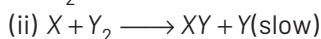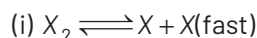# 11
Chemical Kinetics

TOPIC 1
Rate of Chemical Reaction, Rate Expression

01 Mechanism of a hypothetical reaction $X_2 + Y_2 \longrightarrow 2XY$ is given below **[NEET 2017]**

(i) $X_2 \rightleftharpoons X + X$(fast)

(ii) $X + Y_2 \longrightarrow XY + Y$(slow)

(iii) $X + Y \longrightarrow XY$ (fast)

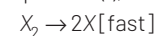The overall order of the reaction will be

(a) 1   (b) 2

(c) 0   (d) 1.5

Ans. *(d)*

We know that, slowest step is the rate determining step.

$\therefore$ Rater $(r) = K_1[X][Y_2]$ ... (i)

Now, from equation. (i), i.e.

$$X_2 \rightarrow 2X[\text{fast}]$$

$$K_{eq} = \frac{[X]^2}{[X_2]}$$

$$[X] = \{K_{eq}[X_2]\}^{1/2} \quad ... (ii)$$

Now, substitute the value of $[X]$ from equation. (ii) in equation. (i), we get

$$\text{Rate } (r) = K_1 (K_{eq})^{1/2} [X_2]^{1/2} [Y_2]$$
$$= K[X_2]^{1/2} [Y_2]$$

$\therefore$ Order of reaction $= \frac{1}{2} + 1 = \frac{3}{2} = 1.5$

02 In a reaction, $A + B \rightarrow$ Product, rate is doubled when the concentration of B is doubled and rate increases by a factor of 8 when the concentrations of both the reactants (A and B) are doubled. Rate law for the reaction can be written as **[CBSE AIPMT 2012]**

(a) rate $= k[A][B]^2$ (b) rate $= k[A]^2[B]^2$

(c) rate $= k[A][B]$ (d) rate $= k[A]^2[B]$

Ans. *(d)*

Let the order of reaction with respect to A and B is x and y respectively. So, the rate law can be given as

$$R = k[A]^x[B]^y \quad ...(i)$$

When the concentration of only B is doubled,

the rate is doubled, so

$$R_1 = k[A]^x[2B]^y = 2R \quad ...(ii)$$

If concentrations of both the reactants A and B are doubled, the rate increases by a factor of 8, so

$$R'' = k[2A]^x[2B]^y = 8R \quad ...(iii)$$

$$\Rightarrow \quad k2^x 2^y [A]^x[B]^y = 8R \quad ...(iv)$$

From Eqs. (i) and (ii), we get

$$\Rightarrow \quad \frac{2R}{R} = \frac{[A]^x[2B]^y}{[A]^x[B]^y}$$

$$2 = 2^y \Rightarrow y = 1$$

rom Eqs. (i) and (iv), we get

$$\Rightarrow \quad \frac{8R}{R} = \frac{2^x 2^y [A]^x[B]^y}{[A]^x[B]^y} \quad \text{or} \quad 8 = 2^x 2^y$$

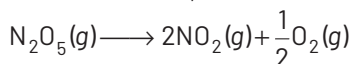Substitution of the value of y gives,

$$8 = 2^x 2^1$$
$$4 = 2^x$$
$$(2)^2 = (2)^x$$
$$\therefore \quad x = 2$$

Substitution of the value of x and y in Eq. (i) gives,

$$R = k[A]^2[B]$$

03 For the reaction,

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$

The value of rate of disappearance of N_2O_5 is given as 6.25×10^{-3} mol $L^{-1}s^{-1}$. The rate of formation of NO_2 and O_2 is given respectively as **[CBSE AIPMT 2010]**

(a) 6.25×10^{-3} mol $L^{-1}s^{-1}$ and 6.25×10^{-3} mol $L^{-1}s^{-1}$

(b) 1.25×10^{-2} mol $L^{-1}s^{-1}$ and 3.125×10^{-3} mol $L^{-1}s^{-1}$

(c) 6.25×10^{-3} mol $L^{-1}s^{-1}$ and 3.125×10^{-3} mol $L^{-1}s^{-1}$

(d) 1.25×10^{-2} mol $L^{-1}s^{-1}$ and 6.25×10^{-3} mol $L^{-1}s^{-1}$

Ans. *(b)*

Key Idea *Rate of disappearance of reactant = rate of appearance of product*

or

$$-\frac{1}{\text{Stoichiometric coefficient of reactant}} \frac{d[\text{reactant}]}{dt}$$

$$= +\frac{1}{\text{Stoichiometric coefficient of product}} \frac{d[\text{product}]}{dt}$$

For the reaction,

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$
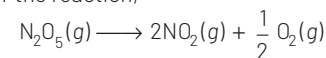
$$\frac{-d[N_2O_5]}{dt} = +\frac{1}{2}\frac{d[NO_2]}{dt} = +\frac{2d[O_2]}{dt}$$

$$\therefore \quad \frac{d[NO_2]}{dt} = -2\frac{d[N_2O_5]}{dt}$$

$$= 2 \times 6.25 \times 10^{-3} \text{ mol } L^{-1} s^{-1}$$
$$= 12.5 \times 10^{-3} \text{ mol } L^{-1} s^{-1}$$
$$= 1.25 \times 10^{-2} \text{ mol } L^{-1} s^{-1}$$

$$\frac{d[O_2]}{dt} = -\frac{d[N_2O_5]}{dt} \times \frac{1}{2}$$

$$= \frac{6.25 \times 10^{-3} \text{ mol } L^{-1}s^{-1}}{2}$$

$$= 3.125 \times 10^{-3} \text{ mol } L^{-1}s^{-1}$$

04 During the kinetic study of the reaction, $2A + B \longrightarrow C + D$, following results were obtained

Run	A/molL^{-1}	B/mol L^{-1}	Initial rate of formation of D/molL^{-1}min^{-1}
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Based on the above data which one of the following is correct?

[CBSE AIPMT 2010]

(a) Rate $=k[A]^2[B]$
(b) Rate $=k[A][B]$
(c) Rate $=k[A]^2[B]^2$
(d) Rate $=k[A][B]^2$

Ans. *(d)*

Let the order of reaction with respect to A is x and with respect to B is y. Thus,

$$\text{rate} = k[A]^x[B]^y$$

(x and y are stoichiometric coefficient)

For the given cases,

I. $\text{rate} = k(0.1)^x(0.1)^y = 6.0 \times 10^{-3}$
II. $\text{rate} = k(0.3)^x(0.2)^y = 7.2 \times 10^{-2}$
III. $\text{rate} = k(0.3)^x(0.40)^y = 2.88 \times 10^{-1}$
IV. $\text{rate} = k(0.4)^x(0.1)^y = 2.40 \times 10^{-2}$

Dividing Eq. (I) by Eq. (IV), we get

$$\left(\frac{0.1}{0.4}\right)^x \left(\frac{0.1}{0.1}\right)^y = \frac{6.0 \times 10^{-3}}{2.4 \times 10^{-2}}$$

or $\left(\frac{1}{4}\right)^x = \left(\frac{1}{4}\right)^1$

$\therefore \qquad x = 1$

On dividing Eq. (II) by Eq. (III), we get

$$\left(\frac{0.3}{0.3}\right)^x \left(\frac{0.2}{0.4}\right)^y = \frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}}$$
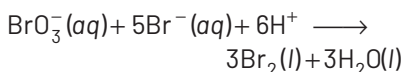
or $\left(\frac{1}{2}\right)^y = \frac{1}{4}$

or $\left(\frac{1}{2}\right)^y = \left(\frac{1}{2}\right)^2$

$\therefore \qquad y = 2$

Thus, rate law is,

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

05 In the reaction,
$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+ \longrightarrow 3Br_2(l) + 3H_2O(l)$$
the rate of appearance of bromine (Br_2) is related to rate of disappearance of bromide ions as following.

[CBSE AIPMT 2009, 2000]

(a) $\dfrac{d[Br_2]}{dt} = -\dfrac{3}{5}\dfrac{d[Br^-]}{dt}$

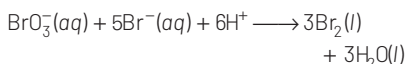(b) $\dfrac{d[Br_2]}{dt} = -\dfrac{5}{3}\dfrac{d[Br^-]}{dt}$

(c) $\dfrac{d[Br_2]}{dt} = \dfrac{5}{3}\dfrac{d[Br^-]}{dt}$

(d) $\dfrac{d[Br_2]}{dt} = \dfrac{3}{5}\dfrac{d[Br^-]}{dt}$

Ans. *(a)*

Rate of appearance/disappearance

$$= \pm \frac{1}{\text{stoichiometric coefficient}} \times \frac{[\text{reactant or product}]}{\text{time taken}}$$
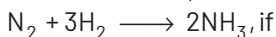
For the reaction,
$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+ \longrightarrow 3Br_2(l) + 3H_2O(l)$$

Rate of appearance of bromine (Br_2)
$$= +\frac{1}{3}\frac{d[Br_2]}{dt}$$

Rate of disappearance of bromide ion (Br^-)
$$= -\frac{1}{5}\frac{d[Br^-]}{dt}$$

or $\dfrac{d[Br_2]}{dt} = -\dfrac{3}{5}\dfrac{d[Br^-]}{dt}$

06 For the reaction,
$N_2 + 3H_2 \longrightarrow 2NH_3$, if
$$\frac{d[NH_3]}{dt} = 2 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}, \text{the}$$
value of $\dfrac{-d[H_2]}{dt}$ would be **[CBSE AIPMT 2009]**

(a) 3×10^{-4} mol L^{-1} s^{-1}
(b) 4×10^{-4} mol L^{-1} s^{-1}
(c) 6×10^{-4} mol L^{-1} s^{-1}
(d) 1×10^{-4} mol L^{-1} s^{-1}

Ans. *(a)*

For the reaction,
$$N_2 + 3H_2 \longrightarrow 2NH_3$$

$$\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

or $-\dfrac{1}{3}\dfrac{d[H_2]}{dt} = +\dfrac{1}{2}\dfrac{d[NH_3]}{dt}$

$$-\frac{d[H_2]}{dt} = \frac{3}{2} \times 2 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$$
$$= 3 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$$

07 For the reaction,
$A + B \longrightarrow$ products, it is observed that

I. On doubling the initial concentration of A only, the rate of reaction is also doubled and

II. On doubling the initial concentrations of both A and B, there is a change by a factor of 8 in the rate of the reaction.

[CBSE AIPMT 2009]

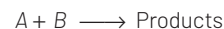The rate of this reaction is, given by

(a) rate $= k[A]^2[B]$
(b) rate $= k[A][B]^2$
(c) rate $= k[A]^2[B]^2$
(d) rate $= k[A][B]$

Ans. *(b)*

For the reaction,
$$A + B \longrightarrow \text{Products}$$
On doubling the initial concentration of A only, the rate of the reaction is also doubled, therefore

$$\text{Rate} \propto [A]^1 \qquad \ldots(i)$$

Let initial rate law is

$$\text{Rate} = k[A][B]^y \qquad \ldots(ii)$$

If concentration of A and B both are doubled, the rate gets changed by a factor of 8.

$$8 \times \text{rate} = k[2A][2B]^y \qquad \ldots(iii)$$
$$[\because \text{ Rate} \propto [A]^1]$$

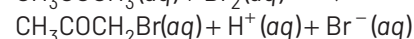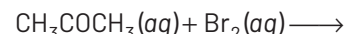Dividing Eq. (iii) by Eq. (ii), we get
$$8 = 2 \times 2^y$$
$$4 = 2^y$$
$$(2)^2 = (2)^y$$
$\therefore \qquad y = 2$

Hence, rate law is, rate $= k[A][B]^2$

08 The bromination of acetone that occurs in acid solution is represented by this equation
$$CH_3COCH_3(aq) + Br_2(aq) \longrightarrow CH_3COCH_2Br(aq) + H^+(aq) + Br^-(aq)$$
These kinetic data were obtained for given reaction concentrations.

Initial concentrations, M

$[CH_3COCH_3]$	$[Br_2]$	$[H^+]$
0.30	0.05	0.05
0.30	0.10	0.05
0.30	0.10	0.10
0.40	0.05	0.20

Initial rate, disappearance of Br_2, Ms^{-1}

$$5.7 \times 10^{-5}$$
$$5.7 \times 10^{-5}$$
$$1.2 \times 10^{-4}$$
$$3.1 \times 10^{-4}$$

Based on these data, the rate equation is **[CBSE AIPMT 2008]**

(a) rate $= k[CH_3COCH_3][H^+]$
(b) rate $= k[CH_2\!=\!COCH_3][Br_2]$
(c) rate $= k[CH_3COCH_3][Br_2][H^+]^2$
(d) rate $= k[CH_3COCH_3][Br_2][H^+]$

Ans. *(a)*

Let the order of reaction wrt CH_3COCH_3, Br_2 and H^+ are x, y and z respectively. Thus,

Rate $(r) = [CH_3COCH_3]^x [Br_2]^y [H^+]^z$

$5.7 \times 10^{-5} = (0.30)^x (0.05)^y (0.05)^z$ ...(i)

$5.7 \times 10^{-5} = (0.30)^x (0.10)^y (0.05)^z$ ...(ii)

$1.2 \times 10^{-4} = (0.30)^x (0.10)^y (0.10)^z$ ...(iii)

$3.1 \times 10^{-4} = (0.40)^x (0.05)^y (0.20)^z$ ...(iv)

From Eqs. (i) and (ii)

$$1 = \left(\frac{1}{2}\right)^y \quad \text{or} \quad 1^\circ = \left(\frac{1}{2}\right)^y$$
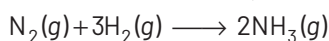
$$y = 0$$

From Eqs. (ii) and (iii)

$$z = 1$$

From Eqs. (i) and (iv)

$$x = 1$$

Thus, rate law $\propto [CH_3COCH_3]^1 [Br_2]^0 [H^+]^1$

$= k[CH_3COCH_3][H^+]$

09 Consider the reaction,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

The equality relationship between $\frac{d[NH_3]}{dt}$ and $-\frac{d[H_2]}{dt}$ is

[CBSE AIPMT 2006]

(a) $\frac{d[NH_3]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt}$

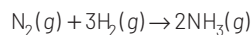(b) $+\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$

(c) $+\frac{d[NH_3]}{dt} = -\frac{3}{2}\frac{d[H_2]}{dt}$

(d) $\frac{d[NH_3]}{dt} = -\frac{d[H_2]}{dt}$

Ans. *(b)*

For the reaction,

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

The rate of reaction wrt

$$N_2 = -\frac{d[N_2]}{dt}$$

[Rate of disappearance]

The rate of reaction with respect to

$$H_2 = -\frac{1}{3}\frac{d[H_2]}{dt}$$

[Rate of disappearance]

The rate of reaction with respect to

$$NH_3 = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

[Rate of appearance]

Hence, at a fixed time

$$-\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

or $+\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$

or $+\frac{d[NH_3]}{dt} = -\frac{2d[N_2]}{dt}$

10 For the reaction,

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

which of the following does not express the reaction rate?

[CBSE AIPMT 2006]

(a) $-\frac{d[C]}{3dt}$

(b) $-\frac{d[B]}{dt}$

(c) $\frac{d[D]}{dt}$

(d) $-\frac{d[A]}{2dt}$

Ans. *(a)*

For the reaction,

$$2A + B \longrightarrow 3C + D$$
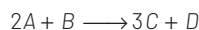
The reaction rate is written as follows:

The reaction rate with respect to

$$A = -\frac{1}{2}\frac{d[A]}{dt}$$

The reaction rate with respect to

$$B = -\frac{d[B]}{dt}$$

The reaction rate with respect to

$$C = +\frac{1}{3}\frac{d[C]}{dt}$$

The reaction rate with respect to

$$D = \frac{d[D]}{dt}$$

Hence, the answer (a) is not correct expression to represent the rate of the reaction.

11 The rate of reaction between two reactants A and B decreases by a factor of 4, if the concentration of reactant B is doubled. The order of this reaction with respect to reactant B is **[CBSE AIPMT 2005]**

(a) -1

(b) -2

(c) 1

(d) 2

Ans. *(b)*

$A + B \rightarrow$ Product

Rate, $r \propto [A]^x [B]^y$ ...(i)

The rate decreases by a factor 4 if the concentration of reactant B is doubled

$$\frac{r}{4} \propto [A]^x [2B]^y$$ ...(ii)

From Eqs. (i) and (ii)

$$4 = \left(\frac{1}{2}\right)^y$$

$$y = -2$$

Hence, order of reaction with respect to B is -2.

12 $3A \longrightarrow 2B$, rate of reaction $+\frac{d[B]}{dt}$ is equal to **[CBSE AIPMT 2002]**

(a) $-\frac{3}{2}\frac{d[A]}{dt}$

(b) $-\frac{2}{3}\frac{d[A]}{dt}$

(c) $-\frac{1}{3}\frac{d[A]}{dt}$

(d) $+2\frac{d[A]}{dt}$

Ans. *(b)*

For reaction,

$$3A \rightarrow 2B$$

$$\text{Rate} = -\frac{1}{3}\frac{d[A]}{dt}$$

[Rate of disappearance]

$$= +\frac{1}{2}\frac{d[B]}{dt}$$

[Rate of appearance]

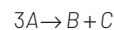$$\therefore \ +\frac{d[B]}{dt} = -\frac{2}{3}\frac{d[A]}{dt}$$

13 $3A \longrightarrow B + C$ It would be a zero order reaction, when

[CBSE AIPMT 2002]

(a) the rate of reaction is proportional to square of concentration of A

(b) the rate of reaction remains same at any concentration of A

(c) the rate remains unchanged at any concentration of B and C

(d) the rate of reaction doubles if concentration of B is increased to double

Ans. *(b)*

For reaction,

$$3A \rightarrow B + C$$

If it is zero order reaction, then the rate remains same at any concentration of A

or $\frac{dx}{dt} = k[A^0]$ $[A^0 = 1]$.

It means that for zero order reaction, rate is independent of concentration of reactants.

14 For the reaction,
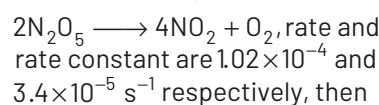
$2N_2O_5 \longrightarrow 4NO_2 + O_2$, rate and rate constant are 1.02×10^{-4} and 3.4×10^{-5} s^{-1} respectively, then concentration of N_2O_5 at that time will be **[CBSE AIPMT 2001]**

(a) 1.732

(b) 3

(c) 1.02×10^{-4}

(d) 3.4×10^5

Ans. *(b)*

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$
$$\frac{-d[N_2O_5]}{dt} = k \cdot [N_2O_5]$$
$$1.02 \times 10^{-4} = 3.4 \times 10^{-5}\ s^{-1} \times [N_2O_5]$$
$$\therefore \quad [N_2O_5] = \frac{1.02 \times 10^{-4}}{3.4 \times 10^{-5}} = 3$$

15 The experimental data for the reaction $2A + B_2 \longrightarrow 2AB$ is

Exp.	[A]	[B₂]	Rate (M s⁻¹)
1.	0.50	0.50	1.6×10^{-4}
2.	0.50	1.00	3.2×10^{-4}
3.	1.00	1.00	3.2×10^{-4}

The rate equation for the above data is **[CBSE AIPMT 1997]**
(a) rate $= k\,[B_2]$ 　　(b) rate $= k\,[B_2]^2$
(c) rate $= k\,[A]^2\,[B]^2$ (d) rate $= k\,[A]^2\,[B]$
Ans. *(a)*

Consider the following rate law equation,
$$\frac{dx}{dt} = k[A]^m\,[B_2]^n$$
$$1.6 \times 10^{-4} = k[0.50]^m\,[0.50]^n \quad ...(i)$$
$$3.2 \times 10^{-4} = k[0.50]^m\,[1.0]^n \quad ...(ii)$$
$$3.2 \times 10^{-4} = k[1.00]^m\,[1.0]^n \quad ...(iii)$$
By dividing Eq. (iii) by (ii) we get,
$$\frac{3.2 \times 10^{-4}}{3.2 \times 10^{-4}} = \frac{k[1.00]^m\,[1.0]^n}{k[0.50]^m\,[1.0]^n}$$
$$1 = 2^m \quad \text{or} \quad 2^0 = 2^m$$
$$\therefore \quad m = 0$$
By dividing Eq. (ii) by (i)
$$\frac{3.2 \times 10^{-4}}{1.6 \times 10^{-4}} = \frac{[0.50]^m\,[1.0]^n}{[0.50]^m\,[0.50]^n}$$
$$2 = 2^n \quad \text{or} \quad 2^1 = 2^n$$
$$\therefore \quad n = 1$$
Hence rate,
$$\left(\frac{dx}{dt}\right) = k\,[A]^0\,[B_2]^1 = k[B_2]$$

TOPIC 2
Order and Molecularity

16 The rate constant for a first order reaction is $4.606 \times 10^{-3}\ s^{-1}$. The time required to reduce 2.0 g of the reactant to 0.2 g is
[NEET (Sep.) 2020]
(a) 200 s 　　　(b) 500 s
(c) 1000 s 　　 (d) 100 s
Ans. *(b)*

For a first order reaction,

Rate constant $(k) = 4.606 \times 10^{-3}\ s^{-1}$
Initial amount $(a_0) = 2g$
Final amount $(a) = 0.2$ g
So, time required,
$$t = \frac{2.303}{k} \log \frac{a_0}{a}$$
$$= \frac{2.303}{4.606 \times 10^{-3}} \times \log \frac{2}{0.2} = 500\ s$$

17 The half-life for a zero order reaction having 0.02 M initial concentration of reactant is 100 s. The rate constant (in mol L⁻¹ s⁻¹) for the reaction is **[NEET (Oct.) 2020]**
(a) 1.0×10^{-4} 　　(b) 2.0×10^{-4}
(c) 2.0×10^{-3} 　　(d) 1.0×10^{-2}
Ans. *(a)*

For a zero order reaction, $t = \frac{1}{k}(a_0 - a)$
$$\Rightarrow \quad t_{50} = \frac{1}{k} \times \frac{a_0}{2}\ [\because \text{at } t_{50}, a = a_0/2]$$
$$\Rightarrow \quad k = \frac{a_0}{2 \times t_{50}} = \frac{0.02\ M}{2 \times 100\ s}$$
$$= 1 \times 10^{-4}\ Ms^{-1} = 1 \times 10^{-4}\ mol\ L^{-1} s^{-1}$$

18 A first order reaction has a rate constant of $2.303 \times 10^{-3}\ s^{-1}$. The time required for 40 g of this reactant to reduce to 10 g will be [Given that $\log_{10} 2 = 0.3010$]
[NEET (Odisha) 2019]
(a) 230.3 s 　　　(b) 301 s
(c) 2000 s 　　　(d) 602 s
Ans. *(d)*

For first order reaction,
$$t = \frac{2.303}{k} \log \frac{a}{a-x} \quad ...(i)$$
Given : $k = 2.303 \times 10^{-3}\ s^{-1}$,
$$a = 40\ g, a - x = 10\ g$$
On substituting the given values in Eq. (i), we get
$$t = \frac{2.303}{2.303 \times 10^{-3}} \log \frac{40}{10}$$
$$= 10^3 \log 2^2 = 2 \times 10^3 \times \log 2$$
$$= 2 \times 10^3 \times 0.3010 = 602\ s$$

Alternative method
For first order reaction,
$$t_{1/2} = \frac{0.693}{k}$$
$$t_{1/2}(t_{50\%}) = \frac{0.693}{2.303 \times 10^{-3}} = 301 s$$
Also, $\quad t_{75\%} = 2t_{50\%}$
$$\therefore \quad t_{75\%} = 2 \times 301 = 602\ s$$

19 If the rate constant for a first order reaction is k, the time (t) required for the completion of 99% of the reaction is given by
[NEET (National) 2019]
(a) $t = 6.909/k$ 　　(b) $t = 4.606/k$
(c) $t = 2.303/k$ 　　(d) $t = 0.693/k$
Ans. *(b)*

Key Idea For first order reaction,
$$t = \frac{2.303}{K} \log \frac{a}{a-x}$$
where, $a =$ initial concentration, $a - x =$ final concentration.
Let the initial concentration $(a) = 100$
After time t, final concentration
$(a - x) = 100 - 99 = 1$
We know that, $t = \frac{2.303}{K} \log \frac{a}{a-x}$

On substituting the given values in above eqn. we get
$$t = \frac{2.303}{K} \log \frac{100}{1} = \frac{2.303}{K} \log 10^2$$
$$= \frac{2.303}{K} \times 2 \log 10 = \frac{4.606}{K}$$
Thus, option (b) is correct.

20 The correct difference between first-and second- order reactions is that **[NEET 2018]**
(a) a first-order reaction can be catalysed; a second-order reaction cannot be catalysed
(b) the half-life of a first-order reaction does not depend on $[A]_0$; the half-life of a second-order reaction does depend on $[A]_0$
(c) the rate of a first-order reaction does not depend on reactant concentrations; the rate of a second-order reaction does depend on reactant concentrations
(d) the rate of a first-order reaction does depend on reactant concentrations; the rate of a second-order reaction does not depend on reactant concentrations
Ans. *(b)*

For first order reactions, the rate of reaction is proportional to the first power of the concentration of the reactant .
For, $A \rightarrow B$
$$\text{Rate} = -\frac{d[A]}{dt} = k[A]$$
$$[\text{where, } k = \text{constant}]$$
Half-life $(t_{1/2}) = \frac{0.693}{k}$

∴ Rate of first order reaction depends upon reactant concentrations and half life does not depend upon initial concentration of reactant, $[A]_0$.

For second order reactions, the rate of reaction is proportional to the second power of the concentration of the reactant.

For, $2A \rightarrow B$

$$\text{Rate} = k[A]^2$$

$$\text{Half-life}\,(t_{1/2}) = \frac{1}{k[A]_0}$$

∴ Rate of second order reaction depends upon reactant concentration and half life also does depend on $[A]_0$.

21 When initial concentration of the reactant is doubled, the half-life period of a zero order reaction **[NEET 2018]**

(a) is tripled
(b) is doubled
(c) is halved
(d) remains unchanged

Ans. *(b)*

For zero order reaction,

$$t_{1/2} = \frac{[R]_0}{2k}$$

where, $[R]_0$ = Initial concentration of the reactant.

k = Rate constant.

Thus, $t_{1/2}$ for zero order reaction is directly proportional to the initial concentration of the reactant.

$$t_{1/2} \propto [R]_0$$

∴ For zero order reaction, when the concentration of reactant is doubled, the half-life $(t_{1/2})$ will also get doubled.

22 A first order reaction has a specific reaction rate of $10^{-2}\,s^{-1}$. How much time will it take for 20 g of the reactant to reduce to 5 g? **[NEET 2017]**

(a) 238.6 s   (b) 138.6 s
(c) 346.5 s   (d) 693.0 s

Ans. *(b)*

For a first order reaction,

$$\text{Rate constant}\,(k) = \frac{2.303}{t}\log\frac{a}{a-x}$$

where, a = initial concentration

$a - x$ = concentration after time 't'

t = time in sec.

Given, $a = 20\,g$, $a - x = 5\,g$, $k = 10^{-2}$

$$\therefore \quad t = \frac{2.303}{10^{-2}}\log\frac{20}{5} = 138.6\,s$$

Alternatively,

Half-life for the first order reaction,

$$\frac{t_{1/2}}{2} = \frac{0.693}{k} = \frac{0.693}{10^{-2}} = 69.3\,s$$

Two half-lives are required for the reduction of 20 g of reactant into 5 g.

$$20\,g \xrightarrow{t_{1/2}} 10\,g \xrightarrow{t_{1/2}} 5\,g.$$

∴ Total time $= 2t_{1/2}$

$$= 2 \times 69.3 = 138.6\,s$$

23 The rate constant of the reaction $A \rightarrow B$ is 0.6×10^{-3} mole per second. If the concentration of A is 5 M then concentration of B after 20 min is **[CBSE AIPMT 2015]**

(a) 1.08 M   (b) 3.60 M
(c) 0.36 M   (d) 0.72 M

Ans. *(d)*

Key Concept *For a zero order reaction unit of rate constant is mole per second. Hence, we can easily calculate concentration of B after 20 min by the following formula,*

$$x = Kt$$

$$x = Kt = 0.6 \times 10^{-3} \times 20 \times 60 = 0.72\,M$$

24 The rate of a first-order reaction is 0.04 mol $L^{-1}\,s^{-1}$ at 10 sec and 0.03 mol $L^{-1}\,s^{-1}$ at 20 sec after initiation of the reaction. The half-life period of the reaction is **[NEET 2016, Phase I]**

(a) 34.1 s   (b) 44.1 s   (c) 54.1 s   (d) 24.1 s

Ans. *(d)*

Given, order of reaction = 1

Rate of reaction at 10 s = 0.04 mol $L^{-1}\,s^{-1}$

Rate of reaction at 20 s = 0.03 mol $L^{-1}\,s^{-1}$

∴ Half-life period $(t_{1/2}) = ?$

We have the equation for rate-constant 'K' in first order reaction.

$$k = \frac{2.303}{t}\log\frac{A_t}{A_0} = \frac{2.303}{105}\log\frac{0.04}{0.03}$$

$$= \frac{2.303}{105} \times 0.124$$

$$k = 0.028\,s^{-1}$$

We know that,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.028773391\,s^{-1}}$$

$$= 24.14\,s \approx 24.1\,s$$

25 The decomposition of phosphine (PH_3) on tungsten at low pressure is a first-order reaction. It is because the **[NEET 2016, Phase II]**

(a) rate is proportional to the surface coverage
(b) rate is inversely proportional to the surface coverage
(c) rate is independent of the surface coverage
(d) rate of decomposition is very slow

Ans. *(a)*

$$PH_3 \xrightarrow{W} P + \frac{3}{2}H_2$$
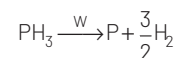
This is an example of surface catalysed unimolecular decomposition.

For the above reaction, rate is given as

$$\text{Rate} = \frac{k\alpha p}{1 + \alpha p}$$

where, p = partial pressure of absorbing substrate.

At low pressure, $\alpha p << 1$ or Rate $= k\alpha p$

So, $(\alpha p + 1)$ can be neglected.

hus, the decomposition is predicted to be first order.

26 When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is **[CBSE AIPMT 2015]**

(a) zero
(b) first
(c) second
(d) more than zero but less than first

Ans. *(b)*

For a zero order reaction $t_{1/2}$ is directly proportional to the initial concentration of the reactant $[R]_0$

$$t_{1/2} \propto [R]_0$$

For a first order reaction

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

at $t_{1/2}$, $[R] = \frac{[R]_0}{2}$

So, the above equation becomes

$$K = \frac{2.303}{t_{1/2}}\log\frac{[R]_0}{[R]_0/2}$$

$$t_{1/2} = \frac{2.303}{K} = \log 2 = \frac{2.303}{K} \times .3010$$

$$t_{1/2} = \frac{.693}{K}$$

i.e., half life period is independent of initial concentration of a reactant.

27 Which one of the following statements for the order of a reaction is incorrect? **[CBSE AIPMT 2011]**

(a) Order is not influenced by stoichiometric coefficient of the reactants
(b) Order of reaction is sum of power to the concentration terms of reactants to express the rate of reaction
(c) Order of reaction is always whole number
(d) Order can be determined only experimentally

Ans. *(c)*

Order of reaction may be zero, whole number or fraction number.

28 Half-life period of a first order reaction is 1386s. The specific rate constant of the reaction is

[CBSE AIPMT 2009]

(a) $5.0 \times 10^{-3} s^{-1}$
(b) $0.5 \times 10^{-2} s^{-1}$
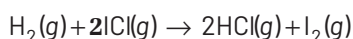(c) $0.5 \times 10^{-3} s^{-1}$
(d) $5.0 \times 10^{-3} s^{-1}$

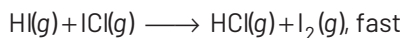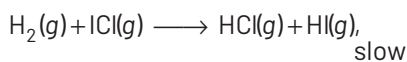**Ans.** *(c)*

Specific rate constant,
$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1386}$$
$$= 0.5 \times 10^{-3} s^{-1}$$

29 The reaction of hydrogen and iodine monochloride is given as
$$H_2(g) + 2ICl(g) \rightarrow 2HCl(g) + I_2(g)$$
This reaction is of first order with respect to $H_2(g)$ and $ICl(g)$, following mechanisms were proposed

Mechanism A
$$H_2(g) + 2ICl(g) \rightarrow 2HCl(g) + I_2(g)$$

Mechanism B
$$H_2(g) + ICl(g) \longrightarrow HCl(g) + HI(g),$$
slow
$$HI(g) + ICl(g) \longrightarrow HCl(g) + I_2(g), \text{ fast}$$

Which of the above mechanism(s) can be consistent with the given information about the reaction?

[CBSE AIPMT 2007]

(a) Only B
(b) Both A and B
(c) Neither A nor B
(d) Only A

Ans. *(a)*

In the reactions which take place in a number of steps, the slowest step is known as the rate determining step. Hence, rate of reaction always depends on slow step.
$$H_2(g) + ICl(g) \longrightarrow HCl(g) + HI(g)$$

is first order reaction with respect to H_2 and ICl. Thus, the mechanism B will be more consistent with the given information.

30 If 60% of a first order reaction was completed in 60 min, 50% of the same reaction would be completed in approximately (log 4 = 0.60, log 5 = 0.69)

[CBSE AIPMT 2007]

(a) 50 min
(b) 45 min
(c) 60 min
(d) 40 min

Ans. *(b)*

From first order reaction,
Rate constant,
$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$
$$k_1 = \frac{2.303}{t_1} \log \frac{a_1}{a_1 - x_1} \qquad ...(i)$$
$$k_2 = \frac{2.303}{t_2} \log \frac{a_2}{a_2 - x_2} \qquad ...(ii)$$
$$x_1 = \frac{60}{100} a_1, t_1 = 60$$
$$x_2 = \frac{50}{100} a_2, t_2 = ?$$

From Eqs. (i) and (ii)
$$\frac{2.303}{t_1} \log \frac{a_1}{a_1 - x_1} = \frac{2.303}{t_2} \log \frac{a_2}{a_2 - x_2}$$
$$\frac{2.303}{60} \log \frac{a_1}{\left(a_1 - \frac{60}{100} a_1\right)} = \frac{2.303}{t_2} \log \frac{a_2}{\left(a_2 - \frac{50}{100} a_2\right)}$$
$$\frac{2.303}{60} \log \frac{100a_1}{40a_1} = \frac{2.303}{t_2} \log \frac{100a_2}{50a_2}$$
$$\frac{1}{60} \log \frac{100}{40} = \frac{1}{t_2} \log \frac{100}{50}$$
$$t_2 = \frac{60 \log \frac{100}{50}}{\log \frac{100}{40}}$$
$$= \frac{60 (\log 10 - \log 5)}{(\log 10 - \log 4)}$$
$$= \frac{60(1 - 0.69)}{(1 - 0.60)} = \frac{60 \times 0.31}{0.40}$$
$$= 1.5 \times 31 = 46.5 \approx 45 \text{ min}$$

31 In a first order reaction, $A \longrightarrow B$, if k is rate constant and initial concentration of the reactant A is 0.5 M, then the half-life is

[CBSE AIPMT 2007]

(a) $\frac{0.693}{0.5k}$
(b) $\frac{\log 2}{k}$
(c) $\frac{\log 2}{k\sqrt{0.5}}$
(d) $\frac{\ln 2}{k}$

Ans. *(d)*

For first order reaction,
Rate constant, $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$
$$t_{1/2} = \frac{2.303}{k} \log \frac{a}{a - \frac{a}{2}} \qquad \left(x = \frac{a}{2}\right)$$
$$= \frac{2.303}{k} \log 2 \quad \text{or} \quad = \frac{\ln 2}{k}$$

32 For a first order reaction, $A \rightarrow B$, the reaction rate at reactant concentration of 0.01 M is found to be 2.0×10^{-5} mol L^{-1}s^{-1}. The half-life period of the reaction is

[CBSE AIPMT 2005]

(a) 220 s
(b) 30 s
(c) 300 s
(d) 347 s

Ans. *(d)*

For first order reaction,
$$A \longrightarrow B$$
$$\text{rate} = k \times [A]$$
$$\text{Rate} = 2.0 \times 10^{-5} \text{ mol L}^{-1}s^{-1}$$
$$[A] = 0.01 \text{ M}$$
So, $2.0 \times 10^{-5} = k \times 0.01$
$$k = \frac{2.0 \times 10^{-5}}{0.01} s^{-1}$$
$$= 2.0 \times 10^{-3} s^{-1}$$
For first order reaction,
$$t_{1/2} = \frac{0.693}{k}$$
$$= \frac{0.693}{2.0 \times 10^{-3}}$$
$$= 346.5 \approx 347 \text{ s}$$

33 The rate of first order reaction is 1.5×10^{-2} mol L^{-1} min^{-1} at 0.5 M concentration of the reactant. The half-life of the reaction is

[CBSE AIPMT 2004]

(a) 0.383 min
(b) 23.1 min
(c) 8.73 min
(d) 7.53 min

Ans. *(b)*

For the first order reaction,
$$\text{Rate}\left(\frac{dx}{dt}\right) = k[A]$$
$[A]$ = concentration of reactant
k = rate constant
Given that,
$$\frac{dx}{dt} = 1.5 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$$
$$k = ?$$
and $[A] = 0.5 \text{ M}$
$\therefore 1.5 \times 10^{-2} = k \times 0.5$

$$\therefore \quad k = \frac{1.5 \times 10^{-2}}{0.5}$$
$$= 3 \times 10^{-2} \, \text{min}^{-1}$$

For first order reaction,

half-life period, $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{3 \times 10^{-2}}$
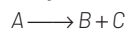
$$= 23.1 \, \text{min}$$

34 If the rate of a reaction is equal to the rate constant, the order of the reaction is **[CBSE AIPMT 2003]**
(a) 2   (b) 3   (c) 0   (d) 1

Ans. *(c)*

Rate of reaction is equal to the rate constant for zero order reaction.

Let us consider the following hypothetical change.

$$A \longrightarrow B + C$$

Suppose this reaction is zero order, then

$$\text{rate} \propto [A]^0$$
$$\therefore \qquad \text{rate} = k[A]^0 = k$$

35 The reaction, $A \rightarrow B$ follows first order kinetics. The time taken for 0.8 mole of A to produce 0.6 mole of B is 1h. What is the time taken for the conversion of 0.9 mole of A to 0.675 mole of B ? **[CBSE AIPMT 2003]**
(a) 0.25 h (b) 2 h   (c) 1 h   (d) 0.5 h

Ans. *(c)*

Rate constant of first order reaction

$$k = \frac{2.303}{t} \log_{10} \frac{(A)_0}{(A)_t}$$

or $\qquad k = \dfrac{2.303}{1} \times \log_{10} \dfrac{0.8}{0.2} \qquad ...(i)$

(because 0.6 mole of B is formed)

Suppose t_1 hour are required for changing the concentration of A from 0.9 mole to 0.675 mole of B.

Remaining mole of $A = 0.9 - 0.675 = 0.225$

$$\therefore \qquad k = \frac{2.303}{t_1} \log_{10} \frac{0.9}{0.225} \qquad ...(ii)$$

From Eqs. (i) and (ii)

$$\frac{2.303}{1} \log_{10} \frac{0.8}{0.2} = \frac{2.303}{t_1} \log_{10} \frac{0.9}{0.225}$$

$$2.303 \log_{10} 4 = \frac{2.303}{t_1} \log_{10} 4 \Rightarrow t_1 = 1\text{h}$$

36 For a first-order reaction, the half-life period is independent of **[CBSE AIPMT 1999]**
(a) initial concentration
(b) cube root of initial concentration

(c) first power of final concentration
(d) square root of final concentration

Ans. *(a)*

$t_{1/2}$ of nth order reaction $\propto \dfrac{1}{a^{n-1}}$

where, $a =$ initial concentration of
        reactant
        $n =$ order of reaction

$\therefore t_{1/2}$ for first order reaction $(n = 1)$

$$t_{1/2} \propto \frac{1}{a^{1-1}}$$

or $\qquad t_{1/2} \propto \dfrac{1}{a^0} \qquad (a^0 = 1)$

So, for a first order reaction half-life is independent on initial concentration of reactants.

37 The plot of concentration of the reactant *versus* time for a reaction is a straight line with a negative slope. This reaction follows **[CBSE AIPMT 1996]**
(a) zero order rate equation
(b) first order rate equation
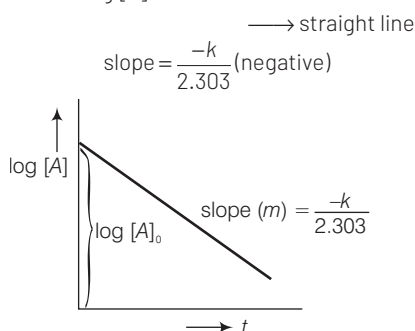(c) second order rate equation
(d) third order rate equation

Ans. *(b)*

For first order reaction, we know that

$$\log[A] = -\frac{kt}{2.303} + \log[A]_0$$

On comparing it with the equation of straight line,

i.e. $\qquad y = mx + c$

Plot of $\log[A]$ *versus* time

$\longrightarrow$ straight line

$$\text{slope} = \frac{-k}{2.303} \text{(negative)}$$

slope $(m) = \dfrac{-k}{2.303}$

38 A substance A decomposes by a first order reaction starting initially with $[A] = 2.00$ m and after 200 min, $[A]$ becomes 0.15 m. For this reaction $t_{1/2}$ is **[CBSE AIPMT 1995]**
(a) 53.49 min   (b) 50.49 min
(c) 48.45 min   (d) 46.45 min

Ans. *(a)*

$[A]_0 = 2.0$ m, $[A] = 0.15$ m, $t = 200$ min

For first order reaction

$A_0 =$ Initial concentration
$A =$ Final concentration

Rate constant, $k = \dfrac{2.303}{t} \log \dfrac{[A]_0}{[A]}$

$$= \frac{2.303}{200} \log \frac{2.0}{0.15}$$

$$= \frac{2.303}{200} (\log 200 - \log 15)$$

$$= \frac{2.303}{200} \times (2.3010 - 1.1761)$$

$$= \frac{2.303 \times 1.1249}{200}$$

$$= 0.01295 \, \text{min}^{-1}$$
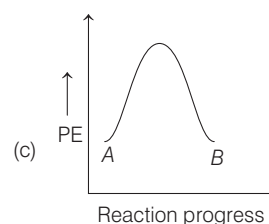
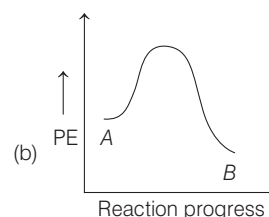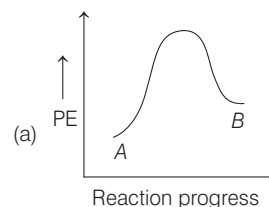Now, half life, $t_{1/2} = \dfrac{0.6932}{k}$

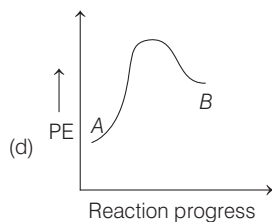$$= \frac{0.6932}{0.01295}$$

$$= 53.50 \, \text{min}$$

TOPIC 3
Activation Energy, Arrhenius and Collision Theory, Factors Affecting Rate of Reaction

39 For a reaction, $A \rightarrow B$, enthalpy of reaction is -4.2 kJ mol^{-1} and enthalpy of activation is 9.6 kJ mol^{-1}. The correct potential energy profile for the reaction is shown in option. **[NEET 2021]**

(a)

(b)

(c)

(d)

Reaction progress

Ans. *(b)*

The enthalpy of reaction is negative, -4.2 kJ mol^{-1}. The reaction is an exothermic reaction i.e. the energy of product B, is less than the energy of reactant A. So, the potential energy profile for the reaction is

Reaction process

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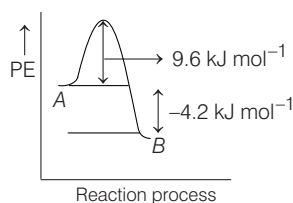
40 The slope of Arrhenius plot $\left(\ln k \, vs \, \dfrac{1}{T}\right)$ of first order reaction is -5×10^3 K. The value of E_a of the reaction is [Given, $R = 8.314$ JK^{-1} mol^{-1}]

[NEET 2021]

(a) 41.5 kJ mol^{-1} (b) 83.0 kJ mol^{-1}
(c) 166 kJ mol^{-1} (d) -83 kJ mol^{-1}

Ans. *(a)*

Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

$$\ln k = \ln A - \dfrac{E_a}{R}\left(\dfrac{1}{T}\right)$$

$\dfrac{-E_a}{R}$ is the slope of Arrhenius plot $\left(\ln k \, vs \, \dfrac{1}{T}\right)$

In A is the intercept
$$\text{Slope} = -5\times10^3 \text{ K}$$
$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$
So, $\quad -\dfrac{E_a}{R} = -5\times10^3 \text{ K}$

$\Rightarrow E_a = 5\times10^3 \times R = 5\times10^3 \times 8.314$
$\qquad = 41.57\times10^3$ J mol^{-1} = 41.5 kJ mol^{-1}

---

41 In collision theory of chemical reaction, Z_{AB} represents

[NEET (Oct.) 2020]

(a) the fraction of molecules with energies greater than E_a
(b) the collision frequency of reactants, A and B
(c) steric factor
(d) the fraction of molecules with energies equal to E_a

Ans. *(b)*

From collision theory of chemical reaction, Arrhenius equation.
We get, $k = A \times e^{-E_a/RT}$

where, $k =$ rate constant,
$e^{-E_a/RT}$ = fraction of molecules with energy greater than E_a at T K. (option-(a))
$A =$ Arrhenius factor or frequency factor
$= P \times Z_{AB}$
when, $P =$ steric factor (option-(c))
Z_{AB} = collision frequency of reactants, A and B
= number of effective binary collisions between A and B in one second in unit volume (option-(b)).
Hence, option (b) is the correct.

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42 For a reaction, activation energy $E_a = 0$ and the rate constant at 200K is 1.6×10^6 s^{-1}. The rate constant at 400 K will be [Given that gas constant $R = 8.314$ JK^{-1} mol^{-1}]

[NEET (Odisha) 2019]

(a) 3.2×10^4 s^{-1} (b) 1.6×10^6 s^{-1}
(c) 1.6×10^3 s^{-1} (d) 3.2×10^6 s^{-1}

Ans. *(b)*

Key Idea Rate constants at two different temperatures is given by Arrhenius equation as follows :

$$\log\dfrac{k_2}{k_1} = \dfrac{E_a}{2.303R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right], T_2 > T_1$$

Given, $E_a = 0$, $T_1 = 200$ K, $k_1 = 1.6\times10^6$ s^{-1}
$\qquad T_2 = 400$ K,
$\qquad R = 8.314$ JK^{-1} mol^{-1}

According to Arrhenius equation,

$$\log\dfrac{k_2}{k_1} = \dfrac{E_a}{2.303R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$$

On substituting the given values in above equation, we get

$$\log\dfrac{k_2}{1.6\times10^6} = \dfrac{0}{2.303\times8.314}\left[\dfrac{1}{200} - \dfrac{1}{400}\right]$$

$$\log\left(\dfrac{k_2}{1.6\times10^6}\right) = 0$$

$$\dfrac{k_2}{1.6\times10^6} = 10^0 = 1$$

$$k_2 = 1.6\times10^6 \text{ s}^{-1} \text{ at 400K}$$

Thus, option (b) is correct.

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43 Which one of the following statements is not correct?

[NEET 2017]

(a) Catalyst does not initiate any reaction
(b) The value of equilibrium constant is changed in the presence of a catalyst in the reaction equilibrium

(c) Enzymes catalyse mainly biochemical reaction
(d) Coenzymes increase the catalytic activity of enzyme

Ans. *(b)*

For a reversible reaction, it accelerates the speed of forward as well as backward reaction to the same extent. Hence, it does not disturb the equilibrium, i.e. does not change the equilibrium constant of the reaction but helps to attain the equilibrium faster.

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44 The addition of a catalyst during a chemical reaction alters which of the following quantities?

[NEET 2016, Phase I]

(a) Internal energy
(b) Enthalpy
(c) Activation energy
(d) Entropy

Ans. *(c)*

A catalyst is a substance which alters the reaction rate but itself remains unchanged in amount and chemical composition at the end of the reaction. It provides a new reaction path with a lower energy barrier (lowering activation energy).

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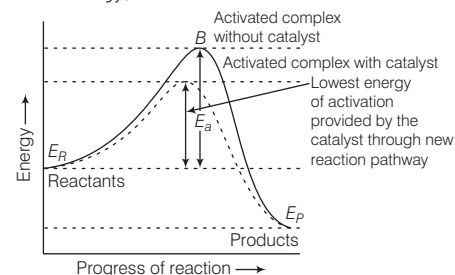
45 The activation energy of a reaction can be determined from the slope of which of the following graphs?

[CBSE AIPMT 2015]

(a) ln K vs T   (b) $\dfrac{\ln K}{T}$ vs T
(c) ln K vs $\dfrac{1}{T}$ (d) $\dfrac{T}{\ln K}$ vs $\dfrac{1}{T}$

Ans. *(c)*

By Arrhenius equation
$$K = Ae^{-Ea/RT}$$

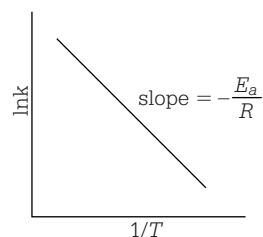where, $E_a =$ energy of activation
Applying log on both the side,

$$\ln k = \ln A - \dfrac{E_a}{RT} \qquad \text{...(i)}$$

or $\qquad \log k = -\dfrac{E_a}{2.303RT} + \log A \quad \text{...(ii)}$

Compare the above equation w.r.t. straight line equation of $y = mx + c$.

Thus, if a plote of $\ln k$ vs $\frac{1}{T}$ is a straight line, the validity of the equation is confirmed.

Slope of the line $= -\dfrac{E_a}{R}$

Thus, measuring the slope of the line, the value of E_a can be calculated.

46 What is the activation energy for a reaction if its rate doubles when the temperature is raised from 20°C to 35°C?

$(R = 8.314\, J\, mol^{-1}\, K^{-1})$ **[NEET 2013]**

(a) 342 kJ mol^{-1}
(b) 269 kJ mol^{-1}
(c) 34.7 kJ mol^{-1}
(d) 15.1 kJ mol^{-1}

Ans. *(c)*

Given, initial temperature,
$$T_1 = 20 + 273 = 293\, K$$
Final temperature,
$$T_2 = 35 + 273 = 308\, K$$
$$R = 8.314\, J\, mol^{-1}\, K^{-1}$$

Since, rate becomes double on raising temperature,

$\therefore$ $\qquad r_2 = 2r_1$ or $\dfrac{r_2}{r_1} = 2$

As rate constant, $k \propto r$

$\therefore$ $\qquad \dfrac{k_2}{k_1} = 2$

From Arrhenius equation, we know that

$$\log \frac{k_2}{k_1} = -\frac{E_a}{2.303\, R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

$$\log 2 = -\frac{E_a}{2.303 \times 8.314}\left[\frac{293 - 308}{293 \times 308}\right]$$

$$0.3010 = -\frac{E_a}{2.303 \times 8.314}\left[\frac{-15}{293 \times 308}\right]$$

$\therefore$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 293 \times 308}{15}$$

$$= 34673.48\, J\, mol^{-1}$$
$$= 34.7\, kJ\, mol^{-1}$$

47 In a zero order reaction for every 10°C rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C, the rate of the reaction will become

[CBSE AIPMT 2012]

(a) 256 times   (b) 512 times
(c) 64 times   (d) 128 times

Ans. *(b)*

For 10° rise in temperature, $n = 1$

so $\qquad$ rate $= 2^n = 2^1 = 2$

When temperature is increased from 10°C to 100°C, change in temperature
$$= 100 - 10 = 90°C$$

i.e. $\qquad n = 9$

So, $\qquad$ rate $= 2^9 = 512$ times

Alternate method with every 10° rise in temperature, rate becomes double,

so $\dfrac{r'}{r} = 2^{\left(\frac{100-10}{10}\right)} = 2^9 = 512$ times.

48 For an endothermic reaction, energy of activation is E_a and enthalpy of reaction is ΔH (both of these in kJ/mol). Minimum value of E_a will be   **[CBSE AIPMT 2010]**

(a) less than ΔH
(b) equal to ΔH
(c) more than ΔH
(d) equal to zero

Ans. *(c)*

Key Idea *In endothermic reactions, energy of reactants is less than that of the products.*

Potential energy diagram for endothermic reactions is
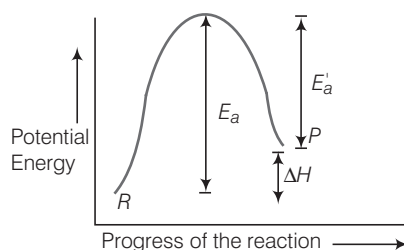
where,
E_a = activation energy of forward reaction

activation energy of backward reaction

ΔH = enthalpy of the reaction.

From the above diagram,
$$E_a = E_a' + \Delta H$$

Thus, $\qquad E_a > \Delta H$

49 The rate constants k_1 and k_2 for two different reactions are $10^{16} \cdot e^{-2000/T}$ and $10^{15} \cdot e^{-1000/T}$, respectively. The temperature at which $k_1 = k_2$ is **[CBSE AIPMT 2008]**

(a) 1000 K   (b) $\dfrac{2000}{2.303}$ K

(c) 2000 K   (d) $\dfrac{1000}{2.303}$ K

Ans. *(d)*

Given, $\quad k_1 = 10^{16} \cdot e^{-2000/T}$
$$k_2 = 10^{15} \cdot e^{-1000/T}$$

On taking log of both the equations we get

$$\log k_1 = 16 - \frac{2000}{2.303T}$$

$$\log k_2 = 15 - \frac{1000}{2.303T}$$

At $k_1 = k_2$
$$16 - \frac{2000}{2.303T} = 15 - \frac{1000}{2.303T}$$

$$T = \frac{1000}{2.303}\, K$$

50 The activation energy for a simple chemical reaction, $A \longrightarrow B$ is E_a in forward direction. The activation energy for reverse reaction **[CBSE AIPMT 2003]**

(a) can be less than or more than E_a
(b) is always double of E_a
(c) is negative of E_a
(d) is always less than E_a

Ans. *(a)*

The energy of activation of reverse reaction is less than or more than energy of activation (E_a) of forward reaction.

$\therefore \qquad \Delta H = (E_a)_F - (E_a)_R$

Because it depends upon the nature of reaction.

If $(E_a)_F > (E_a)_R$, reaction is endothermic or $(E_a)_F < (E_a)_R$, reaction is exothermic

51 The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation, $k = Ae^{-E*/RT}$. Activation energy (E^*) of the reaction can be calculated by plotting **[CBSE AIPMT 2003]**

(a) $\log k$ vs $\dfrac{1}{T}$ (b) $\log k$ vs $\dfrac{1}{\log T}$

(c) k vs T (d) k vs $\dfrac{1}{\log T}$

Ans. *(a)*

Arrhenius equation $k = Ae^{-E^*/RT}$

$$\ln k = \ln A - \frac{E^*}{RT}$$
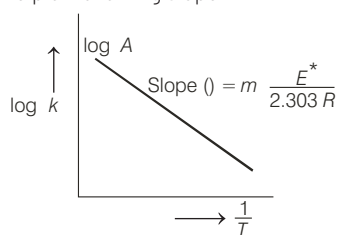
$$(E^* = \text{energy of activation})$$

or $\log k = \log A - \dfrac{E^*}{2.303\,RT}$

Compare this equation with the straight line equation,

i.e. $y = mx + c$

where 'm' is slope and 'c' is intercept

Hence, E^* can be calculated with the help of following slope

52 When a biochemical reaction is carried out in laboratory from outside of human body in the absence of enzyme, the rate of reaction obtained is 10^{-6} times, then activation energy of the reaction in the presence of enzyme is [CBSE AIPMT 2001]

(a) $\dfrac{6}{RT}$

(b) P is required
(c) different from E_a obtained in laboratory
(d) cannot say any things

Ans. *(c)*

When a biochemical reaction is carried out in laboratory from outside of human body in the absence of enzyme, then rate of reaction obtained is 10^{-6} times than activation energy of reaction in the presence of enzyme. It is different from E_a obtained in laboratory because for a given chemical reaction.

$$k = Ae^{-E_a/RT} \text{ (Arrhenius equation)}$$

Also activation energy have different value in absence or presence of enzyme.

53 Activation energy of a chemical reaction can be determined by [CBSE AIPMT 1998]

(a) evaluating rate constant at standard temperature
(b) evaluating velocities of reaction at two different temperatures
(c) evaluating rate constants at two different temperatures
(d) changing concentration of reactants

Ans. *(c)*

Activation energy can be calculated by using Arrhenius equation. The Arrhenius equation is

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

where, k_1 and k_2 = rate constants at two different temperatures, i.e. T_1 and T_2 respectively.

E_a = Activation energy

R = Gas constant

So, activation energy of a chemical reaction can be determined by evaluating rate constants at two different temperatures.

54 In a reversible reaction, the energy of activation of the forward reaction is 50 kcal. The energy of activation for the reverse reaction will be [CBSE AIPMT 1996]

(a) < 50 kcal
(b) 50 kcal
(c) either greater than or less than 50 kcal
(d) > 50 kcal

Ans. *(c)*

The activation energy of a reverse reaction decide whether the given reaction is exothermic or endothermic, so, the energy of activation of reverse reaction is either greater or less than 50 kcal. In case of exothermic reaction, the activation energy for reverse reaction is more than activation energy of the forward reaction and in case of endothermic reaction, the activation energy for reverse reaction is less than activation energy of the forward reaction.

55 A chemical reaction is catalysed by a catalyst X. Hence, X [CBSE AIPMT 1995]

(a) reduces enthalpy of the reaction
(b) decreases rate constant of the reaction
(c) increases activation energy of the reaction
(d) does not affect equilibrium constant of the reaction

Ans. *(d)*

Although a catalyst speeds up the reaction but it does not shift the position of equilibrium. This is due to the fact that the presence of catalyst reduces the height of barrier by providing an alternative path for the reaction and lowers the activation energy. However, the lowering in activation energy is to the same extent for the forward as well as the backward reaction.

56 For exothermic reaction, the energy of activation of the reactants is [CBSE AIPMT 1994]

(a) equal to the energy of activation of products
(b) less than the energy of activation of products
(c) greater than the energy of activation of products
(d) sometimes greater and sometimes less than that of the products

Ans. *(b)*

The plot of activation energy *versus* reaction coordinates is given below for exothermic reaction.
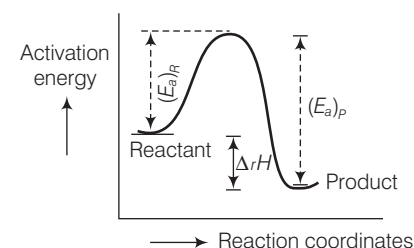
It is clear from the above plot that the activation energy of reactant is less than the activation energy of products.