Chemical Kinetics

This branch of chemistry deals with the study of rates of chemical reactions and the mechanism by which they occur. While studying reaction rates, one deals with :

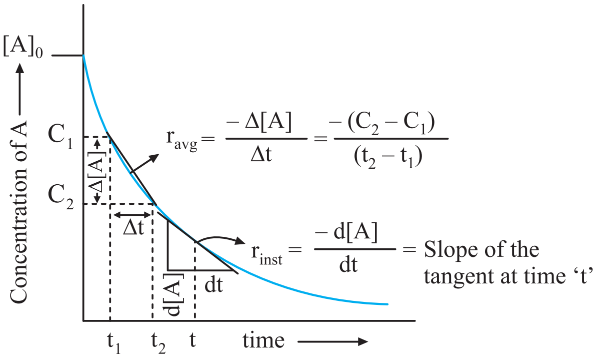
(a) How fast (or slow) the reactants get converted into products

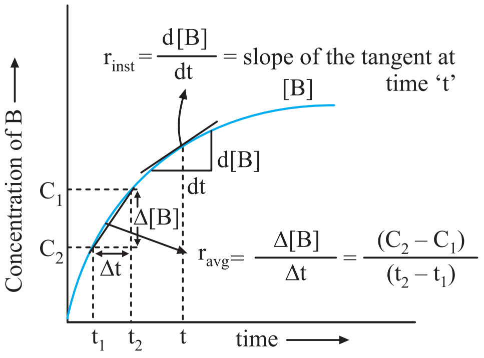
(b) The steps or paths through which the products are formed (*reaction mechanism*)

BASIC Section - 1

Rate of a Reaction :

In general, for a reaction : A $\longrightarrow$ B, the behaviour of the concentration of the reactant and product, as the reaction proceeds, is shown graphically.





From the graph, it is clear that the concentration of the reactant decreases and that of the product increases as the reaction proceeds and the rate of the change of the concentration of the reactant as well as that of the product is also changing.

Rate of a reaction can, now, be defined in two ways :

1. Average Rate of reaction (r_{avg}) given by : $r_{avg} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$

where Δ[A] and Δ[B] represents the change in the concentrations of 'A' and 'B' respectively over a time interval Δt.

The average rate of the reaction between a time interval ($t_2 - t_1 = \Delta t$) can be determined from the above graph by locating the concentration of 'A' or 'B' on this graph at the time instants t_2 and t_1 as shown.

If $[A]_2$ and $[A]_1$ are the concentrations of the reactant 'A' at the time instants t_2 and t_1, then : $r_{avg} = -\left(\frac{[A]_2 - [A]_1}{t_2 - t_1}\right)$

Similarly from the plot of 'B' as a function of 't', we have : $r_{avg} = \left(\frac{[B]_2 - [B]_1}{t_2 - t_1}\right)$

Note : The above expressions for r_{avg} is equivalent to the slope of the line joining the points (t_2, $[A]_2$) and (t_1, $[A]_1$) or (t_2, $[B]_2$) and (t_1, $[B]_1$) as shown.

2. Instantaneous Rate of reaction ($r_{inst.}$) can be calculated from r_{avg} in the limit $\Delta t \longrightarrow 0$ and is represented as :

$$r_{inst} = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$

Note :

- The above expression for $r_{inst.}$ is equivalent to the slope of the tangent from the plot of the concentration of 'A' or 'B' at any time instant 't'.
- The rate of the reaction ($r_{inst.}$ or r_{avg}) is always calculated as a positive quantity.
- The rate of the change of the concentration of the reactant will be a negative quantity since its concentration is decreasing with time.
- The rate of the change of the concentration of the product will be a positive quantity since its concentration is increasing with time.
- The magnitude of the rates of the change of the concentration of reactants and products will be equal in this case, as one mole of 'A' gives one mole of 'B' in the above reaction.
- The rate of a reaction at any temperature depends on the concentration of the reactants and sometimes on the concentration of some foreign substances (e.g a catalyst) being used in the reaction as well. The representation of this dependence of the rate of the reaction on the concentrations is known as *rate law* and this *rate law* is determined experimentally.
- The above expression for $r_{inst.}$ is called as differential rate law.

In general for a reaction :

$$mA + nB \longrightarrow pC + qD$$

The rate of reaction can be expressed as follows :

$$\text{Rate} = -\frac{1}{m}\frac{d[A]}{dt} = -\frac{1}{n}\frac{d[B]}{dt} = +\frac{1}{p}\frac{d[C]}{dt} = +\frac{1}{q}\frac{d[D]}{dt}$$

Illustrating the concept :

The rate of formation of NO(g) in the reaction $2NOBr(g) \longrightarrow 2NO(g) + Br_2(g)$ is found to be 1.6×10^{-4} M/s. Find the rate of overall reaction and rate of consumption of NOBr.

We have : $\frac{d[NO]}{dt} = 1.6 \times 10^{-4}$ M/s.

Now, Rate of overall reaction $= -\frac{1}{2}\frac{d[NOBr]}{dt} = +\frac{1}{2}\frac{d[NO]}{dt} = \frac{1}{1}\frac{d[Br_2]}{dt} = 0.8 \times 10^{-4}$ M/s

Rate of consumption of NOBr $= \frac{d[NOBr]}{dt} = 1.6 \times 10^{-4}$ M/s

Order of a Reaction :

By performing a reaction in actual in laboratory and carefully examining it, it is possible to express the rate law as the product of concentrations of reactants each raised to some power. For example consider the reaction :

$$P + 2Q \longrightarrow R$$

The differential rate law is written as :

$$\text{Rate} = -\frac{d[P]}{dt} = -\frac{1}{2}\frac{d[Q]}{dt}$$

Also, Rate can be expressed as Rate = $k\,[P]^m\,[Q]^n$

where k is called as rate constant or velocity constant or specific reaction rate.
k is a characteristic of a reaction at a given temperature. It changes only when the temperature changes.

The powers m and n are integers or fractions. m is called as order of reaction with respect to P and n is called as order of reaction with respect to Q.

The overall order of reaction = $m + n$

Note : The values of m and n are calculated from the experimental data obtained for a reaction and the powers m and n are not related to the stoichiometric coefficients of the reactants.

Units of *k* :

In general, the rate law for a n^{th} order reaction can be taken as :

$$\frac{dc}{dt} = -kc^n \qquad \left[\text{Note:} \quad r_{\text{inst.}} = -\frac{dc}{dt} = kc^n\right]$$

where k : rate constant ; c : concentration and n : order of reaction

$$\Rightarrow \qquad k = \frac{dc/dt}{c^n}$$

$$\Rightarrow \qquad \text{Units of } k \equiv (\text{mol/L})^{1-n}\,(\text{time})^{-1}$$

For a 'zero' order reaction (n = 0) :

Units of $k \equiv (\text{mol/ L})^1\,(\text{time})^{-1}$

⇒ Units are : mol/L/sec, mol/L/min, ... etc.

For a first order reaction ($n = 1$) :

Units of $k \equiv (\text{time})^{-1}$

⇒ Units are : sec^{-1}, min^{-1}, hrs^{-1} etc.

For a second order reaction ($n = 2$) :

Units of $k \equiv (\text{mol/ L})^{-1}\,(\text{time})^{-1}$

⇒ Units are : L/mol/sec, L/mol/min, ... etc.

Illustration - 1 *From the rate laws for the reactions given below, determine the order with respect to each species and the overall order:*

(i) $2HCrO_4^- + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 8H_2O$

$Rate = k\,[HCrO_4^-][I^-]^2[H^+]^2$

(ii) $H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$

$Rate = k\,[H_2O_2][I^-]$

SOLUTION :

(i) The order of the reaction with respect to $[HCrO_4^-]$ is 1; with respect to $[I^-]$ is 2 and with respect to $[H^+]$ is 2. The overall order of the reaction is $1 + 2 + 2 = 5$

(ii) The order of the reaction with respect to $[H_2O_2]$ is 1 and with respect to $[I^-]$ is 1. The overall order of the reaction is $1 + 1 = 2$

Note :

- In (i) the stoichiometric coefficient of I^- is 6 whereas the power coefficient (n) in the rate law is 2.
- Reaction (i) may not take place in a single step. It may not be possible for all the 22 molecules to be in a state to collide with each other simultaneously. Such a reaction is called a complex reaction.
- A complex reaction takes place in a series of a number of elementary reactions.

Illustration - 2 *For a reaction* $2\,NO(g) + 2\,H_2(g) \longrightarrow N_2(g) + 2\,H_2O(g)$ *; the following data were obtained.*

	$[NO](mol/L)$	$[H_2](mol/L)$	$Rate(mol/L/s)$
1.	5×10^{-3}	2.5×10^{-3}	3×10^{-5}
2.	15×10^{-3}	2.5×10^{-3}	9×10^{-5}
3.	15×10^{-3}	10×10^{-3}	3.6×10^{-4}

(a) *Calculate the order of reaction.*

(b) *Find the rate constant.*

(c) *Find the initial rate if* $[NO] = [H_2] = 8.0 \times 10^{-3}$ M

SOLUTION :

Assuming rate law can be expressed as follows :

$$\text{rate} = k\,[NO]^x\,[H_2]^y$$

By analysing the data :

From observations 1 and 2, we see that $[H_2]$ is constant and when [NO] is tripled, the rate is also tripled.

$\Rightarrow \quad \text{rate}\ (r) \propto [NO] \quad \Rightarrow \quad x = 1$

From observations 2 and 3, we see that [NO] is constant ; when $[H_2]$ is increased four times, the rate also increases four times.

$\text{rate} \propto [H_2] \quad \Rightarrow \quad y = 1$

$\Rightarrow \quad r = k\,[NO]\,[H_2]$

$\Rightarrow$ The order of reaction w.r.t NO and H_2 is 1 and the overall order of reaction is $1 + 1 = 2$.

Initial rate $= k\,[NO]\,[H_2] = 2.4 \times (8 \times 10^{-3})^2 = 1.536 \times 10^{-4}$ mol/L/s.

IN-CHAPTER EXERCISE - A

1. *For a reaction :* $2P + Q \longrightarrow S$; *following data were collected.*

	P(mol/L)	Q(mol/L)	Rate(mol/L/min)
(i)	6×10^{-2}	1×10^{-2}	0.0012
(ii)	6×10^{-2}	2×10^{-2}	0.0024
(iii)	12×10^{-2}	1×10^{-2}	0.0024

Calculate the overall order of the reaction. Also find out the reaction rate constant.

2. *The rate of a reaction :* $A + B \longrightarrow$ *products is studied to give following data.*

Initial [A] in mol/L	Initial [B] in mol/L	rate (mol/L/min)
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

What is the rate law ?

Choose the correct option. Only one choice is correct. Questions marked with '*' may have more than one correct options.

3. *In the following reaction, how is the rate of appearance of the underlined product related to the rate of disappearance of the underlined reactant ?*

$$BrO_3^-(aq) + 5\underline{Br}^-(aq) + 6H^+(aq) \longrightarrow 3\underline{Br_2}(l) + 3H_2O(l)$$

(A) $\frac{d[Br_2]}{dt} = -\frac{5}{3}\frac{d[Br^-]}{dt}$ **(B)** $\frac{d[Br_2]}{dt} = -\frac{d[Br^-]}{dt}$

(C) $\frac{d[Br_2]}{dt} = -\frac{d[Br^-]}{dt}$ **(D)** $\frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$

4. *For the reaction* $H_2(g) + I_2(g) \longrightarrow 2HI(g)$, *the rate of disappearance of* H_2 *is* 1.0×10^{-4} $mol\ L^{-1}\ s^{-1}$. *The rate of appearance of HI will be :*

(A) $1.0 \times 10^{-4}\ mol\ L^{-1}s^{-1}$ **(B)** $0.50 \times 10^{-4}\ mol\ L^{-1}s^{-1}$

(C) $2.0 \times 10^{-4}\ mol\ L^{-1}s^{-1}$ **(D)** $4.0 \times 10^{-4}\ mol\ L^{-1}s^{-1}$

5. *The rate law for a reaction between A and B is given by rate =* $k[A]^n\ [B]^m$. *On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction becomes :*

(A) $2^{1/(m+n)}$ **(B)** $m+n$ **(C)** $m-n$ **(D)** 2^{n-m}

6. *For the chemical reaction* $X \longrightarrow Y$, *it is found that the rate of reaction increases by 2.25 times when the concentration of X is increased by 1.5 times, what is the order w.r.t X ?*

(A) *zero* **(B)** *one* **(C)** *two* **(D)** *three*

***7.** *In a reaction* $2X + Y \longrightarrow X_2Y$, *the reactant X will disappear at :*

(A) *half the rate as that of disappearance of Y* **(B)** *the same rate as that of disappearance of Y*

(C) *twice the rate as that of appearance of* X_2Y **(D)** *twice the rate as that of disappearance of Y*

8. *The units of rate constant and rate of a reaction are identical for :*

(A) *zero-order reaction* **(B)** *first-order reaction*

(C) *second-order reaction* **(D)** *third -order reaction*

nth ORDER REACTIONS Section - 2

Zero Order Reactions :

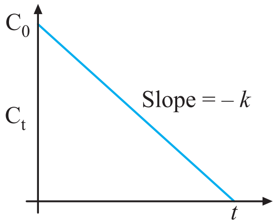
The rate law for zero order reactions ($n = 0$) is written as :

$$\frac{dc}{dt} = -k \qquad \text{.....(i)}$$

Clearly, zero order reactions are those, whose rates are not affected by change in concentrations of reactants (i.e., independent of concentration). The rates of such reactions only depend upon temperature. Most of photochemical reactions are zero order reactions. Other examples are : decomposition of HI over the surface of gold and NH_3 over tungsten.

Equation (i) can be rearranged and integrated to get the variation of the concentration of the reactants as a function of time.

$$\int_{C_0}^{C_t} dc = -\int_0^t k\,dt \quad \Rightarrow \quad [C_t - C_0] = -k\,[t - 0]$$



Thus, $$k = -\frac{[C_t - C_0]}{t} \qquad \text{.....(ii)}$$

where C_0 = Initial concentration of the reactant

and C_t = Concentration of the reactant at any time instant 't' after the reaction started

- From the above expression, it is clear that if we plot C_t as a function of time (t) then it will be a straight line with a negative slope = $-k$ and Y– Intercept of C_0.
- One can also define, Half Life ($t_{1/2}$) which is equal to the time taken for the reactant's concentration to drop to 50% of its initial value.

Putting $C_t = 0.5\,C_0$ in equation (ii), we get $t = t_{1/2} = \dfrac{C_0}{2k}$

Thus, for a Zero order reaction, half life is directly proportional to initial concentration of the reactant.

> **Note :** The equation obtained on integrating the differential rate law is known as Integrated Rate Law. For example : equation (ii) is the Integrated Rate Law for the Zero Order Reaction.