

Rate Law

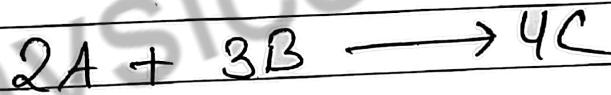
Explains the dependence of Rate of Reaction (ROR) on the concentration of species of reaction

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



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

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

$[A]$ = 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
 $ROR = K[A]^2[B]^3 \rightarrow$ wrong.

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

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

where n = order of reaction

$$\text{Units of } K = \frac{\text{Mol s}^{-1}}{\ell} = \left(\frac{\text{Mol}}{\ell} \right)^{1-n} \text{s}^{-1}$$

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

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

Q) if $K = 3 \times 10^{-3} \ell^2 \text{ mol}^{-2} \text{ s}^{-1}$, find order of reaction.

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

$$1-n = -2$$

$n=3$ Third order Reaction

Order of Reaction (n)

units of K

0 (zero order)

$\frac{\text{mol}}{\text{l}} \text{s}^{-1}$

1 (First order)

$(\frac{\text{mol}}{\text{l}})^0 \text{s}^{-1}$

2 (Second order)

$(\frac{\text{mol}}{\text{l}})^{-1} \text{s}^{-1}$

$-\frac{1}{2}$ (Half order)

$(\frac{\text{mol}}{\text{l}})^{3/2} \text{s}^{-1}$

Order of Reaction :-

i) experimentally determined

ii) can be 0, -ve, +ve & fractional

example $n = 0, -1, -\frac{1}{2}, -\frac{3}{2}, +3, +\frac{7}{3} \text{ etc}$

Q) If $2A + B \rightarrow \text{Products}$
 Order w.r.t $A \rightarrow 2$
 " " $B \rightarrow -1$

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

on rate of reaction if

- Conc of A is doubled alone
- Conc of B is halved alone
- Conc of both A & B is doubled
- Volume of container is halved
- Volume of container is tripled

Solution

$$\text{ROR} = k[A]^2[B]^{-1}$$

$$i) \quad r_1 = k[A]^2[B]^{-1}$$

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

$$\frac{r_2}{r_1} = 4$$

$r_2 = 4r_1$, Increases 4 times
 (see $\text{ROR} \propto A^2$)

$$ii) \quad r_1 = k[A]^2[B]^{-1}$$

$$r_2 = k[A]^2[B_2]^{-1}$$

$$\frac{r_2}{r_1} = 2$$

$r_2 = 2r_1$, Increases 2 times
 (see $\text{ROR} \propto \frac{1}{B}$)

$$\text{iii) } \tau_1 = K[A]^2[B]^{-1}$$

$$\tau_2 = K[2A]^2[2B]^{-1}$$

$$\frac{\tau_2}{\tau_1} = 2$$

$\tau_2 = 2\tau_1$, Increases 2 times

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

⇒ same as above

$$\tau_2 = 2\tau_1, \text{ Increases 2 times}$$

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

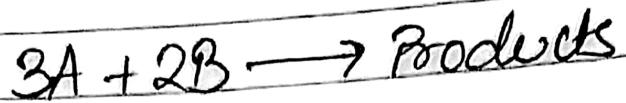
$$\tau_1 = [A]^2[B]^{-1}$$

$$\tau_2 = \left[\frac{A}{3}\right]^2 \left[\frac{B}{3}\right]^{-1}$$

$$\frac{\tau_2}{\tau_1} = \frac{1}{3}$$

$\tau_2 = \frac{\tau_1}{3}$ decreases 3 times

(Q2)



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

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

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

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

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

$$\text{(ii)} \div \text{(i)}$$

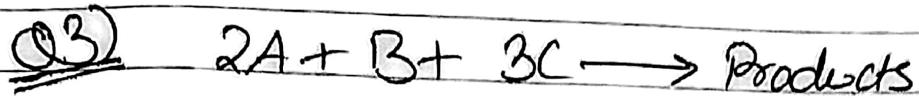
$$2 = 2^x \Rightarrow x = 1$$

$$\text{(iii)} \div \text{(ii)}$$

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

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

$$\text{overall order} = 1+2 = 3$$



On doubling volume of container, rate decreases 8 times

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

$[C] \rightarrow 4 \text{ times} \rightarrow \text{rate Increases 64 times}$

Write correct rate law expression & find order of reaction.

Solution ROR = $K[A]^x[B]^y[C]^z = \gamma$ - (i)

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

$$4\gamma = K(2A)^x\left(\frac{B}{2}\right)^y\left(C\right)^z - (\text{iii})$$

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

$$(\text{ii}) \div (\text{iii}) \quad 8 = 2^{x+y+z} \quad x+y+z = 3$$

$$(\text{iv}) \div (\text{i}) \quad 64 = 4^z \quad z = 3$$

$$(\text{ii}) \div (\text{i}) \quad 4 = 2^{x-y} \quad x-y = 2$$

$$x+y+3=3$$

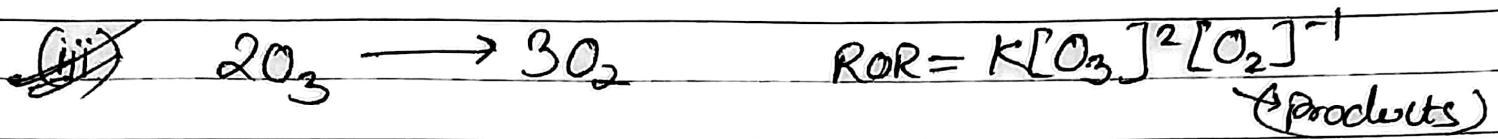
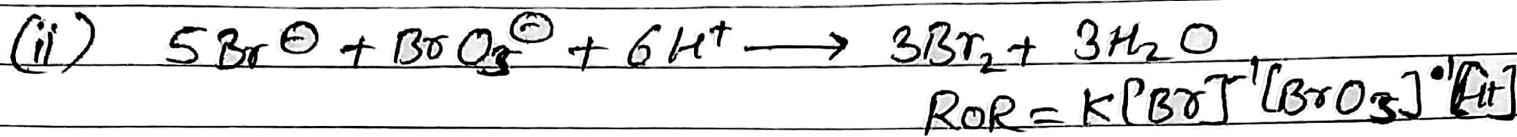
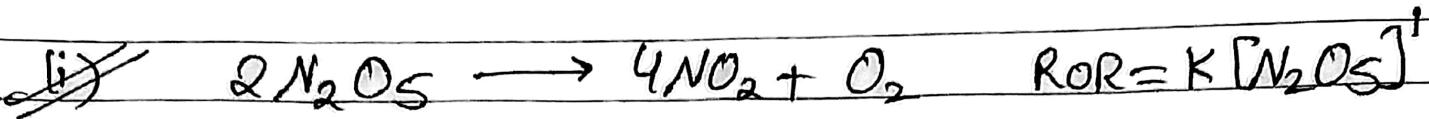
$$x+y=0$$

$$+ x-y=2$$

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

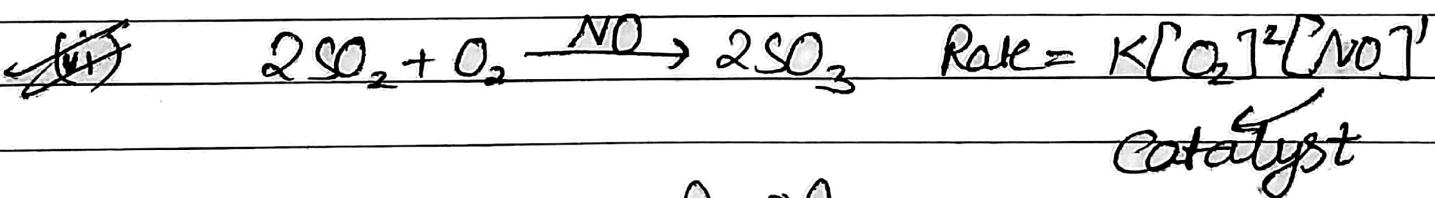
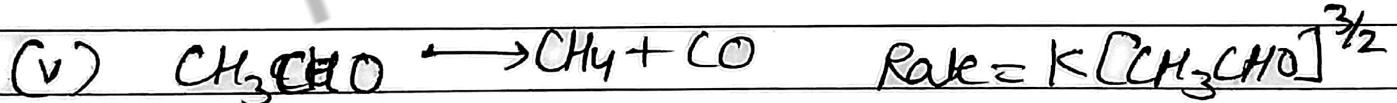
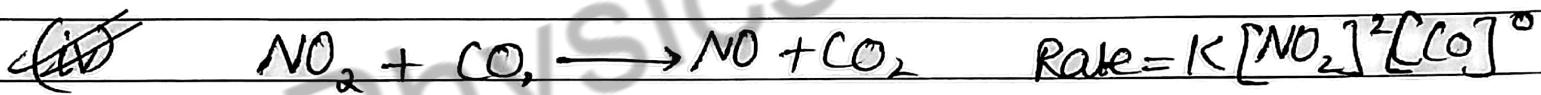
$$\text{ROR} = K[A][B][C]$$

Important examples showing order & rate law



Rate Law \propto Reactant & Product दीनी ही

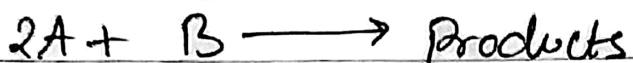
साधारण है.



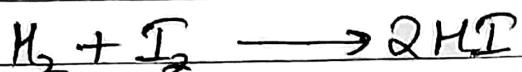
Intermediate नहीं ही

नहीं तो राहि, catalyst तो माना है

Simple / Elementary Single Step Reaction.



$$\text{RoR} = K[A]^2 [B]^1 \Rightarrow \text{Simple}$$



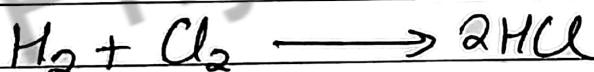
(Stoichiometric coefficient)
used for power

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

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

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

Ex



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

Experimentally
(Actual)

$$\text{Rate} = K[H_2]^0[Cl_2]^0$$
 (correct) ✓

⇒ Not Simple Reaction

Note: Rate Law can be obtained experimentally
only. Don't use Stoichiometric coefficient
unless mentioned as simple / elementary reaction.