Chemical Kinetics

In, Reaction Kinetics we study about the rate of reaction, the mechanism of rxn, and the factor which can be responsible for effect of Rate of Rxn.

	A ⟶	Product
$t = t_1$	x_1	0
$t = t_2$	x_2	

$$\text{Rate of Rxn } (r) = \frac{x_1 - x_2}{t_2 - t_1}$$

$$r = \ominus \frac{\Delta x}{\Delta t}$$

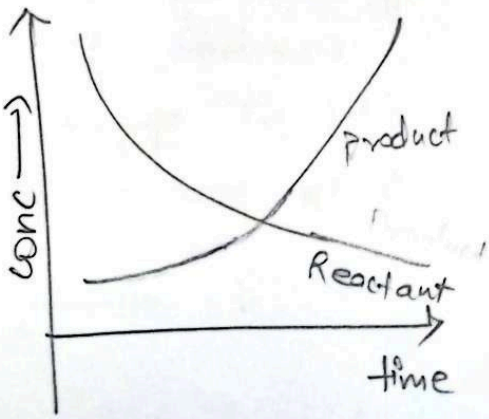
Show that (r) is decreasing

$$r = \frac{\text{conc}}{\text{time}} \quad \text{mol/Lit-sec}$$

$$\text{unit} = \left[\text{mol-Lit}^{-1}.\text{sec}^{-1}\right]$$

Instantaneous Rate of Rxn

$$r = \frac{-dx}{dt}$$



Rate law Expression

	A +	B	⟶ Product
$t=0$	(a) mole	(b) mole	0
$t = t$	$(a-x)$	$(b-x)$	x

$$r = -\frac{dx}{dt} \propto [a-x] \cdot [b-x]$$

It is simply an expression that represents a relationship b/w the rate of rxn and the molar conc^n of reactant molecules. Acc. to rate law expression the R.O.R. at any time (t) is always directly proportional to the molar conc^n. of reactant at time t.

Rate constant

$$r \propto [A][B]$$

$$r = K[A][B]$$

(1)

$$\boxed{r = K}$$

The rate of rxn is equal to the rate constant or velocity constant on the condition if the change in molar concentration of the reactant molecules with time is taken as unity (1).

Factor Affecting the Rate of a chemical Reaction:-

~~1) molar conc^n.~~

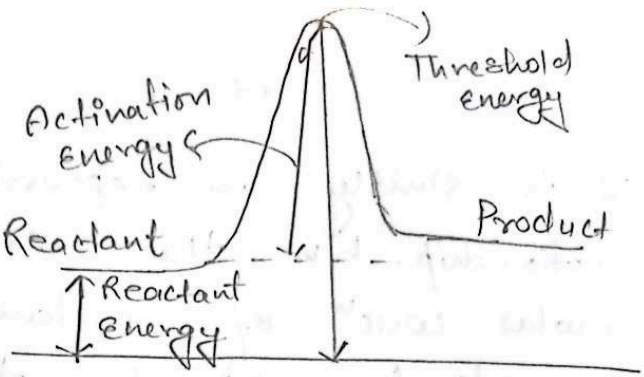
1) Molar conc^n. of Reactant molecules :-

$$n \propto r.o.r.$$

2) Temperature :-

on increasing the temp. R.O.R increases.

For each 10° rise in Temp. The R.O.R. Doubles.



3) Catalyst :-

4) Nature or size of Reactant molecules :-

Smaller size → more R.O.R.

5) Radiation :- inc. the R.O.R

Molecularity :- The total no. of Reactant molecules participating in any chemical Rxn.

Order of Rxn :- It is the no. of those Reactant molecules whose change in conc^n of during the rxn changing the R.O.R.

Molecularity	Rate of Rxn
1) Total no. of Reactant molecules.	1) Total no. of Actively Participate Reactant molecule
2) Theoritical concept	2) Experimental concept
3) Can never be zero (always a whole no.)	3) Can be zero, integer & fraction No. also.
4)	4)

5) not give the information about the mechanism of Rxn.

5) Give Information about the mechanism of Rxn.

Pseudo order Rxn

1) $H_2 + Cl_2 \xrightarrow{hv} 2HCl$

2) Hydrolysis of Ester in Presence of Acid

$CH_3COOC_2H_5 + H_2O \xrightarrow{HCl} CH_3COOH + C_2H_5OH$

Order of Rxn = (1)

3) Hydrolysis of Ester in presence of base

$CH_3COOC_2H_5 + H_2O \xrightarrow{Base} CH_3COOH + C_2H_5OH$

Order Rxn :- (2)

→ Those Rxn. which appears to be of Higher order but actually it follows the kinetics of lower order such Rxn. are known as Pseudo order rxn.

$$r = \frac{-dx}{dt} \propto [CH_3COOC_2H_5]^1 \cdot [H_2]^0$$

order of Rxn = 1+0 = 1

order of Rxn :-
It is the sum of power raised on the molar conc^n. Term of the Reactant molecule in a rate law expression.

Units for Rate constant (K) for different order of Rxn :-

For ~~first~~ Zero order

$A \longrightarrow$ Product

$t=0$	a	0
$t=t$	$(a-x)$	x

$$r = \frac{dx}{dt} \propto [a-x]^0$$

$$\frac{dx}{dt} = K$$

$$K = \frac{\text{conc.}}{\text{time}}$$

$$\boxed{K = \text{mol } L^{-1} \text{sec}^{-1}}$$

For ~~second~~ First order :-

$$r = \frac{dx}{dt} \propto [a-x]^1$$

$$\frac{dx}{dt} = K[a-x]$$

$$K = \frac{1}{dt} = \frac{1}{\text{sec}} = \text{sec}^{-1}$$

General Formula

$$K = [\text{mol} \cdot Lit^{-1}]^{1-n} \text{ sec}^{-1}$$

Derivation For the Rate constant (K) For different order of Rxn :-

→ Zero Order :-

	A	⟶	Product
t = 0	a		0
t = t	(a-x)		x

$$r = \frac{dx}{dt} \propto [a-x]^0$$

$$\frac{dx}{dt} = k$$

on Integration

$$dx = k\,dt$$

$$x = kt + c$$

when $t = 0 \longrightarrow x = 0$; $c = 0$

$$\boxed{k = \frac{x}{t}}$$

$$\left[k = \frac{a-(a-x)}{t}\right]$$

Q The Rate constant of a zero order rxn is .2 mol/L h what will be the initial conc^n of the reactant molecule if after half an hour its conc^n. dropped down to .5 mol/L.

Half life for zero order:-

$t \longrightarrow t_{1/2}$, $x = a/2$

$$k = \frac{x}{t}$$

$$\left[T_{1/2} = \frac{a}{2k}\right]$$

$$\left[T_{1/2} \propto a\right]$$

For First order (Derivation)

Imp. V.V.

	A	⟶ Product
$t=0$	(a)	0
$t=t$	$(a-x)$	x

$$r = \frac{dx}{dt} \propto [a-x]^1$$

$$\frac{dx}{dt} = k[a-x]$$

$$\frac{dx}{a-x} = kt$$

on Integration

$$-\log_e(a-x) = kt + c \quad -(1)$$

when $t=0 \longrightarrow x=0$

$$c = -\log_e a \quad \text{(Put in (1))}$$

$$\log_e a - \log_e(a-x) = kt$$

$$\ln\left(\frac{a}{a-x}\right) = kt$$

$$\frac{a}{a-x} = e^{kt}$$

$$\left[k = \frac{2.303}{t} \log_{10} \frac{a}{a-x} \right]$$

For 1

Q Prove that the time Req. to complete any fraction of a first order rxn is independent on the initial conc^n of the Reactant molecule.

$$k = \frac{2.303}{t_{1/2}} \log_{10} \left(\frac{a}{a - a/2} \right) \quad \left\{ t \to t_{1/2},\ x = a/2 \right.$$

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

$$\left[T_{1/2} = \frac{.693}{k} \right]$$

Q prove that in case of a 1st order rxn the time Req. for 99.9% completion of Rxn is about 10 times more req. for Half completion of Rxn.

Let initial conc^n = 100

$$T_{99.9} = \frac{2.303}{k} \log \left(\frac{100}{100 - 99.9} \right)$$

$$= \frac{2.303}{k} \log (10^3) (100)$$

$$T_{99.9} = \frac{9.303 \times 3}{k} = \frac{6.909}{k}$$

$$T_{1/2} = \frac{.693}{k}$$

$$\text{So, } \frac{T_{99.9}}{T_{1/2}} = \frac{\frac{.693}{k} \times 10}{.693/k} = \frac{100}{10} = 10$$

Q The First order Rxn is 75% in 72 minutes How long will it take for $(\frac{1}{2})$ to complete.

Q The Rate const for a First order Rxn is $(2.2 \times 10^{-5})/s$ determine the time Req. if the Rxn is 15% complete

$$k = \frac{2.303}{t} \log_{10}\left(\frac{a}{a-x}\right)$$

$$2.2 \times 10^{-5} = \frac{2.303}{t} \log_{10}\left(\frac{100}{100-15}\right)$$

$$t = \frac{2.303}{2.2 \times 10^{-5}} \times \log_{10}\left(\frac{100}{85}\right)$$

Q The Rate constant for a first order Rxn involving a compound (A) was Found to be .02/min when the initial conc^{n}. of a is given as .15 mol/L, How long will it take to conc. of a to drop down to (.02) mol/L

$$k = \frac{2.303}{t} \log_{10}\left(\frac{a}{a-x}\right)$$

$$.02 = \frac{2.303}{t} \log_{10}\left(\frac{.15}{.02}\right)$$

$$t = 1.963 \text{ min}$$