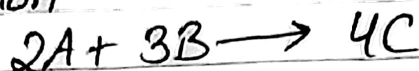


Chemical Kinetics - 07

Initial Rate Method to find Rate Law & Order of Reaction.

we have studied that,
for a Reaction



$$\text{Rate of Reaction} = \text{ROR} = r = K[A]^x[B]^y$$

$K \rightarrow$ Rate Constant

$[A] \rightarrow$ Concentration of A

$[B] \rightarrow$ " " B

$x \rightarrow$ order of Reaction w.r.t A

$y \rightarrow$ " " " " B

$x + y = n =$ overall order of reaction

Rate Law expression $r = K[A]^x[B]^y$ & order (n)
can be obtained experimentally only

For a Reaction $2A + B \rightarrow \text{Products}$
following data is available, write Rate Law
expression & find order of Reaction & rate constant

Initial [A] (in mol/L)	Initial [B] (in mol/L)	Initial (r) Rate of Reaction (in mol/L.s)
0.1	0.1	2×10^{-3}
0.1	0.2	1×10^{-3}
0.2	0.1	4×10^{-3}

Solution Let $ROR = K[A]^x[B]^y$

put the values available

$$2 \times 10^{-3} = K[0.1]^x[0.1]^y \quad \text{--- (i)}$$

$$1 \times 10^{-3} = K[0.1]^x[0.2]^y \quad \text{--- (ii)}$$

$$4 \times 10^{-3} = K[0.2]^x[0.1]^y \quad \text{--- (iii)}$$

$$(ii) \div (i)$$

$$\frac{1}{2} = 2^y \Rightarrow 2^{-1} = 2^y \quad \boxed{y = -1}$$

$$(iii) \div (i)$$

$$2 = 2^x \Rightarrow \boxed{x = 1}$$

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

order of reaction = $1 - 1 = 0$ Zero order

from (i)

$$2 \times 10^{-3} = K[0.1]^1[0.1]^{-1}$$

$$2 \times 10^{-3} = K(0.1)^0$$

$$\boxed{K = 2 \times 10^{-3} \text{ mol s}^{-1}}$$

↓
Rate constant

So,

$$ROR = 2 \times 10^{-3} [A]^1 [B]^{-1}$$

Q2) Find Order of Reaction, Rate constant, write Rate Law expression

Initial [A] (mol/L)	Initial [B] (mol/L)	Initial ROR (mol/Ls)
0.2	0.1	1×10^{-3}
0.2	0.2	4×10^{-3}
0.4	0.2	0.25×10^{-3}

Solution: Let $ROR = K[A]^x[B]^y$

put values;

$$1 \times 10^{-3} = K[0.2]^x[0.1]^y \quad \text{---(i)}$$

$$4 \times 10^{-3} = K[0.2]^x[0.2]^y \quad \text{---(ii)}$$

$$0.25 \times 10^{-3} = K[0.4]^x[0.2]^y \quad \text{---(iii)}$$

$$(ii) \div (i)$$

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

$$(iii) \div (ii) \quad \frac{1}{16} = 2^x \Rightarrow 2^{-4} = 2^x \Rightarrow x = -4$$

$$ROR = K[A]^{-4}[B]^2$$

using (i)

$$1 \times 10^{-3} = K[0.2]^{-4}[0.1]^2$$

$$K = \frac{10^{-3}}{\left(\frac{2}{10}\right)^{-4} \times \left(\frac{1}{10}\right)^2} = \frac{10^{-3} \times \left(\frac{2}{10}\right)^4 \times 10^2}{1} = 16 \times 10^{-5}$$

$$ROR = 16 \times 10^{-5} [A]^{-4} [B]^2$$

Short cut:

$$ROR \propto [B]^{-1}$$

Q1)

[A]	[B]	ROR
0.1	0.1	2×10^{-3}
0.1	0.2	1×10^{-3}
0.2	0.1	4×10^{-3}

Annotations: [A] is constant, [B] is doubled. ROR is halved. ROR is doubled.

$$ROR \propto [A]^1$$

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

Q2)

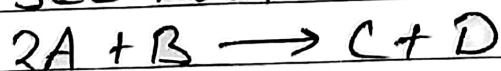
[A]	[B]	ROR
0.2	0.1	1×10^{-3}
0.2	0.2	4×10^{-3}
0.4	0.2	0.25×10^{-3}

Annotations: [A] is constant, [B] is doubled. ROR increases 4 times. ROR decreases 16 times.

$$ROR \propto [A]^{-4}$$

$$ROR = K [A]^{-4} [B]^2$$

Q3) 2014 IIT JEE Main



Initial [A] (mol/l)	Initial [B] (mol/l)	Initial Rate of Formation of C (mol/l)
0.1	0.1	1.2×10^{-3}
0.1	0.2	1.2×10^{-3}
0.2	0.1	2.4×10^{-3}

The rate Law for formation of C

$$\frac{dc}{dt} =$$

a) $k[A][B]$

b) $k[A]^2[B]$

c) $k[A][B]^2$

d) $k[A]$

Solution

[A]	[B]	ROR	ROR $\propto [B]^0$
Constant $\begin{pmatrix} 0.1 \\ 0.1 \end{pmatrix}$	$\begin{pmatrix} 0.1 \\ 0.2 \end{pmatrix}$ double	$\begin{pmatrix} 1.2 \times 10^{-3} \\ 1.2 \times 10^{-3} \end{pmatrix}$ No change	
$\begin{pmatrix} 0.1 \\ 0.2 \end{pmatrix}$ double	Constant $\begin{pmatrix} 0.1 \\ 0.1 \end{pmatrix}$	$\begin{pmatrix} 1.2 \times 10^{-3} \\ 2.4 \times 10^{-3} \end{pmatrix}$ double	ROR $\propto [A]^1$

Note that $2A + B \rightarrow C + D$

$$ROR = -\frac{1}{2} \frac{dA}{dt} = -\frac{1}{1} \frac{dB}{dt} = +\frac{dC}{dt} = +\frac{dD}{dt}$$

So $\frac{dC}{dt} = ROR$

$$\frac{dc}{dt} = ROR = k[A]^1[B]^0 = k[A]$$

Q4) IIT Advance 2014 For $M \rightarrow N$

The Rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of reaction w.r.t M is.

a) 4 b) 3 c) 2 d) 1

Solution) $ROR = -\frac{1}{1} \frac{dM}{dt} = +\frac{1}{1} \frac{dN}{dt}$

ROR = Rate of disappearance of M

M
1
2

ROR
x
8x

$ROR \propto [M]^3$
order w.r.t M $\rightarrow 3$

Home work

Q5) IIT 2004

Initial [A] (mol/L)	Initial [B] (mol/L)	Initial Rate
0.1	0.1	0.05
0.2	0.1	0.1
0.1	0.2	0.05

Write rate equation & find rate constant

Solution:

A	B	ROR	ROR $\propto [A]^1$
0.1	0.1	0.05	\uparrow
0.2	0.1	0.1	double
0.1	0.2	0.05	no change

\downarrow ROR $\propto [B]^0$

$$\text{ROR} = k[A]^1[B]^0$$

$$0.05 = k[0.1]^1[0.1]^0$$

$$[k = 0.5] \text{ Rate constant}$$

$$\text{ROR} = 0.5[A]^1[B]^0$$