Rate Law

↓

Explains the dependence of Rate of Reaction (ROR) on the Concentration of Species of reaction

Note: This dependency is very complex as it changes with change in concentration of species

But, we study the simplest form of dependence of ROR on concentration of reactants & products.

This can be obtained experimentally ONLY

for example, chemical Reaction
⇓

$$2A + 3B \longrightarrow 4C$$

$$\left.\begin{aligned} ROR &\propto [A]^1 \\ ROR &\propto [B]^2 \end{aligned}\right\} \text{experimental conclusions}$$

$$\Rightarrow \boxed{ROR = K[A]^1[B]^2} \text{ Rate Law}$$

$[A]$ = Concentration of A

$[B]$ = " " B

1 = order of Reaction w.r.t A

2 = " " " " B

1+2 = 3 = overall order of reaction → called 'n'

Note: Guldberg & Waage Law of Mass Action suggested to use Stoichiometric Coefficient as power in rate Law → which is wrong

$ROR = K[A]^2[B]^3$ → wrong.

K = Rate Constant / velocity Constant / Specific Reaction Rate.

$$\text{Units of } K = \frac{\text{Rate}}{[A]^1[B]^2} = \frac{\text{Rate}}{(\text{Concentration})^n}$$

where n = order of reaction

$$\text{units of } K = \frac{\frac{Mol}{l}\, s^{-1}}{\left(\frac{Mol}{l}\right)^n} = \left(\frac{Mol}{l}\right)^{1-n} s^{-1}$$

$$\text{units of } K = \left(\frac{Mol}{l}\right)^{1-n} (time)^{-1}$$

Note: By knowing units of K, we can predict order of Reaction

Q) if $K = 3\times10^{-3}\ l^2\,mol^{-2}\,s^{-1}$, find order of Reaction.

$$\left(\frac{mol}{l}\right)^{1-n} s^{-1} = \left(\frac{mol}{l}\right)^{-2} s^{-1}$$

$$1-n = -2$$

$\boxed{n=3}$ Third order Reaction

Order of Reaction (n)	Units of K
0 (zero order)	$\frac{mol}{l} s^{-1}$
1 (First order)	$\left(\frac{mol}{l}\right)^{0} s^{-1}$
2 (second order)	$\left(\frac{mol}{l}\right)^{-1} s^{-1}$
$-\frac{1}{2}$ (Half order)	$\left(\frac{mol}{l}\right)^{3/2} s^{-1}$

Order of Reaction :-

i) experimentally determined

ii) can be 0, −ve, +ve & fractional

<u>example</u> $n = 0, -1, -\frac{1}{2}, -\frac{3}{2}, +3, +\frac{7}{3}$ etc.

Q) If $2A + B \longrightarrow$ Products

order w.r.t $A \longrightarrow 2$

" " $B \longrightarrow -1$

write rate Law expression. Find order of reaction (overall). What will be the effect on rate of reaction if

i) conc of A is doubled alone

ii) conc of B is halved alone

iii) conc of both A & B is doubled

iv) volume of container is halved

v) volume of container is tripled.

Solution

$$ROR = K[A]^2[B]^{-1}$$

i) $r_1 = K[A]^2[B]^{-1}$

$r_2 = K[2A]^2[B]^{-1}$

$\frac{r_2}{r_1} = 4$ $\qquad r_2 = 4r_1$ Increases 4 times

(see $ROR \propto A^2$)

ii) $r_1 = K[A]^2[B]^{-1}$

$r_2 = K[A]^2\left[\frac{B}{2}\right]^{-1}$

$\frac{r_2}{r_1} = 2$ $\qquad r_2 = 2r_1$ Increases 2 times

(see $ROR \propto \frac{1}{B}$)

iii) $r_1 = K[A]^2[B]^{-1}$

$r_2 = K[2A]^2[2B]^{-1}$

$\frac{r_2}{r_1} = 2$ $\quad r_2 = 2r_1$ Increases 2 times

iv) when volume is halved, concentration of both A & B is doubled

⇒ same as above

$r_2 = 2r_1$ Increases 2 times

v) when volume is 3 times, conc of both A & B will be $\frac{1}{3}$ times

$r_1 = [A]^2[B]^{-1}$

$r_2 = \left[\frac{A}{3}\right]^2\left[\frac{B}{3}\right]^{-1}$

$\frac{r_2}{r_1} = \frac{1}{3}$ $\quad r_2 = \frac{r_1}{3}$ decreases 3 times

Q2) $3A + 2B \longrightarrow$ Products

On doubling the concentration of A alone, rate increases 2 times while on doubling the concentration of both A & B rate increases 8 times. Write correct rate law expression & find overall order of reaction.

Solution

Let $\text{Rate} = K[A]^x[B]^y$

$$r = K[A]^x[B]^y \quad \text{—(i)}$$

$$2r = K[2A]^x[B]^y \quad \text{—(ii)}$$

$$8r = K[2A]^x[2B]^y \quad \text{—(iii)}$$

(ii) ÷ (i)

$$2 = 2^x \quad \Rightarrow x = 1$$

(iii) ÷ (ii)

$$4 = 2^y \quad \Rightarrow \quad y = 2$$

$$\text{Rate} = K[A]^1[B]^2$$

overall order $= 1+2 = 3$

Q3) $2A + B + 3C \longrightarrow$ Products

On doubling volume of container, rate decreases 8 times

On doubling conc of A & half conc of B rate Increases 4 times

$[C] \rightarrow 4$ times $\Rightarrow$ rate Increases 64 times

Write correct rate law expression & find order of reaction.

Solution $ROR = K[A]^x[B]^y[C]^z = r$ —(i)

$$\frac{r}{8} = K\left[\frac{A}{2}\right]^x\left[\frac{B}{2}\right]^y\left[\frac{C}{2}\right]^z \quad \text{—(ii)}$$

$$4r = K[2A]^x\left[\frac{B}{2}\right]^y[C]^z \quad \text{—(iii)}$$

$$64r = K[A]^x[B]^y[4C]^z \quad \text{—(iv)}$$

(i) ÷ (ii) $\quad 8 = 2^{x+y+z} \qquad x+y+z = 3$

(iv) ÷ (i) $\quad 64 = 4^z \qquad z = 3$

(iii) ÷ (i) $\quad 4 = 2^{x-y} \qquad x-y = 2$

$x+y+3 = 3$

$x+y = 0$

$+\ x-y = 2$

$\boxed{x=1} \quad \boxed{y=-1} \quad \boxed{z=3}$

$ROR = K[A]^1[B]^{-1}[C]^3$

Important examples showing order & rate Law

(i) $2N_2O_5 \longrightarrow 4NO_2 + O_2$ ROR $= K[N_2O_5]^1$

(ii) $5Br^{\ominus} + BrO_3^{\ominus} + 6H^+ \longrightarrow 3Br_2 + 3H_2O$
ROR $= K[Br^-]^1[BrO_3^-]^1[H^+]$

(iii) $2O_3 \longrightarrow 3O_2$ ROR $= K[O_3]^2[O_2]^{-1}$
(products)

Rate Law में Reactant & Product दोनों हो सकते हैं।

(iv) $NO_2 + CO \longrightarrow NO + CO_2$ Rate $= K[NO_2]^2[CO]^0$

(v) $CH_3CHO \longrightarrow CH_4 + CO$ Rate $= K[CH_3CHO]^{3/2}$

(vi) $2SO_2 + O_2 \xrightarrow{NO} 2SO_3$ Rate $= K[O_2]^2[NO]^1$
Catalyst

Intermediate कभी भी नहीं आ सकता, Catalyst आ सकता है।

Simple / Elementry Single Step Reaction.

$2A + B \longrightarrow$ Products

$ROR = K[A]^2 [B]^1$ $\Rightarrow$ Simple

(Stochiometric coeffecient used for power)

$H_2 + I_2 \longrightarrow 2HI$

$Rate = K[H_2]^1[I_2]^1$ $\Rightarrow$ Simple

This was also suggested by Guldberg & Wagge
Law of Mass Action

But they Predicted this to be true for all reactions which is wrong.

ex

$H_2 + Cl_2 \longrightarrow 2HCl$

Law of Mass Action $Rate = K[H_2]^1[Cl_2]^1$ (wrong) ✗

experimentally (Actual) $Rate = K[H_2]^0[Cl_2]^0$ (Correct ✓)

$\Rightarrow$ Not Simple Reaction

Note: Rate Law can be obtained experimentally only. Don't use Stochiometric coeffecient unless mentioned as Simple / Elementry Reaction.