Chemical Kinetics

Rate of a reaction

The rate (speed or velocity) of a reaction is the change in concentration in per unit time.

$\frac{\Delta x}{\Delta t}$ or $\frac{dx}{dt} = \left(\frac{x_2 - x_1}{t_2 - t_1} \right)$

where Δx or *dx* is the concentration change, *i.e.,* $(x_2 - x_1)$ in the time interval Δt or *dt, i.e.,* $(t_2 - t_1)$.

Law of mass action and Rate constant

Law of mass action states that, the rate at which a substance reacts is directly proportional to its active mass and the rate at which a reaction takes place is proportional to the product of the active masses of the reacting substances.

- Rate constant for the reaction, $aA + bB \rightarrow$ product is

Rate $= \left(\frac{dx}{dt} \right) \propto [A]^a [B]^b$; $\left(\frac{dx}{dt} \right) = k[A]^a [B]^b$

Here, *k* is **rate constant** and it is also known as **velocity constant**.

If $[A] = [B] = 1\, mol\, / litre$, then $\frac{dx}{dt} = k$

Thus, rate constant k is also called **specific reaction rate**.

•   Its value depends on the nature of reactant, temperature and catalyst. It value is independent of reactants concentration.

•Unit of rate constant $= \left[\dfrac{\text{litre}}{\text{mol}}\right]^{n-1} \times \sec^{-1}$

Here, n is order of reaction.

Some Reactions

S. No.	Chemical equation	Rate law
1.	$aA + bB \rightarrow$ product	$\left(\dfrac{dx}{dt}\right) = k[A]^a[B]^b$
2.	$aA + bB \rightarrow$ product	$\left(\dfrac{dx}{dt}\right) = k[A]^2[B]^0$
3.	$2H_2O_2 \xrightarrow{Pt,\Delta} 2H_2O + O_2$	$\left(\dfrac{dx}{dt}\right) = k[H_2O_2]$
4.	$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+}$ $CH_3COOH + C_2H_5OH$	$\left(\dfrac{dx}{dt}\right) = k[CH_3COOC_2H_5]$

5.	$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+}$ Sucrose $C_6H_{12}O_6 + C_6H_{12}O_6$ Glucose Fructose	$\left(\dfrac{dx}{dt}\right) = k[C_{12}H_{22}O_{11}]$
6.	$(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$	$\left(\dfrac{dx}{dt}\right) = k[(CH_3)_3CCl]$
7.	$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$	$\left(\dfrac{dx}{dt}\right) = k[CH_3Cl][OH^-]$
8.	$C_6H_5N_2Cl \xrightarrow{\Delta} C_6H_5Cl + N_2$	$\left(\dfrac{dx}{dt}\right) = k[C_6H_5N_2Cl]$
9.	$CH_3CHO \xrightarrow{\Delta} CH_4 + CO$	$\left(\dfrac{dx}{dt}\right) = k[CH_3CHO]^{3/2}$
10.	$H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$	$\left(\dfrac{dx}{dt}\right) = k[H_2O_2][I^-]$
11.	$2O_3 \rightarrow 3O_2$	$\left(\dfrac{dx}{dt}\right) = k[O_3]^2[O_2]$

Rate constant and other parameters of different order reactions

Order	Rate constant	Unit of rate constant	(Half-life period) $T_{50}=$
0	$k_0 = \dfrac{x}{t}$	conc. time^{-1} (mol L^{-1} s^{-1})	$\dfrac{a}{2k_0}$
1	$k_1 = \dfrac{2.303}{t}\log_{10}\left(\dfrac{a}{a-x}\right)$, $C = C_0 e^{-k_1 t}$	time^{-1} (s^{-1})	$\dfrac{0.693}{k_1}$

		conc time	1
	$N = N_0 e^{-k_1 t}$, $k_1 = \dfrac{2.303}{(t_2 - t_1)} \log_{10} \dfrac{(a - x_1)}{(a - x_2)}$		
2	$k_2 = \dfrac{1}{t}\left[\dfrac{1}{(a - x)} - \dfrac{1}{a}\right] = \dfrac{x}{ta(a - x)}$ (for the case when each reactant has equal concentration) $k_2 = \dfrac{2.303}{t(a - b)} \log_{10}\left[\dfrac{b(a - x)}{a(b - x)}\right]$ (for the case when both reactants have different concentration)	$conc^{-1}$ time^{-1} $(mol\ L^{-1})\ s^{-1}$ $L\ mol^{-1}\ s^{-1}$	$\dfrac{1}{k_2 a}$
3	$k_3 = \dfrac{1}{2t}\left[\dfrac{1}{(a - x)^2} - \dfrac{1}{a^2}\right]$	$conc^{-2}$ time^{-1} $(mol\ L^{-1})^{-2}\ s^{-1}$ $L^2\ mol^{-2}\ s^{-1}$	$\dfrac{3}{2k_3 a^2}$
n	$k_n = \dfrac{1}{(n - 1)t}\left[\dfrac{1}{(a - x)^{n-1}} - \dfrac{1}{(a)^{n-1}}\right]$; $n \geq 2$	$conc^{(1-n)}$ time^{-1} $(mol\ L^{-1})^{(1-n)}\ s^{-1}$ $L^{(n-1)}\ mol^{(1-n)}\ s^{-1}$	$\dfrac{2^{n-1} - 1}{(n - 1)k_n(a)^{n-1}}$

Methods for determination of order of a reaction

Integration method

(i) The value of k is determined and checked for all sets of a, x and t.

(ii) If the value of k is constant, the used equation gives the order of reaction.

(iii) If all the reactants are at the same molar concentration, the kinetic equations are :

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} \qquad \textit{(For first order reactions)}$$

$$k = \frac{1}{t} \left[\frac{1}{a} - \frac{1}{a-x} \right] \qquad \textit{(For second order reactions)}$$

$$k = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right] \qquad \textit{(For third order reactions)}$$

Half-life method: The half-life may be described as the amount of time it takes for a reactant's concentration to fall to half of its original value.

This method is employed only when the rate law involved only one concentration term.

$$t_{1/2} \propto a^{1-n} \; ; \quad t_{1/2} = ka^{1-n} \; ; \quad \log t_{1/2} = \log k + (1-n) \log a$$

If we plot a graph of $\log t_{1/2}$ *vs log a*, we gets a straight line with slope $(1-n)$. We can find the order n by determining the slope.

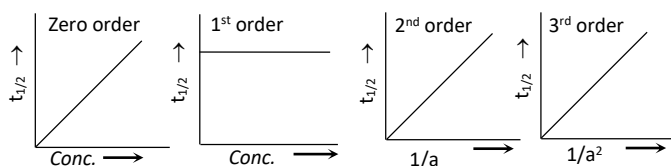If half-life at different concentration is given then,

$$(t_{1/2})_1 \propto \frac{1}{a_1^{n-1}} ; \; (t_{1/2})_2 \propto \frac{1}{a_2^{n-1}} ; \; \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1} \right)^{n-1}$$

$$\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2 = (n-1) \left[\log_{10} a_2 - \log_{10} a_1 \right]$$

$$n = 1 + \frac{\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2}{(\log_{10} a_2 - \log_{10} a_1)}$$

This relation can be used to find the '*n*'.

*Plots of half-lives Vs concentrations ($t_{1/2} \propto a^{1-n}$)*

Graphical method:

A graphical method based on the respective rate laws, can also be used.

(i) If the plot of $\log(a-x)$ Vs t is a straight line, the reaction follows first order.

(ii) If the plot of $\frac{1}{(a-x)}$ Vs t is a straight line, the reaction follows second order.

(iii) If the plot of $\frac{1}{(a-x)^2}$ Vs t is a straight line, the reaction follows third order.

(iv) In general, for a reaction of nth order, a graph of $\frac{1}{(a-x)^{n-1}}$ Vs t must be a straight line.

Plots from integrated rate equations
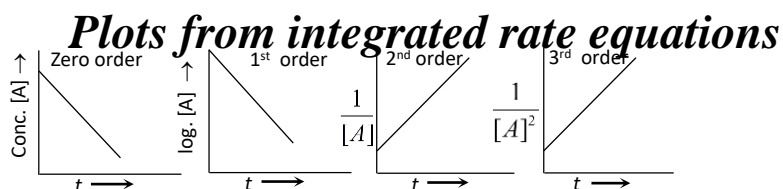
Arrhenius equation

Arrhenius proposed a quantitative relationship between rate constant and temperature as,

$$k = A\, e^{-E_a / RT} \qquad \text{.....(i)}$$

The equation is called *Arrhenius equation*.

In which constant A is known as *frequency factor*. This factor is related to number of binary molecular collision per second per litre.

E_a is the activation energy.

T is the absolute temperature and

R is the gas constant

Both A and E_a are collectively known as *Arrhenius parameters*.

Taking logarithm equation (i) may be written as,

$$\log k = \log A - \frac{E_a}{2.303\ RT} \qquad \text{.....(ii)}$$

The value of activation energy (E_a) increases, the value of k decreases and therefore, the reaction rate decreases.

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2} \right] \qquad \text{.....(iii)}$$

where k_1 and k_2 are rate constant at temperatures T_1 and T_2 respectively $(T_2 > T_1)$.