, FUT, SRT-23]**

A reaction whose rate depends on the reactant concentration raised to the first power is called a first order reaction. Let us consider the following first order reaction,



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Rate law can be expressed as

$$\text{Rate} = k [A]^1$$

Where, k is the first order rate constant.

$$\frac{-d[A]}{dt} = k [A]^1$$

$$\Rightarrow \frac{-d[A]}{[A]} = k dt$$

Integrate the above equation between the limits of time  $t = 0$  and time equal to  $t$ , while the concentration varies from the initial concentration  $[A_0]$  to  $[A]$  at the later time.

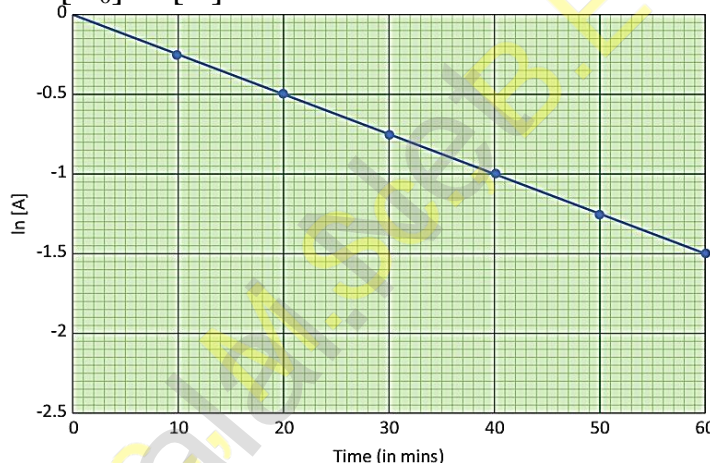
$$\int_{[A_0]}^{[A]} \frac{-d[A]}{[A]} = k \int_0^t dt$$

$$(-\ln[A])_{[A_0]}^{[A]} = k(t)_0^t$$

$$-\ln[A] - (-\ln[A_0]) = k(t-0)$$

$$-\ln[A] + \ln[A_0] = kt$$

$$\ln\left(\frac{[A_0]}{[A]}\right) = kt$$



This equation is in natural logarithm. To convert it into usual logarithm with base 10, we have to multiply the term by 2.303.

$$2.303 \log\left(\frac{[A_0]}{[A]}\right) = kt$$

$$k = \frac{2.303}{t} \log\left(\frac{[A_0]}{[A]}\right)$$

Equation (2) can be written in the form  $y = mx + c$  as below

$$\ln[A_0] - \ln[A] = kt$$

$$\ln[A] = \ln[A_0] - kt$$

$$\Rightarrow y = c + mx$$

If we follow the reaction by measuring the concentration of the reactants at regular time interval 't', a plot of  $\ln[A]$  against 't' yields a straight line with a negative slope. From this, the rate constant is calculated.

### 8. Write the rate law for the following reactions.

(a) A reaction that is 3/2 order in x and zero order in y.

(b) A reaction that is second order in NO and first order in Br<sub>2</sub>.

(a) Rate =  $k[x]^{3/2} [y]^0$

(b) The reaction  $2NO + Br_2 \rightarrow 2NOBr$  is second order in NO and first order in Br<sub>2</sub>.

Rate =  $k[NO]^2 [Br_2]$

### 9. Explain the effect of catalyst on reaction rate with an example. [SEP-20]

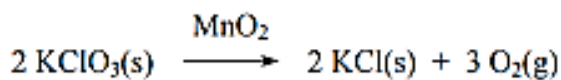
✚ A catalyst is substance which alters the rate of a reaction without itself undergoing any permanent chemical change.

✚ They may participate in the reaction, but again regenerated at the end of the reaction.

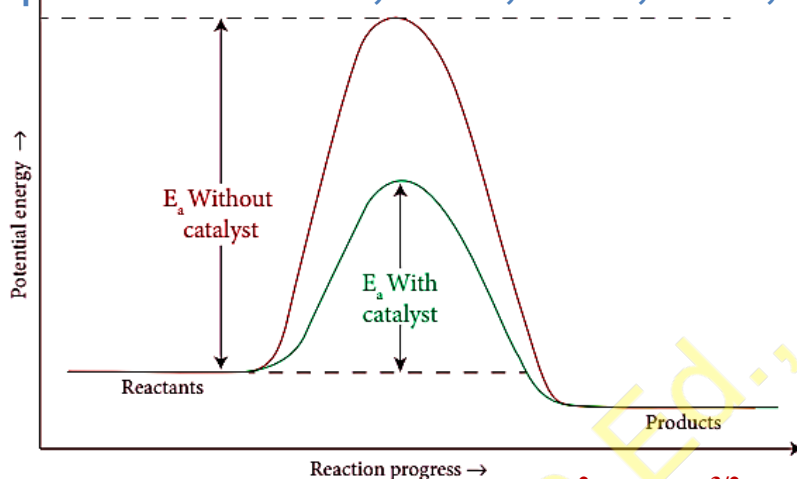
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In the presence of a catalyst, the energy of activation is lowered and hence, greater number of molecules can cross the energy barrier and change over to products, thereby increasing the rate of the reaction.



$\text{MnO}_2$  acts as a catalyst.



**10. The rate law for a reaction of A, B and C has been found to be rate =  $k[A]^2 [B] [L]^{3/2}$ . How would the rate of reaction change when (i) Concentration of [L] is quadrupled (ii) Concentration of both [A] and [B] are doubled (iii) Concentration of [A] is halved (iv) Concentration of [A] is reduced to (1/3) and concentration of [L] is quadrupled.**

$$\text{Rate} = k[A]^2 [B][L]^{3/2} \quad (1)$$

(i) When  $[L] = [4L]$

$$\text{Rate} = k[A]^2 [B][4L]^{3/2}$$

$$\text{Rate} = 8(k[A]^2 [B][L]^{3/2}) \quad (2)$$

Comparing (1) and (2); rate is increased by 8 times.

(ii) When  $[A] = [2A]$  and  $[B] = [2B]$

$$\text{Rate} = k[2A]^2 [2B][L]^{3/2}$$

$$\text{Rate} = 8(k[A]^2 [B][L]^{3/2}) \quad (3)$$

Comparing (1) and (3); rate is increased by 8 times.

(iii) When  $[A] = [A/2]$

$$\text{Rate} = k\left[\frac{A}{2}\right]^2 [B][L]^{3/2}$$

$$\text{Rate} = \left(\frac{1}{4}\right)(k[A]^2 [B][L]^{3/2}) \quad (4)$$

Comparing (1) and (4); rate is reduced to  $\frac{1}{4}$  times.

(iv) When  $[A] = \left[\frac{A}{3}\right]$  and  $[L] = [4L]$

$$\text{Rate} = k\left[\frac{A}{3}\right]^2 [B][4L]^{3/2}$$

$$\text{Rate} = \left(\frac{8}{9}\right)(k[A]^2 [B][L]^{3/2}) \quad (5)$$

Comparing (1) and (5); rate is reduced to  $\frac{8}{9}$  times.

**11. The rate of formation of a dimer in a second order reaction is  $7.5 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$  at  $0.05 \text{ mol L}^{-1}$  monomer concentration. Calculate the rate constant. [PTA-2]**

For a second order reaction  $k = \frac{R}{[A]^2}$

Where  $k$  = rate constant of reaction;

$R$  = rate of reaction;

$[A]$  = concentration of reactant or products using equation

$$k = \frac{7.5 \times 10^{-3}}{(0.05)^2} = \frac{0.0075}{0.0025} = 3 \text{ mol}^{-1} \text{ L s}^{-1}$$



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**12. For a reaction  $x + y + z \rightarrow \text{products}$  the rate law is given by rate  $k = [x]^{3/2}[y]^{1/2}$  what is the overall order of the reaction and what is the order of the reaction with respect to z.**

$$\text{Rate} = k [x]^{(3/2)} [y]^{(1/2)}$$

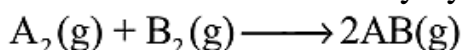
$$\text{Overall order} = \left(\frac{3}{2} + \frac{1}{2}\right) = 2$$

i.e., second order reaction. Since the rate expression does not contain the concentration of z, the reaction is zero order with respect to z.

**13. Explain briefly the collision theory of bimolecular reactions. [QY-22, SRT-23, FRT-24]**

Collision theory is based on the kinetic theory of gases. According to this theory, chemical reactions occur as a result of collisions between the reacting molecules.

Let us understand this theory by considering the following reaction.



If we consider that, the reaction between  $A_2$  and  $B_2$  molecules proceeds through collisions between them, then the rate would be proportional to the number of collisions per second.

Rate  $\propto$  number of molecules colliding per litre per second (collision rate)

The number of collisions is directly proportional to the concentration of both  $A_2$  and  $B_2$ .

Where, Z is a constant. The collision rate in gases can be calculated from kinetic theory of gases.

For a gas at room temperature (298K) and 1 atm pressure, each molecule undergoes approximately  $10^9$  collisions per second, i.e., 1 collision in  $10^{-9}$  second.

Thus, if every collision resulted in reaction, the reaction would be complete in  $10^{-9}$  second. In actual practice this does not happen.

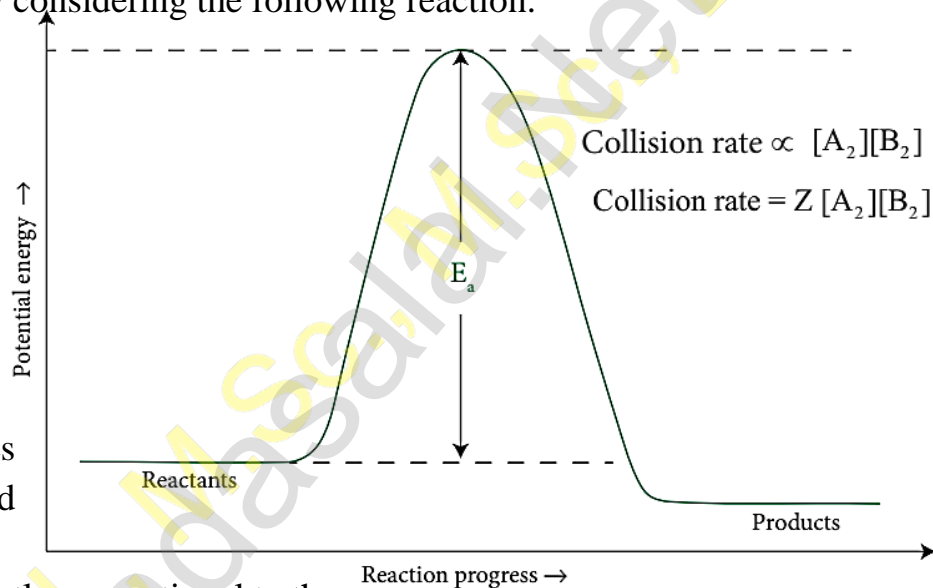
It implies that all collisions are not effective to lead to the reaction. In order to react, the colliding molecules must possess a minimum energy called activation energy.

The molecules that collide with less energy than activation energy will remain intact and no reaction occurs.

Fraction of effective collisions (f) is given by the following expression

$$f = e^{\frac{-E_a}{RT}}$$

To understand the magnitude of collision factor (f), Let us calculate the collision factor (f) for a reaction having activation energy of  $100 \text{ kJ mol}^{-1}$  at 300K.



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$$f = e^{-\left(\frac{100 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}\right)}$$

$$f = e^{-40} \approx 4 \times 10^{-18}$$

✚ Thus, out of  $10^{18}$  collisions only four collisions are sufficiently energetic to convert reactants to products.

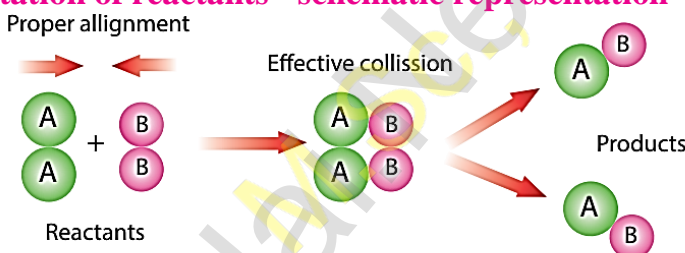
✚ This fraction of collisions is further reduced due to orientation factor i.e., even if the reactant collide with sufficient energy, they will not react unless the orientation of the reactant molecules is suitable for the formation of the transition state.

✚ The figure illustrates the importance of proper alignment of molecules which leads to reaction.

✚ The fraction of effective collisions (f) having proper orientation is given by the steric factor p.

$$\Rightarrow \text{Rate} = p \times f \times \text{collision rate}$$

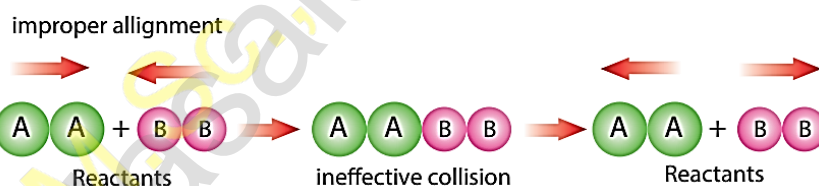
### Orientation of reactants - schematic representation



$$\text{i.e., Rate} = p \times e^{\frac{-E_a}{RT}} \times Z [A_2][B_2] \dots(1)$$

As per the rate law,

$$\text{Rate} = k [A_2] [B_2] \dots(2)$$



✚ Where k is rate constant on comparing equation (1) and (2), the rate constant k is

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

### 14. Write Arrhenius equation and explains the terms involved. [QY-19, QY-22, MAY-22, FUT-23, SRT, MAR-24]

The exact dependence of the rate of a chemical reaction on temperature is given by Arrhenius equation.

$$K = A e^{-E_a/RT}$$

Where,

A = Arrhenius factor or the frequency factor

T = Temperature

R = Gas constant

$E_a$  = Activation energy

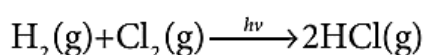
### 15. The decomposition of $\text{Cl}_2\text{O}_7$ at 500K in the gas phase to $\text{Cl}_2$ and $\text{O}_2$ is a first order reaction. After 1 minute at 500K, the pressure of $\text{Cl}_2\text{O}_7$ falls from 0.08 to 0.04 atm. Calculate the rate constant in $\text{s}^{-1}$ .

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]} = \frac{2.303}{1 \text{ min}} \log \frac{[0.08]}{[0.04]} = 2.303 \log 2 = 2.303 \times 0.3010 = 0.6932 \text{ min}^{-1}$$

$$k = \left(\frac{0.6932}{60}\right) \text{ s}^{-1} = 1.153 \times 10^{-2} \text{ s}^{-1}$$

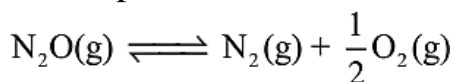
### 16. Give two (or) three examples for zero order reaction. [HY-19, QY-23]

✚ Photochemical reaction between  $\text{H}_2$  and  $\text{I}_2$

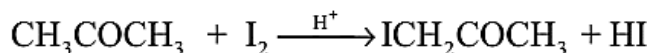


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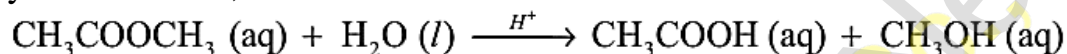
- Decomposition of  $N_2O$  on hot platinum surface



- Iodination of acetone in acid medium is zero order with respect to iodine.

**17.Explain pseudo first order reaction with an example. [QY-19, QY-23]**

Kinetic study of a higher order reaction is difficult to follow, for example, in a study of a second order reaction involving two different reactants; the simultaneous measurement of change in the concentration of both the reactants is very difficult. To overcome such difficulties, a second order reaction can be altered to a first order reaction by taking one of the reactant in large excess, such reaction is called pseudo first order reaction. Let us consider the acid hydrolysis of an ester,



$$\text{Rate} = k [CH_3COOCH_3] [H_2O]$$

If the reaction is carried out with the large excess of water, there is no significant change in the concentration of water during hydrolysis. i.e., concentration of water remains almost a constant. Now, we can define  $k [H_2O] = k'$ ; Therefore the above rate equation becomes

$$\text{Rate} = k' [CH_3COOCH_3]$$

Thus it follows first order kinetics.

**18. Identify the order for the following reactions (i) Rusting of Iron (ii) Radioactive disintegration of  ${}_{92}U^{238}$  (iii)  $2A + 3B \rightarrow \text{products}$ ; rate =  $k [A]^{1/2} [B]^2$** 

(i) Since, Rusting of iron is a very slow reaction, it is difficult its rate.

Hence, it is difficult to write the rate law and difficult to predict the order of rusting of iron.

(ii) Radioactive disintegration of  ${}_{92}U^{238}$  is a first order reaction.

All radio active reaction are first order reactions.

(iii) Order with respect to  $A = \frac{1}{2}$  Order with respect to  $B = 2$

$$\text{Order of overall reaction} = \frac{1}{2} + 2 = \frac{3}{2}$$

**19. A gas phase reaction has energy of activation  $200 \text{ kJ mol}^{-1}$ . If the frequency factor of the reaction is  $1.6 \times 10^{13} \text{ s}^{-1}$ . Calculate the rate constant at  $600\text{K}$ . ( $e^{-40.09} = 3.8 \times 10^{-18}$ )**

$$k = Ae^{-\left(\frac{E_a}{RT}\right)}$$

$$k = 1.6 \times 10^{13} \text{ s}^{-1} e^{-\left(\frac{200 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 600\text{K}}\right)} = 1.6 \times 10^{13} \text{ s}^{-1} e^{-40.1}$$

$$k = 1.6 \times 10^{13} \text{ s}^{-1} \times 3.8 \times 10^{-18} = 6.21 \times 10^{-5} \text{ s}^{-1}$$

**20. For the reaction  $2x + y \rightarrow L$ . Find the rate law from the following data.**

[x] (M)	[y] (M)	Rate ( $M \text{ s}^{-1}$ )
0.2	0.02	0.15
0.4	0.02	0.30
0.4	0.08	1.20

$$\text{Rate} = k[x]^n[y]^m$$

$$0.15 = k[0.2]^n[0.02]^m \quad (1)$$

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$$0.30 = k[0.4]^n [0.02]^m \quad (2)$$

$$1.20 = k[0.4]^n [0.08]^m \quad (3)$$

By dividing equation  $\frac{(3)}{(2)}$

$$\frac{1.2}{0.3} = \frac{k[0.4]^n [0.08]^m}{k[0.4]^n [0.02]^m}$$

$$4 = \left(\frac{[0.08]}{[0.02]}\right)^m = (4)^m$$

$$\therefore m = 1$$

$$\text{Rate} = k[x]^m [y]^n$$

$$0.15 = k[0.2]^m [0.02]^n$$

$$\frac{0.15}{[0.2]^m [0.02]^n} = k$$

$$k = 37.5 \text{ mol L}^{-1}\text{s}^{-1}$$

By dividing equation  $\frac{(2)}{(1)}$

$$\frac{0.30}{0.15} = \frac{k[0.4]^n [0.02]^m}{k[0.2]^n [0.02]^m}$$

$$2 = \left(\frac{[0.4]}{[0.2]}\right)^n = (2)^n$$

$$\therefore n = 1$$

**21. How do concentrations of the reactant influence rate of reaction?**

- ✚ The rate of a reaction increases with the increase in the concentration of the reactants.
- ✚ The effect of concentration is explained on the basis of collision theory of reaction rates.
- ✚ Higher the concentration, greater is the possibility for collision and hence the rate.
- ✚ According to this theory, the rate of a reaction depends upon the number of collisions between the reacting molecules.

**22. How do nature of the reactant influence rate of reaction?**

- ✚ The chemical reaction involves breaking of certain existing bonds of the reactant and forming new bonds which lead to the product.
- ✚ The net energy involved in this process is dependent on the nature of the reactant and hence the rates are different for different reactants.

Let us compare the following two reactions that you carried out in volumetric analysis.

- ✚ Redox reaction between ferrous ammonium sulphate (FAS) and  $\text{KMnO}_4$
- ✚ Redox reaction between oxalic acid and  $\text{KMnO}_4$
- ✚ The oxidation of oxalate ion by  $\text{KMnO}_4$  is relatively slow compared to the reaction between  $\text{KMnO}_4$  and  $\text{Fe}^{2+}$ . In fact heating is required for the reaction between  $\text{KMnO}_4$  and Oxalate ion and is carried out at around  $60^\circ\text{C}$ .
- ✚ The physical state of the reactant also plays an important role to influence the rate of reactions. Gas phase reactions are faster as compared to the reactions involving solid or liquid reactants. For example, reaction of sodium metal with iodine vapours is faster than the reaction between solid sodium and solid iodine.

**23. The rate constant for a first order reaction is  $1.54 \times 10^{-3} \text{ s}^{-1}$ . Calculate its half life time.**

[PTA-6, SEP-20]

$$t_{1/2} = 0.693 / k = 0.693 / (1.54 \times 10^{-3} \text{ sec}^{-1}) = 450 \text{ seconds.}$$

**24. The half life of the homogeneous gaseous reaction  $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$  which obeys first order kinetics is 8.0 minutes. How long will it take for the concentration of  $\text{SO}_2\text{Cl}_2$  to be reduced to 1% of the initial value?**

$$\text{We know that, } k = \frac{0.6932}{t_1} \quad k = \frac{0.6932}{8.0 \text{ minutes}} = 0.087 \text{ min}^{-1}$$

$$\text{For a first order reaction, } t = \frac{2.303}{0.087 \text{ min}^{-1}} \log \left(\frac{100}{1}\right) \quad t = 52.93 \text{ min}$$



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**25. The time for half change in a first order decomposition of a substance A is 60 seconds.**

**Calculate the rate constant. How much of A will be left after 180 seconds?**

(i) Order of a reaction = 1;  $t_{\frac{1}{2}} = 60$  seconds;  $k = ?$

We know that,  $k = \frac{0.6932}{t_{\frac{1}{2}}} = 0.01155 \text{ s}^{-1}$

(ii)  $[A_0] = 100\%$ ;  $t = 180 \text{ s}$ ;  $k = 0.01155 \text{ s}^{-1}$ ;  $[A] = ?$

For the first order reaction

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$0.01155 = \frac{2.303}{180} \log \frac{[A_0]}{[A]}$$

$$\frac{0.01155 \times 180}{2.303} = \log \frac{100}{[A]}$$

$$0.9027 = \log 100 - \log [A]$$

$$\log [A] = 2 - 0.9027$$

$$[A] = \text{antilog of } (1.0973) = 12.5\%$$

After 180 second 12.5% of A will be left over.

**26. A zero order reaction is 20% complete in 20 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?**

Let  $A = 100\text{M}$ ,  $[A_0] - [A] = 20\text{M}$ ,

For the zero order reaction

$$K = \left( \frac{[A_0] - [A]}{t} \right) = \left( \frac{20\text{M}}{20 \text{ min}} \right) = 1\text{M min}^{-1}$$

Rate constant for a reaction = **1M min<sup>-1</sup>**

To calculate the time for 80% of completion

$k = 1\text{M min}^{-1}$ ,  $[A_0] = 100\text{M}$ ,  $[A_0] - [A] = 80\text{M}$ ,  $t = ?$

Therefore,

$$t = \left( \frac{[A_0] - [A]}{k} \right) = \left( \frac{80\text{M}}{1 \text{ M min}^{-1}} \right) = 80 \text{ min.}$$

**27. The activation energy of a reaction 22.5 kcal mol<sup>-1</sup> and the value of rate constant at 40°C is 1.8 x 10<sup>-5</sup> s<sup>-1</sup>. Calculate the frequency factor, A.**

Here, we are given that

$E_a = 22.5 \text{ kcal mol}^{-1} = 22500 \text{ cal mol}^{-1}$ ,  $T = 40^\circ\text{C} = 40 + 273 = 313\text{K}$ ,  $k = 1.8 \times 10^{-5} \text{ sec}^{-1}$

Substituting the values in the equation.

$$\log A = \log k + \left( \frac{E_a}{2.303RT} \right) = \log (1.8 \times 10^{-5}) + \left( \frac{22500}{2.303 \times 1.987 \times 313} \right)$$

$$\log A = \log (1.8)(-5) + (15.7089) = 10.9642$$

$$A = \text{antilog } (10.9642) = 9.208 \times 10^{10} \text{ collisions s}^{-1}$$

**28. Benzene diazonium chloride in aqueous solution decomposes according to the equation  $\text{C}_6\text{H}_5\text{N}_2\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{N}_2$  starting with an initial concentration of 10g L<sup>-1</sup>, the volume of N<sub>2</sub> gas obtained at 50°C at different intervals of time was found to be as under:**

t (min)	6	12	18	24	30	∞
Vol. of N <sub>2</sub> (ml)	19.3	32.6	41.3	46.5	50.4	58.3

**Show that the above reaction follow the first order kinetics. What is the value of the rate constant?**

For a first order reaction  $k = \frac{2.303}{t} \log \frac{[A_0]}{[A]} = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$

In the present case,  $V_\infty = 58.3 \text{ ml}$ .

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The value of  $k$  at different time can be calculated as follows.

t (min)	$V_t$	$V_\infty - V_t$	$\frac{2.303}{t} \log \frac{[A_0]}{[A]}$
6	19.3	$58.3 - 19.3 = 39.0$	$k = \frac{2.303}{6} \log \left( \frac{58.3}{39} \right) = 0.0670 \text{ min}^{-1}$
12	32.6	$58.3 - 32.6 = 25.7$	$k = \frac{2.303}{12} \log \left( \frac{58.3}{25.7} \right) = 0.0683 \text{ min}^{-1}$
18	41.3	$58.3 - 41.3 = 17.0$	$k = \frac{2.303}{18} \log \left( \frac{58.3}{17} \right) = 0.0685 \text{ min}^{-1}$
24	46.5	$58.3 - 46.5 = 11.8$	$k = \frac{2.303}{24} \log \left( \frac{58.3}{11.8} \right) = 0.0666 \text{ min}^{-1}$

Since  $k$  values are nearly constant, the reaction follows first order kinetics. The mean value of  $k = 0.0676 \text{ min}^{-1}$

**29. From the following data, show that the decomposition of hydrogen peroxide is a reaction of the first order:**

t (min)	0	10	20
V (ml)	46.1	29.8	19.3

Where  $t$  is the time in minutes and  $V$  is the volume of standard  $\text{KMnO}_4$  solution required for titrating the same volume of the reaction mixture.

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]} \quad k = \frac{2.303}{24} \log \left( \frac{V_0}{V_t} \right)$$

In the present case,  $V_0 = 46.1 \text{ ml}$ .

The value of  $k$  at each instant can be calculated as follows:

t (min)	$V_t$	$k = \frac{2.303}{24} \log \left( \frac{V_0}{V_t} \right)$
10	29.8	$k = \frac{2.303}{10} \log \left( \frac{46.1}{29.8} \right) = 0.0436 \text{ min}^{-1}$
20	19.3	$k = \frac{2.303}{20} \log \left( \frac{46.1}{19.3} \right) = 0.0435 \text{ min}^{-1}$

Thus, the value of  $k$  comes out to be nearly constant. Hence it is a reaction of the first order.

**30. A first order reaction is 40% complete in 50 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete? [GMQ-19]**

For the first order reaction  $k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$

Assume,  $[A_0] = 100\%$ ,  $t = 50$  minutes

Therefore,  $[A] = 100 - 40 = 60$

$$k = \frac{2.303}{50} \log \left( \frac{100}{60} \right) = 0.010216 \text{ min}^{-1}$$

Hence the value of the rate constant is  **$0.010216 \text{ min}^{-1}$**

$t = ?$ , when the reaction is 80% completed,  $[A] = 100 - 80 = 20\%$

from above,  $k = 0.010216 \text{ min}^{-1}$

$$t = \frac{2.303}{0.010216} \log \left( \frac{100}{20} \right) = 157.58 \text{ min}$$

The time at which the reaction will be 80% complete is **157.58 min.**

### Evaluate Yourself

**1. Write the rate expression for the following reactions, assuming them as elementary reactions.**

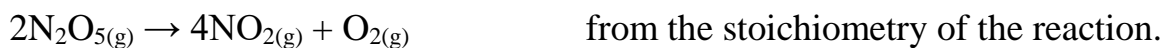


(i) Rate =  $k [A]^3 [B_2]^5$

(ii) Rate =  $k [X_2][Y_2]$

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2. Consider the decomposition of  $N_2O_5(g)$  to form  $NO_2(g)$  and  $O_2(g)$ . At a particular instant,  $N_2O_5$  disappears at a rate of  $2.5 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$ . At what rates are  $NO_2$  and  $O_2$  formed? What is the rate of the reaction?

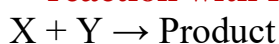


$$\frac{d[N_2O_5]}{dt} = 2.5 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$-\frac{1}{2} \frac{d[N_2O_5]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt} = 2 \left( -\frac{d[N_2O_5]}{dt} \right) = 2 \times 2.5 \times 10^{-2} = 5 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$-\frac{1}{2} \frac{d[N_2O_5]}{dt} = \frac{d[O_2]}{dt} = \frac{1}{2} \left( -\frac{d[N_2O_5]}{dt} \right) = \frac{1}{2} \times 2.5 \times 10^{-2} = 1.25 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$$

3. For a reaction,  $X + Y \rightarrow \text{Product}$  quadrupling  $[x]$ , increases the rate by a factor of 8. Quadrupling both  $[x]$  and  $[y]$  increases the rate by a factor of 16. Find the order of the reaction with respect to  $x$  and  $y$ . what is the overall order of the reaction?



$$\text{Rate law is Rate} = k [X]^m [Y]^n = 1 \quad (1)$$

Quadrupling  $[X]$  ie  $[4X]$ , Rate = 8

$$k [4X]^m [Y]^n = 8$$

$$k 4^m [X]^m [Y]^n = 8 \quad (2)$$

Quadrupling  $[X]$  and  $[Y]$  ie  $[4X]$  and  $[4Y]$ , Rate = 16

$$k [4X]^m [4Y]^n = 16$$

$$k 4^m [X]^m 4^n [Y]^n = 16 \quad (3)$$

Dividing (2) by (1)

$$\frac{k 4^m [X]^m [Y]^n}{k [X]^m [Y]^n} = \frac{8}{1}$$

$$\therefore 4^m = 8$$

$$(2^2)^m = 2^3$$

$$2m = 3$$

$$m = \frac{3}{2} = 1.5$$

$\therefore$  Order of the reaction w.r.t X is 1.5

Dividing (3) by (2)

$$\frac{k 4^m [X]^m 4^n [Y]^n}{k 4^m [X]^m [Y]^n} = \frac{16}{8}$$

$$\therefore 4^n = 2$$

$$(2^2)^n = 2^1$$

$$2n = 1$$

$$n = \frac{1}{2} = 0.5$$

$\therefore$  Order of the reaction w.r.t Y is 0.5

Overall order of the reaction =  $m + n = 1.5 + 0.5 = 2$

4. Find the individual and overall order of the following reaction using the given data.



Experiment Number	Initial concentration		Initial rate NOCl mol L <sup>-1</sup> s <sup>-1</sup>
	NO	Cl <sub>2</sub>	
1	0.1	0.1	$7.8 \times 10^{-5}$
2	0.2	0.1	$3.12 \times 10^{-4}$
3	0.2	0.3	$9.36 \times 10^{-4}$

For experiment 1, the rate law is, Rate 1 =  $k [NO]^m [Cl_2]^n$

$$7.8 \times 10^{-5} = k [0.1]^m [0.1]^n \dots \dots \dots (1)$$

For experiment 2, the rate law is, Rate 2 =  $k [NO]^m [Cl_2]^n$

$$3.12 \times 10^{-4} = k [0.2]^m [0.1]^n \dots \dots \dots (2)$$

For experiment 3, the rate law is, Rate 3 =  $k [NO]^m [Cl_2]^n$

$$9.36 \times 10^{-4} = k [0.2]^m [0.3]^n \dots \dots \dots (3)$$

Dividing (2) by (1)

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$$\frac{3.12 \times 10^{-4}}{7.8 \times 10^{-5}} = \frac{k[0.2]^m[0.1]^n}{k[0.1]^m[0.1]^n} \quad 4 = \left(\frac{0.2}{0.1}\right)^m \quad 4 = 2^m$$

$$\therefore 2^2 = 2^m \quad \therefore m = 2$$

Order w.r.t NO is 2. Dividing (3) by (2)

$$\frac{9.36 \times 10^{-4}}{3.12 \times 10^{-4}} = \frac{k[0.2]^m[0.3]^n}{k[0.2]^m[0.1]^n} \quad 3 = \left(\frac{0.3}{0.1}\right)^n \quad 3 = 3^n$$

$$\therefore 3^1 = 3^n \quad \therefore n = 1$$

Order w.r.t Cl<sub>2</sub> is 1. Overall order of the reaction = m + n = 2 + 1 = 3

**5. In a first order reaction A → products, 60% of the given sample of A decomposes in 40 min. what is the half life of the reaction?**

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]} = \frac{2.303}{40} \log \frac{[100]}{[40]} = \frac{2.303}{40} \log 2.5 = \frac{2.303}{40} \times 0.3979 = 0.0229 \text{ min}^{-1}$$

$$t_{\frac{1}{2}} = \frac{0.6932}{k} = \frac{0.6932}{0.0229} = 30.27 \text{ min}$$

**6. The rate constant for a first-order reaction is 2.3 x 10<sup>-4</sup> s<sup>-1</sup>. If the initial concentration of the reactant is 0.01 M. what concentration will remain after 1 hour?**

Rate constant of a first order reaction k = 2.3 x 10<sup>-4</sup> s<sup>-1</sup>

Initial concentration of the reactant [A<sub>0</sub>] = 0.01 M

Concentration will remain after 1 hour [A] = ?

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]} \quad 2.3 \times 10^{-4} = \frac{2.303}{1 \text{ hour}} \log \frac{[0.01]}{[A]}$$

$$\frac{2.3 \times 10^{-4} \times 1}{2.303} = \log [0.01] - \log [A]$$

$$9.986 \times 10^{-5} = -2 - \log [A]$$

$$11.986 \times 10^{-5} = - \log [A]$$

$$[A] = \text{antilog} (-11.986 \times 10^{-5}) = 0.997 \text{ M}$$

**7. Hydrolysis of an ester in an aqueous solution was studied by titrating the liberated carboxylic acid against sodium hydroxide solution. The concentrations of the ester at different time intervals are given below.**

Time (min)	0	30	60	90
Ester concentration mol L <sup>-1</sup>	0.85	0.80	0.754	0.71

**Show that, the reaction follows first order kinetics.**

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$k_1 = \frac{2.303}{30} \log \frac{0.85}{0.80} = \frac{2.303}{30} \log 1.0625 = \frac{2.303}{30} \times 0.0263 = 2.01 \times 10^{-3} \text{ min}^{-1}$$

$$k_2 = \frac{2.303}{60} \log \frac{0.85}{0.754} = \frac{2.303}{60} \log 1.127 = \frac{2.303}{60} \times 0.0519 = 1.992 \times 10^{-3} \text{ min}^{-1}$$

$$k_3 = \frac{2.303}{90} \log \frac{0.85}{0.71} = \frac{2.303}{90} \log 1.197 = \frac{2.303}{90} \times 0.0781 = 2 \times 10^{-3} \text{ min}^{-1}$$

Since all the k values are constants, the reaction follows first order kinetics.

**8. For a first-order reaction the rate constant at 500K is 8 x 10<sup>-4</sup> s<sup>-1</sup>. Calculate the frequency factor, if the energy of activation for the reaction is 190 kJ mol<sup>-1</sup>.**

$$k = 8 \times 10^{-4} \text{ s}^{-1}; T = 500\text{K}; E_a = 190 \text{ kJ mol}^{-1}; A = ?$$

According to Arrhenius equation,  $k = A e^{\frac{-E_a}{RT}}$        $\log k = \log A - \frac{E_a}{2.303 RT}$

$$\log A = \log k + \frac{E_a}{2.303 RT} = \log (8 \times 10^{-4} \text{ s}^{-1}) + \left( \frac{190 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 500 \text{ K}} \right)$$

$$\log A = -3.096 + 19.8463 = 16.7493$$

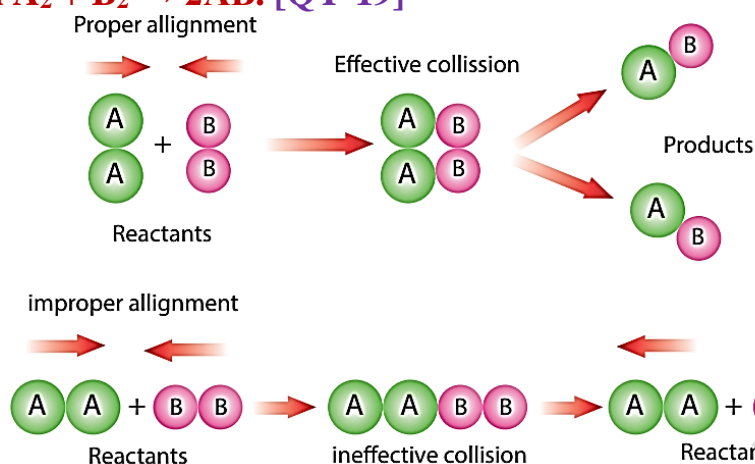
$$A = \text{Antilog} (16.7493) = 5.6 \times 10^{16} \text{ s}^{-1} \text{ (approximately)}$$



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## GOVERNMENT EXAM QUESTION PAPER

1. Give the schematic representation of proper and improper alignment of reactant for a general reaction  $A_2 + B_2 \rightarrow 2AB$ . [QY-19]



2. Give examples for the first order reaction. [MAY-22, SRT-24]

- (i) Decomposition of dinitrogen pentoxide  $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$
- (ii) Decomposition of sulphurylchloride;  $SO_2Cl_2(l) \longrightarrow SO_2(g) + Cl_2(g)$
- (iii) Decomposition of the  $H_2O_2$  in aqueous solution;  $H_2O_2(aq) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$
- (iv) Isomerisation of cyclopropane to propene.

3. The rate of reaction  $x + 2y \rightarrow$  product is  $4 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ , if  $[x] = [y] = 0.2 \text{ M}$  and rate constant at  $400\text{K}$  is  $2 \times 10^{-2} \text{ s}^{-1}$ , what is the overall order of the reaction? [SEP-20]

$$\text{Rate} = k [x]^n [y]^m$$

$$4 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1} = 2 \times 10^{-2} \text{ s}^{-1} (0.2 \text{ mol L}^{-1})^n (0.2 \text{ mol L}^{-1})^m$$

$$\frac{4 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}}{2 \times 10^{-2} \text{ s}^{-1}} = (0.2)^n (0.2)^m \quad (0.2 \text{ mol L}^{-1}) = (0.2)^{n+m}$$

Compare the powers on both sides, we get  $n + m = 1$ ,  $\therefore$  The overall order of the reaction is 1.

4. Show that for a first order reaction the time required for 99.9% completion is about 10 times its half life period. [QY-19, QY-23]

Let

$$[A_0] = 100;$$

$$\text{when } t = t_{99.9\%}; [A] = (100 - 99.9) = 0.1$$

$$k = \frac{2.303}{t} \log \left( \frac{[A_0]}{[A]} \right)$$

$$t_{99.9\%} = \frac{2.303}{k} \log \left( \frac{100}{0.1} \right)$$

$$t_{99.9\%} = \frac{2.303}{k} \log 1000$$

$$t_{99.9\%} = \frac{2.303}{k} (3)$$

$$t_{99.9\%} = \frac{6.909}{k}$$

$$t_{99.9\%} \approx 10 \times \frac{0.69}{k}$$

$$t_{99.9\%} \approx 10 t_{1/2}$$

5. Write the differences between rate and rate constant of a reaction. [PTA-3, AUG-21]

S. NO.	RATE OF A REACTION	RATE CONSTANT OF A REACTION
1	It is measured as decrease in the concentration of the reactants or increase in the concentration of products.	It is equal to the rate of reaction, when the concentration of each of the reactants is unity
2	It depends on the initial concentration of reactants.	It does not depend on the initial concentration of reactants.

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<b>3</b>	It generally decreases with the progress of reaction	It does not depend on the progress of reaction
<b>4</b>	Its unit is $\text{mol L}^{-1}\text{cm}^{-1}$ .	It changes according to order of reaction.

**6. What is an order of a reaction? [MAR-24]**

Order of a reaction is the sum of the powers of concentration terms involved in the experimentally determined rate law. It can be zero (or) fractional (or) integer values. It is assigned for a overall reaction.

**7. Mention the factors that affected the rate of chemical reaction. [QY-23]**

The rate of a reaction is affected by the following factors,

- + Nature and state of the reactant
- + Concentration of the reactant
- + Surface area of the reactant
- + Presence of a catalyst