# 18

# Chemical Kinetics

## TOPIC 1 Rate of Reaction, Rate Laws and Rate Constant

**1.** For the reaction $2A + 3B + \frac{3}{2}C \rightarrow 3P$, which statement is correct? **[Sep. 03, 2020 (II)]**

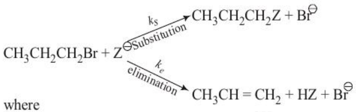
(a) $\frac{dn_A}{dt} = \frac{3}{2}\frac{dn_B}{dt} = \frac{3}{4}\frac{dn_C}{dt}$

(b) $\frac{dn_A}{dt} = \frac{dn_B}{dt} = \frac{dn_C}{dt}$

(c) $\frac{dn_A}{dt} = \frac{2}{3}\frac{dn_B}{dt} = \frac{4}{3}\frac{dn_C}{dt}$

(d) $\frac{dn_A}{dt} = \frac{2}{3}\frac{dn_B}{dt} = \frac{3}{4}\frac{dn_C}{dt}$

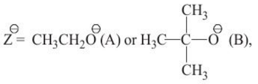
**2.** For the following reactions



$CH_3CH_2CH_2Br + Z^{\ominus} \xrightarrow[\text{Substitution}]{k_S} CH_3CH_2CH_2Z + Br^{\ominus}$

$CH_3CH_2CH_2Br + Z^{\ominus} \xrightarrow[\text{elimination}]{k_e} CH_3CH = CH_2 + HZ + Br^{\ominus}$

where



$$\overset{\ominus}{Z} = CH_3CH_2\overset{\ominus}{O}\,(A) \text{ or } H_3C{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\overset{\ominus}{O}\ (B),$$

$k_s$ and $k_e$, are, respectively, the rate constants for substitution and elimination, and $\mu = \frac{k_s}{k_e}$, the correct option is ________. **[Jan. 07, 2020 (II)]**

(a) $\mu_B > \mu_A$ and $k_e(A) > k_e(B)$

(b) $\mu_A > \mu_B$ and $k_e(B) > k_e(A)$

(c) $\mu_B > \mu_A$ and $k_e(B) > k_e(A)$

(d) $\mu_A > \mu_B$ and $k_e(A) > k_e(B)$

**3.** For the reaction

$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$ the observed rate expression is, rate $= k_f[NO]^2[H_2]$. The rate expression for the reverse reaction is: **[Jan. 07, 2020 (II)]**

(a) $k_b[N_2][H_2O]^2$

(b) $k_b[N_2][H_2O]^2/[NO]$

(c) $k_b[N_2][H_2O]$

(d) $k_b[N_2][H_2O]^2/[H_2]$

**4.** In the following reaction : $xA \rightarrow yB$

$$\log_{10}\left[-\frac{d[A]}{dt}\right] = \log_{10}\left[\frac{d[B]}{dt}\right] + 0.3010$$

'A' and 'B' respectively can be: **[April 12, 2019 (I)]**

(a) *n*-Butane and Iso-butane

(b) $C_2H_2$ and $C_6H_6$

(c) $C_2H_4$ and $C_4H_8$

(d) $N_2O_4$ and $NO_2$

**5.** $NO_2$ required for a reaction is produced by the decomposition of $N_2O_5$ in $CCl_4$ as per the equation,

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$.

The initial concentration of $N_2O_5$ is 3.00 mol $L^{-1}$ and it is 2.75 mol $L^{-1}$ after 30 minutes. The rate of formation of $NO_2$ is : **[April 12, 2019 (II)]**

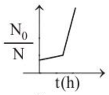
(a) $4.167 \times 10^{-3}$ mol $L^{-1}$ $min^{-1}$

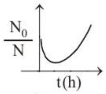
(b) $1.667 \times 10^{-2}$ mol $L^{-1}$ $min^{-1}$

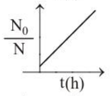
(c) $8.333 \times 10^{-3}$ mol $L^{-1}$ $min^{-1}$

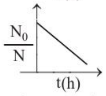
(d) $2.083 \times 10^{-3}$ mol $L^{-1}$ $min^{-1}$

**6.** A bacterial infection in an internal wound grows as $N'(t) = N_0\exp(t)$, where the time t is in hours. A dose of antibiotic, taken orally, needs 1 hour to reach the wound. Once it reaches there, the bacterial population goes down as $\frac{dN}{dt} = -5N^2$. What will be the plot of $\frac{N_0}{N}$ vs. t after 1 hour? **[April 10, 2019 (I)]**

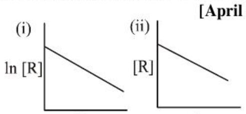
(a) 

(b) 

(c) 

(d) 

**7.** The given plots represents the variation of the concentration of a reactant R with time for two different reactions (i) and (ii). The respective orders of the reactions are: **[April 9, 2019 (I)]**



(a) 1, 0 (b) 1, 1 (c) 0, 1 (d) 0, 2

**8.** For the reaction $2A + B \rightarrow C$, the values of initial rate at different reactant concentrations are given in the table below. The rate law for the reaction is :

| **[A](mol L$^{-1}$)** | **[B](mol L$^{-1}$)** | **Initial Rate(mol L$^{-1}$ s$^{-1}$)** |
|---|---|---|
| 0.05 | 0.05 | 0.045 |
| 0.10 | 0.05 | 0.090 |
| 0.20 | 0.10 | 0.72 |

**[April 8, 2019 (I)]**

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

**9.** For a reaction scheme $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, if the rate of formation of B is set to be zero then the concentration of B is given by : **[April 8, 2019 (II)]**

(a) $(k_1 - k_2)$ [A] (b) $k_1k_2$ [A]
(c) $(k_1 + k_2)$ [A] (d) $\left(\frac{k_1}{k_2}\right)$[A]

**10.** For an elementary chemical reaction, $A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A$, the expression for $\frac{d[A]}{dt}$ is: **[Jan. 10, 2019 (II)]**

(a) $k_1[A_2] - k_{-1}[A]^2$ (b) $2k_1[A_2] - k_{-1}[A]^2$
(c) $k_1[A_2] + k_{-1}[A]^2$ (d) $2k_1[A_2] - 2k_{-1}[A]^2$

**11.** The reaction of ozone with oxygen atoms in the presence of chlorine atoms can occur by a two step process shown below : **[Online April 9, 2016]**

$O_3(g) + Cl^*(g) \rightarrow O_2(g) + ClO^*(g)$ ...(i)
$[K_i = 5.2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}]$
$ClO^*(g) + O^*(g) \rightarrow O_2(g) + Cl^*(g)$ ...(ii)
$[K_{ii} = 2.6 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}]$

The closest rate constant for the overall reaction $O_3(g) + O^*(g) \rightarrow 2O_2(g)$ is :

(a) $1.4 \times 10^{20}$ L mol$^{-1}$ s$^{-1}$ (b) $3.1 \times 10^{10}$ L mol$^{-1}$ s$^{-1}$
(c) $5.2 \times 10^9$ L mol$^{-1}$ s$^{-1}$ (d) $2.6 \times 10^{10}$ L mol$^{-1}$ s$^{-1}$

**12.** The rate law for the reaction below is given by the expression k [A][B]

$$A + B \rightarrow \text{Product}$$

If the concentration of B is increased from 0.1 to 0.3 mole, keeping the value of A at 0.1 mole, the rate constant will be: **[Online April 10, 2016]**

(a) $3k$ (b) $9k$ (c) $k/3$ (d) $k$

**13.** $A + 2B \rightarrow C$, the rate equation for this reaction is given as Rate $= k[A][B]$. **[Online April 11, 2015]**
If the concentration of A is kept the same but that of B is doubled what will happen to the rate itself ?

(a) halved (b) the same
(c) doubled (d) quadrupled

**14.** For the non - stoichiometric reaction $2A + B \rightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K.

| **Initial Concentration (A)** | **Initial Concentration (B)** | **Initial rate of formation of C (mol L$^{-1}$ s$^{-1}$)** |
|---|---|---|
| 0.1 M | 0.1 M | $1.2 \times 10^{-3}$ |
| 0.1 M | 0.2 M | $1.2 \times 10^{-3}$ |
| 0.2 M | 0.1 M | $2.4 \times 10^{-3}$ |

The rate law for the formation of C is: **[2014]**

(a) $\frac{dc}{dt} = k[A][B]$ (b) $\frac{dc}{dt} = k[A]^2[B]$
(c) $\frac{dc}{dt} = k[A][B]^2$ (d) $\frac{dc}{dt} = k[A]$

**15.** In the reaction of formation of sulphur trioxide by contact process $2SO_2 + O_2 \rightleftharpoons 2SO_3$ the rate of reaction was measured as

$\frac{d[O_2]}{dt} = -2.5 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$. The rate of reaction is terms of $[SO_2]$ in mol L$^{-1}$ s$^{-1}$ will be:

**[Online April 11, 2014]**

(a) $-1.25 \times 10^{-4}$ (b) $-2.50 \times 10^{-4}$
(c) $-3.75 \times 10^{-4}$ (d) $-5.00 \times 10^{-4}$

**16.** For the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$, the rate equation can be expressed in two ways $-\frac{d[N_2O_5]}{dt} = k[N_2O_5]$ and $+\frac{d[NO_2]}{dt} = k'[N_2O_5]$
$k$ and $k'$ are related as: **[Online April 11, 2014]**

(a) $k = k'$ (b) $2k = k'$
(c) $k = 2k'$ (d) $k = 4k'$

**17.** For the reaction,
$3A + 2B \rightarrow C + D$,
the differential rate law can be written as:

**[Online April 19, 2014]**

(a) $\frac{1}{3}\frac{d[\mathrm{A}]}{dt}=\frac{d[\mathrm{C}]}{dt}=k[\mathrm{A}]^n[\mathrm{B}]^m$

(b) $-\frac{d[\mathrm{A}]}{dt}=\frac{d[\mathrm{C}]}{dt}=k[\mathrm{A}]^n[\mathrm{B}]^m$

(c) $+\frac{1}{3}\frac{d[\mathrm{A}]}{dt}=-\frac{d[\mathrm{C}]}{dt}=k[\mathrm{A}]^n[\mathrm{B}]^m$

(d) $-\frac{1}{3}\frac{d[\mathrm{A}]}{dt}=\frac{d[\mathrm{C}]}{dt}=k[\mathrm{A}]^n[\mathrm{B}]^m$

**18.** The instantaneous rate of disappearance of $\mathrm{MnO_4^-}$ ion in the following reaction is $4.56 \times 10^{-3}\ \mathrm{Ms^{-1}}$

$\mathrm{2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O}$

The rate of appearance $\mathrm{I_2}$ is : **[Online April 9, 2013]**

(a) $4.56 \times 10^{-4}\ \mathrm{Ms^{-1}}$ (b) $1.14 \times 10^{-2}\ \mathrm{Ms^{-1}}$

(c) $1.14 \times 10^{-3}\ \mathrm{Ms^{-1}}$ (d) $5.7 \times 10^{-3}\ \mathrm{Ms^{-1}}$

**19.** Reaction rate between two substance A and B is expressed as following:

rate $= k[\mathrm{A}]^n[\mathrm{B}]^m$

If the concentration of A is doubled and concentration of B is made half of initial concentration, the ratio of the new rate to the earlier rate will be:

**[Online May 7, 2012, Offline 2003]**

(a) $m+n$ (b) $n-m$

(c) $\frac{1}{2^{(m+n)}}$ (d) $2^{(n-m)}$

**20.** Consider the reaction :

$\mathrm{Cl_2(aq) + H_2S(aq) \rightarrow S(s) + 2H^+(aq) + 2Cl^-(aq)}$

The rate equation for this reaction is

rate $= k[\mathrm{Cl_2}][\mathrm{H_2S}]$

Which of these mechanisms is/are consistent with this rate equation? **[2010]**

A. $\mathrm{Cl_2 + H_2S \rightarrow H^+ + Cl^- + Cl^+ + HS^-}$ (slow)

$\mathrm{Cl^+ + HS^- \rightarrow H^+ + Cl^- + S}$ (fast)

B. $\mathrm{H_2S \rightleftharpoons H^+ + HS^-}$ (fast equilibrium)

$\mathrm{Cl_2 + HS^- \rightarrow 2Cl^- + H^+ + S}$ (Slow)

(a) B only (b) Both A and B

(c) Neither A nor B (d) A only

**21.** For a reaction $\frac{1}{2}\mathrm{A} \rightarrow 2\mathrm{B}$, rate of disappearance of 'A' is related to the rate of appearance of 'B' by the expression **[2008]**

(a) $-\frac{d[\mathrm{A}]}{dt}=\frac{1}{2}\frac{d[\mathrm{B}]}{dt}$ (b) $-\frac{d[\mathrm{A}]}{dt}=\frac{1}{4}\frac{d[\mathrm{B}]}{dt}$

(c) $-\frac{d[\mathrm{A}]}{dt}=\frac{d[\mathrm{B}]}{dt}$ (d) $-\frac{d[\mathrm{A}]}{dt}=4\frac{d[\mathrm{B}]}{dt}$

**22.** The differential rate law for the reaction **[2002]**

$\mathrm{H_2 + I_2 \rightarrow 2HI}$ is

(a) $-\frac{d[\mathrm{H_2}]}{dt}=-\frac{d[\mathrm{I_2}]}{dt}=-\frac{d[\mathrm{HI}]}{dt}$

(b) $\frac{d[\mathrm{H_2}]}{dt}=\frac{d[\mathrm{I_2}]}{dt}=\frac{1}{2}\frac{d[\mathrm{HI}]}{dt}$

(c) $\frac{1}{2}\frac{d[\mathrm{H_2}]}{dt}=\frac{1}{2}\frac{d[\mathrm{I_2}]}{dt}=-\frac{d[\mathrm{HI}]}{dt}$

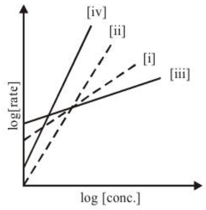
(d) $-2\frac{d[\mathrm{H_2}]}{dt}=-2\frac{d[\mathrm{I_2}]}{dt}=\frac{d[\mathrm{HI}]}{dt}$

## TOPIC 2 Order of Reaction and Half Life Period

**23.** Consider the following reactions

$\mathrm{A \rightarrow P1}$ ; $\mathrm{B \rightarrow P2}$ ; $\mathrm{C \rightarrow P3}$ ; $\mathrm{D \rightarrow P4}$,

The order of the above reactions are (i), (ii), (iii), and (iv), respectively. The following graph is obtained when log [rate] vs. log[conc.] are plotted : **[Sep. 06, 2020 (I)]**



Among the following, the correct sequence for the order of the reactions is:

(a) (iv) > (i) > (ii) > (iii) (b) (i) > (ii) > (iii) > (iv)

(c) (iii) > (i) > (ii) > (iv) (d) (iv) > (ii) > (i) > (iii)

**24.** A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives for A and B are 300 s and 180 s, respectively. If the concentrations of A and B are equal initially, the time required for the concentration of A to be four times that of B (in s) is: (Use ln 2 = 0.693) **[Sep. 05, 2020 (I)]**

(a) 180 (b) 900

(c) 300 (d) 120

**25.** If 75% of a first order reaction was completed in 90 minutes, 60% of the same reaction would be completed in approximately (in minutes) ____________.

(Take : log 2 = 0.30; log 2.5 = 0.40) **[NV, Sep. 04, 2020 (I)]**

**26.** It is true that : **[Sep. 03, 2020 (I)]**

(a) A second order reaction is always a multistep reaction

(b) A zero order reaction is a multistep reaction

(c) A first order reaction is always a single step reaction

(d) A zero order reaction is a single step reaction

**27.** The results given in the below table were obtained during kinetic studies of the following reaction :

$2A + B \rightarrow C + D$ **[Sep. 02, 2020 (II)]**

| Experiment | [A]/ $molL^{-1}$ | [B]/ $molL^{-1}$ | Initial rate/ $molL^{-1}\ min^{-1}$ |
|---|---|---|---|
| I | 0.1 | 0.1 | $6.00 \times 10^{-3}$ |
| II | 0.1 | 0.2 | $2.40 \times 10^{-2}$ |
| III | 0.2 | 0.1 | $1.20 \times 10^{-2}$ |
| IV | X | 0.2 | $7.20 \times 10^{-2}$ |
| V | 0.3 | Y | $2.88 \times 10^{-1}$ |

X and Y in the given table are respectively :

(a) 0.4, 0.4 (b) 0.4, 0.3

(c) 0.3, 0.4 (d) 0.3, 0.3

**28.** During the nuclear explosion, one of the products is $^{90}Sr$ with half life of 6.93 years. If 1 μg of $^{90}Sr$ was absorbed in the bones of a newly born baby in place of Ca, how much time, in years, is required to reduce it by 90% if it is not lost metabolically. **[NV, Jan. 07, 2020 (I)]**

**29.** Decomposition of X exhibits a rate constant of 0.05 μg/year. How many years are required for the decomposition of 5 μg of X into 2.5 μg? **[Jan. 12, 2019 (I)]**

(a) 50 (b) 25 (c) 20 (d) 40

**30.** The reaction $2X \rightarrow B$ is a zeroth order reaction. If the initial concentration of X is 0.2 M, the half-life is 6 h. When the initial concentration of X is 0.5 M, the time required to reach its final concentration of 0.2 M will be : **[Jan. 11, 2019 (II)]**

(a) 9.0 h (b) 12.0 h (c) 18.0 h (d) 7.2 h

**31.** The following results were obtained during kinetic studies of the reaction; **[Jan. 9, 2019 (I)]**

$2A + B \rightarrow$ Products

| Experiment | [A] (in mol $L^{-1}$) | [B] (in mol $L^{-1}$) | Initial Rate of reaction (in mol $L^{-1}$ $min^{-1}$) |
|---|---|---|---|
| I | 0.10 | 0.20 | $6.93 \times 10^{-3}$ |
| II | 0.10 | 0.25 | $6.93 \times 10^{-3}$ |
| III | 0.20 | 0.30 | $1.386 \times 10^{-2}$ |

The time (in minutes) required to consume half of A is:

(a) 5 (b) 10 (c) 1 (d) 100

**32.** For the reaction, 2A + B → products, when the concentrations of A and B both were doubled, the rate of the reaction increased from 0.3 mol $L^{-1}$ $s^{-1}$ to 2.4 mol $L^{-1}s^{-1}$. When the concentration of A alone is doubled, the rate increased from 0.3 and $L^{-1}s^{-1}$ to 0.6 mol $L^{-1}s^{-1}$. Which one of the following statements is correct? **[Jan. 9, 2019 (II)]**

(a) Total order of the reaction is 4

(b) Order of the reaction with respect to B is 2

(c) Order of the reaction with respect to B is 1

(d) Order of the reaction with respect to A is 2

**33.** At 518 °C, the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 Torr, was 1.00 Torr $s^{-1}$ when 5% had reacted and 0.5 Torr $s^{-1}$ when 33% had reacted. The order of the reaction is : **[2018]**

(a) 2 (b) 3 (c) 1 (d) 0

**34.** If 50% of a reaction occurs in 100 seconds and 75% of the reaction occurs in 200 seconds, the order of this reaction is: **[Online April 16, 2018]**

(a) 2 (b) 3 (c) Zero (d) 1

**35.** $N_2O_5$ decomposes to $NO_2$ and $O_2$ and follows first order kinetics. After 50 minutes, the pressure inside the vessel increases from 50 mm Hg to 87.5 mm Hg. The pressure of the gaseous mixture after 100 minutes at constant temperature will be ________. **[Online April 15, 2018 (I)]**

(a) 136.25 mm Hg (b) 106.25 mm Hg

(c) 175.0 mm Hg (d) 116.25 mm Hg

**36.** For a first order reaction, $A \rightarrow P$, $t_{1/2}$ (half-life) is 10 days. The time required for $\frac{1}{4}^{th}$ conversion of A (in days) is:

($\ln 2 = 0.693$, $\ln 3 = 1.1$). **[Online April 15, 2018 (II)]**

(a) 3.2 (b) 2.5 (c) 4.1 (d) 5

**37.** Decomposition of $H_2O_2$ follows a first order reaction. In fifty minutes the concentration of $H_2O_2$ decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of $H_2O_2$ reaches 0.05 M, the rate of formation of $O_2$ will be: **[2016]**

(a) 2.66 L $min^{-1}$ at STP (b) $1.34 \times 10^{-2}$ mol $min^{-1}$

(c) $6.96 \times 10^{-2}$ mol $min^{-1}$ (d) $6.93 \times 10^{-4}$ mol $min^{-1}$

**38.** Higher order (>3) reactions are rare due to : **[2015]**

(a) shifting of equilibrium towards reactants due to elastic collisions

(b) loss of active species on collision

(c) low probability of simultaneous collision of all the reacting species

(d) increase in entropy and activation energy as more molecules are involved

**39.** The reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ follows first order kinetics. The pressure of a vessel containing only $N_2O_5$ was found to increase from 50 mm Hg to 87.5 mm Hg in 30 min. The pressure exerted by the gases after 60 min. will be (assume temperature remains constant) : **[Online April 10, 2015]**

(a) 106.25 mm Hg (b) 150 mm Hg

(c) 125 mm Hg (d) 116.25 mm Hg

**40.** The half-life period of a first order reaction is 15 minutes. The amount of substance left after one hour will be: **[Online April 9, 2014]**

(a) $\frac{1}{4}$ of the original amount

(b) $\frac{1}{8}$ of the original amount

(c) $\frac{1}{16}$ of the original amount

(d) $\frac{1}{32}$ of the original amount

**41.** The rate constant of a zero order reaction is $2.0 \times 10^{-2}$ mol $L^{-1}$ $s^{-1}$. If the concentration of the reactant after 25 seconds is 0.5 M. What is the initial concentration ? **[Online April 23, 2013]**

(a) 0.5 M (b) 1.25 M (c) 12.5 M (d) 1.0 M

**42.** A radioactive isotope having a half - life period of 3 days was received after 12 days. If 3g of the isotope is left in the container, what would be the initial mass of the isotope ? **[Online April 25, 2013]**

(a) 12 g (b) 36 g (c) 48 g (d) 24 g

**43.** For a first order reaction (A) → products, the concentration of A changes from 0.1 M to 0.025 M in 40 minutes. The rate of reaction when the concentration of A is 0.01 M is : **[2012]**

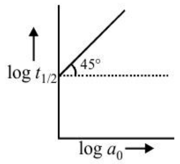
(a) $1.73 \times 10^{-5}$ M/min (b) $3.47 \times 10^{-4}$ M/min

(c) $3.47 \times 10^{-5}$ M/min (d) $1.73 \times 10^{-4}$ M/min

**44.** In a chemical reaction *A* is converted into *B*. The rates of reaction, starting with initial concentrations of *A* as $2 \times 10^{-3}$ M and $1 \times 10^{-3}$ M, are equal to $2.40 \times 10^{-4}$ $Ms^{-1}$ and $0.60 \times 10^{-4}$ $Ms^{-1}$ respectively. The order of reaction with respect to reactant *A* will be **[Online May 12, 2012]**

(a) 0 (b) 1.5 (c) 1 (d) 2

**45.** For a reaction $A \rightarrow$ Products, a plot of log $t_{1/2}$ versus log $a_0$ is shown in the figure. If the initial concentration of *A* is represented by $a_0$, the order of the reaction is **[Online May 19, 2012]**



(a) one (b) zero (c) two (d) three

**46.** The time for half life period of a certain reaction $A \longrightarrow$ Products is 1 hour. When the initial concentration of the reactant 'A' is 2.0 mol $L^{-1}$, how much time does it take for its concentration to come from 0.50 to 0.25 mol $L^{-1}$ if it is a zero order reaction ? **[2010]**

(a) 4 h (b) 0.5 h (c) 0.25 h (d) 1 h

**47.** The half life period of a first order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be (log 2 = 0.301) **[2009]**

(a) 23.03 minutes (b) 46.06 minutes

(c) 460.6 minutes (d) 230.03 minutes

**48.** Consider the reaction, 2A + B → products. When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is **[2007]**

(a) $s^{-1}$ (b) L $mol^{-1}$ $s^{-1}$ (c) no unit (d) mol $L^{-1}$ $s^{-1}$.

**49.** A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial velocity is ten times the permissible value, after how many days will it be safe to enter the room? **[2007]**

(a) 100 days (b) 1000 days

(c) 300 days (d) 10 days.

**50.** The following mechanism has been proposed for the reaction of NO with $Br_2$ to form NOBr :

$$NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$$

$$NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$$

If the second step is the rate determining step, the order of the reaction with respect to NO(g) is **[2006]**

(a) 3 (b) 2 (c) 1 (d) 0

**51.** A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will **[2006]**

(a) increase by a factor of 4

(b) double

(c) remain unchanged

(d) triple

**52.** A reaction involving two different reactants can never be **[2005]**

(a) bimolecular reaction (b) second order reaction

(c) first order reaction (d) unimolecular reaction

**53.** $t_{\frac{1}{4}}$ can be taken as the time taken for the concentration of a reactant to drop to $\frac{3}{4}$ of its initial value. If the rate constant for a first order reaction is *k*, the $t_{\frac{1}{4}}$ can be written as **[2005]**

(a) 0.75/*k* (b) 0.69/*k* (c) 0.29/*k* (d) 0.10/*k*

**54.** The rate equation for the reaction 2A + B → C is found to be: rate = *k*[A][B]. The correct statement in relation to this reaction is that the **[2004]**

(a) rate of formation of C is twice the rate of disappearance of A

(b) $t_{1/2}$ is a constant

(c) unit of *k* must be $s^{-1}$

(d) value of *k* is independent of the initial concentrations of A and B

**55.** For the reaction system : **[2003]**
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
volume is
suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to $O_2$ and second order with respect to NO, the rate of reaction will
(a) diminish to one-eighth of its initial value
(b) increase to eight times of its initial value
(c) increase to four times of its initial value
(d) diminish to one-fourth of its initial value

**56.** The integrated rate equation is **[2002]**
$Rt = \log C_0 - \log C_t$.
The straight line graph is obtained by plotting
(a) time vs $\log C_t$
(b) $\frac{1}{\text{time}}$ vs $C_t$
(c) time vs $C_t$
(d) $\frac{1}{\text{time}}$ vs $\frac{1}{C_t}$

**57.** In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is **[2004]**
(a) 7.5 minutes
(b) 15 minutes
(c) 30 minutes
(d) 60 minutes

**58.** The half-life of a radioisotope is four hours. If the initial mass of the isotope was 200 g, the mass remaining after 24 hours undecayed is **[2004]**
(a) 3.125 g (b) 2.084 g (c) 1.042 g (d) 4.167 g

**59.** The half-life of a radioactive isotope is three hours. If the initial mass of the isotope were 256 g, the mass of it remaining undecayed after 18 hours would be **[2003]**
(a) 8.0 g (b) 12.0 g (c) 16.0 g (d) 4.0 g

**60.** Units of rate constant of first and zero order reactions in terms of molarity M unit are respectively **[2002]**
(a) $sec^{-1}$, $Msec^{-1}$
(b) $sec^{-1}$, M
(c) $Msec^{-1}$, $sec^{-1}$
(d) M, $sec^{-1}$.

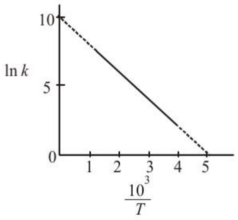
**61.** For the reaction $A + 2B \rightarrow C$, rate is given by $R = [A][B]^2$ then the order of the reaction is **[2002]**
(a) 3 (b) 6 (c) 5 (d) 7

**62.** If half-life of a substance is 5 yrs, then the total amount of substance left after 15 years, when initial amount is 64 grams is **[2002]**
(a) 16 grams
(b) 2 grams
(c) 32 grams
(d) 8 grams

## TOPIC 3 Theories of Rate of Reaction

**63.** The rate of a reaction decreased by 3.555 times when the temperature was changed from 40ºC to 30ºC. The activation energy (in kJ $mol^{-1}$) of the reaction is ______. Take;
$R = 8.314\ J mol^{-1} K^{-1}$ In 3.555 = 1.268 **[NV, Sep. 06, 2020 (II)]**

**64.** The rate constant ($k$) of a reaction is measured at different temperatures ($T$), and the data are plotted in the given figure. The activation energy of the reaction in kJ $mol^{-1}$ is :
($R$ is gas constant) **[Sep. 05, 2020 (II)]**



(a) $2/R$ (b) $1/R$ (c) $R$ (d) $2R$

**65.** The number of molecules with energy greater than the threshold energy for a reaction increases five fold by a rise of temperature from 27°C to 42°C. Its energy of activation in J/ mol is __________. (Take ln 5 = 1.6094; $R = 8.314\ J mol^{-1}K^{-1}$) **[NV, Sep. 04, 2020 (II)]**

**66.** For following reactions:

$A \xrightarrow{700\,K} \text{Product}$

$A \xrightarrow[\text{catalyst}]{500\,K} \text{Product}$

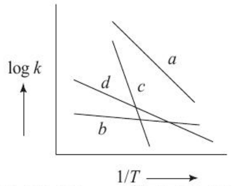
it was found that the $E_a$ is decrease by 30 kJ/mol in the presence of catalyst. If the rate remains unchanged, the activation energy for catalysed reaction is (Assume pre exponential factor is same): **[Jan. 09, 2020 (I)]**
(a) 75 kJ/mol
(b) 105 kJ/mol
(c) 135 kJ/mol
(d) 198 kJ/mol

**67.** A sample of milk splits after 60 min. at 300 K and after 40 min. at 400 K when the population of *lactobacillus acidophilus* in it doubles. The activation energy (in kJ/mol) for this process is closest to _____.

(Given, $R = 8.3\ J mol^{-1} K^{-1}$, $\ln\left(\frac{2}{3}\right) = 0.4$, $e^{-3} = 4.0$)
**[NV, Jan. 09, 2020 (II)]**

**68.** The rate of a certain biochemical reaction at physiological temperature ($T$) occurs $10^6$ times faster with enzyme than without. The change in the activation energy upon adding enzyme is: **[Jan. 08, 2020 (I)]**
(a) –6(2.303)RT
(b) –6RT
(c) +6(2.303)RT
(d) +6RT

**69.** Consider the following plots of rate constant versus $\frac{1}{T}$ for four different reactions. Which of the following orders is correct for the activation energies of these reactions? **[Jan. 08, 2020 (II)]**



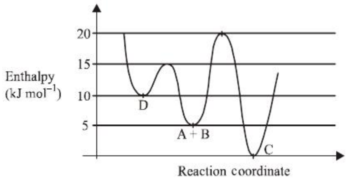
(a) $E_b > E_a > E_d > E_c$  (b) $E_a > E_c > E_d > E_b$
(c) $E_c > E_a > E_d > E_b$  (d) $E_b > E_d > E_c > E_a$

**70.** For the reaction of $H_2$ with $I_2$, the rate constant is $2.5 \times 10^{-4}$ $dm^3\ mol^{-1}\ s^{-1}$ at 327 °C and 1.0 $dm^3\ mol^{-1}\ s^{-1}$ at 527 °C. The activation energy for the reaction, in $kJ\ mol^{-1}$ is : ($R = 8.314 J\ K^{-1}\ mol^{-1}$) **[April 10, 2019 (II)]**

(a) 166 (b) 150 (c) 72 (d) 59

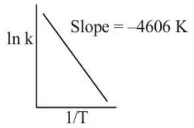
**71.** Consider the given plot of enthalpy of the following reaction between A and B, $A + B \rightarrow C + D$.

Identify the incorrect statement. **[April 9, 2019 (II)]**



(a) Activation enthalpy to form C is 5kJ $mol^{-1}$ less than that to form D.
(b) C is the thermodynamically stable product.
(c) D is kinetically stable product.
(d) Formation of A and B from C has highest enthalpy of activation.

**72.** For a reaction, consider the plot of ln k versus 1/T given in the figure. If the rate constant of this reaction at 400 K is $10^{-5}\ s^{-1}$, then the rate constant at 500 K is : **[Jan. 12, 2019 (II)]**

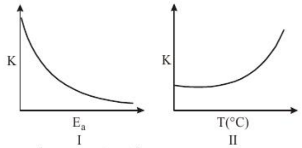


(a) $10^{-6}\ s^{-1}$  (b) $2 \times 10^{-4}\ s^{-1}$
(c) $10^{-4}\ s^{-1}$  (d) $4 \times 10^{-4}\ s^{-2}$

**73.** If a reaction follows the Arrhenius equation, the plot lnk vs $\frac{1}{(RT)}$ gives straight line with a gradient (– y) unit. The energy required to activate the reactant is: **[Jan. 11, 2019 (I)]**

(a) y/R unit  (b) y unit
(c) yR unit  (d) – y unit

**74.** Consider the given plots for a reaction obeying Arrhenius equation (0 °C < T < 300 °C) : (k and $E_a$ are rate constant and activation energy, respectively) **[Jan. 10, 2019 (I)]**



Choose the correct option:
(a) I is right but II is wrong
(b) Both I and II are correct
(c) I is wrong but II is right
(d) Both I and II are wrong

**75.** Two reactions $R_1$ and $R_2$ have identical pre-exponential factors. Activation energy of $R_1$ exceeds that of $R_2$ by 10 $kJ\ mol^{-1}$. If $k_1$ and $k_2$ are rate constants for reactions $R_1$ and $R_2$ respectively at 300 K, then $\ln(k_2/k_1)$ is equal to : ($R = 8.314\ J\ mol^{-1}K^{-1}$) **[2017]**

(a) 8 (b) 12 (c) 6 (d) 4

**76.** The rate of a reaction A doubles on increasing the temperature from 300 to 310 K. By how much, the temperature of reaction B should be increased from 300 K so that rate doubles if activation energy of the reaction B is twice to that of reaction A. **[Online April 8, 2017]**

(a) 9.84 K (b) 4.92 K (c) 2.45 K (d) 19.67 K

**77.** The rate of a reaction quadruples when the temperature changes from 300 to 310 K. The activation energy of this reaction is : (Assume activation energy and pre-exponential factor are independent of temperature; ln 2 = 0.693; $R = 8.314\ J\ mol^{-1}\ K^{-1}$) **[Online April 9, 2017]**

(a) 107.2 $kJ\ mol^{-1}$  (b) 53.6 $kJ\ mol^{-1}$
(c) 26.8 $kJ\ mol^{-1}$  (d) 214.4 $kJ\ mol^{-1}$

**78.** For the equilibrium, $A(g) \rightleftharpoons B(g)$, ΔH is –40 kJ/mol. If the ratio of the activation energies of the forward ($E_f$) and reverse ($E_b$) reactions is $\frac{2}{3}$ then : **[Online April 11, 2015]**

(a) $E_f$ = 80 kJ/mol; $E_b$ = 120 kJ/mol
(b) $E_f$ = 60 kJ/mol; $E_b$ = 100 kJ/mol
(c) $E_f$ = 30 kJ/mol; $E_b$ = 70 kJ/mol
(d) $E_f$ = 70 kJ/mol; $E_b$ = 30 kJ/mol

**79.** The rate coefficient (k) for a particular reactions is $1.3 \times 10^{-4}\ M^{-1}\ s^{-1}$ at 100 °C, and $1.3 \times 10^{-3}\ M^{-1}\ s^{-1}$ at 150 °C. What is the energy of activation ($E_a$) (in kJ) for this reaction? (R = molar gas constant = 8.314 $JK^{-1}\ mol^{-1}$) **[Online April 12, 2014]**

(a) 16 (b) 60 (c) 99 (d) 132

**80.** The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of the reaction will be : (R = 8.314 JK$^{-1}$ mol$^{-1}$ and log 2 = 0.301) **[2013]**

(a) 53.6 kJ mol$^{-1}$ (b) 48.6 kJ mol$^{-1}$
(c) 58.5 kJ mol$^{-1}$ (d) 60.5 kJ mol$^{-1}$

**81.** The reaction X → Y is an exothermic reaction. Activation energy of the reaction for X into Y is 150 kJ mol$^{-1}$. Enthalpy of reaction is 135 kJ mol$^{-1}$. The activation energy for the reverse reaction, Y → X will be : **[Online April 22, 2013]**

(a) 280 kJ mol$^{-1}$ (b) 285 kJ mol$^{-1}$
(c) 270 kJ mol$^{-1}$ (d) 15 kJ mol$^{-1}$

**82.** The activation energy for a reaction which doubles the rate when the temperature is raised from 298 K to 308 K is **[Online May 26, 2012]**

(a) 59.2 kJ mol$^{-1}$ (b) 39.2 kJ mol$^{-1}$
(c) 52.9 kJ mol$^{-1}$ (d) 29.5 kJ mol$^{-1}$

**83.** A reactant (A) froms two products : **[2011RS]**

$A \xrightarrow{k_1} B$, Activation energy $Ea_1$

$A \xrightarrow{k_2} C$, Activation energy $Ea_2$

If $Ea_2 = 2\,Ea_1$, then $k_1$ and $k_2$ are related as :

(a) $k_2 = k_1 e^{Ea_1/RT}$ (b) $k_2 = k_1 e^{Ea_2/RT}$
(c) $k_1 = Ak_2 e^{Ea_1/RT}$ (d) $k_1 = 2k_2 e^{Ea_2/RT}$

**84.** The energies of activation for forward and reverse reactions for $A_2 + B_2 \rightleftharpoons 2AB$ are 180 kJ mol$^{-1}$ and 200 kJ mol$^{-1}$ respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol$^{-1}$. The enthalpy change of the reaction ($A_2 + B_2 \rightarrow 2AB$) in the presence of a catalyst will be (in kJ mol$^{-1}$) **[2007]**

(a) 20 (b) 300 (c) 120 (d) 280

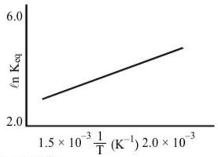
**85.** Rate of a reaction can be expressed by Arrhenius equation as : **[2006]**

$$k = A\,e^{-Ea/RT}$$

In this equation, *Ea* represents

(a) the total energy of the reacting molecules at a temperature, *T*
(b) the fraction of molecules with energy greater than the activation energy of the reaction
(c) the energy above which all the colliding molecules will react
(d) the energy below which all the colliding molecules will react

**86.** A schematic plot of ln$K_{eq}$ versus inverse of temperature for a reaction is shown below **[2005]**



The reaction must be

(a) highly spontaneous at ordinary temperature
(b) one with negligible enthalpy change
(c) endothermic
(d) exothermic

**87.** Consider an endothermic reaction X → Y with the activation energies $E_b$ and $E_f$ for the backward and forward reactions, respectively. In general **[2005]**

(a) there is no definite relation between $E_b$ and $E_f$
(b) $E_b = E_f$
(c) $E_b > E_f$
(d) $E_b < E_f$

**88.** In respect of the equation $k = Ae^{-E_a/RT}$ in chemical kinetics, which one of the following statements is correct ? **[2003]**

(a) *A* is adsorption factor
(b) $E_a$ is energy of activation
(c) *R* is Rydberg's constant
(d) *k* is equilibrium constant

# Hints & Solutions

1. **(c)** For a given reaction,

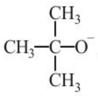
$$\text{rate} = -\frac{1}{2}\frac{dn_A}{dt} = -\frac{1}{3}\frac{dn_B}{dt} = -\frac{2}{3}\frac{dn_C}{dt}$$

$$\text{rate} = \frac{dn_A}{dt} = \frac{2}{3}\frac{dn_B}{dt} = \frac{4}{3}\frac{dn_C}{dt}$$

2. **(b)** Among the given bases (A) and (B), *t*-butoxide being bulky base favours elimination reaction and ethoxide favours substitution reaction.

$\therefore$ when $Z^{\ominus} = CH_3CH_2O^-$, (substitution reaction favoured)

and when $Z^{\ominus} =$



$CH_3-C(CH_3)_2-O^-$ ,(elimination reaction favoured)

Hence, $\mu_A > \mu_B$ and $k_e(B) > k_e(A)$

3. **(d)** Rate of forward reaction $= k_f[NO]^2[H_2]^2$

Observed rate $= k_f[NO]^2[H_2]$

$$\text{Observed rate} = \frac{\text{Rate of forward reaction}}{[H_2]}$$

$$\therefore \text{Rate of backward reaction} = \frac{k_b[N_2][H_2O]^2}{[H_2]}$$

4. **(c)** $xA \rightarrow yB$

$$\therefore \frac{-dA}{xdt} = \frac{1}{y}\frac{dB}{dt}$$

$$\frac{-dA}{dt} = \frac{dB}{dt} \times \frac{x}{y}$$

$$\log\left[\frac{-dA}{dt}\right] = \log\left[\frac{dB}{dt}\right] + \log\left(\frac{x}{y}\right)$$

Comparing this equation with the equation given in question. We get,

$$\log\frac{x}{y} = 0.3010 \quad \text{or} \quad \log\frac{x}{y} = \log 2$$

$$\therefore \frac{x}{y} = 2$$

$\therefore$ The reaction is of type $2A \rightarrow B$.

Hence, option (3) is correct.

5. **(b)** $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

$$\text{rate of reaction} = \frac{-1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

According to the question

$$\frac{-d[N_2O_5]}{dt} = -\frac{(2.75-3)}{30} = \frac{0.25}{30} M\,min^{-1}$$

$$\therefore \frac{d[NO_2]}{dt} = 2 \times \frac{-d[N_2O_5]}{dt} = 2 \times \frac{0.25}{30}$$

$= 1.67 \times 10^{-2-} M\,min^{-1}$

6. **(c)** From 0 to 1h, $N' = N_0e^t$

When drug is administered bacterial growth is given by

$$\frac{dN}{dt} = -5N^2$$

So, at $t = 1$ h, $N' = eN_0$

Integrating the following equation,

$$\frac{dN}{dt} = -5N^2$$

$$\int_{eN_0}^{N}\frac{dN}{N^2} = -5\int_1^t dt$$

$$\frac{1}{N} - \frac{1}{eN_0} = 5(t-1)$$

$$\frac{N_0}{N} - \frac{1}{e} = 5N_0(t-1)$$

$$\frac{N_0}{N} = 5N_0(t-1) + \frac{1}{e}$$

$$\frac{N_0}{N} = 5N_0t + \left(\frac{1}{e} - 5N_0\right)$$

The above equation is similar to straight line equation with positive slope.

Thus $\frac{N_0}{N}$ increases linearly with t.

7. **(a)** In graph (i), ln [Reactant] vs time is linear with positive intercept and negative slope. Hence it is 1st order. In graph (ii), [Reactant] vs time is linear with positive intercept and negative slope. Hence, it is zero order.

8. **(a)** $2A + B \longrightarrow C$

Rate $= k[A]^x[B]^y$

**Exp-1,** $0.045 = k[0.05]^x[0.05]^y$ ...(i)

**Exp-2,** $0.090 = k[0.1]^x[0.05]^y$ ...(ii)

**Exp-3,** $0.72 = k[0.2]^x[0.1]^y$ ...(iii)

Divide equation (i) by equation (ii)

$$\frac{0.045}{0.090} = \left(\frac{1}{2}\right)^x \Rightarrow x = 1$$

Divide equation (i) by equation (iii)

$$\frac{0.045}{0.72} = \left(\frac{0.05}{0.1}\right)^y \left(\frac{0.05}{0.2}\right)^1$$

$$\frac{0.045}{0.72} \times \frac{0.2}{0.05} = \left(\frac{0.05}{0.1}\right)^y$$

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

Rate law $= k[\mathrm{A}]^1[\mathrm{B}]^2$.

**9.** **(d)** $\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}] = 0$$

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]}{k_2}$$

**10.** **(d)** Given: $\mathrm{A}_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\mathrm{A}$

Now, $-\frac{1}{2}\frac{d[\mathrm{A}]}{dt} = k_{-1}[\mathrm{A}]^2 - k_1[\mathrm{A}_2]$

$$\frac{d[\mathrm{A}]}{dt} = -2k_{-1}[\mathrm{A}]^2 + 2k_1[\mathrm{A}_2]$$

$$\Rightarrow \frac{d[\mathrm{A}]}{dt} = 2k_1[\mathrm{A}_2] - 2k_{-1}[\mathrm{A}]^2$$

**11.** **(a)** On adding eq. (i) and eq. (ii) we get

$$\mathrm{O_3(g) + O(g) \longrightarrow 2O_2(g)}$$

Hence overall rate constant $= k_i \times k_{ii}$

$= 5.2 \times 10^9 \times 2.6 \times 10^{10} \approx 1.4 \times 10^{20}\ \mathrm{mol^{-1}\,L\,s^{-1}}$

$$\begin{array}{l} \mathrm{O_3(g) + Cl^{\bullet}(g) \longrightarrow O_2(g) + ClO^{\bullet}(g)},\ k_{\mathrm{i}} \\ \mathrm{ClO^{\bullet}(g) + O^{\bullet}(g) \longrightarrow O_2(g) + Cl^{\bullet}(g)},\ k_{\mathrm{ii}} \\ \hline \mathrm{O_3(g) + O^{\bullet}(g) \longrightarrow 2O_2(g)},\ k_{\mathrm{Rate}} = k_{\mathrm{i}} \times k_{\mathrm{ii}} \end{array}$$

**12.** **(d)** Rate constant is independent of concentration.

**13.** **(c)** Rate $= k[\mathrm{A}][\mathrm{B}] = \mathrm{R}$

$\mathrm{R'} = k[\mathrm{A}][2\mathrm{B}]$

$$\frac{\mathrm{R}}{\mathrm{R'}} = \frac{k[\mathrm{A}][\mathrm{B}]}{k[\mathrm{A}][2\mathrm{B}]} = \frac{k[\mathrm{A}][\mathrm{B}]}{2k[\mathrm{A}][\mathrm{B}]}$$

$\Rightarrow 2\mathrm{R} = \mathrm{R'}$ i.e., rate become doubles.

**14.** **(d)** Let rate of reaction $= \frac{d[C]}{t} = k[A]^x[B]^y$

Now from the given data

$1.2 \times 10^{-3} = k[0.1]^x[0.1]^y$ .....(i)

$1.2 \times 10^{-3} = k[0.1]^x[0.2]^y$ .....(ii)

$2.4 \times 10^{-3} = k[0.2]^x[0.1]^y$ .....(iii)

Dividing equation (i) by (ii)

$$\Rightarrow \frac{1.2 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k[0.1]^x[0.1]^y}{k[0.1]^x[0.2]^y}$$

We find, $y = 0$

Now dividing equation (i) by (iii)

$$\Rightarrow \frac{1.2 \times 10^{-3}}{2.4 \times 10^{-3}} = \frac{k[0.1]^x[0.1]^y}{k[0.2]^x[0.1]^y}$$

We find, $x = 1$

Hence, $\frac{d[C]}{dt} = k[A]^1[B]^0$

**15.** **(d)** From rate law

$$-\frac{1}{2}\frac{d[\mathrm{SO_2}]}{dt} = -\frac{d[\mathrm{O_2}]}{dt} = \frac{1}{2}\frac{d[\mathrm{SO_3}]}{dt}$$

$$\therefore -\frac{d[\mathrm{SO_2}]}{dt} = -2 \times \frac{d[\mathrm{O_2}]}{dt}$$

$= -2 \times 2.5 \times 10^{-4}$

$= -5 \times 10^{-4}\ \mathrm{mol\,L^{-1}\,s^{-1}}$

**16.** **(b)** Rate of disappearance of reactant = Rate of appearance of products

$$-\frac{1}{2}\frac{d[\mathrm{N_2O_5}]}{dt} = \frac{1}{4}\frac{d[\mathrm{NO_2}]}{dt}$$

$$\frac{1}{2}k[\mathrm{N_2O_5}] = \frac{1}{4}k'[\mathrm{N_2O_5}]$$

$$\frac{k}{2} = \frac{k'}{4}$$

$$\therefore k' = 2k$$

**17.** **(d)** For the reaction

$3\mathrm{A} + 2\mathrm{B} \longrightarrow \mathrm{C} + \mathrm{D}$

Rate of disappearance of A = Rate of appearance of C reaction

$$= -\frac{1}{3}\frac{d[\mathrm{A}]}{dt} = \frac{d[\mathrm{C}]}{dt} = k[\mathrm{A}]^n[\mathrm{B}]^m$$

**18.** **(b)** Given $-\frac{d[\mathrm{MnO_4^-}]}{dt} = 4.56 \times 10^{-3}\ \mathrm{Ms^{-1}}$

From the reaction given,

$$-\frac{1}{2}\frac{d[\mathrm{MnO_4^-}]}{dt} = \frac{4.56 \times 10^{-3}}{2}\mathrm{Ms^{-1}}$$

$$-\frac{1}{2}\frac{d[\mathrm{MnO_4^-}]}{dt} = \frac{1}{5}\frac{d\mathrm{I_2}}{dt}$$

$$\therefore -\frac{5}{2}\frac{d[\mathrm{MnO_4^-}]}{dt} = \frac{d\mathrm{I_2}}{dt}$$

On substituting the given value

$$\therefore \frac{dI_2}{dt} = \frac{4.56\times10^{-3}\times5}{2} = 1.14\times10^{-2}\text{ M/s}$$

**19.** **(d)** $\text{Rate}_1 = k[A]^n[B]^m$

$$\text{Rate}_2 = k[2A]^n\left[\frac{1}{2}B\right]^m$$

$$\therefore \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[2\text{A}]^n\left[\frac{1}{2}\text{B}\right]^m}{k[\text{A}]^n[\text{B}]^m} = (2)^n\left(\frac{1}{2}\right)^m$$

$$= 2^n\,.\,(2)^{-m} = 2^{n-m}$$

**20.** **(d)** Since the slow step is the rate determining step, hence if we consider mechanism A. We find

$\text{Rate} = k[\text{Cl}_2][\text{H}_2\text{S}]$

Now, if we consider mechanism B. We find

$\text{Rate} = k[\text{Cl}_2][\text{HS}^-]$ ...(i)

From step 1 (fast equilibrium) of mechanism B.

$$k = \frac{[\text{H}^+][\text{HS}^-]}{\text{H}_2\text{S}}$$

$$\text{or } [\text{HS}^-] = \frac{k[\text{H}_2\text{S}]}{\text{H}^+}$$

Substituting this value in equation (i) we find

$$\text{Rate} = k[\text{Cl}_2]k\frac{[\text{H}_2\text{S}]}{\text{H}^+} = k'\frac{[\text{Cl}_2][\text{H}_2\text{S}]}{[\text{H}^+]}$$

Hence, only mechanism A is consistent with the given rate equation.

**21.** **(b)** The rate of reaction for the reaction

$$\frac{1}{2}\text{A} \longrightarrow 2\text{B}$$

can be written either as

$-2\frac{d}{dt}[\text{A}]$ with respect to 'A' or $\frac{1}{2}\frac{d}{dt}[\text{B}]$ with respect to 'B'

From the above, we have

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

$$\text{or } -\frac{d}{dt}[\text{A}] = \frac{1}{4}\frac{d}{dt}[\text{B}]$$

**22.** **(d)** Rate of appearance of HI $= \frac{1}{2}\frac{d[\text{HI}]}{dt}$

Rate of disappearance of $\text{H}_2 = \frac{-d[\text{H}_2]}{dt}$

Rate of disappearance of $\text{I}_2 = \frac{-d[\text{I}_2]}{dt}$

$$\text{hence } -\frac{d[\text{H}_2]}{dt} = -\frac{d[\text{I}_2]}{dt} = \frac{1}{2}\frac{d[\text{HI}]}{dt}$$

$$\text{or } -2\frac{d[\text{H}_2]}{dt} = -2\frac{d[\text{I}_2]}{dt} = \frac{d[\text{HI}]}{dt}$$

**23.** **(d)** $\text{Rate} = k[\text{A}]^n$

$\log[\text{Rate}] = \log k + n\log[\text{A}]$

Slope $= n$ [$n$ is order of the reaction]

$\therefore$ Correct sequence for the order of the reaction is (iv) > (ii) > (i) > (iii)

**24.** **(b)** $C_t = C_0e^{-kt};\ k = \frac{\ln 2}{t_{1/2}}$

$$(C_t)_A = (C_0)_Ae^{-k_At};\ k_A = \frac{\ln 2}{300}$$

$$(C_t)_B = (C_0)_Be^{-k_Bt};\ k_B = \frac{\ln 2}{180}$$

$$\frac{(C_t)_B}{(C_t)_A} = \frac{(C_0)_B}{(C_0)_A}\times e^{(k_B-k_A)t}$$

$$\Rightarrow 4 = e^{(k_B-k_A)t}$$

$$\Rightarrow 2\ln 2 = \left[\frac{\ln 2}{180}-\frac{\ln 2}{300}\right]t$$

$$\Rightarrow 2\ln 2 = \ln 2\left[\frac{1}{180}-\frac{1}{300}\right]t$$

$$\Rightarrow 2 = \left(\frac{120}{180\times300}\right)t \Rightarrow t = \frac{2\times180\times300}{120} = 900\text{ sec}$$

**25.** **(60)**

$$t = \frac{2.303}{k}\log\left[\frac{100}{100-x\%}\right]$$

$$t_{75\%} = \frac{2.303}{k}\log\left[\frac{100}{25}\right] = 90$$

$$t_{60\%} = \frac{2.303}{k}\log\left[\frac{100}{40}\right]$$

$$\frac{t_{75\%}}{t_{60\%}} = \frac{2\log 2}{\log 2.5} \Rightarrow \frac{90}{t_{60\%}} = \frac{2\times0.3}{0.4}$$

$$\Rightarrow t_{60\%} = \frac{90\times4}{6} = 60\text{ min.}$$

**26.** **(b)** Zero order reaction is always multi step reaction.

**27.** **(c)** Rate (R) = $\text{k}[\text{A}]^\text{a}[\text{B}]^\text{b}$

$\text{Exp I} \Rightarrow 6.0\times10^{-3} = \text{k}[0.1]^\text{a}[0.1]^\text{b}$

$\text{Exp II} \Rightarrow 24.0\times10^{-3} = \text{k}[0.1]^\text{a}[0.2]^\text{b}$

$\text{Exp III} \Rightarrow 12.0\times10^{-3} = \text{k}[0.2]^\text{a}[0.1]^\text{b}$

$\text{Exp IV} \Rightarrow 72\times10^{-3} = \text{k}[\text{X}]^\text{a}[0.2]^\text{b}$

$\text{Exp V} \Rightarrow 288\times10^{-3} = \text{k}[0.3]^\text{a}[\text{Y}]^\text{b}$

From Exp I & II,

$$\Rightarrow \frac{6.0\times10^{-3}}{24\times10^{-3}}=\frac{k[0.1]^a[0.1]^b}{k[0.1]^a[0.2]^b}$$

$$\Rightarrow \frac{1}{4}=\left(\frac{0.1}{0.2}\right)^b \Rightarrow \left(\frac{1}{2}\right)^2=\left(\frac{1}{2}\right)^b$$

$\therefore b = 2$

Similarly, from exp I & III we get

$$\frac{1}{2}=\left(\frac{1}{2}\right)^a \Rightarrow a = 1$$

From Exp. II & IV,

$$\Rightarrow \frac{24\times10^{-3}}{72\times10^{-3}}=\frac{k[0.1]^a[0.2]^b}{k[X]^a[0.2]^b}$$

$$\Rightarrow \frac{1}{3}=\left(\frac{0.1}{X}\right)^a \Rightarrow \frac{1}{3}=\left(\frac{0.1}{X}\right)^1$$

$\therefore X = 0.3$

From Exp. I & V,

$$\Rightarrow \frac{6.0\times10^{-3}}{288\times10^{-3}}=\left(\frac{0.1}{0.3}\right)^a\left(\frac{0.1}{Y}\right)^b$$

$$\Rightarrow \frac{1}{48}=\left(\frac{1}{3}\right)^1\left(\frac{0.1}{Y}\right)^2$$

$$\Rightarrow \frac{3}{48}=\left(\frac{0.1}{Y}\right)^2 \Rightarrow \frac{1}{16}=\left(\frac{0.1}{Y}\right)^2$$

$$\Rightarrow \left(\frac{1}{4}\right)^2=\left(\frac{0.1}{Y}\right)^2 \Rightarrow \frac{1}{4}=\frac{0.1}{Y}$$

$\therefore Y = 0.4$

**28.** **(23.03)** $t_{1/2} = 6.93$ years,

$a = 10^{-6}$ g

$$t_{1/2}=\frac{0.693}{K}$$

$$\Rightarrow \quad K=\frac{0.693}{t_{1/2}}=\frac{0.693}{6.93}=0.1$$

For Ist order reaction,

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

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

$$=\frac{2.303}{0.1}\log\frac{10^{-6}}{10^{-7}}$$

$$=\frac{2.303}{0.1}=23.03 \text{ years}$$

**29.** **(a)** Rate constant of decomposition of $X = 0.05$ μg/year. Unit of rate constant confirms that the decomposition of $X$ is a zero order reaction.

For zero order kinetics,

$[X] = [X]_0 - kt$

$kt = [X]_0 - [X]$

$$t=\frac{[X]_0-[X]}{k}$$

$$t=\frac{5-2.5}{0.05}$$

$$=\frac{2.5}{0.05}=50 \text{ years}$$

**30.** **(c)** For the reaction $2X \rightarrow B$, follow zeroth order

Rate equation is

$Kt = [A]_0 - [A]$

For the half-life; $t = t_{1/2}$ and $[A] = 0.1$

$K\,t_{1/2} = 0.2 - 0.1$

$$\frac{0.2-0.1}{6}=\frac{0.1}{6}\,M\,hr^{-1}$$

$\therefore$ Time required to reach from 0.5 M to 0.2 M

$Kt = [A]_0 - [A]$

$$\frac{0.1}{6}\times t=(0.5-0.2);\ t=18 \text{ hour}$$

**31.** **(a)** From experiment I and II, it is observed that order of reaction w.r.t. (B) is zero.

From experiment II and III, $x$ can be calculated as:

$$\frac{6.93\times10^{-3}}{13.86\times10^{-3}}=\left(\frac{0.1}{0.2}\right)^x\left(\frac{0.25}{0.3}\right)^y$$

$\because$ Order of reaction w.r.t. $B = 0$, so $y = 0$

$$\therefore \quad \frac{6.93\times10^{-3}}{13.86\times10^{-3}}=\left(\frac{0.1}{0.2}\right)^x$$

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

$x = 1$

Now, Rate $= K[A]^1[B]^o$

or, $6.93\times10^{-3} = K[0.1]^1[0.2]^o$

$K = 6.93\times10^{-2}$

For the reaction, $2A + B \rightarrow$ Products

$$2Kt=\ln\frac{[A]_0}{[A]}$$

$$\therefore \quad t_{1/2}=\frac{0.693}{2K}=\frac{0.693}{0.693\times10^{-2}\times2}$$

**32.** **(2)** $r = K[A]^x[B]^y$

$$\frac{r_2}{r_1}=2^x.2^y=8 \Rightarrow x+y=3$$

$$\frac{r_3}{r_1}=2x=2 \Rightarrow x=1$$

$\therefore \quad y = 2$

$t_{1/2} = 5$

**33.** **(a)** $CH_3CHO \longrightarrow CH_4 + CO$

Generally $r \propto (a-x)^m$

m = order of reaction

a – x = unreacted

$r_1 = 1$ torr $s^{-1}$, when 5% reacted

$r_2 = 0.5$ torr $s^{-1}$, when 33 % reacted

$(a-x_1) = 0.95$(unreacted)

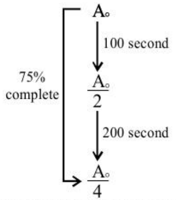
$(a-x_2) = 0.67$(unreacted)

$$\frac{r_1}{r_2} = \left[\frac{(a-x_1)}{(a-x_2)}\right]^m ; \frac{1}{0.5} = \left(\frac{0.95}{0.67}\right)^m$$

$2 = (1.41)^m \Rightarrow 2 = (\sqrt{2})^m$

$\Rightarrow m = 2$

**34.** **(d)**



First order reaction as half life is constant.

**35.** **(b)**

| | $N_2O_5$ | $\rightarrow$ | $2NO_2$ | $+ \frac{1}{2}O_2$ |
|---|---|---|---|---|
| At t = 0 | 50 | | 0 | 0 |
| At t = 50 min | $50-p_1$ | | $2p_1$ | $\frac{p_1}{2}$ |

Total pressure at 50 minutes

$$= 50 - p_1 + 2p_1 + \frac{p_1}{2} = 87.5$$

$$50 + \frac{3p_1}{2} = 87.5$$

$$\frac{3p_1}{2} = 37.5$$

$$\therefore \quad p_1 = \frac{37.5 \times 2}{3} = 25$$

At, t = 100 min $\quad 50 - p_2 \quad 2p_2 \quad \frac{p_2}{2}$

50 minutes is half life period

For 100 minutes i.e. for 2 half lives $50 - p_2 = 12.5$

$\therefore p_2 = 37.5$ mm of Hg

Total pressure at 100 minutes

$$= 50 - p_2 + 2p_2 + \frac{p_2}{2}$$

$$= 50 + \frac{3p_2}{2} = 50 + \frac{3}{2} \times 37.5$$

= 50 + 56.25

= 106.25 mm of Hg

**36.** **(c)** The half life $t_{1/2} = 10$ days

The decay constant

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10\text{days}} = 0.0693 \text{ days}^{-1}$$

The time required for one fourth conversion

$$t = \frac{2.303}{k}\log_{10}\frac{a}{a-x}$$

$$= \frac{2.303}{0.0693 \text{ day}^{-1}}\log_{10}\frac{1}{1-(1/4)} = 4.1 \text{ days}$$

**37.** **(d)** $H_2O_2(aq) \rightarrow H_2O(aq) + \frac{1}{2}O_2(g)$

For a first order reaction

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

Given a = 0.5, (a – x) = 0.125, t = 50 min

$$\therefore \ k = \frac{2.303}{50}\log\frac{0.5}{0.125}$$

$$= 2.78 \times 10^{-2} \text{ min}^{-1}$$

$r = k[H_2O_2] = 2.78 \times 10^{-2} \times 0.05 = 1.386 \times 10^{-3}$ mol min$^{-1}$

Now

$$-\frac{d[H_2O_2]}{dt} = \frac{d[H_2O]}{dt} = \frac{2d[O_2]}{dt}$$

$$\therefore \quad \frac{2d[O_2]}{dt} = -\frac{d[H_2O_2]}{dt}$$

$$\therefore \quad \frac{d[O_2]}{dt} = -\frac{1}{2} \times \frac{d[H_2O_2]}{dt}$$

$$= \frac{1.386 \times 10^{-3}}{2} = 6.93 \times 10^{-4} \text{ mol min}^{-1}$$

**38.** **(c)** Reactions of higher order (>3) are very rare due to very less chances of many molecules to undergo effective collisions.

**39.** **(a)** Rate law for first order reaction = $k[N_2O_5]$

| | $2N_2O_5(g) \longrightarrow$ | $4NO_2(g)$ | $+O_2(g)$ |
|---|---|---|---|
| t = 0 min<br>(Pressure in mm Hg) | 50 | 0 | 0 |
| t = 30 min<br>(Pressure in mm Hg) | $50-2p$ | $4p$ | $p$ |

Total pressure $50 - 2p + 4p + p = 50 + 3p$

$= 87.5$ mm Hg

$\therefore p = 12.5$ mm Hg

$\therefore p_0 = 50$ & $p$ (t = 30 min) = 25 for $N_2O_5$ reactant

$$\therefore \quad k = \frac{2.303}{30\,\text{min}} \times \log\left(\frac{50}{25}\right) = \frac{2.303}{60\,\text{min}} \times \log\left(\frac{50}{x}\right)$$

On solving $x = 12.5$ mm Hg $= 50 - 2p$

$\therefore p = 18.75$ mm Hg

$\therefore$ Total pressure $= 50 + 3p = 106.25$ mm Hg

**40.** **(c)** Given $t_{1/2} = 15$ minutes

Total time $(T) = 1$ hr = 60 min

From $T = n \times t_{1/2}$

$n = \frac{60}{15} = 4$

Now from the formula $\frac{N}{N_0} = \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^4 = \frac{1}{16}$

Where $N_0$ = initial amout

N = amount left after time $t$

Hence the amount of substance left after 1 hour will be

$\frac{1}{16}$

**41.** **(d)** For a zero order reaction

Rate constant $= k = \frac{a-x}{t}$

$2 \times 10^{-2} = \frac{a-0.5}{25}$

$a - 0.5 = 0.5$

$a = 1.0\ \text{M}$

**42.** **(c)** Given $t_{1/2} = 3$

Total time T = 12

No. of half lives $(n) = \frac{12}{3} = 4$

$\left(\frac{1}{2}\right)^n = \frac{N}{N_o}$

$\therefore \left(\frac{1}{2}\right)^4 = \frac{3}{N}$

$\frac{3}{N} = \frac{1}{16}$

$N = 48\ \text{g}$

**43.** **(b)** For a first order reaction

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{40}\log\frac{0.1}{0.025}$$

$$= \frac{2.303}{40}\log 4 = \frac{2.303 \times 0.6020}{40}$$

$$= 3.47 \times 10^{-2}$$

$R = k\,(A)^1 = 3.47 \times 10^{-2} \times 0.01$

$= 3.47 \times 10^{-4}$

**44.** **(d)** $A \longrightarrow B$

| Initial concentration | Rate of reaction |
|---|---|
| $2 \times 10^{-3}$ M | $2.40 \times 10^{-4}$ Ms$^{-1}$ |
| $1 \times 10^{-3}$ M | $0.60 \times 10^{-4}$ Ms$^{-1}$ |

rate of reaction

$r = k[A]^x$

where $x$ = order of reaction

hence

$2.40 \times 10^{-4} = k\,[2 \times 10^{-3}]^x$ ......(i)

$0.60 \times 10^{-4} = k\,[1 \times 10^{-3}]^x$ ......(ii)

On dividing eqn.(i) from eqn. (ii) we get

$4 = (2)^x$

$\therefore\ x = 2$

i.e. order of reaction = 2

**45.** **(b)** Plot given is for zero order reaction.

**46.** **(c)** For the reaction

$A \rightarrow$ Product

Given $t_{1/2} = 1$ hour

For a zero order reaction

$$t_{\text{completion}} = \frac{[A_0]}{k} = \frac{\text{Initial conc.}}{\text{Rate constant}}$$

$$\therefore t_{1/2} = \frac{[A_0]}{2k}$$

$$\text{or } k = \frac{[A_0]}{2t_{1/2}} = \frac{2}{2 \times 1} = 1\ \text{mol lit}^{-1}\,\text{hr}^{-1}$$

Further for a zero order reaction

$$k = \frac{dx}{dt} = \frac{\text{change in concentration}}{\text{time}}$$

$$1 = \frac{0.50 - 0.25}{\text{time}}$$

$\therefore$ time = 0.25 hr.

**47.** **(b)** For first order reaction,

$$k = \frac{2.303}{t}\log\frac{100}{100-99}$$

$$\frac{0.693}{6.93} = \frac{2.303}{t}\log\frac{100}{1}$$

$$\frac{0.693}{6.93} = \frac{2.303 \times 2}{t}$$

$t = 46.06$ min

**48.** **(b)** For a first order reaction, $t_{1/2} = \frac{0.693}{K}$ i.e. for a first order reaction $t_{1/2}$ does not depend up on the concentration. From the given data, we can say that order of reaction with respect to $B = 1$ because change in concentration of $B$ does not change half life.

Order of reaction with respect to $A = 1$ because rate of reaction doubles when concentration of B is doubled keeping concentration of $A$ constant.

$\therefore$ Order of reaction = 1 + 1 = 2 and units of second order reaction are L mol$^{-1}$ sec$^{-1}$.

**49.** **(a)** Suppose activity of safe working = A

Given $A_0 = 10A$

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{30}$$

$$t_{1/2} = \frac{2.303}{\lambda}\log\frac{A_0}{A} = \frac{2.303}{0.693/30}\log\frac{10A}{A}$$

$$= \frac{2.303 \times 30}{0.693} \times \log 10 = 100 \text{ days.}$$

**50.** **(b)** (i) $NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$

(ii) $NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$

Rate law equation $= k[NOBr_2]\,[NO]$

But $NOBr_2$ is intermediate and must not appear in the rate law equation.

From Ist step, $K_c = \frac{[NOBr_2]}{[NO][Br_2]}$

$\therefore [NOBr_2] = K_c [NO][Br_2]$

$\therefore$ Rate law equation $= k.K_c [NO]^2 [Br_2]$

Hence order of reaction w.r.t. NO is 2.

**51.** **(a)** Since the reaction is 2nd order w.r.t CO. Thus, rate law is given as.

$r = k[CO]^2$

Let initial concentration of CO is $a$

i.e. $[CO] = a$

$\therefore \quad r_1 = k(a)^2 = ka^2$

When concentration becomes doubled, i.e. $[CO] = 2a$

$\therefore \quad r_2 = k(2a)^2 = 4ka^2 \quad \therefore \; r_2 = 4r_1$

So, the rate of reaction becomes 4 times.

**52.** **(d)** The molecularity of a reaction is the number of reactant molecules taking part in a single step of the reaction.

**Note :** The reaction involving two different reactants can never be unimolecular.

**53.** **(c)** $t_{1/4} = \frac{2.303}{K}\log\frac{1}{3/4} = \frac{2.303}{K}\log\frac{4}{3}$

$$= \frac{2.303}{K}(\log 4 - \log 3)$$

$$= \frac{2.303}{K}(2\log 2 - \log 3)$$

$$= \frac{2.303}{K}(2 \times 0.301 - 0.4771) = \frac{0.29}{K}$$

**54.** **(d)** The velocity constant depends on temperature only. It is independent of concentration of reactants.

**55.** **(b)** $r = k[O_2][NO]^2$. When the volume is reduced to 1/2, the conc. will double

$\therefore$ New rate $= k[2O_2][2NO]^2 = 8k[O_2][NO]^2$

The new rate increases to eight times of its initial.

**56.** **(a)** $Rt = \log C_0 - \log C_t$

It is clear from the equation that if we plot a graph between $\log C_t$ and time, a straight line with a slope equal to $-\frac{k}{2.303}$ and intercept equal to $\log [C_0]$ will be obtained.

**57.** **(c)** As the concentration of reactant decreases from 0.8 to 0.4 in 15 minutes hence the $t_{1/2}$ is 15 minutes. To fall the concentration from 0.1 to 0.025 we need two half lives i.e., 30 minutes.

**58.** **(a)** $N_t = N_0\left(\frac{1}{2}\right)^n$ where n is number of half life periods.

$$n = \frac{\text{Total time}}{\text{half life}} = \frac{24}{4} = 6$$

$$\therefore N_t = 200\left(\frac{1}{2}\right)^6 = 3.125 \text{ g}$$

**59.** **(d)** $t_{1/2} = 3$ h, $T = 18$ h

$\because T = n \times t_{1/2}$

$\therefore n = \frac{18}{3} = 6$

Initial mass $(C_0) = 256$ g

$$\therefore C_n = \frac{C_0}{2^n} = \frac{256}{(2)^6} = \frac{256}{64} = 4 \text{g}$$

**60.** **(a)** For a zero order reaction.

rate $= k[A]^o$ i.e. rate $= k$

hence unit of $k = \text{M.sec}^{-1}$

For a first order reaction.

rate $= k[A]$

$\therefore \quad k = \text{M.sec}^{-1}/\text{M} = \text{sec}^{-1}$

**61.** **(a)** **Note :** Order is the sum of the power of the concentration terms in rate law expression.

Hence the order of reaction is $= 1 + 2 = 3$

**62.** **(d)** $t_{1/2} = 5$ years, T = 15 years.

Hence total number of half life periods $= \frac{15}{5} = 3$

$\therefore$ Amount left $= \frac{64}{(2)^3} = 8$ g

**63.** **(100)** The Arr henices equation is

$$k = Ae^{\frac{E_a}{RT}}$$

Assuming $A$ and $E_a$ to be independent of temperature

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln 3.555 = \frac{E_a}{8.314}\left(\frac{1}{303} - \frac{1}{313}\right)$$

$$\Rightarrow E_a = \frac{1.268 \times 8.314 \times 303 \times 313}{10}$$

$$= 99980.7 = 99.98 \text{ kJ/mol}$$

**64.** **(d)** Arrhenius equation :

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

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

$$\ln k = \ln A - \left(\frac{E_a}{R \times 10^3}\right) \times \frac{10^3}{T}$$

Slope of graph $= \frac{-E_a}{R \times 10^3} = \frac{-10}{5}$

$E_a = 2R \times 10^3 \text{ J} = 2R \text{ kJ}$

**65.** **(84297.48)**

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

$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \Rightarrow \ln 5 = \frac{E_a}{R}\left(\frac{1}{300}-\frac{1}{315}\right)$

$\Rightarrow E_a = \frac{1.6094 \times 8.314 \times 300 \times 315}{15} = 84297.48$ J/mol.

**66.** **(a)** $\text{A} \xrightarrow{700\text{K}(k_1)} \text{Product}$

$\text{A} \xrightarrow[\text{Catalyst}]{500\text{K}(k_2)} \text{Product}$

Given: $k_1 = k_2$

$\text{A}e^{-\frac{\text{E}_{a_1}}{\text{RT}_1}} = \text{A}e^{-\frac{\text{E}_{a_2}}{\text{RT}_2}}$

$\frac{\text{E}_{a_1}}{\text{T}_1} = \frac{\text{E}_{a_2}}{\text{T}_2}$

$\text{E}_{a_2} = \text{E}_{a_1} - 30$

$\Rightarrow \text{E}_{a1} = \text{E}_{a_2} + 30$

$\frac{\text{E}_{a_2}+30}{\text{T}_1} = \frac{\text{E}_{a_2}}{\text{T}_2}$

$\frac{\text{E}_{a_2}+30}{700} = \frac{\text{E}_{a_2}}{500}$

$\Rightarrow 150 = 2\text{E}_{a_2}$

$\text{E}_{a_2} = 75\text{kJ / mol}$

**67.** **(– 3.98)**

For a first order reaction, $\text{kt} = \ln\frac{[\text{A}]}{[\text{A}_0]}$

At 300 K, $\text{k}_1 \times 60 = \ln\frac{[\text{A}]}{[\text{A}_0]}$ ...(1)

At 400 K, $\text{k}_2 \times 40 = \ln\frac{[\text{A}]}{[\text{A}_0]}$ ...(2)

From equation (1) and (2),

$\frac{\text{k}_2}{\text{k}_1} = \frac{60}{40}$

$\ln\frac{\text{k}_2}{\text{k}_1} = \frac{\text{E}_a}{\text{R}}\left[\frac{1}{\text{T}_1}-\frac{1}{\text{T}_2}\right]$

$\ln\left(\frac{60}{40}\right) = \frac{\text{E}_a}{8.3} \times \frac{100}{400 \times 300}$

$\ln\left(\frac{3}{2}\right) \times 8.3 \times 1200 = \text{E}_\text{a}$

Given : $\ell\text{n}\,\frac{2}{3} = 0.4$

Then, $\ell\text{n}\,\frac{3}{2} = -0.4$

$\Rightarrow \text{E}_\text{a} = -0.4 \times 8.3 \times 1200$

$\Rightarrow \text{E}_\text{a} = -3984$ J/mol.

$\Rightarrow \text{E}_\text{a} = -3.984$ kJ/mol.

**68.** **(a)** The rate constant of a reaction is given by

$\text{k} = \text{Ae}^{-\text{E}_\text{a}/\text{RT}}$

The rate constant in tpresence of catalyst is given by

$\text{k}' = \text{Ae}^{-\text{E}'_\text{a}/\text{RT}}$

$\frac{\text{k}'}{\text{k}} = \text{e}^{-(\text{E}'_\text{a}-\text{E}_\text{a})/\text{RT}}$

$10^6 = \text{e}^{-(\text{E}'_\text{a}-\text{E}_\text{a})/\text{RT}}$

$\ell\text{n}\,10^6 = -\frac{(\text{E}'_\text{a}-\text{E}_\text{a})}{\text{RT}}$

$\text{E}'_\text{a} - \text{E}_\text{a} = -6(2.303)\text{RT}$

**69.** **(c)** Arrhenius equation, $k = \text{A}e^{-\text{Ea/RT}}$

$\log k = \log \text{A} - \frac{\text{E}_a}{2.303\ \text{RT}}$

$\text{slope} = -\frac{\text{E}_a}{2.303\ \text{R}}$

∴ More negative the slope greater will be the $\text{E}_a$.

So correct order is $\text{E}_c > \text{E}_a > \text{E}_d > \text{E}_b$

**70.** **(a)** $K = e^{-\frac{E_a}{RT}}$ or $\log K = \frac{-E_a}{2.303RT}$

So, $\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$

$\log\frac{1}{2.5\times10^{-4}} = \frac{E_a}{8.314\times2.303}\left(\frac{1}{600}-\frac{1}{800}\right)$

$3.6 = \frac{E_a}{8.314\times2.303} \times \frac{200}{600\times800}$

$E_a = 165.4$ kJ/mol H" 166 kJ/mol

**71.** **(a)** As we can see from the graph that activation enthalpy to form D from A + B is 15 – 5 = 10 kJ mol$^{-1}$, whereas, to form C from A + B is 20 – 5 = 15 kJ mol$^{-1}$. Therefore, activation enthalpy to form C is 5 kJ more than that to form D.

**72.** **(c)** From Arrhenius equation,

$$\ln K = \ln A - \frac{E_a}{RT}$$

$$\text{Slope} = \frac{-E_a}{R} = -4606\ \text{K}$$

$$\log\left(\frac{K_2}{K_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log\left(\frac{K_2}{10^{-5}}\right) = \frac{1}{2.303} \times 4606\left(\frac{1}{400} - \frac{1}{500}\right)$$

$$= \frac{4606 \times (100)}{2.303 \times 400 \times 500} = 1$$

$$\Rightarrow \log\left(\frac{K_2}{10^{-5}}\right) = 1;\ \frac{K_2}{10^{-5}} = \text{Antilog}\ (1)$$

$$\frac{K_2}{10^{-5}} = 10$$

$$\Rightarrow K_2 = 10^{-5} \times 10 = 10^{-4}\ \text{s}^{-1}$$

**73.** **(b)** From Arrhenius equation,

$$\text{k} = \text{Ae}^{-\text{E}_\text{a}/\text{RT}}$$

$$\ln\text{k} = \ln \text{A} - \frac{\text{E}_\text{a}}{\text{RT}}$$

slope $= -y$ (given)

$-y = -\text{E}_\text{a}$

$\Rightarrow \text{E}_\text{a} = y$

**74.** **(b)** From Arrhenius equation,

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

So, as $\text{E}_\text{a}$ increases, $e^{-E_a/RT}$ decreases, $k$ decreases

and as T increases, $\frac{E_a}{RT}$ decreases, $e^{-E_a/RT}$ increases.

**75.** **(d)** From Arrhenius equation,

$$\text{k} = \text{A.e}^{\frac{-\text{Ea}}{\text{RT}}}$$

$$\text{so,}\quad \text{k}_1 = \text{A}\cdot\text{e}^{-\text{E}_{\text{a}_1}/\text{RT}} \qquad .....(\text{i})$$

$$\text{k}_2 = \text{A}\cdot\text{e}^{-\text{E}_{\text{a}_2}/\text{RT}} \qquad .....(\text{ii})$$

On dividing equation (ii) by (i)

$$\Rightarrow \frac{\text{k}_2}{\text{k}_1} = \text{e}^{\frac{(\text{E}_{\text{a}_1} - \text{E}_{\text{a}_2})}{\text{RT}}}$$

$$\ln\left(\frac{\text{k}_2}{\text{k}_1}\right) = \frac{\text{E}_{\text{a}_1} - \text{E}_{\text{a}_2}}{\text{RT}} = \frac{10,000}{8.314 \times 300} = 4$$

**76.** **(b)** $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

For reaction $A$ -

Given, $\frac{k_2}{k_1} = 2,\ T_1 = 300\ \text{K},\ T_2 = 310\ \text{K}$

$$\log 2 = \frac{E_a}{2.303R}\left[\frac{1}{300} - \frac{1}{310}\right] \qquad ...(\text{i})$$

For reaction $B$ -

Given, $\frac{k_2}{k_1} = 2,\ E_a = 2E_a,\ T_1 = 300\ \text{K},\ T_2 = ?$

$$\log 2 = \frac{E_a}{2.303R}\left[\frac{1}{300} - \frac{1}{T_2}\right] \qquad ...(\text{ii})$$

From equation (i) and (ii),

$$\frac{2E_a}{2.303R}\left[\frac{1}{300} - \frac{1}{T_2}\right] = \frac{E_a}{2.303R}\left[\frac{1}{300} - \frac{1}{310}\right]$$

$$\Rightarrow 2\left[\frac{1}{300} - \frac{1}{T_2}\right] = \frac{310 - 300}{300 \times 310}$$

$$\Rightarrow T_2 = 304.92\ \text{K}$$

$T_1 = 300\ \text{K},\ T_2 = 304.92\ \text{K}$

$\Delta T = T_2 - T_1 = 4.92\ \text{K}.$

**77.** **(a)** $\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_1}, -\frac{1}{T_2}\right)$

$$\ln 4 = \frac{E_a}{8.314}\left(\frac{310 - 300}{310 \times 300}\right)$$

$$2\ln 2 = \frac{E_a}{8.314}\left(\frac{310 - 300}{310 \times 300}\right)$$

$$E_a = \frac{0.693 \times 2 \times 8.314 \times 300 \times 310}{10} = 107.2\ \text{kJ/mol}$$

**78.** **(a)** $\text{A(g)} \rightleftharpoons \text{B(g)}\ \Delta\text{H} = -40\ \text{kJ}$

If activation energy of the reaction = x

since, $\frac{\text{E}_\text{f}}{\text{E}_\text{b}} = \frac{2}{3}$, therefore, $\text{E}_\text{f} = \frac{2\text{x}}{5}$ and $\text{E}_\text{b} = \frac{3\text{x}}{5}$

$\text{E}_\text{b} - \text{E}_\text{f} = +40$

$$= \frac{3\text{x}}{5} - \frac{2\text{x}}{5} = 40;\ \frac{\text{x}}{5} = 40;\ \text{x} = 200$$

Therefore

$$\text{E}_\text{b} = \frac{3\text{x}}{5} = \frac{3 \times 200}{5} = 120\ \text{kJ mol}^{-1}$$

$$\text{E}_\text{f} = \frac{2\text{x}}{5} = \frac{2 \times 200}{5} = 80\ \text{kJ mol}^{-1}$$

**79.** **(b)** According to Arrhenius equation

$$\log\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$\log\frac{1.3\times10^{-3}}{1.3\times10^{-4}}=\frac{E_a}{2.303\times8.314}\left[\frac{1}{373}-\frac{1}{423}\right]$$

$$1=\frac{E_a}{2.303\times8.314}\left[\frac{1}{373}-\frac{1}{423}\right]$$

$E_a = 60\text{ kJ / mol}$

**80.** **(a)** Activation energy can be calculated from the equation

$$\frac{\log k_2}{\log k_1}=\frac{E_a}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

Given $\frac{k_2}{k_1}=2$; $T_2 = 310\text{ K}$; $T_1 = 300\text{ K}$

$$\therefore\quad \log 2=\frac{E_a}{2.303\times8.314}\left(\frac{1}{300}-\frac{1}{310}\right)$$

$E_a = 53598.6\text{ J/mol} = 53.6\text{ kJ/mol}.$

**81.** **(b)** $X \longrightarrow Y$; $\Delta H = -135\text{ kJ/mol}$,

$E_a = 150\text{ kJ/mol}$

For an exothermic reaction

$E_{a(\text{F.R.})} = \Delta H + E'_{a(\text{B.R.})}$

$150 = -135 + E'_{a(\text{B.R.})}$

$E'_{a(\text{B.R.})} = 285\text{ kJ/mol}$

**82.** **(c)** Activation energy can be calculated from the equation

$$\frac{\log k_2}{\log k_1}=\frac{E_a}{2.303\,R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

Given, $\frac{\log k_2}{\log k_1}=2$ $T_2 = 308$; $T_1 = 298$

$$\therefore\quad \log 2=\frac{E_a}{2.303\times8.314}\left(\frac{1}{298}-\frac{1}{308}\right)$$

$E_a = 52.9\text{ kJ mol}^{-1}$

**83.** **(c)** $k_1 = A_1 e^{-Ea_1/RT}$ .....(i)

$k_2 = A_2 e^{-Ea_2/RT}$ .....(ii)

On dividing eqn. (i) by eqn. (ii)

$$\frac{k_1}{k_2}=\frac{A_1}{A_2}(E_{a_2}-E_{a_1})/RT \quad .....(iii)$$

Given $Ea_2 = 2Ea_1$

On substituting this value in eqn. (iii)

$k_1 = k_2 A \times e^{Ea_1/RT}$

**84.** **(a)** $\Delta H_R = E_f - E_b = 180 - 200 = -20\text{ kJ/mol}$

The nearest correct answer given in choices may be obtained by neglecting sign.

**85.** **(c)** In Arrhenius equation, $k = A\,e^{-Ea/RT}$, $E_a$ is the energy of activation, which is required by the colliding molecules to react resulting in the formation of products.

**86.** **(d)** The graph shows that reaction is exothermic.

$$\log k=\frac{-\Delta H}{RT}+1$$

For exothermic reaction $\Delta H < 0$

$\therefore$ log k Vs $\frac{1}{T}$ would be negative straight line with positive slope.

**87.** **(d)** Enthalpy of reaction $(\Delta H) = E_f - E_b$

For an endothermic reaction, $\Delta H$ = +ve hence for $\Delta H$ to be negative

$E_b < E_f$

**88.** **(b)** In equation $k = Ae^{-E_a/RT}$;

$A$ = Frequency factor

$k$ = velocity constant, $R$ = gas constant and $E_a$ = energy of activation