CHEMICAL KINETICS

1. Rate of Reaction :

The rate of a reaction means the speed with which the reaction takes place. This is expressed either in terms of decrease in the concentration of a reactant per unit time or increase in the concentration of a product per unit time. Hence the rate of a reaction may be defined as follows :

The rate of reaction is the change in the concentration of any one of the reactants or products per unit time i.e.,

Rate of reaction = $\frac{\text{Decrease in the concentration of a reactant}}{\text{Time interval}}$ or = $\frac{\text{Increase in the concentration of a product}}{\text{Time interval}}$

Time interval

For example, consider the reaction,

 $PCl_5 \longrightarrow PCl_3 + Cl_2$

Suppose in a time interval Δt , decrease in concentration of PCl₅ is Δ [PCl₅] and increase in the concentration of PCl₃ and Cl₂ are Δ [PCl₃] and Δ [Cl₂] respectively, where square brackets indicate molar concentrations (moles/litre) of the substances involved. Then we have,

Rate of reaction = $-\frac{\Delta[PCl_5]}{\Delta t} = +\frac{\Delta[PCl_3]}{\Delta t} = +\frac{\Delta[Cl_2]}{\Delta t}$

It may be emphasized that the rate of reaction is always positive. The minus sign alongwith the first term is used simply to show that the concentration of the reactant (PCl_5) is decreasing while plus sign along with the other two terms is used to show that the concentration of the products (PCl_3) and (Cl_2) is increasing.

In general, for any reaction of the type

 $A + B \longrightarrow C + D$

Rate of reaction = $-\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = +\frac{\Delta[C]}{\Delta t} = +\frac{\Delta[D]}{\Delta t}$

Units of the Rate of Reaction :

Since concentration is usually expressed in moles/litre and the time is taken in seconds or minutes, the unit of the rate of reaction is moles litre⁻¹ sec⁻¹ (mol $L^{-1} s^{-1}$) or moles litre⁻¹ min⁻¹ (mol $L^{-1} min^{-1}$).

In case of gaseous reactions, pressures are used in place of molar concentrations. As pressures are expressed in atmospheres, therefore the units of the rate of reaction are atm min^{-1} or atm s^{-1} etc. The relationship between partial pressure of a gas in a reaction mixture

and its molar concentration follows from the relationship PV = nRT i.e. $\frac{n}{V} = \frac{P}{RT}$

Where partial pressure, $P = \frac{\text{No. of moles of the gas}}{\text{Total no. of moles}} \times \text{Total pressure}$

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Average Rate and Instantaneous Rate of Reaction :

A difficulty arises in stating the rate of reaction as above. This is because according to the Law of Mass Action, the rate of reaction depends upon the molar concentrations of reactants which keep on decreasing with the passage of time (while those of the products keep on increasing). Therefore, the rate of reaction does not remain constant throughout. Thus the rate of reaction as defined above is the 'average rate of reaction' during the time

interval chosen.

To know the rate of reaction at any instant of time during the course of a reaction, we introduce the term 'instantaneous rate of reaction' which may be defined as follows :

The rate of reaction at any instant of time is the rate of change of concentration (i.e. change of concentration per unit time) of any one of the reactants or products at that particular instant of time.

To express the instantaneous rate of reaction, as small interval of time (dt) is chosen at that particular instant of time during which the rate of reaction is supposed to be almost constant. Suppose the small change in concentration is dx in the small interval of time dt. Then

the rate of reaction at that instant is given by $\frac{dx}{dt}$.

Measurement of the Rate of Reaction :

In order to measure the rate of a reaction, the progress of the reaction is followed by studying the concentration of one of the reactants or products at different intervals of time. the most common practice to do so is to withdraw small amount of the reaction mixture (2 cm³ or 5 cm³) at different intervals of time, cool it down immediately to nearly 0° C to arrest the reaction (called freezing the reaction) and then find out the concentration of the reactant or the product by suitable method usually by titration against a suitable reagent. However, this method is not preferred when some observable property like volume, pressure, optical rotation etc. changes with time and can be observed directly at different intervals of time without stopping the reaction. it is important to mention that except concentration, all other factors (like temperature etc.) which affect the rate of the reaction are kept constant during the kinetic study of the reaction.



If concentration of one of the reactants is studied at different intervals of time and these values are plotted against the corresponding times, a graph of the type shown in figure is obtained.

Calculation of instantaneous rate of reaction :

To know the rate of the reaction at any time t, a tangent is drawn to the curve at the point corresponding to that time figure and it is extended on either side so as to cut the axes, say at the points A and B. then

Rate of reaction =
$$\frac{\text{Change in the concentration}}{\text{Time}}$$

$$=\frac{\Delta A}{\Delta t} = \frac{\Theta A}{\Theta B}$$
 Slope of the tangent

Thus the slope of the tangent gives the rate of reaction.

For example, from the (figure) in the present case, at time t = 10 minutes, $\Delta x = 0.04$ mole and $\Delta t = 20$ minutes = $20 \times 60 = 1200$ seconds, therefore, rate of reaction at the end of 10 minutes will be $0.04/1200 = 3.33 \times 10^{-5}$ mol L⁻¹ s⁻¹.

Calculation of the average rate of reaction :

To calculate the average rate of reaction between any two instants of time say t_1 and t_2 , the corresponding concentrations x_1 and x_2 are noted from the graph. Then

Average rate of reaction =
$$\frac{x_2 - x_1}{t_2 - t_1}$$

For example, from the (figure) between the time interval 5 to 15 minutes,

Average rate
$$=\frac{0.03 - 0.012}{15 - 5} = \frac{0.018}{10} = 0.0018$$
 and mol L⁻¹ min⁻¹

If concentration of one of the products is plotted against time, the type of curve obtained and the rate of reaction at any instant of time are calculated as shown in the figure.



Example 1 :

In a reaction the concentration of a reactant (A) changes from 0.200 mol litre⁻¹ to 0.150 mol litre⁻¹ in 10 minutes. What is the average rate of reaction during this interval? Solution :

$$\Delta[A] = [A]_{\text{final}} - [A]_{\text{initial}}$$

= [0.150 - 0.200]
= -0.050 mol litre⁻¹
$$\Delta t = 10 \text{ minutes}$$

Average rate of reaction = $\frac{-\Delta[A]}{\Delta t} = \frac{0.50}{10} = 0.005 \text{ mol litre}^{-1} \text{ min}^{-1}$

Example 2 :

Decomposition of $N_{2}O_{5}$ is expressed by the equation,

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

If in a certaion time interval, rate of decomposition of N_2O_5 is 1.8×10^{-3} mol litre⁻¹ min⁻¹, what will be the rates of formation of NO_2 and O_2 during the same interval ? Solution :

The rate expression for the decomposition of N_2O_5 is

$$-\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2} \frac{\Delta[NO_2]}{\Delta t} = 2 \times \frac{\Delta[O_2]}{\Delta t}$$

So

$$\frac{\Delta[\text{NO}_2]}{\Delta t} = 2 \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = 2 \times 1.8 \times 10^{-3}$$
$$= 3.6 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$$

and

$$\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2} \times 1.8 \times 10^{-3}$$
$$= 0.9 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$$

[Rate is always positive and hence = $\frac{\Delta [N_2 O_5]}{\Delta t}$ is taken positive.

Example 3 :

If the decomposition of nitrogen (V) oxide $2N_2O_5 \longrightarrow 4NO_2 + O_2$, following a first order kinetics.

- (i) Calculate the rate constant for a 0.04 M solution, if the instantaneous rate is 1.4×10^{-6} mol L s⁻¹.
- (ii) Also calculate the rate of reaction when the concentration of N_2O_5 is 1.20 M.
- (iii) What concentration of N_2O_5 , would give a rate of 2.45 × 10⁵ mol $L^{-1}s^{-1}$?

Solution :

or

(i) As the given reaction is of first order, therefore,

Rate = $k[N_2O_5]$

$$k = \frac{\text{rate}}{[N_2O_5]} = \frac{1.4 \times 10^{-6}}{0.04} \qquad [M = \text{conc. in mol } L^{-1}]$$
$$= 3.5 \times 10^{-5} \text{s}^{-1}$$

(ii) Now if the concentration of N₂O₅ is 1.20 M, then rate = $k[N_2O_5]$ = 3.5 × 10⁻⁵ × 1.20 = 4.2 × 10⁻⁵ mol L⁻¹ s⁻¹

(iii) To obtain concentration of N_2O_5 when the rate is 2.45×10^{-5} mol⁻¹ s⁻¹, we note that

$$[N_2O_5] = \frac{\text{Rate}}{\text{k}} = \frac{2.45 \times 10^{-5}}{3.5 \times 10^{-5}} = 0.7 \text{ mol } \text{L}^{-1} \text{ or } 0.7 \text{ M}$$

Factors Affecting the Reaction Rate :

The rate of any particular reaction depends upon the following factors:

- (i) **Concentration of the reactants :** Greater the concentrations of the reactants, faster is the reaction. Conversely, as the concentrations of the reactants decrease, the rate of reactions also decreases.
- (ii) **Temperature :** The rate of reaction increases with increase of temperature. In most of the cases, the rate of reaction becomes nearly double for 10 K rise of temperature. In some cases, reactions do not take place at room temperature but take place at higher temperature.

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- **Presence of Catalyst :** A catalyst generally increases the speed of a reaction without (iii) itself being consumed in the reaction. In case of reversible reactions, a catalyst helps to attain the equilibrium quickly without disturbing the state of equilibrium.
- (iv) Surface area of the reactants : For a reaction involving a solid reactant or catalyst, the smaller is the particle size, i.e., greater is the surface area, the faster is the reaction.
- **Presence of light :** Some reactions do not take place in the dark but take place in the **(v)** presence of light e.g., $H_2 + Cl_2 \longrightarrow 2HCl$. Such reactions are called "photochemical reactions". Now we shall discuss the quantitative effect of concentration and temperature on the rate of reaction. The study of quantitative effect of concentration on the rate of reaction leads to the introduction of a number of new terms such as order of reaction, specific reaction rate (rate constant) and molecularity of reaction. It also leads to the study of mechanism of the reactions. These different aspects are discussed in the following sections.

2. Molecularity and Order :

Single step reaction is called *elementary* reaction while a reaction occurring in two or more steps is called *complicated* or *consecutive* reaction. Each step of a complicated reaction is an elementary reaction.

The minimum number of molecules, atoms or ions of reactants required for an elementary reaction to occur is indicated by the sum of the stoichiometric coefficients of the reactant(s) in the chemical equation, is known molecularity of the reaction. Thus for an elementary reaction represented by the general chemical equation.

 $aA + bB \longrightarrow products$ molecularity = a + bReactions Examples: Molecularity $PCl_5 \implies PCl_3 + Cl_2 = 1$ $H_2 + I_2 \implies 2HI$

A complicated reaction has no molecularity of its own but molecularity of each of the steps involved in its mechanism.

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For example :

The reaction : $2NO + 2H_2 \implies N_2 + 2H_2O$, takes place in the sequence of following three steps . I. NO + NO \implies N₂O₂ (fast and reversible)

II.
$$N_2O_2 + H_2 \longrightarrow N_2O + H_2O$$
 (slow)
III. $N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast)

The molecularity of each step involved in mechanism is 2 i.e., each step is bimolecular. So as regards the molecularity of the reaction under consideration we simply say that the reaction has mechanism and each step involved in it is bimolecular

However, there is another view also, according to which molecularity of a complicated reaction is taken to be equal to the number of molecules, atoms or ions of reactant(s) and/or intermediates coming into contact and colliding simultaneously in the slowest step i.e. the ratedetermining step (RDS) of the reaction.

For example the reaction ROH + HCl $\xrightarrow{ZnCl_2}$ RCl + H₂O, which actually is a nucleophilic substitution reaction

 $\overrightarrow{ROH} + H^{\oplus} \rightleftharpoons \overrightarrow{ROH}_2$ Ι (fast)

II
$$R \stackrel{f}{=} \stackrel{\overset{\oplus}{O}}{O}H_2 \implies R^{\oplus} + H_2 \stackrel{\dot{O}}{O}$$
 (slow)

 $R^{\oplus} + : \dot{Cl}: \longrightarrow R - \dot{Cl}:$ III (fast)

Here the step II is the slowest step and hence the R.D.S. the molecularity of which is one. Therefore, the mechanism is called unimolecular nucleophilic substitution (S_N^1) and the reaction is said to follow S_N^1 mechanism.

The mathematical equation showing the relation of rate of reaction with concentration of reactant(s) is called rate-law of the reaction. For example, the kinetic experiment carried on the reaction.

$$2 \operatorname{NO} + 2 \operatorname{H}_2(g) \longrightarrow \operatorname{N}_2(g) + 2 \operatorname{H}_2\operatorname{O}(g)$$

has shown that :

- (i) rate increases 4 fold when conc. of NO is doubled keeping the conc. of H_2 constant
- (ii) rate gets just doubled when conc. of H₂ is doubled keeping that of NO constant, and
- (iii) rate increases 8 fold when concentrations of both NO and H_2 are doubled simultaneously. These experimental rate data fit into following equation.

Rate α [NO]²[H₂]

This equation is called experimentally observed "Rate law" of the reaction.

Order of reaction is defined as the sum of the powers of the concentration terms appearing in experimentally observed rate law.

Thus for the reaction (reduction of nitric oxide by hydrogen) considered above.

Order w.r.t. NO = 2 Order w.r.t. $H_2 = 1$

Overall order = 2 + 1 = 3

In general, let a reaction represented by the chemical equation:

 $aA + bB \longrightarrow Products$

obeys the following rate law.

Rate α [A]^m [B]ⁿ, or Rate = k[A]^m [B]ⁿ

Where k = rate constant of reaction, a constant at constant temp and is actually the rate of reaction when conc. of each reactant is equal to unity k is also called **velocity constant** or **specific reaction** rate.

Note that m and n are experimental quantities which may or may not be equal to the respective stoichiometric coefficients.

Also note that if either of A or B is taken in large excess as compared to another, the order w.r.t this reactant will be zero so order = m (when B is in large excess), and order = n (when A is large excess), i.e.,

Rate = $k'[A]^m$, $k' = k[B]^n$ another constant, when B is in large excess.

Order w.r.t.
$$A = m$$

Order w.r.t.
$$B = 0$$

Rate = $k''[B]^n$, $k'' = k[A]^m$ = another constant, when A is in large excess.

Order w.r.t. A = 0

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Order w.r.t. B = n
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k' or k'' is actually known as pseudo rate constant

Thus, a bimolecular reaction conforms to the first - order when one of the reactants is taken in large excess and the reaction is said to be pseudo unimolecular or pseudo first order.

An example of this is the hydrolysis of ester by dil. acid i.e.

 $CH_3COOC_2H_5 + H_3O^+ \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

The reaction is originally of second - order obeying the kinetics.

Rate = $k [CH_3COOC_2H_5] [H_2O]$

But the reaction is usually carried out taking dilute aqueous solution of ester and acid (HCl) such that in the reaction mixture water exists in large excess as compared to ester or better to say, water has almost its maximum concentration of 55.5 mole L^{-1} . So there is no appreciable change in the concentration of water and the same remains practically constant.

 $k[H_2O]$ becomes another constant (k') called pseudo rate constant and reactions obeys the following 1st order kinetics

Rate = k' [CH₃COOC₂H₅]

Thus, the molecularity of the above reaction is 'two' but its order is 'one;.

In the light of the above concept one may define order of reaction as " the number of molecules of the reactant(s) whose concentration alters during the chemical change is the order of reaction".

Distinction between Molecularity and Order

- (i) Molecularity is a theoretical property while order is an experimental property.
- (ii) Molecularity concerns to mechanism, order concerns to kinetics
- (iii) Molecularity is always a whole number and never zero while order may be any number zero, fractional and integral.
- (iv) Molecularity is invariant but order may vary with change in experimental condition. As for example, the isomerisation of cyclo propane represented by the chemical equation given below is a first order reaction at high cyclo propane pressure and is a second order reaction at low cyclo propane pressure.



(v) Reactions of higher molecularity is rare since the chance of coming into contact and colliding simultaneously decreases as the number of molecules involved in collision increases.

Unit of rate constant

$$nA \longrightarrow Product$$

$$\frac{dx}{dt} = k[conc.]^{n}$$

$$\frac{[conc.]}{sec} = k[conc.]^{n}$$

$$k = [conc.]^{1-n} sec^{-1}$$

$$= [mole/litre]^{1-n} sec^{-1}$$

Example 4:

State the order w.r.t. each reactant, order of overall reaction and units of rate constant in each of the following reactions

(i) $H_2O_2 + 3I^- + 2H^+ \longrightarrow 2H_2O + I_3^-(aq)$ $Rate = k [H_2O_2] [I^-]$ (ii) $CO + CI_2 \longrightarrow COCI$

(ii)
$$CO + Cl_2 \longrightarrow COCl_2$$

Rate = $k[CO]^2[Cl_2]^{1/2}$

Solution :

(i) Rate = $k[H_2O_2][I^-]$ Order w.r.t. H_2O_2 =1; Order w.r.t. I^- = 1 Overall order = 2 Units of k = (mol L⁻¹)¹⁻² s⁻¹ = mol⁻¹ Ls⁻¹ (ii) Rate = $k[CO]^2 [Cl_2]^{1/2}$ Order w.r.t. to CO = 2; Order w.r.t. $Cl_2 = \frac{1}{2}$ Overall order = 2.5

Example 5 :

For the reaction, $2 \text{ NO} + \text{Cl}_2 \longrightarrow 2 \text{ NOCl}$ at 300 K following data are obtained

Initial Concentration		Initial nata
[NO]	[Cl ₂]	Inilial rate
0.010	0.010	1.2 ×10-4
0.010	0.020	2.4×10^{-4}
0.020	0.020	9.6 ×10-4
	Initial Con [NO] 0.010 0.010 0.020	Initial Concentration [NO] [Cl2] 0.010 0.010 0.010 0.020 0.020 0.020

Write rate law for the reaction. What is the order of the reaction? Also calculate the specific rate constant.

Solution :

Let the rate law for the reaction be

 $\begin{aligned} & \text{Rate} = k[\text{NO}]^{x}[\text{Cl}_{2}]^{y} \\ & \text{From Expt. (1)}, \quad 1.2 \times 10^{-4} = k[0.010]^{x}[0.010]^{y} & \dots (i) \\ & \text{From Expt. (2)}, \quad 2.4 \times 10^{-4} = k[0.010]^{x}[0.020]^{y} & \dots (ii) \\ & \text{Dividing Eq. (ii) by Eq. (i),} \end{aligned}$

$$\frac{2.4 \times 10^{-4}}{1.2 \times 10^{-4}} = \frac{[0.020]^{y}}{[0.100]^{y}}$$
$$2 = 2^{y}$$
$$y = 1$$

From Expt. (2), $2.4 \times 10^{-4} = k[0.010]^{x}[0.020]^{y}$ (ii) From Expt. (3), $9.6 \times 10^{-4} = k[0.020]^{x}[0.020]^{y}$ (iii) Dividing Eq. (iii) by Eq. (ii),

$$\frac{9.6 \times 10^{-4}}{2.4 \times 10^{-4}} = \frac{[0.020]^{x}}{[0.100]^{y}}$$

$$4 = 2^{x}$$

$$x = 2$$
Order of reaction = x + y = 2 + 1 = 3
Rate law for the reation is , Rate = k [NO]²[Cl₂]
Considering Eq. (i) (again) , $1.2 \times 10^{-4} = k[0.010]^{2}[0.010]$

k =
$$\frac{1.2 \times 10^{-4}}{[0.010]^3}$$
 = 1.2 × 10² mol⁻² litre² sec⁻¹

Example 6 :

For the hypothetical reaction, $2A + B \longrightarrow$ products The following data are obtained :

Expt No.	Initial conc. of (A)	initial conc. of (B)	initial rate
	(mol L^{-1})	(mol L ⁻¹)	(mol $L^{-1}s^{-1}$)
1.	0.10	0.20	3×10^{2}
2.	0.30	0.40	3.6 × 10 ³
3.	0.30	0.80	1.44 × 104
4.	0.10	0.40	•••••
5.	0.20	0.60	•••••
6.	0.30	1.20	•••••

Find out how the rate of the reaction depends upon the concentration of A and B and fill in the blanks.

Solution :

From Expt (2) and (3), it is clear that when concentration of A is kept constant and that of B is doubled, the rate increases four times. This show that the reaction is of second order with respect to B.

Similarly, from Expt. (1) and (2), it is observed that when concentration of A is increased three times and that of B two times, the rate becomes twelve times. Hence, the reaction is first order with respect to A.

Thus the rate law for the reaction is :

Rate = $k [A] [B]^2$

Fill in the blanks: Substituting the values of Expt. (1) in the rate equation,

$$3 \times 10^2 = k[0.10][0.20]^2$$

or

or
$$k = \frac{3 \times 10^2}{[0.10][0.20]^2} = 7.5 \times 10^4 L^2 mol^{-2} s^{-1}$$

Expt.(4): Rate = k[0.10][0.40]²
= 7.5 × 10⁴ × 0.10 × 0.40 × 0.40
= 1.2 × 10³ mol L⁻¹ s^{-1}
Expt (5): Rate = k[0.20] [.60]²
= 7.5 × 10⁴ × 0.20 × 0.60 × 0.60
= 5.4 × 10³ mol L⁻¹ s^{-1}
Expt (6): Rate = k[0.30] [1.20]²
= 7.5 × 10⁴ × 0.30 × 1.20 × 1.20
= 3.24 × 10⁴ mol L⁻¹ s^{-1}

3. Rate Law and Mechanism :

As already mentioned in the reaction:

 $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$ Obeys the following third order kinetics Rate α [NO]² [H₂]

The kinetics is not in tune with chemical equation. As the law of mass action suggests each concentration term should be raised to power 2. Neither experimental facts nor those coming from Law of mass action can be unacceptable to us. Under this condition we are led to believe that the reaction does not occur according to the chemical equation as written. That is the reaction is not elementary but is complicated. In order to explain the observed rate law following mechanism has been proposed.

Ι	$NO + NO \implies N_2O_2$	(fast and reversible)
II	$N_2O_2 + H_2 \longrightarrow N_2O + H_2O$	O (slow)
III	$N_2O + H_2 \longrightarrow N_2 + H_2O$	(fast)
ep II being t	he slowest i.e., the rate - detern	nining step (R.D.S.). N

. Note that the rate of The step formation of N_2 cannot be faster than the rate of formation of N_2O . So, the rate of overall reaction or rate of formation of N₂ will be equal to the rate of step II which according to law of mass action may be given as.

Rate of overall reaction = Rate of step II = $k[N_2O_2]$ [H₂]

Where k = rate constant of step II

The conc. of the intermediate (N_2O_2) may be evaluated by applying law of mass action upon the equilibrium existing in step I as mentioned below.

$$K_{c} = \frac{[N_{2}O_{2}]}{[NO]^{2}}$$
 or $[N_{2}O_{2}] = K_{c} [NO]^{2}$

Putting this in the rate expression, we get Rate = $k.k_c[NO]^2[H_2] = k_{obs}[NO]^2[H_2]$ Where $k_{obs} = k.k_c$ = observed rate constant of the reaction Rate $\alpha [NO]^2 [H_2]$

This is the same rate - law as observed experimentally.

Example 7:

The possible mechanism for the reaction $2 NO + Br_2 \longrightarrow 2 NOBr$ is $NO + Br_2 \longrightarrow NOBr_2$ (fast) $NOBr_2 + NO \longrightarrow 2 NOBr$ (slow). Establish the rate law.

Solution :

As the slowest step is the rate determining step, therefore the rate law is $R = k[NOBr_2][NO]$

Now since NOBr_2 is an intermediate its concentration can be calculated from step 1 as follows:

$$K = \frac{[NOBr_2]}{[NO][Br_2]} \qquad [K = eq. constant]$$

or
$$[NOBr_2] = K [NO] [Br_2]$$

Substituting this value in above equation

Substituting this value in above equation

 $r = k. K[NO]^2[Br_2]$

or rate = $k' [NO]^2 [Br_2]$ [Q $k \cdot K$ = constant k']

 $\therefore \qquad \text{Rate} = \mathbf{k}' \ [\text{NO}]^2 \ [\text{Br}_2]$

Example 8:

Rate law for ozone layer depletion is

$$\frac{d[O_3]}{dt} = \frac{K[O_3]^2}{[O_2]}$$

Give the probable mechanism of reaction?

Solution :

$$O_{3} \longleftrightarrow O_{2} + O \quad \text{(fast reaction)}$$

$$O_{3} + O \longrightarrow 2O_{2} \quad \text{(slow reaction, rate constant k)}$$

$$Rate = k [O_{3}][O] \qquad \qquad \dots [1]$$

$$K_c = \frac{[O_2][O]}{[O_3]}$$
 or $[O] = K_c \frac{[O_3]}{[O_2]}$, (equilibrium constant K_c)

putting the value in (1)

From (1) Rate = k ·
$$[O_3]$$
 · kc $\frac{[O_3]}{[O_2]}$ = k · $K_c \cdot \frac{[O_3]^2}{[O_2]}$ = K $\cdot \frac{[O_3]^2}{[O_2]}$
k = k × K_c .

Example 9:

In hypothetical reaction $A_2 + B_2 \longrightarrow 2AB$ follows the mechanism as given below: $A_2 \rightleftharpoons A + A$ (fast reaction) $A + B_2 \longrightarrow AB + B$ (slow reaction) $A + B \longrightarrow AB$ (fast reaction)

Give the rate law and order of reaction.

Soluton :

Slowest step is rate determining. Rate = $k[A][B_2]$ Here [A] should be eleminated.

$$K_{c} = \frac{[A][A]}{[A_{2}]} = \frac{[A]^{2}}{[A_{2}]}$$

$$[A] = K_{c}^{1/2} [A_{2}]^{1/2}$$
From (1). Rate = $k K_{c}^{1/2} [A_{2}]^{1/2} [B_{2}]$

$$= K[A_{2}]^{1/2} [B^{2}] ; \qquad [K = k \cdot K_{c}]$$
Order = $1 + 1/2 = 3/2$

Example 10 :

For the formation of phosgene from CO(g) and chlorine, $CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$ The experimentally determined rate equation is,

$$\frac{d[COCl_2]}{dt} = k[CO][Cl_2]^{3/2}$$

Is the following mechanism consistent with the rate equation?

(i)
$$Cl_2 \Longrightarrow 2Cl$$
 (fast)
(ii) $Cl + CO \Longrightarrow COCl$ (fast)
(iii) $COCl + Cl_2 \Longrightarrow COCl_2 + Cl$ (slow)

Solution :

Multiplying equation (ii) by 2 and adding (i), we get: $Cl_2 + 2CO \implies 2COCl$

$$K = \frac{[COCI]^{2}}{[Cl_{2}][CO]^{2}}$$

$$[COCI] = (K)^{1/2} [Cl_{2}]^{1/2} [CO] \qquad \dots \dots (1)$$
Slowest step is rate determining, hence
Rate = k[COCI][Cl_{2}] \qquad \dots \dots (2)
From (1) and (2), we get
Rate = kK^{1/2} [Cl_{2}]^{1/2} [Cl_{2}] [CO]
Rate = k'[Cl_{2}]^{3/2} [CO] \qquad [k' = k.k^{1/2}]
Thus, rate law is in accordance with the mecahnism.

.....(1)

<u>EXERCISE-I</u> <u>RATE OF REACTION AND STOICHIOMETRIC COEFFICIENT</u>

Q.1 In a catalytic experiment involving the Haber process, $N_2 + 3H_2 \longrightarrow 2NH_3$, the rate of reaction was measured as

$$Rate = \frac{\Delta[NH_3]}{\Delta t} = 2 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}.$$

If there were no sides reactions, what was the rate of reaction expressed in terms of (a) N_2 , (b) H_2 ?

Q.2 For the reaction $3BrO^- \rightarrow BrO_3^- + 2Br^-$ in an alkaline aquesous solution, the value of the second order (in BrO⁻) rate constant at 80°C in the rate law for $-\frac{\Delta[BrO^-]}{\Delta t}$ was found to be 0.056L mol⁻¹s⁻¹.

What is the rate of constant when the rate law is written for (a) $\frac{\Delta[BrO_3^-]}{\Delta t}$, (b) $\frac{\Delta[Br^-]}{\Delta t}$?

Q.3 Dinitropentaoxide decomposes as follows :

$$\begin{aligned} N_2O_5(g) &\longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g) \\ \text{Given that} & -d\left[N_2O_5\right] / dt = k_1[N_2O_5] \\ & d\left[NO_2\right] / dt = k_2[N_2O_5] \\ & d\left[O_2\right] / dt = k_3[N_2O_5] \end{aligned}$$

What is the relation between k_1 , k_2 and k_3 ?

- Q.4 The reaction $2A + B + C \rightarrow D + E$ is found to be first order in A second order in B and zero order in C.
- (i) Give the rate law for the reaction in the form of differential equation.
- (ii) What is the effect in rate of increasing concentrations of A, B, and C two times?
- Q.5 For the elementary reaction $2A + B_2 \longrightarrow 2AB$. Calculate how much the rate of reaction will change if the volume of the vessel is reduced to one third of its original volume?
- Q.6 Ammonia and oxygen reacts at higher temperatures as $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$ In an experiment, the concentration of NO increases by 1.08×10^{-2} mol litre⁻¹ in 3 seconds. Calculate.
- (i) rate of reaction.
- (ii) rate of disappearance of ammonia
- (iii) rate of formation of water
- Q.7 In the following reaction $2H_2O_2 \longrightarrow 2H_2O + O_2$ rate of formation of O_2 is 3.6 M min⁻¹.
- (a) What is rate of formation of H_2O ?
- (b) What is rate of disappearance of H_2O_2 ?
- Q.8 The reaction $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A & B are $P_A = 0.6$ and $P_B = 0.8$ atm, if $P_C = 0.2$ atm then calculate the ratio of rate of reaction relative to initial rate.

Answer Key

- Q.1 (a) $1 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$, (b) $3 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$
- $Q.2 \qquad (a) \ 0.019 \ mol \ L^{-1} \ s^{-1}, (b) \ 0.037 \ mol \ L^{-1} \ s^{-1}$
- Q.3 $2k_1 = k_2 = 4k_3$ Q.4 (i) $\frac{dx}{dt} = k[A][B]^2$, (ii) rate increases by 8 times
- Q.5 rate increase by 27 times
- Q.6 (i) $r = \frac{1}{4} \frac{d[NO]}{dt} = 9 \times 10^{-4} \text{mol litre}^{-1} \sec^{-1}$, (ii) $36 \times 10^{-4} \text{mol litre}^{-1} \sec^{-1}$, (iii) $54 \times 10^{-4} \text{ mol litre}^{-1}$
- Q.7 (i) 7.2 mol litre⁻¹min⁻¹, (ii) 7.2 mol litre⁻¹ min⁻¹ Q.8 1/6