





The energy required to form the intermediate called activated complex is known as activation energy. Activation energy = Threshold energy – Average energy of the reactants

Decreases

Decreases

Decreases

Gibbs energy ( $\Delta G$ ) of a reaction?

CBSE (AI) 2017

No effect

Rate of reaction

Q. 1. What do you understand by 'Rate of reaction'?

The change in the concentration of any one of the reactants or products per unit time is termed as the rate of reaction.

Average rate

Average rate becomes equal to instantaneous rate when the interval,  $\Delta t$ , approaches zero, i.e., it becomes infinitesimally small. Thus,

$$r_{inst} \text{ i.e., } \left( \frac{dx}{dt} \right) = \lim_{\Delta t \rightarrow 0} \frac{\Delta x}{\Delta t}.$$

Instantaneous rate

Instantaneous rate

Instantaneous rate is measured over a very small interval of time, hence, it does not change when a part of solution is taken out.

For the reaction  $X_2 + 3Y_2 \rightarrow 2XY_3$ , the rate of reaction is measured as  $-\frac{d[X_2]}{dt} = -\frac{1}{3} \frac{d[Y_2]}{dt} = +\frac{1}{2} \frac{d[XY_3]}{dt}$

HOTS

Rate =

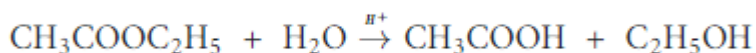
$$\text{Rate} = - \frac{d [X_2]}{dt} = - \frac{1}{3} \frac{d [Y_2]}{dt} = + \frac{1}{2} \frac{d [XY_3]}{dt}$$

$$\text{Rate of disappearance of } Y_2 = - \frac{d[Y_2]}{dt} = - 3 \frac{d[X_2]}{dt} = + \frac{3}{2} \frac{d[XY_3]}{dt}$$

Rate of disappearance of  $Y_2 = - \frac{d[Y_2]}{dt} = - 3 \frac{d[X_2]}{dt} = + \frac{3}{2} \frac{d[XY_3]}{dt}$

Rate of appearance of  $XY_3 = + \frac{2}{3} \frac{d[Y_2]}{dt} = + \frac{2}{3} \frac{d[X_2]}{dt}$

Acid catalysed hydrolysis of ethyl acetate:

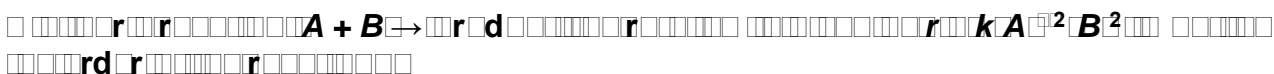


$$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5]$$

Rate of disappearance of ethyl acetate is directly proportional to its concentration.

Rate of appearance of ethanol is same as rate of disappearance of ethyl acetate.

If the reaction is an elementary reaction, order is same as molecularity.



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Order of reaction =  $\frac{1}{2} + 2 = \frac{5}{2}$

$$\text{Order of reaction} = \frac{1}{2} + 2 = \frac{5}{2}$$

Rate of disappearance of  $\text{A} = - \frac{d[\text{A}]}{dt}$  and rate of appearance of  $\text{C} = + \frac{d[\text{C}]}{dt}$

Rate of disappearance of  $\text{B} = - \frac{d[\text{B}]}{dt}$

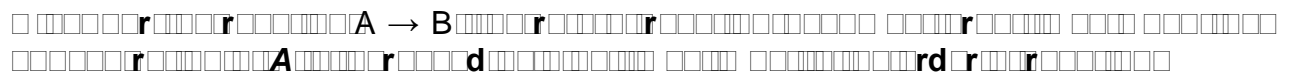
A bimolecular reaction may become kinetically of first order if one of the reactants is in excess.

Rate of disappearance of  $\text{A} = - \frac{d[\text{A}]}{dt}$  and rate of appearance of  $\text{C} = + \frac{d[\text{C}]}{dt}$

Rate law is an experimental law. On the other hand, law of mass action is a theoretical law based on the balanced chemical reaction.

Rate of disappearance of  $\text{A} = - \frac{d[\text{A}]}{dt}$  and rate of appearance of  $\text{C} = + \frac{d[\text{C}]}{dt}$

Specific reaction rate is the rate of reaction when the molar concentration of each of the reactants is unity.



**HOTS**

□□□□

Let,  $r = k [A]^n$  ... (i)

Given,  $3r = k [9A]^n$  ... (ii)

Dividing equation (ii) by (i), we get

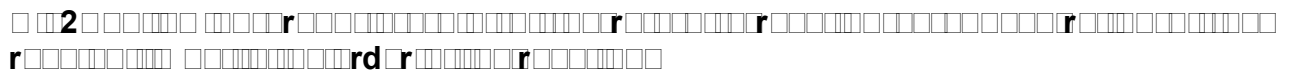
$$\frac{3r}{r} = \frac{k/9A^n}{k/A^n} = \frac{9^n k/A^n}{k/A^n}$$

$$3 = 9^n \quad \text{or} \quad 3^1 = 3^{2n}$$

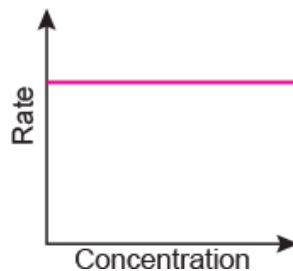
$$\Rightarrow 2n = 1 \quad \text{or} \quad n = \frac{1}{2}$$

$$\therefore \text{Rate, } r = k[A]^{1/2}$$

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



**HOTS**



Zero order reaction, as the rate of reaction is independent of concentration of reactant.

Rate of reaction  $\propto [A][B]^2$

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**HOTS**

During an elementary reaction, the number of atoms or ions colliding to react is referred to as molecularity. Had this been an elementary reaction the order of reaction with respect to B would have been 1, but in the given rate law it is  $\frac{3}{2}$ . This indicates that the reaction is not an elementary reaction.

Rate of reaction  $\propto [A]^2[B]$

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As  $t_{75\%} = 2t_{50\%}$

Therefore, it is a first order reaction.

Rate of reaction  $\propto [A][B]$

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At higher temperatures, larger fraction of colliding particles can cross the energy barrier (*i.e.*, the activation energy), which leads to faster rate.

Rate of reaction  $\propto [A][B]$

**NCERT Exemplar**

The probability of more than three molecules colliding simultaneously is very small. Hence, possibility of molecularity being three is very low.

Rate of reaction  $\propto [A][B]$

**NCERT Exemplar**

Thermodynamically the conversion of diamond to graphite is highly feasible but this reaction is very slow because its activation energy is high.

Rate of reaction  $\propto [A][B]$

**HOTS**



Order of reaction is the sum of powers of concentration of reactants in the rate law expression.

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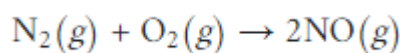
□

Order of reaction is the sum of powers of concentration of reactants in the rate law expression.

□ The reaction which takes place in a single step is called an elementary reaction.

□ For example,

The reaction which takes place in a single step is called an elementary reaction. For example,



□ 2 molecules of reactants.

CBSE (AI) 2009; (F) 2010

The rate of reaction may be defined as the decrease in concentration of reactant or increase in concentration of product per unit time.

For a hypothetical reaction,  $R \rightarrow P$

$$\text{Rate of reaction} = \frac{-\Delta[R]}{\Delta t} = \frac{+\Delta[P]}{\Delta t}$$

differences between 'order of reaction' and 'molecularity of reaction'.

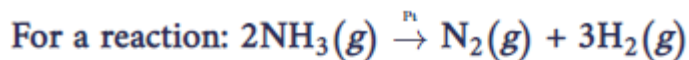
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Differences between order and molecularity of reaction:

Order	Order	Molecularity
i	It is the sum of the powers of the concentration of the reactants in the rate law expression.	It is the number of reacting species taking part in an elementary reaction, which must collide simultaneously so as to result into a chemical reaction.
ii	It is determined experimentally.	It is a theoretical concept.
iii	It can be zero or a fraction.	It cannot be zero or a fraction.
iv	Order is applicable to elementary as well as complex reactions.	Molecularity is applicable only for elementary reactions. For complex reactions it has no meaning.

□





Rate =  $k$

- i. Write the order and molecularity of this reaction.
- ii. Write the unit of  $k$ .

CBSE South 2016

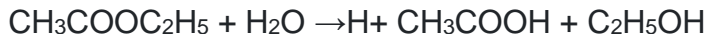
Answer

- Order, bimolecular
- $\text{mol L}^{-1} \text{s}^{-1}$

Q. A reaction which is not truly of first order but under certain conditions becomes a reaction of first order is called pseudo first order reaction, e.g., acid hydrolysis of ethyl acetate.

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Rate  $\propto [\text{CH}_3\text{COOC}_2\text{H}_5]$  as  $\text{H}_2\text{O}$  is in excess.

Q. A reaction which is not truly of first order but under certain conditions becomes a reaction of first order is called pseudo first order reaction, e.g., acid hydrolysis of ethyl acetate.

CBSE Delhi 2014

The half life ( $t_{1/2}$ ) of a reaction is the time in which the concentration of reactant is reduced to one half of its initial concentration  $[R]_0$ .

For a first order reaction,  $t_{1/2} = \frac{0.693}{k}$ , i.e., independent of  $[R]_0$ .

For a zero order reaction,  $t_{1/2} = \frac{[R]_0}{2k}$ , i.e.,  $t_{1/2} \propto [R]_0$ .

Answer the following questions:

Q. A



$$\frac{r'}{r} = \frac{k [R]^2}{4k [R]^2} = \frac{1}{4}$$

$r' = \frac{1}{4}r$ , i.e., rate of reaction becomes  $\frac{1}{4}$ th of the initial rate.

The unit of rate constant is  $\text{mol}^{-1} \text{L s}^{-1}$ .

Due to high activation energy for the reaction.

Rate =  $k[A_2]^0[B_2]^0$  or Rate =  $k$

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CBSE (AI) 2017

Rate =  $k[A_2]^0[B_2]^0$  or Rate =  $k$

Due to high activation energy for the reaction.

CBSE (F) 2016

Due to high activation energy for the reaction.

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$\frac{t_{99.9\%}}{t_{50\%}} = \frac{\frac{2.303}{k} \log \frac{100}{100 - 99.9}}{\frac{2.303}{k} \log \frac{100}{100 - 50}} = \frac{\log \frac{100}{0.1}}{\log \frac{100}{50}}$$

$$= \frac{\log 10^3}{\log 2} = \frac{3 \log 10}{0.3010}$$

$$\frac{t_{99.9\%}}{t_{50\%}} = \frac{30}{3.01} \simeq 10$$

$$t_{99.9\%} = 10t_{50\%}$$

Due to high activation energy for the reaction.



$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]} \quad \text{as} \quad [R] = \frac{[R]_0}{10}$$

$$\therefore t = \frac{2.303}{k} \log \frac{[R]_0}{\frac{[R]_0}{10}} = \frac{2.303}{60} \times \log 10 = \frac{2.303}{60} \times 1 = 3.838 \times 10^{-2} \text{ s}$$

2.  $k = 0.0030 \text{ mol L}^{-1} \text{ s}^{-1}$ ,  $[R]_0 = 0.10 \text{ M}$ ,  $[R] = 0.075 \text{ M}$

CBSE (F) 2010

□□□□□

Given:  $[R_0] = 0.10 \text{ M}$        $[R] = 0.075 \text{ M}$

$$k = 0.0030 \text{ mol L}^{-1} \text{ s}^{-1}, t = ?$$

We know that  $k = \frac{[R_0] - [R]}{t}$

or  $t = \frac{[R_0] - [R]}{k} = \frac{0.10 - 0.075}{0.0030} = 8.33 \text{ s.}$

□□□□□

2.  $k = 0.0030 \text{ mol L}^{-1} \text{ s}^{-1}$ ,  $[R]_0 = 0.10 \text{ M}$ ,  $[R] = 0.075 \text{ M}$

NCERT Exemplar

The rate of reaction depends on the concentration of reactants. As the reaction progresses, reactants start getting converted to products so the concentration of reactants decreases hence the rate of reaction decreases.

2. A complex reaction proceeds through several elementary reactions. Number of molecules involved in each elementary reaction may be different, i.e., the molecularity of each step may be different. Therefore, discussion of molecularity of overall complex reaction is meaningless. On the other hand, order of a complex reaction is determined

NCERT Exemplar

by the slowest step in its mechanism and is not meaningless even in the case of complex reactions.

Example:  $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$

**NCERT Exemplar**

No, the molecularity can never be equal to zero or a fractional number. Molecularity is the number of molecules involved in each elementary reaction which may be different, i.e., the molecularity of each step may be different.

Example:  $\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O}$

Example:

Symbol	Definition	Notes
$r$	Rate of reaction is the change in concentration of a reactant or product in a unit interval of time.	It is the rate of reaction when the molar concentration of each of the reactants is unity.
$k$	The rate of reaction at any instant of time depends upon the molar concentrations of the reactants at that time.	The rate constant does not depend upon the concentrations of the reactants.
Units	Its units are always $\text{mol litre}^{-1} \text{time}^{-1}$ .	Its units depend upon the order of reaction.



Rate of reaction =  $k[\text{Cl}_2][\text{NO}]^2$

Order with respect to  $\text{Cl}_2 = 1$ , Order with respect to  $\text{NO} = 2$ ,

Overall order =  $1 + 2 = 3$

Example:  $\text{A} + \text{B} \rightarrow \text{C}$

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

Example:

- i. Order =  $\frac{1}{2} + \frac{3}{2} = 2$ , i.e., second order.
- ii. Order =  $\frac{3}{2} + (-1) = \frac{1}{2}$ , i.e., half order.



$$\frac{dx}{dt} = k [\text{Ester}] [\text{H}^+]^0$$

(i) The rate of reaction will be doubled. (ii) No effect on rate.

NCERT Exemplar

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

For completion,  $[R] = 0$

$$\therefore t = \frac{[R]_0}{k}$$

$$k = 0.0030 \text{ mol L}^{-1}\text{s}^{-1}, [R]_0 = 0.10 \text{ M}, [R] = 0.075 \text{ M}$$

We know that

$$[R] = -kt + [R]_0$$

$$0.075 = -0.0030t + 0.10$$

$$\Rightarrow 3t = 100 - 75 \Rightarrow t = 8.33 \text{ seconds}$$









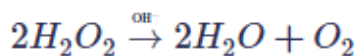




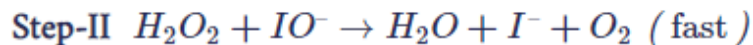
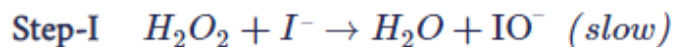


$R]_0 - [R] = 100 - 83.5 = 16.5$ , i.e., 16.5% of initial concentration has changed into products.

2



This reaction takes place in two steps as given below:



- i. Write the rate law expression and determine the order of reaction w.r.t.  $H_2O_2$ .
- ii. What is the molecularity of each individual step?

i. Rate =  $k [H_2O_2]^1 [I^-]^1$

Order of reaction w.r.t  $H_2O_2 = 1$

ii. Molecularity of step I = 2 and step II = 2.



Thus at equilibrium,

$$\begin{aligned}[\text{NO}] &= 2x = 2 \times 6.324 \times 10^{-4} \\ &= 12.648 \times 10^{-4} \text{ mol L}^{-1}\end{aligned}$$

$$\begin{aligned}[\text{N}_2] &= 0.8 - 6.324 \times 10^{-4} \text{ mol L}^{-1} \\ &= 0.799 \text{ mol L}^{-1}\end{aligned}$$

$$[\text{O}_2] = 0.2 - 6.324 \times 10^{-4} \text{ mol L}^{-1}$$

$$= \dots\dots\dots$$

.....  
.....

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T} \text{ K}$$

.....  
.....

$$\dots\dots\dots R \dots\dots\dots$$

**CBSE Delhi 2016**

.....

Comparing the equation,  $\log k = 14.2 - \frac{1.0 \times 10^4}{T} \text{ K}$  with the equation,  $\log k = \log A - \frac{E_a}{2.303 RT}$ , we get

$$\frac{E_a}{2.303 RT} = \frac{1.0 \times 10^4 K}{T} \text{ or } E_a = 1.0 \times 10^4 \text{ K} \times 2.303 \times R$$

$$E_a = 1.0 \times 10^4 \text{ K} \times 2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 19.1471 \times 10^4 \text{ J mol}^{-1}$$

$$= 191.47 \text{ kJ mol}^{-1}$$

$$\text{For a first order reaction, } t_{1/2} = \frac{0.693}{k} \text{ or } k = \frac{0.693}{t_{1/2}}$$





2

CBSE Patna 2015

Substituting  $k_1 = 2 \times 10^{-2}$ ,  $k_2 = 4 \times 10^{-2}$ ,  $T_1 = 300 \text{ K}$ ,  $T_2 = 310 \text{ K}$ ,  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$  in the expression

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left( \frac{T_2 - T_1}{T_1 T_2} \right), \text{ we get}$$

$$\log \frac{4 \times 10^{-2}}{2 \times 10^{-2}} = \frac{E_a}{2.303 \times 8.314} \left( \frac{310 - 300}{300 \times 310} \right)$$

$$\log 2 = \frac{E_a}{19.147} \times \frac{10}{300 \times 310}$$

$$E_a = 0.3010 \times 19.147 \times 300 \times 31 = 53598 \text{ J mol}^{-1}$$

$$E_a = 53.598 \text{ kJ mol}^{-1}$$

$A + 2B \rightarrow C + 2D$   $r$   $d$   $B$   $^{-2}$

- $r$
- $d$

i. As  $\frac{-d[B]}{dt} = 1 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$

$$\therefore \text{Rate} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{2} \times 1 \times 10^{-2} = 0.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

ii.  $\text{Rate} = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = +\frac{1}{3} \frac{d[C]}{dt}$

Rate of change in concentration of A

$$= - \frac{d[A]}{dt} = - \frac{1}{2} \frac{d[B]}{dt}$$

$$= 0.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

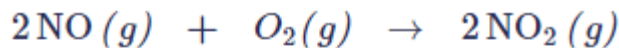
Rate of change in concentration of C

$$= + \frac{d[C]}{dt} = - \frac{3}{2} \frac{d[B]}{dt} = \frac{3}{2} \times 1 \times 10^{-2}$$

$$= 1.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

□ 2 □ □ r □ □ □ □ d □ □ □ □ □ r □ □ □ □ □ □ □ □ □ □ □ r □ d □ □ □ □ □ r □ □ □ □ □ d □ □ □ □ d □ □ □

□ **HOTS** □



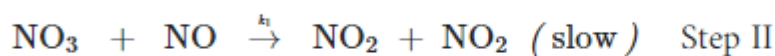
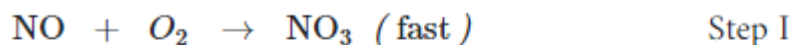
The rate law for this reaction is:

$$\text{Rate} = k [\text{NO}]^2 [\text{O}_2]$$

Propose a mechanism for the reaction.

□ □ □ □ □ □

The probable proposed mechanism may be,



Since slowest reaction is the rate determining step, therefore

$$\text{Rate} = k_1 [\text{NO}_3] [\text{NO}]$$

$$K = \frac{[\text{NO}_3]}{[\text{NO}] [\text{O}_2]}$$

□

□



The rate constant of a reaction is independent of concentration.
  The rate constant of a reaction is dependent on concentration.
  The rate constant of a reaction is independent of temperature.
  The rate constant of a reaction is dependent on temperature.
  The rate constant of a reaction is independent of the nature of the reaction.
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  The rate constant of a reaction is independent of the physical state of the reactants.
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  The rate constant of a reaction is independent of the pressure.
  The rate constant of a reaction is dependent on the pressure.
  The rate constant of a reaction is independent of the catalyst.
  The rate constant of a reaction is dependent on the catalyst.
  The rate constant of a reaction is independent of the surface area of the reactants.
  The rate constant of a reaction is dependent on the surface area of the reactants.
  The rate constant of a reaction is independent of the frequency of collision.
  The rate constant of a reaction is dependent on the frequency of collision.
  The rate constant of a reaction is independent of the activation energy.
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  The rate constant of a reaction is independent of the orientation of collision.
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  The rate constant of a reaction is independent of the concentration of the reactants.
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$k$	$20^\circ\text{C}$	$23.8$	$0.048$
$k$	$30^\circ\text{C}$	$23.8$	$0.048$

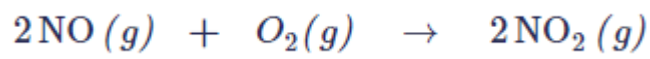
The rate constant of a reaction is independent of concentration.
  The rate constant of a reaction is dependent on concentration.

The rate constant of a reaction is independent of temperature.
  The rate constant of a reaction is dependent on temperature.

i.  $k = \frac{2.303}{10} \log \frac{23.8}{14.7} = \frac{2.303}{10} \times 0.2093 = 0.048 \text{ min}^{-1}$   
 ii.  $k = \frac{2.303}{20} \log \frac{23.8}{9.1} = \frac{2.303}{20} \times 0.4176 = 0.048 \text{ min}^{-1}$

Since the value of  $k$  comes out to be constant in both the cases, therefore the reaction is of first order.

The rate constant of a reaction is independent of concentration.
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The rate constant of a reaction is independent of concentration.
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  The rate constant of a reaction is dependent on the concentration of the products.
  The rate constant of a reaction is independent of the concentration of the catalyst.
  The rate constant of a reaction is dependent on the concentration of the catalyst.
  The rate constant of a reaction is independent of the concentration of the solvent.
  The rate constant of a reaction is dependent on the concentration of the solvent.
  The rate constant of a reaction is independent of the concentration of the medium.
  The rate constant of a reaction is dependent on the concentration of the medium.
  The rate constant of a reaction is independent of the concentration of the reactants and products.
  The rate constant of a reaction is dependent on the concentration of the reactants and products.
  The rate constant of a reaction is independent of the concentration of the reactants, products and catalyst.
  The rate constant of a reaction is dependent on the concentration of the reactants, products and catalyst.
  The rate constant of a reaction is independent of the concentration of the reactants, products, catalyst and solvent.
  The rate constant of a reaction is dependent on the concentration of the reactants, products, catalyst and solvent.
  The rate constant of a reaction is independent of the concentration of the reactants, products, catalyst, solvent and medium.
  The rate constant of a reaction is dependent on the concentration of the reactants, products, catalyst, solvent and medium.

**HOTS**

The rate constant of a reaction is independent of concentration.
  The rate constant of a reaction is dependent on concentration.

$$\text{Rate} = k [\text{NO}]^2 [\text{O}_2]$$

Let initially, moles of NO =  $a$ , moles of  $\text{O}_2 = b$ , volume of the vessel =  $V$ . Then

$$[\text{NO}] = \frac{a}{V} \text{ M}, [\text{O}_2] = \frac{b}{V} \text{ M}$$

$\therefore$  Rate ( $r_1$ ) =  $k \left( \frac{a}{V} \right)^2 \left( \frac{b}{V} \right) = k \frac{a^2 b}{V^3}$  ... (i)

Now, new volume =  $\frac{V}{3}$





We know that,

$$\log k_2 - \log k_1 = \frac{E_a}{2.303 R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log k_2 = \log k_1 + \frac{E_a}{2.303 R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log k_2 = \log (1.60 \times 10^{-5} \text{ s}) + \frac{209000 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left[ \frac{1}{600 \text{ K}} - \frac{1}{700 \text{ K}} \right]$$

$$\log k_2 = -4.796 + 2.599 = -2.197 \text{ or } k_2 = \text{Antilog}(\bar{3}.803)$$

$$k_2 = 6.36 \times 10^{-3} \text{ s}^{-1}$$

Rate of reaction is  $k_2$  times concentration of reactants. The rate of reaction is directly proportional to the concentration of reactants. The rate of reaction is  $k_2$  times concentration of reactants.

Rate of reaction is  $k_2$  times concentration of reactants.

**HOTS**

Q. No. 10

For a first order reaction,  $k = \frac{0.693}{t_{1/2}}$

$$T_1 = 300 \text{ K,} \quad k_1 = \frac{0.693}{20} = 3.456 \times 10^{-2} \text{ min}^{-1}$$

$$T_2 = 350 \text{ K,} \quad k_2 = \frac{0.693}{5} = 1.386 \times 10^{-1} \text{ min}^{-1}$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{T_2 - T_1}{T_2 T_1} \right]$$

$$\log \frac{1.386 \times 10^{-1}}{3.456 \times 10^{-2}} = \frac{E_a}{2.303 \times 8.314} \left( \frac{350 - 300}{350 \times 300} \right)$$

$$\log 4 = \frac{E_a}{2.303 \times 8.314} \left( \frac{50}{350 \times 300} \right)$$



$$0.602 = \frac{E_a}{19.147} \left( \frac{50}{350 \times 300} \right)$$

$$E_a = \frac{0.602 \times 19.147 \times 350 \times 300}{50}$$

$$= 24205.63 \text{ J mol}^{-1} = 24.206 \text{ kJ mol}^{-1}$$

□ □ □ □ □

${}_{92}^{238}\text{U}$  changes to  ${}_{82}^{206}\text{Pb}$  by successive radioactive decay. A sample of uranium ore was analysed and found to contain 1.0 g of  ${}^{238}\text{U}$  and 0.1 g of  ${}^{206}\text{Pb}$  had accumulated due to decay of  ${}^{238}\text{U}$ , find out the age of the ore. (Half-life of  ${}^{238}\text{U} = 4.5 \times 10^9$  years)

[HOTS] □

□ □ □ □ □

$[A]_0 = \text{Initial amount of } {}^{238}\text{U} = \text{amount of } {}^{238}\text{U} \text{ left at time } t + \text{amount of } {}^{238}\text{U} \text{ decayed}$

$[A]_0 = 1.0 + \text{amount of } {}^{238}\text{U} \text{ decayed}$

Now, amount of  ${}^{238}\text{U}$  decayed =  $\frac{0.1 \times 238}{206} \text{ g} = 0.1155 \text{ g}$

$\therefore [A]_0 = 1.0 \text{ g} + 0.1155 \text{ g} = 1.1155 \text{ g}$

Determination of  $k$ :  $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9} = 0.154 \times 10^{-9} \text{ year}^{-1}$

Determination of time:  $t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$

Substituting the values of  $[A]_0 = 1.1155 \text{ g}$  and  $k = 0.154 \times 10^{-9} \text{ year}^{-1}$

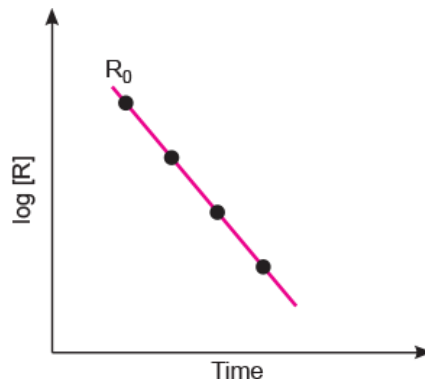
$$t = \frac{2.303}{0.154 \times 10^9} \log \frac{1.1155}{1}$$

$$= 0.7099 \times 10^9 \text{ year}$$

$$= 7.099 \times 10^8 \text{ year}$$

□

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The slope of the line is  $-2.0 \times 10^{-6} \text{ s}^{-1}$ .

Answer

i.  $\text{Slope} = -\frac{k}{2.303}$  or  $k = -2.303 \times \text{Slope}$

$$\therefore k = -2.303 \times (-2.0 \times 10^{-6} \text{ s}^{-1})$$

$$k = 4.606 \times 10^{-6} \text{ s}^{-1}$$

ii. For a zero order reaction

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

$$\text{At } t = t_{1/2}, [R] = \frac{[R]_0}{2}$$

$$\therefore t_{1/2} = \frac{[R]_0 - \frac{[R]_0}{2}}{k} \quad \text{or} \quad t_{1/2} = \frac{[R]_0}{2k}$$

□

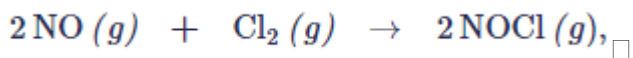
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□**CBSE Delhi 2012**□□

□□□□Suppose order w.r.t. NO is  $m$  and order w.r.t.  $\text{Cl}_2$  is  $n$ . Then the rate will be

$$\text{Rate} = k [\text{NO}]^m [\text{Cl}_2]^n$$

Substituting the values of experiment 1 to 3 in the rate expression, we get

$$0.60 = k(0.15)^m (0.15)^n \quad \dots(i)$$

$$1.20 = k(0.15)^m (0.30)^n \quad \dots(ii)$$

$$2.40 = k(0.30)^m (0.15)^n \quad \dots(iii)$$

Dividing equation (iii) by (i), we get

$$\frac{2.40}{0.60} = \frac{k (0.30)^m (0.15)^n}{k (0.15)^m (0.15)^n}$$

$$4 = 2^m \text{ or } 22 = 2^m \text{ or } m = 2$$

Dividing equation (ii) by (i), we get

$$\frac{1.20}{0.60} = \frac{k (0.15)^m (0.30)^n}{k (0.15)^m (0.15)^n}$$

$$2 = 2^n \text{ or } n = 1$$

i. Rate law expression is, Rate =  $k[\text{NO}]^2 [\text{Cl}_2]$

ii.  $0.60 \text{ mol L}^{-1} \text{ min}^{-1} = k(0.15 \text{ mol L}^{-1})^2 (0.15 \text{ mol L}^{-1})$

$$k = 177.77 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$$

iii. Rate =  $177.77 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1} \times (0.25 \text{ mol L}^{-1})^2 (0.25 \text{ mol L}^{-1})$

$$= 2.778 \text{ mol L}^{-1} \text{ min}^{-1}$$

2.  $\text{A} + \text{B} \rightarrow \text{P}$

$\text{A} + \text{B} \rightarrow \text{P}$

Rate,  $r = k[\text{A}][\text{B}]^2$

If concentration of B is doubled, then

$$\text{Rate, } r = k[\text{A}][\text{B}]^2$$

If concentration of B is doubled, then

$$r' = k[\text{A}][2\text{B}]^2$$

$$r' = 4k[\text{A}][\text{B}]^2, \text{ i.e., } r' = 4r$$

As A is present in large excess therefore, order of the reaction w.r.t. A will be zero.

$$\text{Rate} = k[\text{A}]^0 [\text{B}]^2 = k[\text{B}]^2$$

$\therefore$  Order of reaction = 2

Rate,  $r = k[\text{A}][\text{B}]^2$



For a first order reaction

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$\therefore k = \frac{2.303}{20} \log \frac{0.400}{0.289}$$

$$\Rightarrow k = \frac{2.303}{20} \log \frac{4.00}{2.89}$$

$$\Rightarrow k = \frac{2.303}{20} [\log 4.00 - \log 2.89]$$

$$\Rightarrow k = \frac{2.303}{20} [0.6021 - 0.4609]$$

$$\Rightarrow k = \frac{2.303}{20} \times 0.1412$$

$$\Rightarrow k = 2.303 \times 0.00706 = 0.016259 \text{ min}^{-1}$$

$$\Rightarrow k = 1.6259 \times 10^{-2} \text{ min}^{-1}$$

ii. 
$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

Here,  $[R]_0 = 0.400 \text{ mol}^{-1}$ ,  $t = 100 \text{ min}$ ,  $k = 1.626 \times 10^{-2} \text{ min}^{-1}$

$$100 = \frac{2.303}{1.626 \times 10^{-2}} \log \frac{0.400}{[R]}$$

$$\frac{100 \times 1.626 \times 10^{-2}}{2.303} = \log \frac{0.4}{[R]} \Rightarrow 0.7060 = \log \frac{0.4}{[R]}$$

$$\text{Antilog}(0.7060) = \frac{0.4}{[R]}$$

$$5.082 = \frac{0.4}{[R]} \Rightarrow [R] = \frac{0.4}{5.082} = 0.0787 \text{ M}$$

iii. Initial rate, *i.e.*, rate of reaction when  $t = 0$

When,  $t = 0.00 \text{ min}$ ,  $[R] = 0.400 \text{ mol L}^{-1}$



As the value of  $k$  is same in both the cases, therefore, hydrolysis of methylacetate in aqueous solution follows pseudo first order reaction.

$$\begin{aligned} \text{ii. Average rate} &= - \frac{\Delta / \text{CH}_3 \text{COOCH}_3 /}{\Delta t} \\ &= \frac{-/0.15 - 0.30/}{60 - 30} = \frac{0.15}{30} \end{aligned}$$

Average rate =  $\frac{0.15}{30}$

For a first order reaction,  $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$

For a first order reaction,  $t_{3/4} = \frac{2.303}{k} \log \frac{100}{25} = \frac{2.303}{k} \log 4 = 0.6021 \frac{2.303}{k}$

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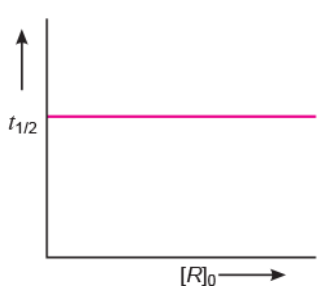
For a first order reaction,  $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$

$$\text{For a first order reaction, } t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

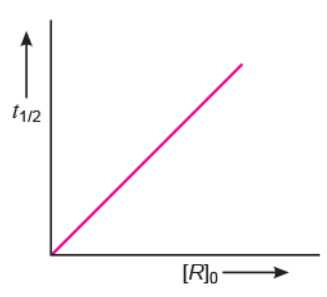
$$\therefore \frac{t_{3/4}}{t_{1/2}} = \frac{\frac{2.303}{k} \log \frac{100}{25}}{\frac{2.303}{k} \log \frac{100}{50}} = \frac{\log 4}{\log 2} = \frac{0.6021}{0.3010}$$

$$\frac{40 \text{ min}}{t_{1/2}} = 2 \quad \text{or} \quad t_{1/2} = 20 \text{ min .}$$

(a)



(b)



For a first order reaction,  $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$

For a first order reaction,  $t_{3/4} = \frac{2.303}{k} \log \frac{100}{25} = \frac{2.303}{k} \log 4 = 0.6021 \frac{2.303}{k}$

For a first order reaction,  $t_{3/4} = 2 t_{1/2}$

(a) First order

(b) Zero order





$$C = [R]_0$$

Substituting the value of  $C$  in equation (i)

$$[R] = -kt + [R]_0 \quad \dots(ii)$$

$$kt = [R]_0 - [R]$$

$$\Rightarrow t = \frac{[R]_0 - [R]}{k}$$

On completion of reactions,  $[R] = 0$

$$\therefore t = \frac{[R]_0}{k}$$

iii. From equation (ii), we have slope of curve

$$\text{Slope} = \frac{d[R]}{dt} = -k \quad \square$$

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

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

$$2. \frac{d[A]}{dt} = -k[A]$$

the rate of appearance of C at time 't' is  $1.3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

$\frac{d[C]}{dt} = 1.3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

$\frac{d[A]}{dt} = -1.3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

$\frac{d[B]}{dt} = 2.6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

$\frac{d[C]}{dt} = 1.3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

$$a. \text{Rate} = \frac{1}{3} \frac{d[C]}{dt}$$

$$= \frac{1}{3} \times 1.3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} = 0.43 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$b. \text{Rate} = \frac{-d[A]}{dt} = \frac{2}{3} \times \frac{d[C]}{dt}$$

$$= \frac{2}{3} \times 1.3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} = 0.86 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

2. For a first order reaction, the concentration of the reactant decreases from 0.25 M to 0.125 M in 2 minutes. Calculate the rate constant of the reaction.

Solution

$$[R]_0 = 0.25 \text{ M}, t = 2 \text{ min} = 2 \times 60 \text{ s} = 120 \text{ s}, k = 5.0 \times 10^{-4} \text{ s}^{-1}$$

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$5.0 \times 10^{-4} = \frac{2.303}{120} \log \frac{0.25}{[R]} \text{ or } \log \frac{0.25}{[R]} = 0.026$$

$$\log \frac{[R]}{0.25} = -0.026 \text{ or } \frac{[R]}{0.25} = \text{Antilog}(\bar{1}.974)$$

$$\frac{[R]}{0.25} = 0.9419 \text{ or } [R] = 0.235 \text{ M}$$

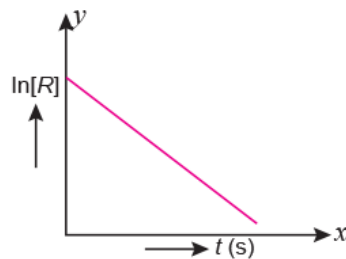
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5 \times 10^{-4} \text{ s}^{-1}} = 1386 \text{ s}$$

3. For a first order reaction, the concentration of the reactant decreases from 0.25 M to 0.125 M in 2 minutes. Calculate the half-life of the reaction.

**HOTS**

Solution

- 1. For a first order reaction, the concentration of the reactant decreases from 0.25 M to 0.125 M in 2 minutes. Calculate the rate constant of the reaction.
- 2. For a first order reaction, the concentration of the reactant decreases from 0.25 M to 0.125 M in 2 minutes. Calculate the half-life of the reaction.
- 3. For a first order reaction, the concentration of the reactant decreases from 0.25 M to 0.125 M in 2 minutes. Calculate the time taken for the concentration of the reactant to decrease to 0.0625 M.
- 4. For a first order reaction, the concentration of the reactant decreases from 0.25 M to 0.125 M in 2 minutes. Calculate the time taken for the concentration of the reactant to decrease to 0.03125 M.





Thus, from Arrhenius equation we find that increasing the temperature or decreasing the activation energy will result in an exponential increase in rate constant.

$k = 4.5 \times 10^{11} s^{-1} e^{-28000 K/T}$

$$k = (4.5 \times 10^{11} s^{-1}) e^{-28000 K/T}$$

$E_a$

□

Comparing with Arrhenius equation  $k = A e^{-E_a/RT}$ , we get

$$-\frac{E_a}{RT} = -\frac{28000 K}{T} \text{ or } E_a = 28000 K \times R$$

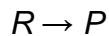
$$E_a = 28000 K \times 8.314 J K^{-1} mol^{-1} = 232792 J mol^{-1}$$

$$E_a = 232.79 kJ mol^{-1}$$

□

□

□ Consider the first order reaction,



For this reaction, rate law which relates the rate of reaction to the concentration of reactants can be given as

$$\text{Rate} = \frac{-d[R]}{dt} = k[R]$$

For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}, \text{ where } [R]_0 = \text{initial concentration, } [R] = \text{concentration at time } t.$$

At  $t_{1/2}$ ,  $[R] = [R]_0 / 2$

So, the above equation becomes





**Alternative Method:**

For a first order reaction,  $t_{3/4} = 2 \times t_{1/2}$

$$\therefore t_{3/4} = 2 \times \frac{0.693}{k}$$

$$t_{3/4} = \frac{2 \times 0.693}{2.54 \times 10^{-3} \text{ s}} = 545.67 \text{ s}$$

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