N.B All the radio-activity is 1st order rkn.

$$^{226}_{88}Ra \xrightarrow{-\alpha} {}^{222}_{86}Rn + {}^{4}_{2}He$$

First order rkn:

VVI

# Expression for the rate const of 1st order rkn

$$\boxed{K = \frac{2.303}{t} \log \frac{a}{(a-x)}}$$

$$t = \frac{2.303}{d} \log \frac{N_0}{N_t} \quad (\text{In Phy})$$

Suppose first order reaction is represented as:→

| | | R | ⟶ | P |
|---|---|---|---|---|
| Initially | $t = 0$ | a mol/lit | | 0 |
| After | $t = t$ | $(a-x)$ mol/lit | | $x$ mol/lit |

$$\text{Rate} = -\frac{d}{dt}(a-x) \propto [a-x]^1$$

$$\Rightarrow -\frac{da}{dt} + \frac{dx}{dt} = k \cdot [a-x]^1$$

$$\Rightarrow 0 + \frac{dx}{dt} = k(a-x)$$

$$\Rightarrow \frac{dx}{dt} = k(a-x)$$

Reactant ——→ Product

Rate ∝ [Reactant]¹

rate = k [R]²

order = 1

eg – (i) $PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$

rate ∝ $[PCl_5]^1$

rate = k · $[PCl_5]^1$

order = 1

molecularity = 1

(ii) $2HI \xrightarrow{\Delta} H_2 + I_2$

rate ∝ $[HI]^1$

order = 1 , molecularity = 2

(iii) $CH_3-COOC_2H_5 + H_2O \rightarrow CH_3-COOH + C_2H_5OH$

rate ∝ $[CH_3-COOC_2H_5]^1 [H_2O]^0$

order = 1 + 0 = 1 , molecularity = 2

(iv) $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

rate ∝ $[C_{12}H_{22}O_{11}]^1 [H_2O]^0$

order = 1 , molecularity = 2

(v) $2N_2O_5 \xrightarrow{\Delta} 4NO_2 + O_2$

rate ∝ $[N_2O_5]^1$

order = 1 , Molecularity = 2

(vi) $C_6H_5N{=}N{-}Cl + H_2O \longrightarrow C_6H_5OH + N_2 + HCl$

rate = k $[C_6H_5N_2Cl]^1$ $[H_2O]^0$

Order = 1

Molecularity = 2.

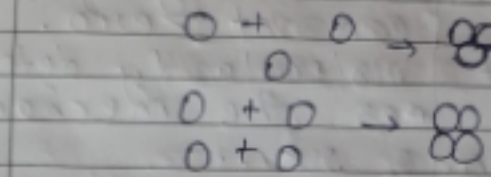
| Order | Molecularity |
| --- | --- |
| i) It is the sum of powers of con$^{n}$ of reactant mol. appearing in rate law eqn. | It is no. of reacting species undergoing simultaneously collision in the elementary or simple rkn. |
| ii) Order is an experimental quantity | It is theoritical concept. |
| iii) Order may be fractional. It is not a whole no. | It has whole no. value only 1, 2, 3... |
| iv) Order of rkn can be zero. | Molecularity of rkn can not zero. |
| v) Order does not determine the mechanism of rkn. | Molecularity determines the mechanism of rkn. |
| vi) Order is affected by the temperat. ure & concentra$^{n}$ | It is unaffected by the temp$^{r}$ & concent$^{n}$ |
| vii) Order is valid for elementary as well as complex rkn | It is applicable for only elementary rkn. |

9) **First Order Reaction:**

Those chemical reaction whose rate is directly proportional to 1st power of conc$^{n}$ of reactant is called 1st order rkn.

- If molecularity is 1, then it is known as unimolecularity.
- If molecularity is 2, then it is known as bimolecularity
- If molecularity is 3, then it is known as trimolecularity.

more than 3 molecularity is not possible because more than 3 molecules can not collide simultaneously.




## Characteristics of molecularity -

(i) It is a theoritical quantity. (ii) It can never be zero or fractional. (iii) It determines the mechanism of reaction (iv) It is not applicable for complex reaction (v) It is applicable for elementary rxn.
(vi) It is independent from conc$^{n}$ & temp$^{e}$.

Q. What is difference b/w order & Molecularity ?

Overall order of reaction: $x+y$

⇒ Order: Sum of powers of conc of all the reactant molecules appearing in rate law expression is called order of rkn.

→ Order may be +ve, -ve, zero & fraction.

→ It is experimental quantity.

⇒ It depends on temperature & conc.

## VI Characteristics of order of Reaction:-

i. Order is an experimental quantity.

ii. It is applicable for both elementary or complex reaction.

iii. Order may be +ve, -ve, zero or fraction.

Ex. It does not determine the mechanism of rkn.

v. Order depends upon temp & conc.

* Molecularity - The total no. of reacting species (atoms, molecules, ions) which collides simultaneously to bring a chemical change is called molecularity.

⇒ It is a theoretical quantity.

⇒ It can never be zero or fractional

It is independent from the conc & temperature.

(i.e. $h\nu$)

Reacting species absorb UV light (photonic energy) which uses the energy of reacting species. Therefore rate of rxn uses

e.g. - $H_2(g) + Cl_2(g) \xrightarrow{\text{presence of UV}} 2HCl$

$H_2 + Cl_2 \xrightarrow{\text{absence of UV}}$ no rxn

$CH_3-C(=O)-CH_3 \xrightarrow{UV} CH_3-CH_3 + CO$

$CH_4 + Cl_2 \xrightarrow{\text{diffused sunlight}} CH_3Cl + H-Cl$

i) $CH_4 + Cl_2 \xrightarrow{\text{dark}}$ no rxn

ii) $CH_4 + 4Cl_2 \xrightarrow{\text{open sunlight}} CCl_4 + 4HCl$

→ Lesser activation energy - higher will be rate of rxn, higher activation energy, lower rate of rxn

## Order & Molecularity :→

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

rate $\propto [A]^x [B]^y$

∴ rate $= k \cdot [A]^x \cdot [B]^y$ → this is known as rate law expression.

where x is the order of reaction w.r.t reactant A.

y is the order of reaction w.r.t reactant B.

→ Catalyst adsorb one of the reactant molecules on its surface which decreases the bond energy provide large surface area for the rxn by lowering the activation energy which increases the rate of rxn.

$$A + B + [C] \longrightarrow \left[\begin{array}{c} A \cdots C \\ \vdots \\ B \end{array}\right] \rightarrow \begin{array}{c} A \cdots B \\ \diagdown\ \diagup \\ C \end{array}$$

$$\rightarrow A\text{-}B + [C]$$

(iv) Surface area - With ↑ing surface area contact of molecules ↑ses so, rate of rxn ↑ses.

→ Rate of rxn gaseous > liquid > solid

Similarly

homogeneous system has higher rate of rxn than heterogeneous system.

e.g i) a log of wood burns slowly than the chips of wood.

ii) $\underset{\text{2 sc}}{2NO} + O_2 \longrightarrow 2NO_2$

larger no of bonds.

iii) $\underset{\text{1 sc}}{CH_4} + O_2 \longrightarrow CO_2 + 2H_2O$

(v) Light or Radiation - Those chemical rxn which occurs in the ↑nce of sunlight or UV light known as photochemical rxn.