SOLVED EXAMPLES

Ex.1 For a reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$. If the reactions are of 1st order then $\frac{d[B]}{dt}$ is equal to

(A) $-k_2[B]$ **(B)** $+k[A]$ **(C)** $k_1[A]-k_2[B]$ **(D)** $k_1[A]+k_2[B]$

Sol. Rate of increase in $[B] = k_1[A]$

Similarly rate of decrease in $[B] = k_2[B]$

Thus, $$\frac{d[B]}{dt} = k_1[A]-k_2[B]$$

Hence the answer is [C]

Ex.2 The half life period $t_{1/2}$ is independent of initial concentration of reactant when the order of reaction is

(A) Negative **(B)** 0 **(C)** 1 **(D)** Fractional

Sol. $t_{½}$ of a reaction of an order n is related to initial concentration by the expression

$$t_{½} \propto \frac{1}{C_0^{\,n-1}} \qquad \text{(Here, } n = \text{order of reaction)}$$

for n = 1, $t_{½}$ is independent of concentration term. Hence the answer is [C].

Ex.3 For a first order reaction, $A \longrightarrow B$, the rate of reaction at $[A] = 0.1$ M is 1.0×10^{-1} mol L^{-1} min^{-1}. The half-life period for the reaction is

(A) 42 sec **(B)** 21 sec **(C)** 20 sec **(D)** 28 sec

Sol. $r = k[A]$

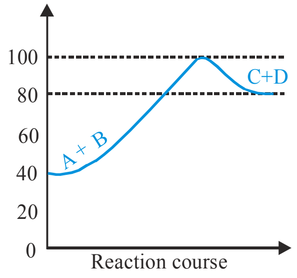
$$k = \frac{r}{[A]} = \frac{10^{-1}}{0.1} = 1$$

$$t_{½} = \frac{0.693}{k} = \frac{0.693}{1} = 0.693 \text{ min} = 0.693 \times 60 \approx 42 \text{ sec}$$

Hence, **(A)** is the correct answer.

Ex.4 Find the activation energy [kJ/mol] for the reaction, $A(g) + B(g) \rightarrow C(g) + D(g)$.

From the plot given below :



(A) 20 **(B)** 60 **(C)** 40 **(D)** 80

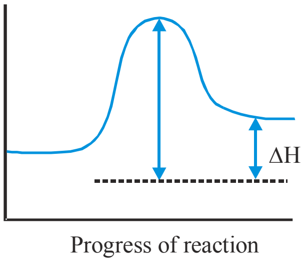
Sol. $E_a = 100 - 40 = 60$ kJ mol^{-1}

Hence the answer is [B].

Ex.5 In an endothermic reaction, ΔH represents the enthalpy of reaction in kJ/mol, the minimum value for the energy of activation will be.

(A) less than ΔH **(B)** zero **(C)** more than ΔH **(D)** equal to ΔH

Sol.



E_a> HΔ

Hence, **(C)** is the correct answer.

Ex.6 Consider the following first order competing reactions

$A \longrightarrow B,\ C \longrightarrow D,$

the ratio of $\frac{k_1}{k_2}$, if only 25% of A have been reacted whereas 50% of C has been reacted, calculate the ratio of $\frac{k_1}{k_2}$

(A) 0.415 **(B)** 0.246 **(C)** 2.06 **(D)** 0.06

Sol. $k_1 = \frac{2.303}{t_1} \log \frac{100}{75}$ for 25% **(A)** reacted

$k_2 = \frac{2.303}{t_2} \log \frac{100}{50}$ for 50% **(C)** reacted

$\therefore \frac{k_1}{k_2} = \frac{t_2}{t_1} \times \frac{0.1249}{0.3010}$

Since $t_2 = t_1$

$\therefore \frac{k_1}{k_2} = \frac{0.1249}{0.3010} = 0.415$

Hence, **(A)** is the correct answer.

Ex.7 A catalyst lowers the activation energy of a reaction from 30 kJ mol^{-1} to 15 kJ mol^{-1}. The temperature at which the uncatalysed reaction will have the same rate as that of the catalysed at 27°C is

(A) –123°C **(B)** 327°C **(C)** –327°C **(D)** +23°C

Sol. $\frac{E'_a}{T_1} = \frac{E_a}{T_2} \Rightarrow \frac{15}{300} = \frac{20}{T_2}$

$\therefore T_2 = 600\ K = 327°C$

Hence, **(B)** is the correct answer.

Ex.8 $SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$, is the first order gas reaction with $k = 2.2 \times 10^{-5}\ sec^{-1}$ at 270°C. The percentage of SO_2Cl_2 decomposed on heating for 50 minutes is

(A) 1.118 **(B)** 0.1118 **(C)** 18.11 **(D)** 6.39

Sol. $k = \frac{2.303}{t} \log \frac{a}{(a-x)} \Rightarrow \log \frac{a}{(a-x)} = \frac{kt}{2.303}$

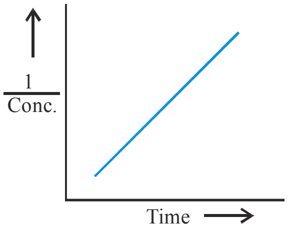
$\Rightarrow \log \frac{a}{a-x} = \frac{2.2 \times 10^{-5} \times 50 \times 60}{2.303} = 0.0286$

Hence, $\frac{a}{(a-x)} = 1.068 \Rightarrow \frac{a-x}{a} = 0.936$

$\Rightarrow 1 - \frac{x}{a} = 0.936 \Rightarrow \frac{x}{a} = 0.068 = 6.39\ \%$

Hence, **(D)** is the correct answer.

Ex.9 In the decomposition of N_2O_5, the plot between the reciprocal of concentration of the reactant and the time was found to be linear as shown in figure. Determine the order of reaction.



Sol. The reaction is of second order, because for II order,

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)} \quad \text{or} \quad t = \frac{1}{k} \cdot \frac{x}{a(a-x)}$$

or time (t) vs. $\frac{1}{\text{conc.}}$ graph is linear

Ex.10 The activation energies of two reactions are E_a and E_a' with $E_a > E_a'$. If the temperature of the reacting systems is increased from T_1 and T_2 predict which alternative is correct. k_1' and k_2' are rate constants at higher temperature. Assume A being the same for both the reactions.

(A) $\frac{k_1'}{k_1} = \frac{k_2'}{k_2}$ **(B)** $k_1 < k_2$ and $k_1' < k_2'$ **(C)** $k_1 > k_2$ and $k_1' < k_2'$ **(D)** $\frac{k_1'}{k_1} < \frac{2k_2'}{k_2}$

Sol. More is energy of activation lesser is rate constant.

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

$k_1 < k_2$ and $k_1' < k_2'$

Hence, **(B)** is the correct answer.

Ex.11 Fill in the blank :

$${}^{235}_{92}U + {}^{1}_{0}n \longrightarrow ? + {}^{92}_{36}Kr + 3\,{}^{1}_{0}n$$

(A) ${}^{141}_{56}Ba$ **(B)** ${}^{139}_{56}Ba$ **(C)** ${}^{139}_{54}Ba$ **(D)** ${}^{141}_{54}Ba$

Sol. $92 + 0 = Z + 36 + 0 \Rightarrow Z = 56$

$235 + 1 = A + 92 + 3$

$\therefore A = 141$

Missing nucleide is ${}^{141}_{56}Ba$

Hence, **(A)** is the correct answer.

Ex.12 In the nuclear reaction, ${}^{234}_{92}U \longrightarrow {}^{222}_{86}Rn$, the number of α and β-particles lost would be :

(A) 1, 3 **(B)** 2, 3 **(C)** 3, 0 **(D)** 0, 3

Sol. ${}^{234}_{92}U \longrightarrow {}^{222}_{86}Rn + x\,{}^{4}_{2}\alpha + y\,{}^{0}_{-1}\beta$

$234 = 222 + 4x \Rightarrow x = 3$

$92 = 86 + 2x - y$ or $y = 0$

Hence, **(C)** is the correct answer.

Ex.13 The inversion of cane sugar proceeds with half-life of 250 minutes at pH = 4 for any concentration of sugar. However, if pH = 5, the half-life changes to 25 minutes. The rate law expression for the sugar inversion can be written as

(A) $r = k\,[\text{sugar}]^2\,[H]^6$ **(B)** $r = k\,[\text{sugar}]^1\,[H^+]^0$ **(C)** $r = k\,[\text{sugar}]^1\,[H^+]^1$ **(D)** $r = k\,[\text{sugar}]^0\,[H^+]^1$

Sol. At pH = 4, the half-life is 250 minutes for all concentrations of sugar that is $t_{1/2} \propto [\text{sugar}]^0$.

The reaction is first order with respect to sugar.

Let, rate = $k[\text{sugar}]^1\,[H^+]^x$

For $[H^+]$ $t_{1/2} \propto [H^+]^{1-x}$

$\Rightarrow 250 \propto (10^{-4})^{(1-x)}$ ......(1)

At pH = 5, the half life is 25 minutes so $50 \propto (10^{-5})^{1-x}$ ......(2)

$\therefore\ \ 10 = 10^{(1-x)} \Rightarrow (1-x) = 1 \ \therefore\ x = 0$

Therefore, rate = $k\,[\text{sugar}]^1\,[H^+]^0$

Hence, **(B)** is the correct answer.

Ex.14 In a hypothetical reaction x → y, the activation energies for the forward and backward reactions are 13 and 8 kJ/mol respectively. The potential energy of x is 10 kJ/mol, then

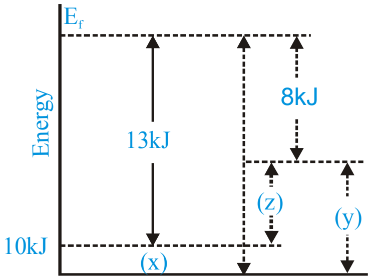
(A) the threshold energy of the reaction is 23 kJ/mol

(B) potential energy of y is 15 kJ

(C) heat of reaction is 5 kJ

(D) the reaction is endothermic

Sol.



Hence, **(A)**, **(B)**, **(C)** and **(D)** are correct answer.

Ex.15 The reactions, $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$, is

(A) biomolecular reaction **(B)** second order reaction **(C)** third order reaction **(D)** none of the above

Sol. **(A)** and **(B)**

Ex.16 The rate constant of a reaction is given by $k = 3.2 \times 10^{10}\, e^{-\frac{2700}{2.303R}}$

It means that

(A) log k vs $^1/_T$ will be straight line with slope $= \dfrac{-2700}{2.303R}$

(B) log k vs $^1/_T$ will be a straight line with intercept on log k axis = $\log 3.2 \times 10^{10}$

(C) the number of effective collisions are $3.2 \times 10^{10}\ \text{cm}^{-3}\ \text{sec}^{-1}$

(D) half-life of the reaction increases with increase in temperature

Sol. **(A)** and **(B)** are correct, **(C)** is wrong because frequency factor gives total number of collisions and not the effective collision $\text{cm}^{-3}\ \text{sec}^{-1}$, **(D)** is wrong because half-life of the reaction decreases with increase in temperature (as reaction becomes faster).

Hence, **(A)** and **(B)** are correct answer.

Ex.17 Two substances x and y are present such that $[x_0] = 2[y_0]$ and half-life of x is 6 minutes and that of y is 18 minutes. If they start decaying at the same time following first order kinetics how much time later will the concentration of both of them would be same?

(A) 15 minutes **(B)** 9 minutes **(C)** 5 minutes **(D)** 12 minutes

Sol. Amount of x left in n_1 half-lives $= \left(\frac{1}{2}\right)^{n_1} [x_0]$

Amount of y left in n_2 half-lives $= \left(\frac{1}{2}\right)^{n_2} [y_0]$

At the end, $\frac{[x_0]}{2^{n_1}} = \frac{[x_0]}{2^{n_2}}$

$\Rightarrow \frac{2}{2^{n_1}} = \frac{1}{2^{n_2}}$, $\{[x_0] = 2[y_0]\}$

$\therefore \frac{2^n}{2^n} = 2 \Rightarrow 2^{n_1 - n_2} = (2)^1$

$\therefore n_1 - n_2 = 1$

$n_2 = (n_1 - 1)$ ...(1)

Also, $t = n_1 \times t_{1/2(x)}$; $t = n_2 \times t_{1/2(y)}$

(Let, concentration of both become equal after time t)

$\therefore \frac{n_1 \times t_{1/2(x)}}{n_2 \times t_{1/2(y)}} = 1 \Rightarrow \frac{n_1 \times 6}{n_2 \times 18} = 1 \Rightarrow \frac{n_1}{n_2} = 3$ ...(2)

From Eqs. (1) and (2), we get

$n_2 = 0.5$, $n' = x^{1.5}$

$t = 0.5 \times 18 = 9$ minutes

Hence **(B)** is the correct answer.

Ex.18 Consider a gaseous reaction, the rate of which is given by k[x] [y], the volume of the reaction vessel containing these gases is suddenly increased to 3rd of the initial volume. The rate of reaction relative to the original rate would be

(A) 9/1 **(B)** 1/9 **(C)** 6/1 **(D)** 1/6

Sol. By increasing volume to 3rd the concentration will become $\frac{1}{3}$ times, hence rate $\frac{1}{9}$ times.

Hence, **(B)** is the correct answer.

Ex.19 The rate of reaction is doubled for every 10° rise in temperature. The increase in reaction rate as a result of temperature rise from 10° to 100° is.

(A) 112 **(B)** 512 **(C)** 400 **(D)** 614

Sol. Increase in steps of 10° has been made 9 times. Hence, rate of reaction should increase 2^9 times i.e., 512 times.

Hence, **(B)** is the correct answer.

Ex20. Van't Hoff equation is

(A) $(d/dT) \ln K = (-\Delta E/RT^2)$ **(B)** $(d/dT) \ln K = + (E/RT^2)$

(C) $(d/dT) \ln K = -(\Delta E/RT)$ **(D)** $K = Ae^{-E_a/RT}$

Sol. **(B)** and **(D)**.

Ex.21 The rate of chemical reaction (except zero order)

(A) decreases from moment to moment **(B)** remains constant throughout

(C) depends upon the order of reaction **(D)** none of the above

Sol. **(A)** and **(C)**

Ex.22 The rate constant for the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$, is $4.0 \times 10^{-5}\ \text{sec}^{-1}$. If the rate of reaction is $4.80 \times 10^{-5}\ \text{molL}^{-1}\ \text{sec}^{-1}$, the concentration of N_2O_5 (molL^{-1}) is :

(A) 1.4 **(B)** 1.2 **(C)** 0.04 **(D)** 0.8

Sol. $r = k\,[N_2O_5]$

$$\therefore [N_2O_5] = \frac{r}{k} = \frac{4.80 \times 10^{-5}}{4.0 \times 10^{-5}} = 1.2\ \text{molL}^{-1}$$

Hence, **(B)** is the correct answer.

Ex.23 The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are 2×10^{-4}, s^{-1}, 114.4 kJ mol^{-1} and $6.0 \times 10^{14}\ s^{-1}$ respectively, the value of the rate constant at $T \to \infty$ is.

(A) $2.0 \times 10^{18}\ s^{-1}$ **(B)** $3.6 \times 10^{30}\ s^{-1}$ **(C)** ∞ **(D)** $6.0 \times 10^{14}\ s^{-1}$

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

When $T \to \infty$

$k \to A$

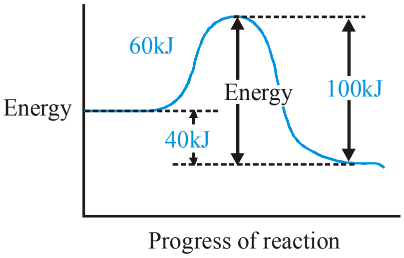
$A = 6 \times 10^{14}\ s^{-1}$

Hence, **(D)** is the correct answer.

Ex.24 If a reaction $A + B \to C$, is exothermic to the extent of 40 kJ/mol and the forward reaction has an activation energy 60 kJ/mol, the activation energy for the reverse reaction is

(A) 30 kJ/mol **(B)** 40 kJ/mol **(C)** 70 kJ/mol **(D)** 100 kJ/mol

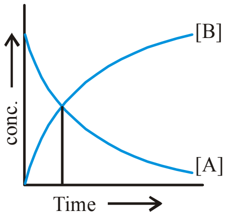
Sol.



Activation energy for backward reaction = 100 kJ

Hence, **(D)** is the correct answer.

Ex.25 The accompanying figure depicts the change in concentration of species A and B for the reaction $A \to B$, as a function of time the point of inter section of the two curves represents.



(A) $t_{1/2}$ **(B)** $t_{3/4}$ **(C)** $t_{2/3}$ **(D)** data insufficient to predict

Sol. The intersection point indicates that half life of the reactant A is converted into B.

Hence the answer is [A].

Ex.26 For the reaction, $A + B \longrightarrow C$, the following data were obtained. In the first experiment, when the initial concentrations of both A and B are 0.1 M, the observed initial rate of formation of C is 1×10^{-4} mol litre^{-1} minute^{-1}. In second experiment when the initial concentrations of (A) and (B) are 0.1 M and 0.3 M, the initial rate is 3.0×10^{-4} mollitre^{-1} minute^{-1}. In the third experiment, when the initial concentrations of both A and B are 0.3 M, the initial rate is 2.7×10^{-3} mol litre^{-1} minute^{-1}.

(A) Write rate law for this reaction.

(B) Calculate the value of specific rate constant for this reaction.

Sol. Let, Rate = $k[A]^x [B]^y$

$r_1 = 1 \times 10^{-4} = k(0.1)^x (0.1)^y$ ...(1)

$r_2 = 3 \times 10^{-4} = k(0.1)^x (0.3)^y$ ...(2)

$r_3 = 2.7 \times 10^{-3} = k(0.3)^x (0.3)^y$ ...(3)

By Eqs. (1) and (2), $\frac{r_1}{r_2} = \frac{1\times10^{-4}}{3\times10^{-4}} = \left(\frac{1}{3}\right)^y \quad \therefore y = 1$

By Eqs. (2) and (3),

$$\frac{r_2}{r_3} = \frac{3\times10^{-4}}{27\times10^{-4}} = \left(\frac{1}{3}\right)^x \quad \therefore x = 2$$

$\therefore$ Rate = $k[A]^2 [B]^1$

Also, $1 \times 10^{-4} = k\,(0.1)^2 (0.1)^1$

$\therefore k = 10^{-1} = 0.1\ L^2 mol^{-1} min^{-1}$

Ex.27 The chemical reaction, $2O_3 \rightarrow 3O_2$ proceeds as follows :

$O_3 \rightleftharpoons O_2 + O$ .... (Fast)

$O + O_3 \rightarrow 2O_2$ .... (Slow)

The rate law expression should be

(A) $r = k[O_3]^2$ **(B)** $r = k[O_3]^2 [O_2]^{-1}$ **(C)** $r = k[O_3][O_2]$ **(D)** Unpredictable

Sol. Rate of reaction (r) = k [O] [O_3]

The rate of formation if [O] depends on first step

$\therefore$ Since $K_{eq} = \frac{[O_2][O]}{[O_3]}$

$\therefore$ $[O] = K_{eq} \frac{[O_3]}{[O_2]}$

or $r = kk_{eq} \frac{[O_3][O_3]}{[O_2]} = k \,.\, [O_3]^2 [O_2]^{-1}$

Ex.28 Disintegration of radium takes place at an average rate of 1.42×10^{13} α-particles per minute. Each α-particle takes up 2 electrons from the air and becomes a neutral helium atom. After 420 days, the He gas collected was 0.5×10^{-3} L measured at 300 K and 750 mm of mercury pressure. From the above data, calculate Avogadro's number.

Sol. No. of α-particles (or) He formed = 1.42×10^{13} min^{-1}

$\therefore$ No. of He particles formed in 420 days $= 1.42 \times 10^{13} \times 420 \times 1440 = 8.588 \times 10^{18}$

Also at 27°C and 750 mm ; He = 0.5 mL

Using PV = nRT

$$\frac{750}{760} \times \frac{0.5}{1000} = n \times 0.0821 \times 300 \quad \Rightarrow \quad n = 2.0 \times 10^{-5} \text{ moles}$$

2.0×10^{-5} moles of He = 8.588×10^{18} particles of He

$$\Rightarrow 1 \text{ mole of He} = \frac{8.588\times10^{18}}{2.0\times10^{-5}} \quad \Rightarrow \quad 4.294 \times 10^{22} \text{ particles}$$

$\therefore$ Avogadro's number = 4.294×10^{22} particles/mol

Ex.29 For the non-equilibrium process, A + B → Products, the rate is first order with respect to A and second order with respect to B. If 1.0 mol each of A and B are introduced into a 1 litre vessel, and the initial rate were 1.0×10^{-2} mol/litre-sec, calculate the rate when half of the reactants have been used.

Sol. $\text{Rate}_1 = k\,[A]\,[B]^2$

∴ $10^{-2} = k\,[1]\,[1]^2$

or $k = 10^{-2}\ \text{litre}^2\ \text{mol}^{-2}\ \text{sec}^{-1}$

Now $\text{Rate}_{II} = 10^{-2} \times 0.5 \times (0.5)^2$

or New rate $= 1.2 \times 10^{-3}$ mol/litre-sec

Ex.30 The energy of activation for a certain reaction is 100 kJ/mol. Presence of catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 25°C, other things being equal ?

Sol. $k = A\,e^{\frac{-E_a}{RT}},\ k_1 = A\,e^{\frac{-100}{RT}},\ k_2 = A\,e^{\frac{-25}{RT}}$

$$\therefore\ \frac{k_1}{k_2} = \frac{e^{\frac{-100}{RT}}}{e^{\frac{-25}{RT}}} = e^{\frac{-75}{RT}}$$

$$\log_e \frac{k_2}{k_1} = \log_e e^{\frac{75}{RT}}$$

$$\therefore\ \log \frac{k_2}{k_1} = \frac{75}{RT} = \frac{75 \times 10^3}{8.314 \times 298}$$

$$\frac{k_2}{k_1} = 1.4020 \times 10^{13},\ \text{As } r = k(\text{conc})^n$$

$$\frac{r_2}{r_1} = \frac{k_2}{k_1} = 1.4020 \times 10^{13}$$

Ex.31 Show that for a first order reaction, time required for 99% completion is twice for the time required for the completion of 90% of the reaction.

Sol.

$$t_{99\%} = \frac{2.303}{k}\log_{10}\frac{100}{100-99} \quad .....(1)$$

$(\because a = 100;\ x = 99)$

$$t_{90\%} = \frac{2.303}{k}\log_{10}\frac{100}{100-90} \quad ....(2)$$

$(\because a = 100;\ x = 90)$

∴ By Eqs. (1) and (2),

$$\frac{t_{99\%}}{t_{90\%}} = \frac{\log_{10}100}{\log_{10}10} = 2$$

∴ $t_{99\%} = 2 \times t_{90\%}$

Ex.32 The optical rotations of sucrose in 0.5 N HCl at 35°C at various time intervals are given below. Show that the reaction is of first order :

Time (minutes)	0	10	20	30	40	∞
Rotation (degrees)	+32.4	+28.8	+25.5	+22.4	+19.6	–11.1

Sol. The inversion of sucrose will be first order reaction if the above data confirm to the equation,

$k_1 = \dfrac{2.303}{t} \log \dfrac{r_0 - r_\infty}{r_t - r_\infty}$ where r_0, r_t and r_∞ represent optical rotations initially, at the commencement of the reaction after time t and at the completion of the reaction respectively.

In this case, $a_0 = r_0 - r_\infty = +32.4 - (-11.1) = +43.5$

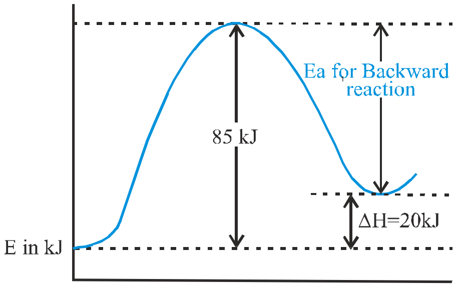
The value of k at different times is calculated as follows :

Time	**r_t**	**$r_t - r_\infty$**	**k**
10 min	+28.8	39.9	$\dfrac{2.303}{10} \log \dfrac{43.5}{39.9} = 0.008625\ \text{min}^{-1}$
20 min	+25.5	36.6	$\dfrac{2.303}{20} \log \dfrac{43.5}{36.6} = 0.008625\ \text{min}^{-1}$
30 min	+22.4	33.5	$\dfrac{2.303}{30} \log \dfrac{43.5}{33.5} = 0.008694\ \text{min}^{-1}$
40 min	+19.6	30.7	$\dfrac{2.303}{40} \log \dfrac{43.5}{30.7} = 0.008717\ \text{min}^{-1}$

The constancy of k_1 indicates that the inversion of sucrose is a **first order** reaction.

Ex.33 For $A + B \rightarrow C + D$; $\Delta H = 20\ \text{kJ mol}^{-1}$; the activation energy of the forward reaction is 85 kJ/mol. Calculate activation energy of the reverse reaction.

Sol.



ΔH of forward reaction = $20\ \text{kJ mol}^{-1}$.

Energy of activation for forward reaction (E_a) = $85\ \text{kJ mol}^{-1}$

∴ Energy of activation for backward reaction $= E_a - \Delta H$

$= 85 - 20$

$= 65\ \text{kJ mol}^{-1}$

Ex.34 The reaction given below is observed to be first order with rate constant 5.26×10^{-3} sec^{-1}. Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise 0.145 atm and also find the total pressure after 100 sec.

$2A(g) \rightarrow 4B(g) + C(g)$

Sol.

	$2A(g)$	$\rightarrow$	$4B(g)$	+	$C(g)$
Initial	P_0		0		0
At time t	$P_0 - P'$		$2P'$		$P'/2$

$$P_{\text{total}} = P_0 - P' + 2P' + P'/2 = P_0 + \frac{3P'}{2}$$

$$P' = \frac{2}{3}(0.145 - 0.1) = 0.03 \text{ atm}$$

$$k = \frac{2.303}{t} \log \frac{P_0}{P_0 - P'}$$

$$t = \frac{2.303}{5.26 \times 10^{-3}} \log\left(\frac{0.1}{0.07}\right) = 67.82 \text{ sec}$$

$$\text{Also, } k = \frac{2.303}{t} \log\left(\frac{0.1}{P_0 - P'}\right)$$

$$5.26 \times 10^{-3} = \frac{2.303}{100} \log\left(\frac{0.1}{0.1 - P'}\right)$$

$0.1 - P' = .059$

$P' = 0.041$

$$P_{\text{total}} = 0.1 + \frac{3}{2}(0.041) \approx 0.162 \text{ atm.}$$

Ex.35 The time required for 10% completion of first order reaction at 298 K is equal to that required for its 76% completion at 308 K. If the pre-exponential factor for the reaction is 3.56×10^{9} s^{-1}, calculate its energy of activation.

Sol. For first order reactions,

$$t = \frac{2.303}{k} \log \frac{N_0}{N_1}$$

$$\text{At 298 K ; } t = \frac{2.303}{k_{298}} \log \frac{100}{90}$$

$$\text{At 309 k ; } t = \frac{2.303}{k_{308}} \log \frac{100}{76}$$

Since time is same

$$\frac{2.303}{k_{298}} \log \frac{100}{90} = \frac{2.303}{k_{308}} \log \frac{100}{76}$$

$$\text{or } \frac{0.0458}{k_{298}} = \frac{0.1191}{k_{308}}$$

or $\frac{k_{308}}{k_{298}} = \frac{0.1191}{0.0458} = 2.60$

According to Arrhenius equation,

$$2.303 \log \frac{k_{308}}{k_{298}} = \frac{E_a}{8.314}\left[\frac{1}{298} - \frac{1}{308}\right]$$

$$\text{or } 2.303 \log 2.60 = \frac{E_a}{8.314}\left[\frac{10}{298 \times 308}\right]$$

$E_a = 72.93$ kJ

Ex.36 In a reaction, the decrease in reactant's concentration is 20% in 20 minute and 40% in 40 minute. Calculate order of reaction and rate constant.

Sol. For zero order reaction : $t = \frac{x}{k}$ or $k = \frac{x}{t}$

If $t = t_{20\%} = 20$ minute, $x = 20$

Then $k = \frac{20}{20} = 1$ mol litre^{-1} minute^{-1}

If $t = t_{40\%} = 40$ minute, $x = 40$

Then $k = \frac{40}{40} = 1$ mol litre^{-1} minute^{-1} ; Thus, reaction is of zero order.

Ex.37 The rate constant for the decomposition of a certain substance is 2.80×10^{-3} m^{-1} s^{-1} at 30°C and 1.38×10^{-1} m^{-1}s^{-1} at 50°C. Evaluate the Arrhenius parameters of the reaction. ($R = 8.314 \times 10^{-3}$ kJmol^{-1} K^{-1})

Sol. Energy of activation (E_a) and pre-exponential factor A are Arrhenius parameters.

$k_1 = 2.80 \times 10^{-3}$ m^{-1} s^{-1} at 303 K

$k_2 = 1.38 \times 10^{-2}$ m^{-1} s^{-1} at 323 K

$$\text{As } \log_{10}\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 \times T_2}\right]$$

$$\therefore E_a = \frac{2.303 R\, T_1 T_2}{(T_2 - T_1)} \log_{10}\frac{k_2}{k_1}$$

$$E_a = \frac{2.303 \times 8.314 \times 10^{-3} \times 303 \times 323}{(323 - 303)} \log_{10}\left(\frac{1.38 \times 10^{-2}}{2.80 \times 10^{-3}}\right) = 64.91 \text{ kJ mol}^{-1}$$

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

or $A = k\, e^{Ea/RT} = 2.80 \times 10^{-3}\, e^{64.91\ 10^3/8.314\ \ 303} = 4.34 \times 10^8$ s^{-1}

Ex.38 For a reaction 3A → Products, it is found that the rate of reaction doubles if concentration of A is increased four times, calculate order of reaction.

Sol. Rate = k [Reactant]^n if [Reactant] = a; rate = r_1

$r_1 = k[a]^n$ if [Reactant] = 4a; rate = $2r_1$

$2r_1 = k[4a]^n$

$$\therefore \frac{1}{2} = \left[\frac{1}{4}\right]^n \qquad \therefore n = \frac{1}{2}$$

Ex.39 The amount of ${}^{14}_{6}C$ isotope in a piece of wood is found to be one fifth of that present in a fresh piece of wood. Calculate the age of the piece of wood (half-life of ${}^{14}_{6}C$ = 5577 year).

Sol. $t = \frac{2.303}{\lambda} \log \frac{N_0}{N}$

$$\Rightarrow t = \frac{2.303 \times t_{1/2}}{0.693} \log \frac{N_0}{N}$$

$$t = \frac{2.303 \times 5577}{0.693} \log \frac{N_0}{N_0 / 5} \Rightarrow \frac{2.303 \times 5577}{0.693} \times 0.6989$$

$= 12.953$ years

Ex.40 In a reaction, $2A \rightarrow$ Products, the concentration of A decreases from 0.5 mol litre^{-1} to 0.4 mol litre^{-1} in 10 minute. Calculate rate during this interval.

Sol. Rate of reaction $= \frac{1}{2} \times$ rate of disappearance of A

$$= \frac{1}{2}\left(-\frac{d[A]}{dt}\right) = \frac{1}{2}\left[\frac{0.5 - 0.4}{10}\right] = 0.005 \text{ mol litre}^{-1} \text{ minute}^{-1}$$

Ex.41 Calculate the order of reaction for which rate becomes half if volume of container having same amount of reactant is doubled. (Assume gaseous phase reaction)

Sol. $\text{Rate} = k[a]^n$

For Case I : Let a mole of reactant in vessel of V litre

$$\therefore \quad r_1 = k\left[\frac{a}{V}\right]^n \quad \text{......(1)}$$

For Case II : The volume is doubled, rate becomes half

$$\therefore \quad \frac{r_1}{2} = k\left[\frac{a}{2V}\right]^n \quad \text{.....(2)}$$

$\therefore$ By Eqs. (1) and (2),

or $2 = (2)^n$

$\therefore$ $n = 1$

Ex.42 Rate constant of a first order reaction, $A \longrightarrow B$, is 0.0693 min^{-1}. Calculate rate (i) at start and (ii) after 20 minutes. Initial concentration of A is 1.0 M.

Sol. $k_1 = 0.0693 \text{ min}^{-1}$

$$t_{\frac{1}{2}} = \frac{0.693}{k_1} = \frac{0.693}{0.0693} = 10 \text{ min}$$

Since $C = C_0\left(\frac{1}{2}\right)^n \qquad \left(n = \frac{t}{t_{1/2}}\right)$

$n = \frac{20}{10} = 2 \qquad C_0 = 1$ M

$$\therefore C = 1 \times \left(\frac{1}{2}\right)^2 = \frac{1}{4} M$$

Rate of the reaction at the start of the reaction $= k_1 \times C_0$

$= 10 \times 0.0693 \times 1 = 0.693 \text{ M min}^{-1}$

Rate after 30 min. $= k_1 C = 0.0693 \times \frac{1}{4} = 17.33 \times 10^{-3} \text{ M min}^{-1}$

Ex.43 Two reactants A and B separately show two chemical reactions. Both reactions are made with same initial concentration of each reactant. Reactant A follows first order kinetics whereas reactant B follows second order kinetics. If both have same half-lives, compare their rates at the start of reactions.

Sol. For A : rate = k_A [A] ...(i)

$$t_{½(A)} = \frac{0.693}{k_A} \quad ...(ii)$$

For B : rate = $k_B[B]^2$ ...(iii)

$$t_{½(B)} = \frac{1}{k_B \times a} \quad ...(iv)$$

Initial rate of A $r_A = k_A \times a$

Initial rate of B $r_B = k_B \times a^2$

$$\therefore \frac{r_A}{r_B} = \frac{k_A \times a}{k_B \times a^2} = \frac{k_A}{k_B \times a} \quad ...(v)$$

If $t_{½(A)} = t_{½(B)}$, then $\frac{0.693}{k_A} = \frac{1}{k_B \times a}$

$$\therefore \frac{k_A}{k_B} = 0.693 \times a$$

$$\therefore \frac{r_A}{r_B} = \frac{0.693 \times a}{a} = 0.693$$

Ex.44 A first order reaction takes 69.3 minute for 50% completion. How much time will be needed for 80% completion ?

Sol. $\because$ $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.3}$ minute^{-1} $(\because t_{½} = 69.3 \text{ min})$

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

Now $k = \frac{2.303}{t} \log_{10} \frac{100}{20}$; [if a = 100, x = 80 and a – x = 20]

$\frac{0.693}{69.3} = \frac{2.303}{t} \log_{10} 5$; t = 160.97 minute

Ex.45 The half-life of the nucleide ^{220}Rn is 693 s. What mass of radon is equivalent to a 1 millicurie (mci) ?

Sol. $t_{½} = \frac{0.693}{\lambda} \Rightarrow \lambda = \frac{0.693}{t_{½}} = \frac{0.693}{693} \times 10^{-3} s^{-1}$

$1 \text{ mci} = 3.7 \times 10^7$ disintegration $s^{-1} = -\frac{dN}{dt} \Rightarrow -\frac{dN}{dt} = \lambda N$

$$N = -\frac{dN/dt}{\lambda} = \frac{3.7 \times 10^7 s^{-1}}{10^{-3} s^{-1}} = 3.7 \times 10^{10}$$

Mass of ^{220}Rn $= \frac{3.7 \times 10^{10} \times 220}{6.022 \times 10^{23}} = 1.35 \times 10^{-11}$ g $= 1.06 \times 10^{-14}$ kg

Ex.46 For the reaction $A \longrightarrow B + C$

Time	t	∞
Total pressure of (B + C)	P_2	P_3

Calculate k.

Sol.

	$A \longrightarrow$	B +	C
At t = 0	P_1	0	0
At t = t	$P_1 - x$	x	x
At t = ∞	0	P_1	P_1

$\therefore \quad 2P_1 = P_3$

$\Rightarrow \quad P_1 = \dfrac{P_3}{2}$

$$2x = P_2 \Rightarrow x = \frac{P_2}{2}$$

$$\therefore P_1 - x = \frac{P_3}{2} - \frac{P_2}{2} = \frac{P_3 - P_2}{2}$$

$$\therefore k = \frac{1}{t}\ln\frac{[A]_0}{[A]_t} = \frac{1}{t}\ln\frac{P_3}{(P_3 - P_2)}$$

Ex.47 The rate of a certain reaction depends on concentration according to equation $-\dfrac{d[A]}{dt} = \dfrac{k_1[A]}{1 + k_2[A]}$

What will be the order of reaction when (i) concentration is very high (ii) very low?

Sol. Given, $-\dfrac{d[A]}{dt} = \dfrac{k_1[A]}{1 + k_2[A]} \Rightarrow \dfrac{-d[A]}{dt} = \dfrac{k_1}{\dfrac{1}{[A]} + k_2}$

(i) When [A] is very high $\dfrac{1}{[A]}$ is very small, and thus negligible

$$\therefore -\frac{d[A]}{dt} = \frac{k_1}{k_2} = \text{constant}$$

Thus, order of reaction is zero.

(ii) When [A] is very low

$[1 + k_2[A] = k'$

$$\therefore -\frac{d[A]}{dt} = \frac{k_1[A]}{k'} = k''[A]$$

Thus, order of reaction is one.

Ex.48 Pseudo first order rate for the reaction, $A + B \longrightarrow$ Product, when studied in 0.1 M of B is given by $-\frac{d[A]}{dt} = k[A]$, where, $k = 1.25 \times 10^4\ \text{sec}^{-1}$, calculate the value of second order rate constant.

Sol. $A + B \longrightarrow$ Product

$$-\frac{d[A]}{dt} = k[A] \Rightarrow -\frac{d[A]}{dt} = 1.25 \times 10^4 \times [A] \qquad \text{....(i)}$$

Assuming the reaction to be of second order

$$-\frac{d[A]}{dt} = k'[A][B] \Rightarrow -\frac{d[A]}{dt} = k'[A][0.1] \qquad \text{....(ii)}$$

Dividing Eq. (i) by (ii), we get

$$1 = \frac{1.25 \times 10^4}{k' \times (0.1)}$$

$$\therefore k' = 1.25 \times 10^5\ \text{L mol}^{-1}\ \text{s}^{-1}$$

Ex.49 N_2O_5 decomposes according to equation, $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$

(A) What does $\frac{-d[N_2O_5]}{dt}$ denote ? **(B)** What does $\frac{d[O_2]}{dt}$ denote ? **(C)** What is the units of rate of this reaction?

Sol. **(A)** Rate of decomposition of N_2O_5. **(B)** Rate of formation of O_2. **(C)** Unit of rate = mol litre^{-1} time^{-1}.

Ex.50 Derive a relation between $t_{1/2}$ and temperature for an nth order reaction where $n > 2$?

Sol. $\ln k = \ln A - \frac{E_a}{RT}$ (Arrhenius equation) ....(i)

$$t_{1/2} = \frac{\left(2^{n-1} - 1\right)}{k(n-1)a_0^{n-1}} \qquad \text{...(ii)}$$

$$\therefore \ln\left(t_{1/2}\right) = \ln\frac{2^{n-1} - 1}{(n-1)a_0^{n-1}} - \ln k \qquad \text{...(iii)}$$

From the Eqs. (i) and (iii)

$$\ln\left(t_{1/2}\right) = \ln\frac{2^{n-1} - 1}{(n-1)a_0^{n-1}} - \ln A + \frac{E_a}{RT}$$

$$\Rightarrow \ln\left(t_{1/2}\right) = \ln A + \frac{E}{RT}$$

$$\text{where } A = \frac{2^{n-1} - 1}{(n-1)a_0^{n-1} \times A}$$

That is $t_{1/2}$ decreases with increase in temperature.

A plot of $t_{1/2}$ vs $\frac{1}{T}$ gives a straight line with slope E_a.

Exercise # 1

[Single Correct Choice Type Questions]

1. $aA + bB \longrightarrow$ Product, $dx/dt = k\,[A]^a\,[B]^b$. If concentration of A is doubled, rate is four times. If concentration of B is made four times, rate is doubled. What is relation between rate of disappearance of A and that of B ?

(A) $-\{d\,[A]/dt\} = -\{d\,[B]/dt\}$ **(B)** $-\{d\,[A]/dt\} = -\{4\,d\,[B]/dt\}$

(C) $-\{4\,d\,[A]/dt\} = -\{d\,[B]/dt\}$ **(D)** None of these

2. For the reaction, $2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$ the rate expression can be written in the following ways:

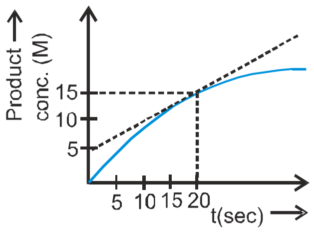
$\{d[N_2]/dt\} = k_1\,[NO][H_2]$; $\{d[H_2O]/dt\} = k[NO][H_2]$; $\{-d[NO]/dt\} = k'_1\,[NO]\,[H_2]$; $\{-d[H_2]/dt\} = k''_1\,[NO][H_2]$

The relationship between k, k_1 , k'_1 and k''_1. is :

(A) $k = k_1 = k'_1 = k''_1$ **(B)** $k = 2k_1 = k'_1 = k''_1$

(C) $k = 2k'_1 = k_1 = k''_1$ **(D)** $k = k_1 = k'_1 = 2\,k''_1$

3.



Rate of formation of product at t = 20 seconds is

(A) $0.5\ MS^{-1}$ **(B)** $1\ M\ S^{-1}$ **(C)** $1.5\ M\ S^{-1}$ **(D)** $2MS^{-1}$

4. In the following reaction : $xA \longrightarrow yB$

$$\log\left[-\frac{d[A]}{dt}\right] = \log\left[\frac{d[B]}{dt}\right] + 0.3$$

where –ve sign indicates rate of disappearance of the reactant. Thus, x : y is :

(A) 1 : 2 **(B)** 2 : 1 **(C)** 3 : 1 **(D)** 3 : 10

5. Rate of formation of SO_3 in the following reaction $2SO_2 + O_2 \rightarrow 2SO_3$ is $100\ g\ min^{-1}$. Hence rate of disappearance of O_2 is :

(A) $50\ g\ min^{-1}$ **(B)** $40\ g\ min^{-1}$ **(C)** $200\ g\ min^{-1}$ **(D)** $20\ g\ min^{-1}$

6. For a reaction $pA + qB \rightarrow$ products, the rate law expression is $r = k[A]^l\,[B]^m$, then :

(A) $(p+1) < (1+m)$ **(B)** $(p+q) > (1+m)$

(C) $(p+q)$ may or may not be equal to $(1+m)$ **(D)** $(p+q) = (1+m)$

7. If rate constant is numerically the same for the three reactions of first, second and third order respectively. Assume all the reactions of the kind $A \rightarrow$ products. Which of the following is correct :

(A) if $[A] = 1$ then $r_1 = r_2 = r_3$ **(B)** if $[A] < 1$ then $r_1 > r_2 > r_3$

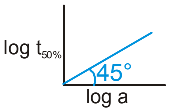
(C) if $[A] > 1$ then $r_3 > r_2 > r_1$ **(D)** All

8. For the irreversible process, $A + B \longrightarrow$ products, the rate is first–order w.r.t. A and second–order w.r.t. B. If 1.0 mol each of A and B introduced into a 1.0 L vessel, and the initial rate was $1.0 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}$, rate when half reactants have been turned into products is :

(A) $1.25 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}$ **(B)** $1.0 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}$

(C) $2.50 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}$ **(D)** $2.0 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}$

9. What will be the order of reaction and rate constant for a chemical change having log $t_{50\%}$ vs log concentration of **(A)** curves as :



(A) 0, 1/2 **(B)** 1, 1 **(C)** 2, 2 **(D)** 3, 1

10. For a reaction 2A + B → product, rate law is $-\frac{d[A]}{dt} = k[A]$. At a time when $t = \frac{1}{k}$, concentration of the reactant is (C_0 = initial concentration)

(A) $\frac{C_0}{e}$ **(B)** C_0e **(C)** $\frac{C_0}{e^2}$ **(D)** $\frac{1}{C_0}$

11. Two substances A ($t_{1/2}$ = 5 min) and B ($t_{1/2}$ = 15 min) are taken in such a way that initially [A] = 4[B]. The time after which both the concentration will be equal is : (Assume that reaction is first order)

(A) 5 min **(B)** 15 min
(C) 20 min **(D)** concentration can never be equal

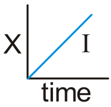
12. The rate constant of the reaction A → 2B is 1.0×10^{-3} mol lit^{-1} min^{-1}, if the initial concentration of A is 1.0 mole lit^{-1} what would be the concentration of B after 100 minutes.

(A) 0.1 mol lit^{-1} **(B)** 0.2 mol lit^{-1} **(C)** 0.9 mol lit^{-1} **(D)** 1.8 mol lit^{-1}

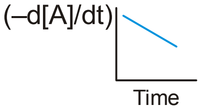
13. A drop of solution (volume 0.05 mL) contains 3.0×10^{-6} moles of H^+. If the rate constant of disappearance of H^+ is 1.0×10^7 mole $litre^{-1}$ sec^{-1}. How long would it take for H^+ in drop to disappear :

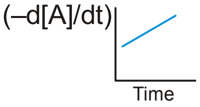
(A) 6×10^{-8} sec **(B)** 6×10^{-7} sec **(C)** 6×10^{-9} sec **(D)** 6×10^{-10} sec

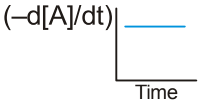
14. Graph between concentration of the product and time of the reaction A → B is of the type

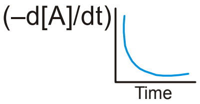


Hence graph between – d[A]/dt and time will be of the type :

(A)


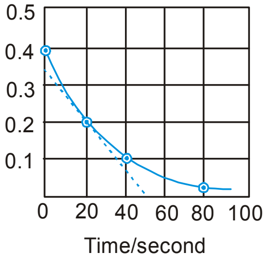
(B)


(C)


(D)


15. A reaction follows the given concentration (M)–time graph. The rate for this reaction at 20 seconds will be :

(A) 4×10^{-3} M s^{-1}
(B) 8×10^{-2} M s^{-1}
(C) 2×10^{-2} M s^{-1}
(D) 7×10^{-3} M s^{-1}



16. In a first order reaction the reacting substance has half-life period of ten minutes. What fraction of the substance will be left after an hour the reaction has occurred ? :

(A) 1/6 of initial concentration **(B)** 1/64 of initial concentration
(C) 1/12 of initial concentration **(D)** 1/32 of initial concentration

17. A certain reaction $A + B \longrightarrow C$, the first order with respect to each reactant $k = 10^{-3}$. Determine the final concentration of A after 100 s, if the initial concentration of A was 0.1 M and that of B was 0.2 M.

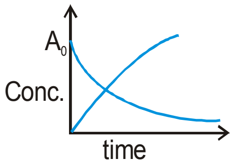
(A) 0.098 M **(B)** 0.088 M **(C)** 0.078 M **(D)** 0.068 M

18. For the reaction $2NO_2 \longrightarrow N_2O_2 + O_2$, rate expression is as follows

$-\dfrac{d[NO_2]}{dt} = K\,[NO_2]^n$, where $K = 3 \times 10^{-3}$ mol^{-1} L sec^{-1}. If the rate of formation of oxygen is 1.5×10^{-4} mol L^{-1} sec^{-1}, then the molar concentration of NO_2 in mole L^{-1} is

(A) 1.5×10^{-4} **(B)** 0.0151 **(C)** 0.214 **(D)** 0.316

19. At the point of intersection of the two curves shown, the conc. of B is given by.......for, $A \rightarrow nB$:



(A) $\dfrac{nA_0}{2}$ **(B)** $\dfrac{A_0}{n-1}$ **(C)** $\dfrac{nA_0}{n+1}$ **(D)** $\left(\dfrac{n-1}{n+1}\right)A_0$

20. A reaction, which is second order, has a rate constant of 0.002 L mol^{-1} s^{-1}. If the initial conc. of the reactant is 0.2 M. how long will it take for the concentration to become 0.0400 M ?

(A) 1000 s **(B)** 400 s **(C)** 200 s **(D)** 10, 000 s

21. Which is not true for a second order reaction ?

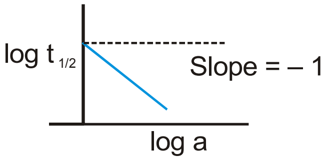
(A) It can have rate constant 1×10^{-2} L mol^{-1} s^{-1}

(B) Its half-life is inversely proportional to its initial concentration

(C) Time to complete 75% reaction is twice of half-life

(D) $T_{50} = \dfrac{1}{K \times \text{Initial conc.}}$

22. A graph between log $t_{1/2}$ and log a (abscissa) a being the initial concentration of A in the reaction For reaction $A \rightarrow$ Product, is the rate law is :



(A) $\dfrac{-d[A]}{dt} = K$

(B) $\dfrac{-d[A]}{dt} = K\,[A]$

(C) $\dfrac{-d[A]}{dt} = K\,[A]^2$

(D) $\dfrac{-d[A]}{dt} = K\,[A]^3$

23. **Statement-1 :** The ratio of $\frac{t_{3/4}}{t_{1/2}}$ for third order reaction is equal to 5 : 1

Statement-2 : $t_{1/2}$ & $t_{3/4}$ of a reaction depends only on order, not on the concentration of reactant.

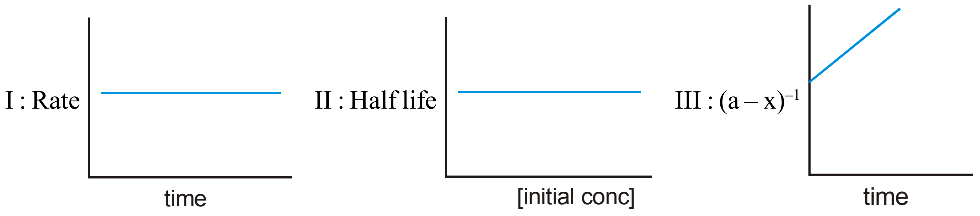
(A) Statement 1 and statement 2 are correct and statement 2 is the correct explanation of statement 1.

(B) Statement 1 and statement 2 are correct but the statement 2 is not correct explanation of statement 1.

(C) statement 1 is correct but statement 2 is false.

(D) statement 1 is false but statement 2 is correct.

24. Match the graphical study with the order of the reactions :



A : First
B : Second
C : Zero

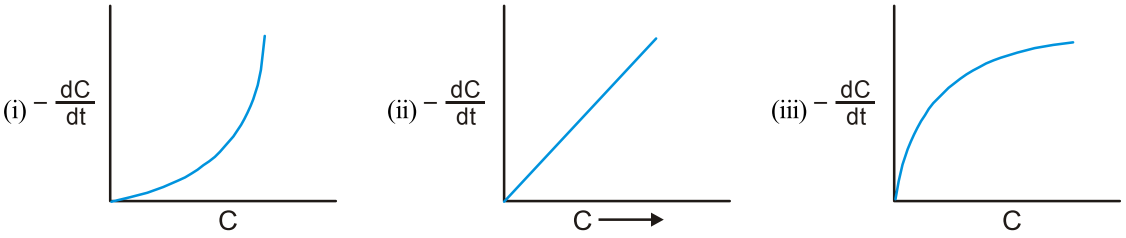
	I	II	III
(A)	A	B	C
(B)	B	C	A
(C)	C	B	A
(D)	C	A	B

25. The data for the reaction $A + B \rightarrow C$ is

Exp.	$[A]_0$	$[B]_0$	initial rate
1	0.012	0.035	0.10
2	0.024	0.035	0.80
3	0.012	0.070	0.10
4	0.024	0.070	0.80

(A) $r = k[B]^3$ **(B)** $r = k[A]^3$ **(C)** $r = k[A][B]^4$ **(D)** $r = k[A]^2[B]^2$.

26. In three different reactions, involving a single reactant in each case, a plot of rate of the reaction on the y–axis, versus concentration of the reactant on the x–axis, yields three different curves shown below.



What are the possible orders of the reactions (i), (ii), (iii).

(A) 1, 2, 3 **(B)** 2, 1, 1/2 **(C)** 0, 1, 2 **(D)** 0, 1, 1/2

27. Which integrated equation is correct for the following Ist order reaction started with only A(g) in a closed rigid vessel.

$$A(g) \longrightarrow B(g) + C(g) + D(g)$$

P_i = initial pressure ; P_t = total pressure at time t

(A) $K = \frac{2.303}{t}\log_{10}\left[\frac{P_i}{P_t}\right]$ **(B)** $K = \frac{2.303}{t}\log_{10}\left[\frac{P_t}{P_i}\right]$

(C) $K = \frac{2.303}{t}\log_{10}\left[\frac{2P_i}{3P_i - P_t}\right]$ **(D)** $K = \frac{2.303}{t}\log_{10}\left[\frac{3P_i}{2P_i - 3P_t}\right]$

28. The decompostion NH_3 gas on a heated tungsten surface gave the following results :

Initial pressure (mm)	65	105	y	185
Half-life (sec)	290	x	670	820

Calculate approximately the values of x and y.

(A) x = 410 sec, y = 115 mm
(B) x = 467 sec, y = 150 mm
(C) x = 490 sec, y = 120 mm
(D) x = 430 sec, y = 105 mm

29. In the reaction $NH_4NO_2\,(aq.) \rightarrow N_2\,(g) + 2\,H_2O\,(l)$ the volume of N_2 after 20 min and after a long time is 40 ml and 70 ml respectively. The value of rate constant is :

(A) (1/20) In (7/4) min^{-1}
(B) (2.303 /1200) log (7/3) sec^{-1}
(C) (1/20) log (7/3) min^{-1}
(D) (2.303 / 20) log (11/7) min^{-1}

30. At 373 K, a gaseous reaction $A \rightarrow 2B + C$ is found to be of first order. Starting with pure A, the total pressure at the end of 10 min. was 176 mm and after a long time when A was completely dissociated, it was 270 mm. The pressure of A at the end of 10 minutes was :

(A) 94 mm
(B) 47 mm
(C) 43 mm
(D) 90 mm

31. The reaction $A(s) \rightarrow 2\,B(g) + C(g)$ is first order. The pressure after 20 min. and after very long time are 150 mm Hg and 225 mm Hg. The value of rate constant and pressure after 40 min. are :

(A) 0.05 In 1.5 min^{-1} ,200 mm
(B) 0.5 ln 2 min^{-1} ,300 mm
(C) 0.05 In 3 min^{-1}, 300 mm
(D) 0.05 In 3 min^{-1} , 200 mm

32. Half life of reaction : $H_2O_2(aq) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$ is independent of initial concentration of H_2O_2 volume of O_2 gas after 20 minute is 5L at 1 atm and 27°C and after completion of reaction 50L. The rate constant is

(A) $\frac{1}{20}\log 10\,min^{-1}$
(B) $\frac{2.303}{20}\log 10\,min^{-1}$
(C) $\frac{2.303}{20}\log\frac{50}{45}min^{-1}$
(D) $\frac{2.303}{20}\log\frac{45}{50}min^{-1}$

33. The decomposition of N_2O_5 in chloroform was followed by measuring the volume of O_2 gas evolved : $2N_2O_5\,(CCI_4) \rightarrow 2N_2O_4\,(CCI_4) + O_2\,(g)$. The maximum volume of O_2 gas obtained was 100 cm^3. In 500 minutes, 90 cm^3 of O_2 were evolved. The first order rate constant (in min^{-1}) for the disappearance of N_2O_5 is :

(A) $\frac{2.303}{500}$
(B) $\frac{2.303}{500}\log\frac{100}{90}$
(C) $\frac{2.303}{500}\log\frac{90}{100}$
(D) $\frac{100}{10\times500}$

34. For a reaction $A \longrightarrow B + C$, it was found that at the end of 10 minutes from the start the total optical rotation of the system was 50° and when the reaction is complete, it was 100°. Assuming that only B and C are optically active and dextrorotatory. calculate the rate constant of this first order reaction.

(A) 0.693 min^{-1}
(B) 0.0693 sec^{-1}
(C) 0.0693 min^{-1}
(D) 0.00693 sec^{-1}

35. In the above question solution is optically inactive when :

(A) $r_t = a$
(B) $r_t = 0$
(C) $r_t = x$
(D) $r_t = (a + x)$

36. The following data were obtained in an experiment on inversion of cane sugar (a first order kinetics)

Time (min)	0	10	After a long time
Total angle of rotation (degree)	+40	+15	– 10

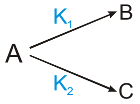
The rate constant (in $second^{-1}$) is [ln 2 = 0.693]

(A) 0.0693
(B) 1.15×10^{-3}
(C) 0.693
(D) 1.15×10^{-2}

37. The rate constant for two parallel reactions were found to be $1.0 \times 10^{-2} dm^3\,mol^{-1}\,s^{-1}$ and $3.0 \times 10^{-2}\,dm^3\,mol^{-1}s^{-1}$. If the corresponding energies of activation of the parallel reactions are 60.0 kJ mol^{-1} and 70.0 kJ mol^{-1} respectively, what is the apparent overall energy of activation ?

(A) 130.0 kJ mol^{-1}
(B) 67.5 kJ mol^{-1}
(C) 100.0 kJ mol^{-1}
(D) 65.0 kJ mol^{-1}

38. The substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as :

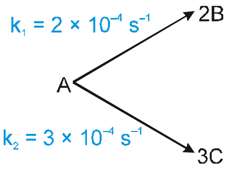


$K_1 = 1.26 \times 10^{-4}\ \text{sec}^{-1}$ and $K_2 = 3.8 \times 10^{-5}\ \text{sec}^{-1}$

The percentage distribution of B and C

(A) 80% B and 20% C
(B) 76.83% B and 23.17%C
(C) 90% B and 10% C
(D) 60% B and 40% C

39. For the follwing parallel chain reaction



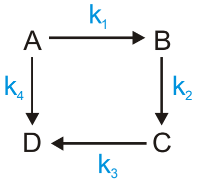
if the sum of the concentration of B and C at any time is 2M then what will be $[B]_t$ and $[C]_t$ respectively?

(A) $\frac{11}{12}M, \frac{13}{12}M$
(B) $\frac{3}{4}M, \frac{5}{4}M$
(C) $\frac{4}{5}M, \frac{6}{5}M$
(D) $\frac{8}{13}M, \frac{18}{13}M$

40. For the system $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$, $A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C$ which was started with only A the equilibrium concentration $[A]_{eq}$ is correctly related to $[B]_{eq}$ and $[C]_{eq}$ as :

(A) $\frac{k_{-1}[B]_{eq} + k_{-2}[C]_{eq}}{(k_1 + k_2)}$
(B) $\frac{k_{-1}[B]_{eq} - k_{-2}[C]_{eq}}{(k_1 - k_2)}$
(C) $\frac{k_{-1}[B]_{eq} + k_{-2}[C]_{eq}}{(k_1 - k_2)}$
(D) $\frac{k_{-1}[B]_{eq} - k_{-2}[C]_{eq}}{(k_1 + k_2)}$

41. Consider the elementary reaction sequence shown in figure. Which of the following equations are correct?



(A) $\frac{d[A]}{dt} = -k_1[A] + k_4[D]$
(B) $\frac{d[C]}{dt} = k_2[B] - k_3[C]$
(C) $\frac{d[D]}{dt} = k_4[D] + k_3[D]$
(D) Nothing can be said about order of reactions in this problem

42. At a given temperature, $k_1 = k_2$ for the reaction

$$A + B \rightleftharpoons C + D$$

If $\left[\frac{dx}{dt}\right] = k_1\,[A]\,[B] - k_2[C]\,[D]$ in which set of the concentration reaction ceases?

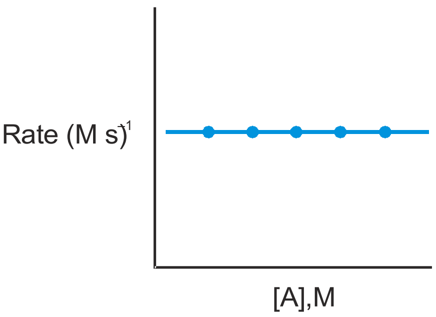
	[A]	[B]	[C]	[D]
(A)	0.1 M	0.2 M	0.3 M	0.4 M
(C)	0.2 M	0.2 M	0.3 M	0.2 M

	[A]	[B]	[C]	[D]
(B)	0.4 M	0.25 M	0.2 M	0.5 M
(D)	0.2 M	0.2 M	0.4 M	0.2 M

43. Following reaction can take place in both direction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$,

Graph is given for the forward reaction :

and for the backward reaction following data are given



[B]	**Rate**
0.01 M	1×10^{-2} Ms^{-1}
0.02 M	2×10^{-2} Ms^{-1}

Hence, net reaction rate of B is :

(A) $= k_1 [A] - k_2 [B]$ **(B)** $= k_1 - k_2 [B]$

(C) $= k_1 [A] - k_2$ **(D)** $= k_1 - k_2$

44. For the complex $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2{}^+]$

$$\left(\frac{dx}{dt}\right) = 2 \times 10^7\ L^2\ mol^{-2}\ s^{-1}\ [Ag^+]\ [NH_3]^2 - 1 \times 10^{-2}\ s^{-1}\ [Ag(NH_3)_2{}^+]$$

Hence, ratio of rate constants of the forward and backward reactions is :

(A) 2×10^7 L^2 mol^{-2} **(B)** 2×10^9 L^2 mol^{-2} **(C)** 1×10^{-2} L^2 mol^{-2} **(D)** 0.5×10^{-9} L^2 mol^{-2}

45. The rate constant K_1 of a reaction is found to be double that of rate constant K_2 of another reaction. The relationship between corresponding activation energies of the two reactions at same temperature (E_1 and E_2) can be represented as :

(A) $E_1 > E_2$ **(B)** $E_1 < E_2$ **(C)** $E_1 = E_2$ **(D)** None of these

46. When a graph between log K and 1/T is drawn a straight line is obtained. The point at which line cuts y -axis and x -axis respectively correspond to the temp :

(A) $0, E_a / 2.303\ R \log A$ **(B)** $\infty, Ea / (R \ln A)$ **(C)** $0, \log A$ **(D)** None of these.

47. How much faster would a reaction proceed at 25°C than at 0°C if the activation energy is 65 kJ?

(A) 2 times **(B)** 5 times **(C)** 11 times **(D)** 16 times

48. The rate constant, the activation energy and the frequency factor of a chemical reaction at 25°C are 3.0×10^{-4} s^{-1}, 104.4 KJ mol^{-1} and 6.0×10^{14} s^{-1} respectively. The value of the rate constant as $T \to \infty$ is :

(A) 2.0×10^{18} s^{-1} **(B)** 6.0×10^{14} s^{-1} **(C)** infinite **(D)** 3.6×10^{30} s^{-1}

49. Following are the values of E_a and ΔH for three reactions carried out at the same temperature :

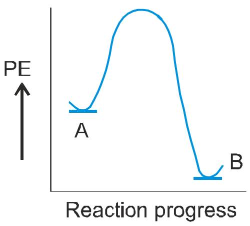
I : $E_a = 20$ kJ mol^{-1} , $\Delta H = -60$ kJ mol^{-1}
II : $E_a = 10$ kJ mol^{-1} , $\Delta H = -20$ kJ mol^{-1}
III: $E_a = 40$ kJ mol^{-1} , $\Delta H = +15$ kJ mol^{-1}

If all the three reaction have same frequency factor then fastest and slowest reactions are :

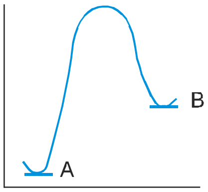
	Fastest	**Slowest**
(A)	I	II
(B)	II	III
(C)	I	III
(D)	can't be predicted.	

50. For a reaction A → B, $E_a = 10\ \text{kJ mol}^{-1}$, $\Delta H = 5\ \text{kJ mol}^{-1}$. Thus, potential energy profile for this reaction is :

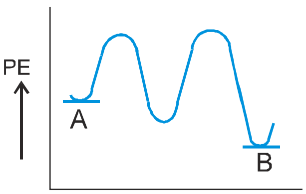
(A)



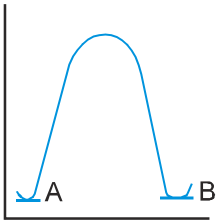
(B)



(C)



(D)



51. For a certain reaction the variation of the rate constant with temperature is given by the equation

$$\ln k_t = \ln k_0 + \left(\frac{\ln 3}{10}\right) t \qquad (t \geq 0°C)$$

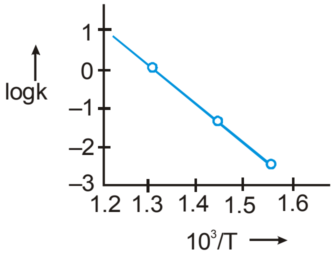
The value of the temperature coefficient of the reaction rate is therefore

(A) 4 **(B)** 3 **(C)** 10 **(D)** 2

52. The E_a of a reaction in presence of a catalyst is 4.15 kJ mol^{-1} and in absence of a catalyst is 8.3 kJ mol^{-1}. What is slope of the plot of $\ln k$ vs $\frac{1}{T}$ in the absence of catalyst

(A) +1 **(B)** –1 **(C)** +1000 **(D)** –1000

53. For the decomposition of HI the following logarithmic plot is shown : [R = 1.98 cal/mol-K]
The activation energy of the reaction is about



(A) 45600 cal

(B) 13500 cal

(C) 24600 cal

(D) 32300 cal

54. The reaction of hydrogen, and iodine monochloride is represented by the equation :

$$H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$$

This reaction is first–order in $H_2(g)$ and also first–order in ICl(g). Which of these proposed mechanism can be consistent with the given information about this reaction ?

Mechanism I : $H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$

Mechanism II : $H_2(g) + ICl(g) \xrightarrow{\text{Slow}} HCl(g) + HI(g)$

$HI(g) + ICl(g) \xrightarrow{\text{fast}} HCl(g) + I_2(g)$

(A) I only **(B)** II only **(C)** both I and II **(D)** neither I nor II

55. Reaction $A + B \longrightarrow D + E$ take place as

$A + B \xrightarrow{K_1} 2C$; $C + B \xrightarrow{K_2} 2D$

$C + A \xrightarrow{K_3} 2E$

The rate of disapperance of C is given by

(A) $-\dfrac{d[C]}{dt} = K_2[B][C] + K_3[A][C] - 2K_1[A][B]$

(B) $-\dfrac{d[C]}{dt} = K_2[B][C] + K_3[E] - K_1[C]$

(C) $-\dfrac{d[C]}{dt} = K_2[D]O + K_3[E] - K_1[C]$

(D) $-\dfrac{d}{dt}[C] = 2K_1[A][B] - K_2[B][C] - K_3[A][C]$

56. The steady state concentration of the activated molecule [A] in the following sequence of steps is given by:

$A + A \xrightarrow{K_1} A + A$; $A + A \xrightarrow{K_2} 2A$

(A) $\dfrac{K_2[A]}{K_1}$ **(B)** $\dfrac{K_1[A]}{K_2}$ **(C)** $K_1K_2[A]$ **(D)** $\dfrac{K_1K_2}{[A]}$

57. For the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ the experiment data suggested that $r = k[H_2][Br_2]^{1/2}$

The molecularity and order of the reaction are respectively :

(A) 2, 3/2 **(B)** 3/2 , 3/2 **(C)** Not defined, 3/2 **(D)** 1,1/2

58. The reaction of NO_2 (g) and O_3 (g) is first-order in NO_2 (g) and O_3 (g)

$$2\,NO_2(g) + O_3(g) \longrightarrow N_2O_5(g) + O_2(g)$$

The reaction can take place by mechanism :

I : $NO_2 + O_3 \xrightarrow{\text{Slow}} NO_3 + O_2$

$NO_3 + NO_2 \xrightarrow{\text{fast}} N_2O_5$

II : $O_3 \underset{k_b}{\overset{k_a\ \text{fast}}{\rightleftharpoons}} O_2 + [O]$

$NO_2 + O \xrightarrow{\text{Slow}} NO_3$

$NO_3 + NO_2 \xrightarrow{\text{fast}} N_2O_5$

Select correct mechanism.

(A) I only **(B)** II only **(C)** both I and II **(D)** None of I and II

59. A hypothetical reaction $X_2 + Y_2 \longrightarrow 2XY$ follows the mechanism given below.

$X_2 \rightleftharpoons X + X$ [Fast]

$X + Y_2 \longrightarrow XY + Y$ [Slow]

$X + Y \longrightarrow XY$ [Fast]

The order of overall reaction is

(A) 2 **(B)** 1 **(C)** 1.5 **(D)** Zero

60. A radioactive element has a half life of one day. After three days the amount of the element left will be :

(A) 1/2 of the original amount **(B)** 1/4 of the original amount

(C) 1/8 of the original amount **(D)** 1/16 of the original amount

61. The activity per ml of a solution of radioactive substance is x. How much water be added to 200 ml of this solution so that the acitivity falls to x/20 per ml after 4 half-lives ?
(A) 100 ml **(B)** 150 ml **(C)** 80 ml **(D)** 50 ml.

62. The α activity in 1g sample of ^{226}Ra ($t_{1/2}$ = 1600 years) is equal to :
(A) 2.19×10^{12} dpm **(B)** 2.19×10^{14} dpm **(C)** 2.19×10^{16} dpm **(D)** 4.96×10^{12} dpm

63. Radioactivity is affected by :
(A) temperature **(B)** Pressure
(C) electric and magnetic field **(D)** none of these

64. Half life period of 10 gm radioactive element is 20 days. Then half life period of 100 gm of this element is :
(A) 20 days **(B)** 200 days **(C)** 100 days **(D)** 10 days

65. Determine the average life of U^{238} having $t_{0.5}$ = 138.5 day.
(A) 138.5 day **(B)** 199.86 day **(C)** 238 day **(D)** None of these

66. A sample of rock from moon contains equal number of atoms of uranium and lead ($t_{1/2}$ for U = 4.5×10^9 years). The age of the rock would be :
(A) 9.0×10^9 years **(B)** 4.5×10^9 years **(C)** 13.5×10^9 years **(D)** 2.25×10^9 years

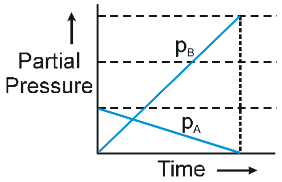
67. The half-life of ^{99}Tc is 6.0 h. The total residual activity in a patient after receiving an injection containing ^{99}Tc must not be more than 0.01 μCi , after 36.0 hours. What is the maximum activity (in μCi) that the sample injected can have?
(A) 0.06 **(B)** 0.16 **(C)** 0.32 **(D)** 0.64

68. A radioactive isotope X with half - life of 6.93×10^9 years decay to Y which is stable. A sample of rock from the moon was found to contain both the element X and Y in the mole ratio 1 : 7.What is the age of the rock?
(A) 2.079×10^{10} years **(B)** 1.94×10^{10} years **(C)** 1.33×10^9 years **(D)** 10^{10} years

69. The half−life of a radioactive isotope is 3 hours . If the initial mass of the isotope were 256 gm , the mass of it remaining undecayed after 18 hours would be :
(A) 4 gm **(B)** 8 gm **(C)** 12 gm **(D)** 16 gm

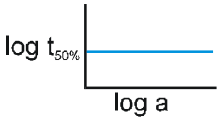
70. The radioactive decay is first order reaction. Its rate, on increasing 10°C temperature
(A) increases 2-3 times **(B)** decreases 2-3 times
(C) does not change **(D)** increases 10 times

71. If for a reaction in which A(g) converts to B(g) the reaction carried out at const. V & T results into the following graph.



(A) then the reaction must be $A(g) \rightarrow 3B(g)$ and is a first order reaction.
(B) then the reaction must be $A(g) \rightarrow 3B(g)$ and is a second order reaction.
(C) then the reaction must be $A(g) \rightarrow 3B(g)$ and is a zero order reaction.
(D) then the reaction must be $A(g) \leftrightarrow 3B(g)$ and is a first order reaction.

72. A graph plotted between log $t_{50\%}$ vs. log concentration is a straight line. What conclusion can you draw from this graph.



(A) n = 1 ; $t_{1/2} \propto a$ **(B)** n = 2, $t_{1/2} \propto 1/a$
(C) n = 1 ; $t_{1/2} = (0.693/k)$ **(D)** None of these

73. Concentration of the reactant in first-order is reduced to $\frac{1}{e^2}$ after : (Natural life = $\frac{1}{K}$)
(A) one natural life-time **(B)** two-natural life-time
(C) three natural life-time **(D)** four natural life-time

74. For a chemical reaction A $\rightarrow$ products, the rate of disappearance of A is given by :

$\frac{-dC_A}{dt} = \frac{K_1C_A}{1+K_2C_A}$ At low C_A the reaction is of the ..... order with rate constant.....(Assume K_1, K_2 are lesser than 1)

(A) I, $\frac{K_1}{K_2}$ **(B)** I, K_1 **(C)** II, K_1/K_2 **(D)** II, $\frac{K_1}{K_1+K_2}$

75. The reaction A(g) + 2B(g) $\rightarrow$ C(g) is an elementary reaction. In an experiment involving this reaction, the initial partial pressures of A and B are P_A = 0.40 atm and P_B = 1.0 atm respectively. When pressure of C becomes 0.3 atm in the reaction the rate of the reaction relative to the initial rate is :

(A) $\frac{1}{12}$ **(B)** $\frac{1}{50}$ **(C)** $\frac{1}{25}$ **(D)** none of these

76. The rate law for the dimerisation of NO_2 is

$$-\frac{d[NO_2]}{dt} = k[NO_2]^2$$

which of the following changes will change the value of the specific rate constant , k :

(A) Doubling the total pressure on the system

(B) Doubling the temperature

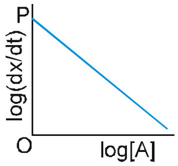
(C) Both of **(A)** and **(B)**

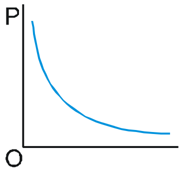
(D) None of the above

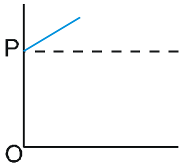
77. In a reaction involving one single reactant, the fraction of the reactant consumed may be defined as $f = \left(1-\frac{C}{C_0}\right)$ where C_0 and C are the concentrations of the reactant at the start and after time, t. For a first order reaction

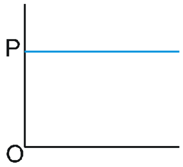
(A) $\frac{df}{dt} = k(1-f)$ **(B)** $-\frac{df}{dt} = kf$ **(C)** $-\frac{df}{dt} = k(1-f)$ **(D)** $\frac{df}{dt} = kf$

78. A $\rightarrow$ Product and $\left(\frac{dx}{dt}\right) = k[A]^2$. If $\log\left(\frac{dx}{dt}\right)$ is plotted against log [A], then graph is of the type :

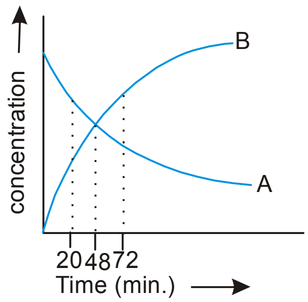
(A)


(B)


(C)


(D)


79. For a first order reaction, nA $\longrightarrow$ B whose concentration vs time curve is as shown in the figure. If half life for the reaction is 24 minutes . Find out the value of n.



(A) 1 **(B)** 2 **(C)** 3 **(D)** 4

80. Acid catalysed hydrolysis of ester is first-order reaction and rate constant is given by

$$k = \frac{2.303}{t}\log\frac{V_\infty - V_0}{V_\infty - V_t}$$

where V_0, V_t and V_∞ are the volume of standard NaOH required to neutralise acid present at a given time ; if ester is 50% hydrolysed then :

(A) $V_\infty = V_t$ **(B)** $V = (V_t - V_0)$ **(C)** $V_\infty = 2V_t - V_0$ **(D)** $V_\infty = 2V_t + V_0$

81. In a hypothetical reaction, $A(aq) \rightleftharpoons 2B(aq) + C(aq)$ (1st order decomposition)
'A' is optically active (dextro-rototory) while 'B' and 'C' are optically inactive but 'B' takes part in a titration reaction (fast reaction) with H_2O_2. Hence, the progress of reaction can be monitored by measuring rotation of plane polarised light or by measuring volume of H_2O_2 consumed in titration.
In an experiment the optical rotation was found to be $\theta = 40°$ at $t = 20$ min and $\theta = 10°$ at $t = 50$ min. from start of the reaction. If the progress would have been monitored by titration method, volume of H_2O_2 consumed at $t = 15$ min. (from start) is 40 ml then volume of H_2O_2 consumed at $t = 60$ min will be:

(A) 60 ml **(B)** 75 ml **(C)** 52.5 ml **(D)** 90 ml

82. Inversion of sucrose ($C_{12}H_{22}O_{11}$) is first-order reaction and is studied by measuring angle of rotation at different instant of time

$$\underset{\substack{\text{Sucrose}\\ d}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\substack{\text{Glucose}\\ d}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose}\\ l}}{C_6H_{12}O_6}$$

If $(r_\infty - r_0) = a$ and $(r_\infty - r_t) = (a - x)$ (where r_0, r_t and r_∞ are the angle of rotation at the start, at the time t and at the end of the reaction respectively, then there is 50% inversion when :

(A) $r_0 = 2r_t - r_\infty$ **(B)** $r_0 = r_t - r_\infty$ **(C)** $r_0 = r_t - 2r_\infty$ **(D)** $r_0 = r_t + r_\infty$

83. The inversion of cane sugar proceeds with half life of 50 minute at pH = 5 for any concentration of sugar. However if pH = 6, the half life changes to 500 minute of any concentration of sugar. The rate law expression for the inversion of cane sugar is written as : $r = K\,[\text{sugar}]^1\,[H^+]^y$. Determine the value of y.

(A) $r = K\,[\text{sugar}]^1\,[H^+]^{-1}$ **(B)** $r = K\,[\text{sugar}]^1\,[H^+]^2$

(C) $r = K\,[\text{sugar}]^1\,[H^+]^1$ **(D)** $r = K\,[\text{sugar}]^1\,[H^+]^0$.

84. The following data is for the decomposition of ammonium nitrite in aqeous solution.

Volume of N_2 in cc.	Time (minutes)
6.25	10
9.00	15
11.40	20
13.65	25
35.05	infinity

The order of the reaction is

(A) zero **(B)** one **(C)** minus one **(D)** minus two

85. Formation of NO_2F from NO_2 and F_2 as per the reaction $2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$ is a second order reaction, first order with respect to NO_2 and first order with respect to F_2. If NO_2 and F_2 are present in a closed vessel in ratio 2 :1 maintained at a constant temperature with an initial total pressure of 3 atm, what will be the total pressure in the vessel after the reaction is complete?

(A) 1atm **(B)** 2 atm **(C)** 2.5 atm **(D)** 3 atm

86. For a first order reaction $A \rightarrow B + 2C + 3D$ (A is optically inactive and B, C and D are dextrorotary), the optical rotation at time t and ∞ are r_t and r_∞ respectively, the expression for rate constant is

(A) $K = \frac{1}{t} \ln \frac{r_t}{r_\infty - r_t}$

(B) $k = \frac{1}{t} \ln \frac{r_\infty}{r_\infty - r_t}$

(C) $k = \frac{1}{t} \ln \frac{r_\infty - r_t}{r_t}$

(D) none of these

87. For the decomposition of $H_2O_2(aq)$ it was found that V_{O_2} (t = 15 min.) was 100 mL (at 0ºC and 1 atm) while V_{O_2} (maximum) was 200 mL (at 0ºC and 2 atm). If the same reaction had been followed by the titration method and if $V_{KMnO_4}^{(cM)}$ (t = 0) had been 40 mL, what would $V_{KMnO_4}^{(cM)}$ (t = 15 min) have been ?

(A) 30 mL **(B)** 25 mL **(C)** 20 mL **(D)** 15 mL

Exercise # 2 Part # I [Multiple Correct Choice Type Questions]

1. A reaction takes place in three steps. The rate constant of the three steps are K_1, K_2 and K_3 respectively. The overall rate constant $K = \frac{K_1K_3}{K_2}$.

The energy of activation for the three steps are 40, 30 and 20 KJ respectively. Therefore :

(A) Overall energy of activation is 10 KJ

(B) Overall energy of activation is 30 KJ

(C) The reaction mechanism is $2A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} A^* + A \,;\, A^* \xrightarrow[\text{rds}]{K_3}$ product and overall order is one.

(D) The reaction mechanism is $A \xrightarrow{K_1} B \,;\, B \xrightarrow{K_2} C \,;\, C \xrightarrow{K_3}$ product and overall order is one

2. For the reaction $CH_4 + Br_2 \rightarrow CH_3Br + HBr$ the experimental data require the following rate equation :

$$\frac{d}{dt}[CH_3Br] = \frac{k_1[CH_4][Br_2]}{1 + k_2[HBr]/[Br_2]}$$

Which of the following is/are true regarding this ?

(A) The reaction is a single step reaction

(B) The reaction is 2nd order in the initial stages $\{[HBr] \approx 0\}$

(C) The reaction is 2nd order in the final stages $\{[Br_2] \approx 0\}$

(D) The molecularity of the reaction is two

3. Rate of radioactive disintegration (–dN/dt) is also known as :

(A) Activity **(B)** Radioactivity **(C)** Half-life period **(D)** Average life period

4. Decomposition of $3\,A(g) \longrightarrow 2\,B(g) + 2C(g)$ follows first order kinetics. Initially only A is present in the container. Pressure developed after 20 min. and infinite time are 3.5 and 4 atm respectively. Which of the following is true.

(A) $t_{50\%} = 20$ min **(B)** $t_{75\%} = 40$ min **(C)** $t_{99\%} = 64/3$ min **(D)** $t_{87.5\%} = 60$ min

5. The polarimeter readings in an experiment to measure the rate of inversion of cane suger (1st order reaction) were as follows

time (min)	:	0	30	∞
angle (degree)	:	30	20	– 15

Identify the true statement (s) log 2 = 0.3, log 3 = 0.48, log 7 = 0.84

(A) the half life of the reaction is 75 min.

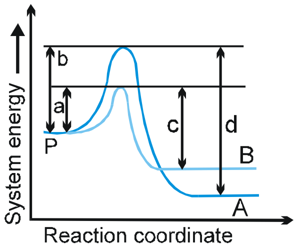
(B) the solution is optically inactive at 120 min.

(C) The equimolar mixture of the products is dextrorotatory.

(D) The angle would be 7.5° at half time.

6. Consider the decay of P to A and B by two parallel first order reactions as shown in Fig. Given

Reaction	ΔH	Rate constant	Energy of activation
$P \rightarrow A$	ΔH_A	k_A	E_A
$P \rightarrow B$	ΔH_B	k_B	E_B



Which of the following is(are) true?

(A) $a = E_B$ **(B)** $b = E_A$ **(C)** $\Delta H_A = b - d$ **(D)** $\Delta H_B = c - a$

7. Rate constant k varies with temperature by equation , $\log k(\text{min}^{-1}) = 5 - \frac{2000}{T(K)}$. We can conclude:

(A) pre–exponential factor A is 5 **(B)** E_a is 2000 kcal

(C) pre–exponential factor A is 10^5 **(D)** E_a is 9.212 kcal

8. Activation energy of a chemical reaction can be determined by :

(A) evaluating rate constant at standard temperature

(B) evaluating velocities of reaction at two different temperatures

(C) evaluating rate constant at two different temperatures

(D) changing concentration of reactants

9. Which of the following statements are correct ?

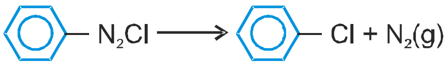
(A) Law of mass action and rate law expressions are same for single step reactions.

(B) Order of the slowest elementary reaction of a complex reaction gives the order of the complex reaction

(C) Both order and molecularity have normally a maximum value of 3

(D) Molecularity of a complex reaction, $A + 2B \longrightarrow C$ is 3.

10. Table I (reactions) and table II (method) have been matched

Table I (reactions)		**Table II (method)**	
P :	$A(g) \longrightarrow B(g) + C(g)$	X :	Titration method
Q :	$RCOOR' + H_2O \xrightarrow{H^+} RCOOH + R'OH$	Y :	Pressure measurement
R :		Z :	Volume measurement

Correct matching is :

	P	Q	R		P	Q	R
(A)	X	Y	Z	**(B)**	Y	X	Z
(C)	Z	X	Y	**(D)**	Z	Y	X

11. Which of the following statements are correct about half–period.

(A) It is proportional to initial concentration for zeroth order

(B) Average life = 1.44 half–life for first order reaction.

(C) Time of 75% completion of reaction is thrice of half–life(initial half life) period in second order reaction

(D) 99.9% reaction takes place in 100 minutes for the case when rate constant is 0.0693 min^{-1}

12. $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

Half–life period is independent of concentration of zinc at constant pH. For the constant concentration of Zn, rate becomes 100 times when pH is decreased from 3 to 2. Hence ,

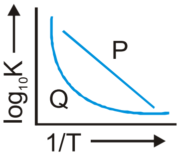
(A) $\frac{dx}{dt} = k[Zn]^0[H^+]^2$

(B) $\left(\frac{dx}{dt}\right) = k[Zn][H^+]^2$

(C) rate is not affected if concentration of zinc is made four times and that of H^+ ion is halved

(D) rate becomes four times if concentration of H^+ ion is doubled at constant Zn concentration

13. Which of the following statement are true regarding the log K vs. 1/T plot shown in the given diagram ?



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

(A) Plot P shows that the energy of activation is independent of temperature.

(B) Plot Q describes the behaviour of temperature dependence of energy of activation

(C) Arrhenius behaviour is described by P

(D) The slope of curve P gives the value $-\frac{E_a}{R}$

14. If the rate of reaction, $2SO_2(g) + O_2(g) \xrightarrow{Pt} 2SO_3(g)$ is given by : Rate $= K\frac{[SO_2]}{[SO_3]^{1/2}}$

which statements are correct :

(A) The overall order of reaction is –1/2

(B) The overall order of reaction is +1/2

(C) The reaction slows down as the product SO_3 is build up

(D) The rate of reaction does not depend upon concentration of SO_3 formed

15. For a second order reaction plots are made for $\frac{1}{[A]}$ vs time for the reaction, $2A \longrightarrow$ Product. Pick up the correct sentences.

(A) the graph will show straight line with slope K

(B) the graph will show straight line with intercept $[A]_0$

(C) the graph will show straight line with slope $[A]_0$

(D) the graph will show straight line with intercept $\frac{1}{[A]_0}$

16. $A(aq) \rightarrow B(aq) + C(aq)$ is a first order reaction.

Time	t	∞
moles of reagent	n_1	n_2

Reaction progress is measure with the help of titration of reagent 'R'.If all A, B and C reacted with reagent and have 'n' factors $\left[\text{n factors; eq.wt.} = \frac{\text{mol. wt}}{n}\right]$ in the ratio of 1 : 2 : 3 with the reagent.The k in terms of t, n_1 and n_2 is :

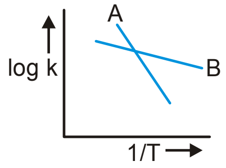
(A) $k = \frac{1}{t}\ln\left(\frac{n_2}{n_2 - n_1}\right)$ **(B)** $k = \frac{1}{t}\ln\left(\frac{2n_2}{n_2 - n_1}\right)$ **(C)** $k = \frac{1}{t}\ln\left(\frac{4n_2}{n_2 - n_1}\right)$ **(D)** $k = \frac{1}{t}\ln\left(\frac{4n_2}{5(n_2 - n_1)}\right)$

17. $A \xrightarrow{K=2\times10^{-5}\,s^{-1}} B \xrightarrow{K=8\times10^{-6}\,s^{-1}} C \xrightarrow{K=3\times10^{-3}\,s^{-1}} D$

The rate determing step of the reaction is :

(A) $A \longrightarrow B$ **(B)** $C \longrightarrow D$ **(C)** $B \longrightarrow C$ **(D)** $A \longrightarrow D$

18. The Arrhenius relationship of two different reactions is shown below. Which reaction is faster at a lower temperature and which is more sensitive to changes of temperature ?



(A) B faster, A more sensitive **(B)** B in both cases

(C) A in both cases **(D)** A faster, B more sensitive

19. Consider the following reactions at 300 K.

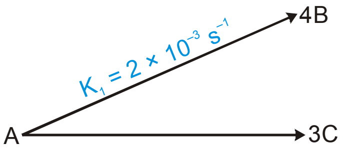
$A \rightarrow B$ (uncatalysed reaction)

$A \xrightarrow{\text{catalyst}} B$ (catalyst reaction)

The activation energy is lowered by 8.314 KJ mol^{-1} for the catalysed reaction. How many times the rate of this catalysed reaction greater than that of uncatalysed reaction ? (Given $e^{3.33} = 28$)

(A) 15 times **(B)** 38 times **(C)** 22 times **(D)** 28 times

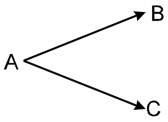
20. For the following parallel chain reaction



what will be that value of overall half-life of A in minutes? $\left[\text{Given that } \frac{[B]_t}{[C]_t} = \frac{16}{9}\right]$

(A) 3.3 **(B)** 6.3 **(C)** 3.6 **(D)** None

21. For the follwing parallel chain reaction



the overall half life of A is 12 hours If rate of formation of C is 60% of a rate of decomposition of A then what will be half life of A while it is converting into B ?

(A) 40 hours **(B)** 60 hours **(C)** 50 hours **(D)** 30 hours

22. At what time will B be present in greatest concentration ?

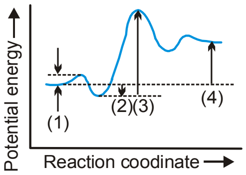
(A) $\frac{k_1}{K_2 - K_1}$ **(B)** $\frac{1}{K_1 - K_2} \ln \frac{k_1}{k_2}$ **(C)** $\frac{1}{K_2 - K_1} \ln \frac{k_1}{k_2}$ **(D)** None of these

23. For the same mechanism as Problem refer to the given Fig. and choose the correct set of identifications.

$$\underset{\text{(enzyme)}}{E} + \underset{\text{(reactant)}}{S} \rightleftharpoons \underset{\text{(intermediate-1)}}{ES}$$

$$\underset{\text{(intermediate-1)}}{ES} \rightleftharpoons \underset{\text{(intermediate-2)}}{EP}$$

$$\underset{\text{(intermediate-2)}}{EP} \rightleftharpoons \underset{\text{(enzyme)}}{E} + \underset{\text{(product)}}{P}$$



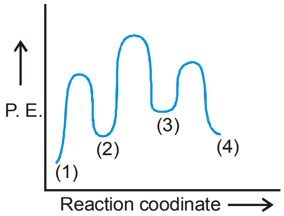
	(1)	(2)	(3)	(4)
(A)	ΔE for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	$\Delta E_{\text{overall}}$ for $S \rightarrow P$	E_a for $EP \rightarrow E + P$
(B)	E_a for $E + S \rightarrow ES$	ΔE for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	$\Delta E_{\text{overall}}$ for $S \rightarrow P$
(C)	E_a for $ES \rightarrow EP$	E_a for $EP \rightarrow E + P$	$\Delta E_{\text{overall}}$ for $S \rightarrow P$	ΔE for $EP \rightarrow E + P$
(D)	E_a for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	E_a for $EP \rightarrow E + P$	$\Delta E_{\text{overall}}$ for $S \rightarrow P$
(E)	ΔE for $E + S \rightarrow ES$	$\Delta E_{\text{overall}}$ for $S \rightarrow P$	ΔE for $_1$ $EP \rightarrow E + P$	E_a for $EP \rightarrow E + P$

24. A simple mechanism for enzyme-catalyzed reaction is given by the following set of equations

$$\underset{\text{(enzyme)}}{E} + \underset{\text{(reactant)}}{S} \rightleftharpoons \underset{\text{(intermediate-1)}}{ES}$$

$$\underset{\text{(intermediate-1)}}{ES} \rightleftharpoons \underset{\text{(intermediate-2)}}{EP}$$

$$\underset{\text{(intermediate-2)}}{EP} \rightleftharpoons \underset{\text{(enzyme)}}{E} + \underset{\text{(product)}}{P}$$

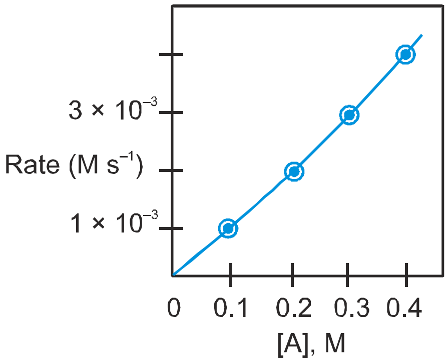


This is known as the Michaelis–Menten mechanism. The potential energy diagram is shown in the fig. Which of the following sets of identifications is correct ? (Assume that the temperature and pressure are constant).

	(1)	(2)	(3)	(4)
(A)	E + P.	EP	ES	E + S
(B)	ES	Activated complex	EP	Activated complex
(C)	EP	Activated complex	ES	Activated complex
(D)	E + S	ES	EP	E + P

25. Rate law of the reaction A → Product is, rate = k[A].

Graphically it is represented as



Hence, rate constant is :

(A) 3×10^{-4} s^{-1}

(B) 1×10^{-2} s^{-1}

(C) 3×10^{-2} s^{-1}

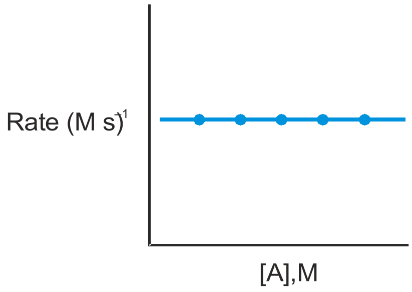
(D) 1×10^{-4} s^{-1}

26. For a given reaction A → Product, rate is 1×10^{-4} M s^{-1} when [A] = 0.01 M and rate is 1.41×10^{-4} M s^{-1} when [A] = 0.02 M. Hence, rate law is :

(A) $-\frac{d[A]}{dt} = k[A]^2$ **(B)** $-\frac{d[A]}{dt} = k[A]$ **(C)** $-\frac{d[A]}{dt} = \frac{k}{4}[A]$ **(D)** $-\frac{d[A]}{dt} = k[A]^{1/2}$

27. Following reaction can take place in both direction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$,

It is given that for the forward reaction :



and for the backward reaction

[B]	**Rate**
0.01 M	1×10^{-2} Ms^{-1}
0.02 M	2×10^{-2} Ms^{-1}

Hence, net reaction rate of B is :

(A) $= k_1[A] - k_2[B]$ **(B)** $= k_1 - k_2[B]$ **(C)** $= k_1[A] - k_2$ **(D)** $= k_1 - k_2$

28. For the complex $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2^+]$

$$\left(\frac{dx}{dt}\right) = 2 \times 10^7 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1} [Ag^+][NH_3]^2 - 1 \times 10^{-2} \text{ s}^{-1} [Ag(NH_3)_2^+]$$

Hence, ratio of rate constants of the forward and backward reactions is :

(A) 2×10^7 L^2 mol^{-2} **(B)** 2×10^9 L^2 mol^{-2} **(C)** 1×10^{-2} L^2 mol^{-2} **(D)** 0.5×10^{-9} L^2 mol^{-2}

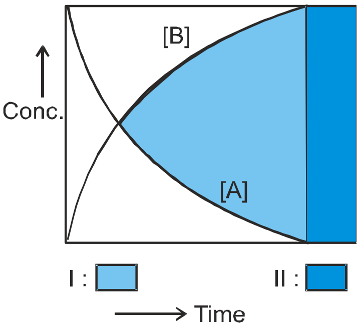
29. In the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$\left(\frac{dx}{dt}\right) = 1 \times 10^2 [N_2][H_2]^3 - 1 \times 10^{-3} [NH_3]^2 \text{ and at some instant if } \frac{[N_2][H_2]^3}{[NH_3]^2} = 10^{-5} \text{ M}^2$$

then at this instant value of $\left(\frac{dx}{dt}\right)$ is :

(A) 0 **(B)** 1×10^5 **(C)** 1×10^{-5} **(D)** 1×10^{-3}

30. In the following graphical representation for the reaction $A \longrightarrow B$ there are two types of regions :



(A) I and II both represent kinetic region at different interval
(B) I and II both represent equilibrium regions at different time interval
(C) I represents kinetic while II represents equilibrium region
(D) I represents equilibrium while II represents kinetic region

31. For the following reaction

$(CH_3)_3CCl + H_2O \longrightarrow (CH_3)_3\,COH + HCl$, $\left(\frac{dx}{dt}\right) = k[(CH_3)_3CCl]$, hence, rate determining step can be:

(A) $(CH_3)_3CCl \longrightarrow (CH_3)_3C^+ + Cl^-$
(B) $(CH_3)_3CCl + H_2O \longrightarrow (CH_3)_3COH + HCl$
(C) $(CH_3)_3C^+ + H_2O \longrightarrow (CH_3)_3COH + H^+$
(D) $H^+ + Cl^- \longrightarrow HCl$

32. For the non-equilibrium process, $A + B \rightarrow$ products, the rate is first-order w.r.t. A and second-order w.r.t. B. If 1.0 mole each of A and B introduced into a 1.0 L vessel and the initial rate was 1.0×10^{-2} mol L^{-1} s^{-1}, rate when half reactants have been turned into products is :

(A) 1.25×10^{-3} mol L^{-1} s^{-1}
(B) 1.0×10^{-2} mol L^{-1} s^{-1}
(C) 2.50×10^{-3} mol L^{-1} s^{-1}
(D) 2.0×10^{-2} mol L^{-1} s^{-1}

33. Select the correct statements out of I, II and III for zero order reaction
I : Quantity of the product formed is directly proportional to time
II : Larger the initial concentration of the reactant, greater the half-life period
III : If 50% reaction takes place in 100 minutes, 75% reaction take place in 150 minutes.

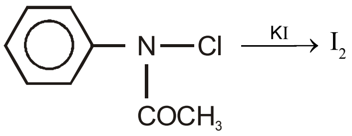
(A) I only
(B) I and II only
(C) II and III only
(D) I, II and III

34. For the first-order reaction T_{av} (average life), T_{50} and T_{75} in the increasing order are :

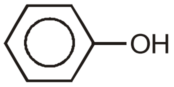
(A) $T_{50} < T_{av} < T_{75}$
(B) $T_{50} < T_{75} < T_{av}$
(C) $T_{av} < T_{50} < T_{75}$
(D) $T_{av} = T_{50} < T_{75}$

35. Which is not true for a second order reaction ?

(A) It can have rate constant 1×10^{-2} L mol^{-1} s^{-1}
(B) Its half-life is inversely proportional to its initial concentration
(C) Time to complete 75% reaction is twice of half-life
(D) $T_{50} = \frac{1}{K \times \text{Initial conc.}}$

36. 

Kinetics can be studied by titration using :

(A) $Na_2S_2O_3$
(B) $KMnO_4$
(C) $H_2C_2O_4$
(D) 

37. A certain zero order reaction has $k = 0.025$ M s^{-1} for the disappearance of A. What will be the concentration of A after 15 seconds if the initial concentration is 0.50 M ?

(A) 0.50 M
(B) 0.375 M
(C) 0.125 M
(D) 0.060 M

38. A reaction of first-order completed 90% in 90 minutes, hence, it is completed 50% in approximately :

(A) 50 min
(B) 54 min
(C) 27 min
(D) 62 min

39. T_{50} (Half-life period) of first-order reaction is 10 minute. Starting with 10 mol L^{-1}, rate after 20 minute is :

(A) 0.0693 mol L^{-1} min^{-1} **(B)** 0.0693×2.5 mol L^{-1} min^{-1}

(C) 0.0693×5 mol L^{-1} min^{-1} **(D)** 0.0693×10 mol L^{-1} min^{-1}

40. $^{M}_{Z}A(g) \longrightarrow {}^{M-8}_{Z-4}B(g) + (\alpha\text{ - particles})$

(α-particles are helium nuclei, so will form helium gas by trapping electrons)

The radioactive disintegration follows first-order kinetics Starting with 1 mol of A in a 1-litre closed flask at 27ºC pressure developed after two half-lives is approximately :

(A) 25 atm **(B)** 12 atm **(C)** 61.5 atm **(D)** 40 atm

41. A.G.M. counter is used to study the radioactive process of first-order. In absence of radioactive substance A, it counts 3 disintegration per second (dps). When A is placed in the G.M. counter, it records 23 dps at the start and 13 dps after 10 minutes. It records x dps after next 10 minutes and A has half-life period y minutes. x and y are :

(A) 8 dps, 10 min **(B)** 5 dps, 10 min **(C)** 5 dps, 20 min **(D)** 5 dps, 5 min

42. Saponification of ethyl acetate ($CH_3COOC_2H_5$) by NaOH (Saponification of ethyl acetate by NaOH is second order Rxn) is studied by titration of the reaction mixture initially having 1:1 molar ratio of the reactants. If 10 mL of 1 N HCl is required by 5 mL of the solution at the start and 8 mL of 1 N HCl is required by another 5 mL after 10 minutes, then rate constant is :

(A) $k = \frac{2.303}{10} \log \frac{10}{8}$ **(B)** $k = \frac{2.303}{10} \log \frac{10}{2}$ **(C)** $k = \frac{1}{10}\left[\frac{1}{8} - \frac{1}{10}\right]$ **(D)** $k = \frac{1}{10}\left[\frac{1}{2} - \frac{1}{10}\right]$

43. Following are the values of E_a and ΔH for three reactions carried out at the same temperature :

I : $E_a = 20$ kJ mol^{-1} , $\Delta H = -60$ kJ mol^{-1}

II : $E_a = 10$ kJ mol^{-1} , $\Delta H = -20$ kJ mol^{-1}

III: $E_a = 40$ kJ mol^{-1} , $\Delta H = +15$ kJ mol^{-1}

If all the three reaction have same frequency factor then fastest and slowest reactions are :

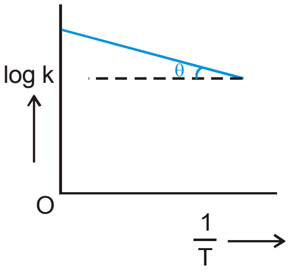
	Fastest	**Slowest**
(A)	I	II
(B)	II	III
(C)	I	III
(D)	can't be predicted.	

44. Milk turns sour at 40^{0}C three times as faster as 0^{0}C. Hence E_a in cal of process of turning of milk sour is :

(A) $\frac{2.303 \times 2 \times 313 \times 273}{40} \log 3$ **(B)** $\frac{2.303 \times 2 \times 313 \times 273}{40} \log\left(\frac{1}{3}\right)$

(C) $\frac{2.303 \times 2 \times 40}{273 \times 313} \log 3$ **(D)** None of the above

45. Graph between log k and $\frac{1}{T}$ (k is rate constant in s^{-1} and T is the temperature in K) is a straight line. As shown in figure if OX = 5 and slope of the line $= -\frac{1}{2.303}$ then E_a is :



(A) 2.303×2 cal **(B)** $\frac{2}{2.303}$ cal

(C) 2 cal **(D)** None of these

46. For the reaction $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ $\frac{dx}{dt} = k[A][B]^2$

Initial pressure of A and B are respectively 0.60 atm and 0.80 atm. At a time when pressure of C is 0.20 atm, rate of the reaction, relative to the initial value is :

(A) $\frac{1}{6}$ **(B)** $\frac{1}{48}$ **(C)** $\frac{1}{4}$ **(D)** $\frac{1}{24}$

47. If $\left(\frac{dx}{dt}\right) = k[H^+]^n$ and rate becomes 100 times when pH changes from 2 to 1. Hence, order is :

(A) 1 **(B)** 2 **(C)** 3 **(D)** 0

48. Consider following reaction, $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

Half–life period is independent of concentration of Zn at constant pH. At constant Zn concentration, half–life is 10 minutes at pH = 2 and half–life is 100 minutes at pH = 3. Hence , rate law is :

(A) $k[Zn][H^+]$ **(B)** $k[Zn][H^+]^2$ **(C)** $k[Zn]^0[H^+]$ **(D)** $k[Zn]^0[H^+]^2$

49. If the fermentation of sugar in an enzymatic solution that is 0.12 M , the concentration of the sugar is reduced to 0.06 M in 10 h and to 0.03 M in 20 h. What is the order of the reaction ?

(A) 1 **(B)** 2 **(C)** 3 **(D)** 0

50. A reaction is catalysed by H^+ ion;and in the rate law the dependence of rate is of first order with respect to the concentration of H^+ ions, in presence of HA rate constant is 2×10^{-3} min^{-1} and in presence of HB rate constant is 1×10^{-3} min^{-1}. HA and HB have relative strength as :

(A) 0.5 **(B)** 0.002 **(C)** 0.001 **(D)** 2

51. For the first-order reaction ($C = C_0 e^{-k_1 t}$) and $T_{av} = k_1^{-1}$. After two average lives concentration of the reactant is reduced to :

(A) 25% **(B)** 75% **(C)** $\frac{100}{e}$ % **(D)** $\frac{100}{e^2}$ %

52. $A(g) \longrightarrow B(g) + C(g)$

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

At the start pressure is 100 mm and after 10 min , pressure is 120 mm. hence , rate constant (min^{-1}) is :

(A) $\frac{2.303}{10}\log\frac{120}{100}$ **(B)** $\frac{2.303}{10}\log\frac{100}{20}$ **(C)** $\frac{2.303}{10}\log\frac{100}{80}$ **(D)** $\frac{2.303}{10}\log\frac{100}{120}$

53. The rate law for the dimerisation of NO_2 is

$$-\frac{d[NO_2]}{dt} = k[NO_2]^2$$

which of the following changes will change the value of the specific rate constant , k :

(A) Doubling the total pressure on the system **(B)** Doubling the temperature

(C) Both of **(A)** and **(B)** **(D)** None of the above

54. In the following reaction, how is the rate of appearance of the underlined product related to rate of disappearance of the underlined reactant :

$$BrO_3^-\,(aq) + 5\,\underline{Br^-}\,(aq) + 6\,H^+\,(aq) \longrightarrow 3\,\underline{Br_2}\,(\ell) + 3\,H_2O\,(\ell)$$

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

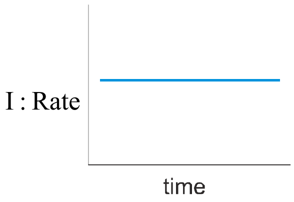
(B) $\frac{d[Br_2]}{dt} = -\frac{d[Br^-]}{dt}$

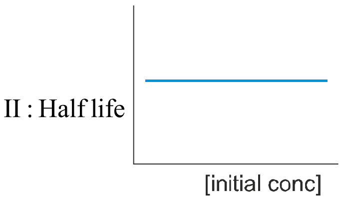
(C) $\frac{d[Br_2]}{dt} = -\frac{d[Br^-]}{dt}$

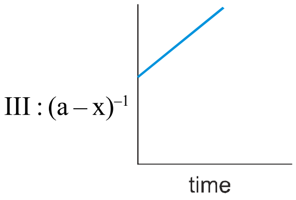
(D) $\frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$

55. Number of natural life times (T_{av}) required for a first-order reaction to achieve 99.9% level of completion is :
(A) 2.3 **(B)** 6.9 **(C)** 9.2 **(D)** 0.105

56. Match the graphical study with the order of the reactions :







A : First
B : Second
C : Zero

	I	II	III		I	II	III
(A)	A	B	C	**(B)**	B	C	A
(C)	C	B	A	**(D)**	C	A	B

57. The bromination of acetone that occurs in acid solution is represented by

$$CH_3COCH_3\,(aq) + Br_2\,(aq) \longrightarrow CH_3COCH_2Br\,(aq) + HBr\,(aq)$$

Given :

Initial concentrations			Initial Rate of Disapperance of Br_2 , Ms^{-1}
Br_2	$[CH_3COCH_3]$	M $[H^+]$	
0.050	0.30	0.050	5.7×10^{-5}
0.10	0.30	0.050	5.7×10^{-5}
0.10	0.30	0.10	1.2×10^{-4}
0.050	0.40	0.20	3.1×10^{-4}

Based on the above data , rate law is :

(A) $\left(\frac{dx}{dt}\right) = k\,[CH_3COCH_3]\,[Br_2]\,[H^+]$

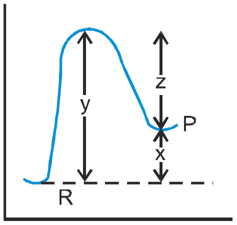
(B) $\left(\frac{dx}{dt}\right) = k\,[CH_3COCH_3]\,[H^+]$

(C) $\left(\frac{dx}{dt}\right) = k\,[CH_3COCH_3]\,[Br_2]$

(D) $\left(\frac{dx}{dt}\right) = k\,[CH_3COCH_3]\,[Br_2]\,[H^+]^2$

58. $3A \longrightarrow B + C$, It would be a zero order reaction when :
(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

59. The potential energy diagram for a reaction R $\longrightarrow$ P is given below :



ΔH^0 of the reaction corresponds to the energy –

(A) x **(B)** y **(C)** z **(D)** (x+y)

60. Read the following industrial methods for the preparation of H_2SO_4 and answer the question at the end.

Professor Molina of the Massachusetts Institute of Technology won the 1995 Nobel Prize in Chemistry for his work on atmospheric chemistry. One reaction that he has studied in detail is the acid rain reaction which produces H_2SO_4 in the atmosphere. He has proposed two possible stoichiometric reactions :

Proposal A : $H_2O(g) + SO_3(g) \longrightarrow H_2SO_4(g)$

Proposal B : $2H_2O(g) + SO_3(g) \longrightarrow H_2SO_4(g) + H_2O(g)$

Using simple collision theory , what reaction orders would be expected for proposal B ?

Proposal B is thought to proceed by the following two-step process :

$$SO_3 + 2H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO_3.2H_2O \text{ (fast)}$$

$$SO_3.2H_2O \xrightarrow{k_2} H_2SO_4 + H_2O \text{ (slow)}$$

($SO_3.2H_2O$ is a complex which is stabilized by hydrogen bonds and $k_2 << k_1$ or k_{-1}).

(A) $k[H_2O][SO_3]$ **(B)** $k[H_2O]^2[SO_3]$ **(C)** $k[SO_3]$ **(D)** $k[H_2O]$

61. In gaseous reactions important for the understanding of the upper atmosphere H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and E_a is 77 kJ mol^{-1}, then E_a for the bimolecular recombination of two OH radicals to form H_2O and O is :

(A) 3 kJ mol^{-1} **(B)** 4 kJ mol^{-1} **(C)** 5 kJ mol^{-1} **(D)** 7 kJ mol^{-1}

62. A reaction takes place in three steps having rate constants K_1, K_2, K_3 respectively. The overall rate constant $K = \frac{K_1K_3}{K_2}$. If energies of activations for the three steps are 40, 30, 20 kJ respectively, the overal energy of activation is :

(A) 10 **(B)** 15 **(C)** 30 **(D)** 60

63. Two reaction, A $\longrightarrow$ products and B $\longrightarrow$ products have rate constants K_a and K_b at temperature T and activation energies E_a and E_b respectively. If $K_a > K_b$ and $E_a < E_b$ and assuming that A for both the reactions is same then

(A) At higher temperatures K_a will be greater than K_b

(B) At lower temperature K_a and K_b will differ more and $K_a > K_b$

(C) As temperature rises K_a and K_b will be close to each other in magnitude

(D) All of the above

64. At room temperature, the reaction between NO and O_2 to give NO_2 is fast, while that between CO and O_2 is slow. It is due to :

(A) CO is smaller in size that of NO

(B) CO is poisonous

(C) The activation energy for the reaction, $2NO + O_2 \longrightarrow 2NO_2$ is less then $2CO + O_2 \longrightarrow 2CO_2$.

(D) None of the above

65. The rate law for a reaction between the substances A and B is given by rate = $K[A]^n [B]^m$. On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as :

(A) $1/2^{m+n}$ **(B)** $(m+n)$ **(C)** $(n-m)$ **(D)** $2^{(n-m)}$

66. Which of the following statement is/are correct ?

(A) A second order reaction must be a bimolecular elementary reaction
(B) A bimolecular elementary reaction must be a second order reaction
(C) Zero order reaction must be a complex reaction
(D) First order reaction may be complex or elementary reaction

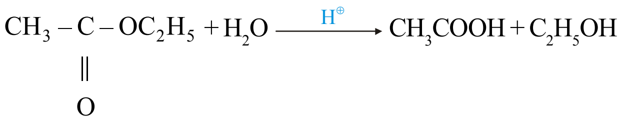
67. For the reaction $2A + B \longrightarrow C$ with the rate law $\frac{d[C]}{dt} = k[A]^1[B]^{-1}$ and started with A and B in stoichiometric proportion. Which is/are true?

(A) unit of k is Ms^{-1}
(B) [A], [B] and [C] all will be linear functions of time
(C) $[C] = 2kt$
(D) $[C] = kt$

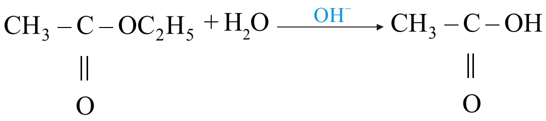
68. For a second order reaction plots are made for $\frac{1}{[A]}$ vs time for the reaction, $2A \longrightarrow$ Product. Pick up the correct sentences.

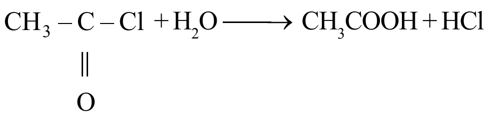
(A) the graph will show straight line with slope K
(B) the graph will show straight line with intercept $[A]_0$
(C) the graph will show straight line with slope $[A]_0$
(D) the graph will show straight line with intercept $\frac{1}{[A]_0}$

69. Which of the following are example of Pseudo uni molecular reaction?

(A)

$CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5+H_2O\xrightarrow{H^{\oplus}}CH_3COOH+C_2H_5OH$

(B) $C_{12}H_{22}O_{11}+H_2O\xrightarrow{H^{\oplus}}C_6H_{12}O_6\text{ (glucose)}+C_6H_{12}O_6\text{ (fructose)}$

(C)

$CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5+H_2O\xrightarrow{OH^{-}}CH_3-\underset{\underset{O}{\|}}{C}-OH$

(D)

$CH_3-\underset{\underset{O}{\|}}{C}-Cl+H_2O\longrightarrow CH_3COOH+HCl$

70. In the following gaseous phase first order reaction

$$A(g) \longrightarrow 2B(g) + C(g)$$

initial pressure was found to be 400 mm and it changed to 1000 mm after 20 min. Then :

(A) Half life for A is 10 min **(B)** Rate constant is $0.0693\ min^{-1}$
(C) Partial pressure of C at 30 min is 350 mm **(D)** Total pressure after 30 min is 1100 mm

71. For the consecutive reaction $A\xrightarrow{k_1(\text{time}^{-1})}B\xrightarrow{k_2(\text{time}^{-1})}C$ following curves were obtained depending upon the relative values of k_1 & k_2

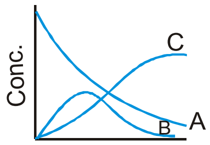


Figure 1

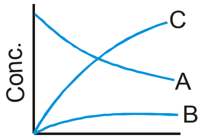


Figure 2

Now which of the following is the correct match

(A) figure 1 – ($k_1 < k_2$)

(B) figure 2 – ($k_1 < k_2$)

(C) figure 2 – ($k_1 >> k_2$)

(D) figure 1 – ($k_1 >> k_2$)

72. A large increase in the rate of a reaction for a rise in temperature is due to

(A) increase in the number of collisions

(B) the increase in the number of activated molecules

(C) The shortening of mean free path

(D) the lowering of activation energy

73. Which of the following statements about the arrhenius equation are correct ?

(A) The pre exponential factor become equal to the rate constant of the reaction at temperature T $\rightarrow \infty$

(B) When the activation energy of the reaction $\rightarrow$ zero, the rate becomes independent of temperature.

(C) The term $e^{-Ea/RT}$ represents the fractions of the molecules having energy is excess of the threshold value.

(D) On raising temperature , rate constant of the reaction of greater activation energy increases less rapidly than that of the reaction of smaller activation energy.

74. Select the correct statements :

(A) the molecularity of an elementary reaction indicates how many reactant molecules take part in the step.

(B) the rate law of an elementary reaction can be predicted by simply seeing the stoichiometry of reaction.

(C) the slowest elementary step in sequence of the reactions governs the overall rate of formation of product.

(D) a rate law is often derived from a proposed mechanism by imposing the steady state approximation or assuming that there is a pre-equilibrium.

75. Which of the following are true about rate of a reaction?

(A) Rate of a reaction cannot be negative

(B) Rate of a reaction is change in concentration of the reactant per unit time per mol

(C) Average rate and instantaneous rate can never be equal.

(D) Rate depends upon surface area of the reactants.

Part # II [Assertion & Reason Type Questions]

Each question has 5 choices (A), (B), (C), (D) and (E) out of which only one is correct.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(C) Statement-1 is True, Statement-2 is False.
(D) Statement-1 is False, Statement-2 is True.
(E) Statement-1 and Statement-2 both are False.

1. **Statement-1 :** If the activation energy of reaction is zero temperature will have no effect on the rate constant
Statement-2 : Lower the activation energy faster is the reaction

2. **Statement-1 :** In $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

If half life of A is very less as compared to B, so the net reaction is $A \longrightarrow C$ with rate constant $(k_1 \times k_2)$

Statement-2 : Slowest step is the rate determining step so $B \longrightarrow C$ is rate determining step.

3. **Statement-1 :** For $A + 2B \longrightarrow C$ (rate$= K[A]^1[B]^0$), the half life time of reaction is only defined when conc. of A and B are in stoichiometric ratio
Statement-2 : For above given order half life of reaction is directly proportional to conc. of A and not to conc. of B due to its zero order.

4. **Statement-1 :** Many reactions occurring on solid surface are zero order reactions.
Statement-2 : $N_2O(g) \xrightarrow{Au} N_2(g) + 1/2O_2$; rate $= k[N_2O]^0 = k =$ constant is a zero order reaction.

5. **Statement-1 :** Half life of a certain radioactive element is 100 days. After 200 days, fraction left undecaye will be 25%.
Statement-2 : $\frac{C_t}{C_0} = \left(\frac{1}{2}\right)^n$, where symbols have standard meaning.

6. **Statement-I :** The pre-exponential factor A has the same units for all reactions.
Statement-II : $e^{-E_a/RT}$ has no unit.

7. **Statement-I :** Disintegration ${}_1H^3$ (tritium) is accompained by β-emission.
Statement-II : Tritium has high n/p ratio.

8. **Statement-I :** Neutrons are the best bombarding particles.
Statement-II : Neutrons are neutral particles.

9. **Statement-I :** The order of reaction can have fractional value.
Statement-II : For an elementary reaction, the partial orders are determined by the reaction stoichiometry.

10. **Statement-I :** Catalyst can increase that rate constant to a large extent.
Statement-II : By using suitable catalyst, we can significantly increase yield.

11. **Statement-I :** Product can form only when the required orientation and energy conditions are met.
Statement-II : All collisions between reactants yield the desired product.

Exercise # 3 Part # I [Matrix Match Type Questions]

1. Match the following :

Column-I	**Column-II**
(A) $A + B \longrightarrow C + D$ $r = k_1 [A] [B]$	**(p)** Unit of rate constant possess concentration unit
(B) $A + B \longrightarrow C + D$ $r = k_2 [A] [B]^o$	**(q)** Rate constant for the reaction of both the reactants are equal
(C) $A + B \longrightarrow C + D$ $r = k_3 [A]^o [B]^o$	**(r)** Rate of consumption of at least one of the reactants is equal to rate of production of at least one of the products
(D) $2A + B \longrightarrow 2C + 3D$ $r = k_3 [A]^o [B]^o$	**(s)** If both reactants are taken in stoichiometric ratio, half life for both reactants are equal.

2. Match the following :

Column-I **(Graph)**	**Column-II** **(Slope)**
(A) C Vs t (abscissa) for zero order	**(p)** unity
(B) log C Vs t (abscissa) for first order	**(q)** zero
(C) $\left(\frac{-dc}{dt}\right)$ Vs c for zero order	**(r)** $-k$
(D) $\ln\left(\frac{-dc}{dt}\right)$ Vs ℓnc for first order	**(s)** $-\frac{k}{2.303}$

3. Match the following :

Column-I	**Column-II**
(A) If the activation energy is 65 kJ then how much time faster a reaction proceed at 25°C than at 0°C	**(p)** 2
(B) Rate constant of a first - order reaction is $0.0693\ \text{min}^{-1}$. If we start with $20\ \text{mol L}^{-1}$, it is reduced to $2.5\ \text{mol L}^{-1}$ in how many minutes	**(q)** Zero
(C) Half - lives of first - order and zero order reactions are same. Ratio of rates at the start of reaction is how many times of 0.693 Assume initial concentration to be same for the both.	**(r)** 11
(D) the half-life periods are given , (see data below) order of the reaction is	**(s)** 30

(D) data:

$[A]_0$	(M)	0.0677	0.136	0.272
$t_{1/2}$	(sec)	240	480	960

4. The decomposition of ammonia on platinum surface follow the change,

$2NH_3 \rightarrow N_2 + 3H_2$; $K = 2.5 \times 10^{-4}\ Ms^{-1}$ & $-\dfrac{d[NH_3]}{dt} = \dfrac{K_1[NH_3]}{1+K_2[NH_3]}$,

where K_1 and K_2 are constant.

	Column-I		**Column-II**
(A)	$\dfrac{-d[NH_3]}{dt}$	**(p)**	Rate of formation of H_2
(B)	$\dfrac{d[N_2]}{dt}$	**(q)**	2.5×10^{-4} M sec^{-1}
(C)	$\dfrac{d[H_2]}{dt}$	**(r)**	Rate of decompositon of NH_3
(D)	If the decomposition is zero order, the rate of production of N_2	**(s)**	First
(E)	If the decomposition is zero order, the rate of production of H_2	**(t)**	Rate of formation of N_2
(F)	the order for decomposition of NH_3 if $[NH_3]$ is very very less	**(u)**	Zero
(G)	the order for decomposition of NH_3 if $[NH_3]$ very very high	**(v)**	7.5×10^{-4} M sec^{-1}

Part # II [Comprehension Type Questions]

Comprehension # 1

Set-I (Without catalyst)

Reaction	Temperature	E (activation)	k
$A \rightarrow B$	T_1K	Ea_1	k_1
$A \rightarrow B$	T_2K	Ea_2	k_2

Set-II (With catalyst)
(Consider catalyst being positive only)

Reaction	Temperature	E (activation)	k
$A \rightarrow B$	T_1K	Ea_3	k_3
$A \rightarrow B$	T_2K	Ea_4	k_4

1. For the (Set-1) :

(A) if $T_1 > T_2$, $k_1 > k_2$ always

(B) if $T_1 > T_2$, $k_1 > k_2$ (for exothermic reaction)

(C) if $T_1 > T_2$, $k_1 < k_2$ (for endothermic reaction)

(D) $Ea_1 \neq Ea_2$

2. For the (Set-1) :

(A) $Ea_1 > Ea_2$ if $T_1 > T_2$ **(B)** $Ea_1 < Ea_2$ if $T_1 > T_2$

(C) $Ea_1 = Ea_2$ **(D)** $Ea_1 = 0.5\ Ea_2$

3. Comparing set-I and II :

(A) $k_4 > k_3$ & $k_2 > k_1$, if $T_2 > T_1$ (endothermic) **(B)** $k_4 < k_3$ & $k_2 > k_1$, if $T_2 < T_1$ (endothermic)

(C) $k_4 > k_3$ & $k_2 > k_1$, if $T_2 < T_1$ (exothermic) **(D)** $k_4 < k_3$ & $k_2 < k_1$, if $T_2 > T_1$ (exothermic)

Comprehension # 2

$$A(g) \longrightarrow 2B(g) + C(g)$$

Initially at $t = 0$ gas A was present along with some amount of gas **(C)**. At $t = 0$ mole fraction of gas C is 1/3. After some time $t = t_1$, total pressure is half of the final total pressure at $t = t_x$ (a very long time). Assume this decomposition is a first order, at a constant temperature. It is also given at $t = t_x$, final total pressure is 35 bar.

1. At $t = t_1$ pressure of gas B is :
(A) 2.5 bar **(B)** 1.25 bar **(C)** 5.0 bar **(D)** data is insufficient

2. Rate constant (k) = (log 64 – log 49) s^{-1}. Value of t_1 in seconds is :
(A) 2.15 s **(B)** 1.5 s **(C)** 2.3 s **(D)** 1.15 s

3. Ratio of rate constant at $t = 0$ to $t = t_1$ to $t = t_x$ is :
(A) 2 : 3 : 4 **(B)** 1 : 1 : 1 **(C)** 1 : 3 : 5 **(D)** 1 : 3 : 5

Comprehension # 3

Competing First-Order Reactions

Frequently a species can react in different ways to give a variety of products. For example, toluene can be nitrated at the ortho, meta, or para positions, We shall consider the simplest case, that of two competing irreversible first-order reactions :

$$A \xrightarrow{k_1} C \text{ and } A \xrightarrow{k_2} D$$

where the stoichiometric coefficients are taken as unity for simplicity. The rate law is

$$\left(\frac{d[A]}{dt}\right) = -k_1[A] - k_2[A] = -(k_1 + k_2)[A] \qquad \Rightarrow \qquad [A] = [A]_0 e^{-(k_1+k_2)t}.$$

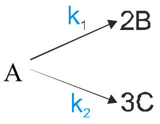
For C, we have $\left(\frac{d[C]}{dt}\right) = k_1[A] = k_1[A]_0 e^{-(k_1+k_2)t}$. Multiplication by dt and integration from time 0

(where $[C]_0 = 0$) to an arbitary time t gives $\quad [C] = \dfrac{k_1[A]_0}{k_1 + k_2}(1 - e^{-(k_1+k_2)t})$

Similarly, integration of $\left(\frac{d[D]}{dt}\right)$ gives $\quad [D] = \dfrac{k_2[A]_0}{k_1 + k_2}(1 - e^{-(k_1+k_2)t})$

The sum of the rate constants $k_1 + k_2$ appears in the exponentials for both [C] and [D].

At any time we also have $\dfrac{[C]}{[D]} = \dfrac{k_1}{k_2}$

1. 

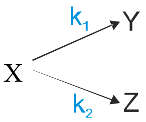
starting initially with only A Which of the following is correct at time t

(A) $[A]_0 = [A]_t + [B]_t + [C]_t$

(B) $[A]_0 = [A]_t + 2[B]_t + 3[C]_t$

(C) $[A]_0 = [A]_t + \dfrac{[B]_t}{2} + \dfrac{[C]_t}{3}$

(D) $[A]_0 = \dfrac{2}{3}[A]_t + [B]_t + [C]_t$

2. X 

starting with only 'X', ratio $\frac{[X]_t}{[Y]_t+[Z]_t}$

(A) Independent of time **(B)** $\frac{1}{(e^{kt}-1)}$

(C) Depends upon initial concentration of X **(D)** $[A]_0\,(e^{kt}-1)$

3. At high temperature acetic acid decomposes into CO_2 & CH_4 and simultaneously into CH_2CO (ketene) and H_2O

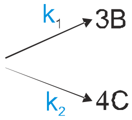
(i) $CH_3COOH \xrightarrow{k_1=3s^{-1}} CH_4+CO_2$

(ii) $CH_3COOH \xrightarrow{k_2=4s^{-1}} CH_2CO+H_2O$

What is the fraction of acetic acid reacting as per reaction (i) ?

(A) $\frac{3}{4}$ **(B)** $\frac{3}{7}$

(C) $\frac{4}{7}$ **(D)** none of these

4. For A 

starting with pure A ratio of rate of production of B to C is

(A) Independent of time
(B) Independent of temperature
(C) Depends upon initial concentration of A
(D) Independent of mechanism of reaction

Comprehension # 4

Study the two photochemical reactions and answer the question at the end.
For the overall reaction between A and B to yield C and D , two mechanisms are proposed :

I. $A+B \longrightarrow AB^* \longrightarrow C+D$, $k_1 = 1\times10^{-5}\ M^{-1}\ s^{-1}$

II. $A \longrightarrow A^* \longrightarrow E$, $k_1 = 1\times10^{-4}\ s^{-1}$

$E+B \longrightarrow C+D$, $k_2 = 1\times10^{10}\ M^{-1}\ s^{-1}$

(species with * are short-lived)

1. Rate according to mechanism I when concentration of each reactant is 0.1 M will be :
(A) $1\times10^{-7}\ Ms^{-1}$ **(B)** $1\times10^{-6}\ Ms^{-1}$
(C) $1\times10^{-5}\ Ms^{-1}$ **(D)** $1\times10^{-4}\ Ms^{-1}$

2. Rate according to mechanism II when concentration of each reactant is 1 M will be :
(A) $1\times10^{-4}\ Ms^{-1}$ **(B)** $1\times10^{10}\ Ms^{-1}$
(C) $1\times10^{-6}\ Ms^{-1}$ **(D)** $1\times10^{-10}\ Ms^{-1}$

3. At what concentration of B, rates of two mechanism are equal :
(A) 1 M **(B)** 5 M **(C)** 7 M **(D)** 10 M

Comprehension # 5

Study the following experiment and answer the questions at the end of it.
The following reactions was studied at 25^{0}C in benzene solution containing 0.10 M pyridine

$$\underset{A}{CH_3OH} + \underset{B}{(C_6H_5)_3\,CCl} \longrightarrow \underset{C}{(C_6H_5)_3\,C\,.\,OCH_3} + HCl$$

The following sets of data were observed :

Set	Initial concentration		time difference	Final concentration [C]
	[A]0	[B]0		
I	0.10 M	0.05 M	25 min	0.0033 M
II	0.10 M	0.10 M	15 min	0.0039 M
III	0.20 M	0.10 M	7.5 min	0.0077 M

1. Rates $\frac{d[C]}{dt}$ in sets I , II and III are respectively (in M min^{-1}) :

	I	II	III
(A)	1.30×10^{-4}	2.6×10^{-4}	1.02×10^{-3}
(B)	0.033	0.0039	0.0077
(C)	0.02×10^{-4}	0.04×10^{-4}	0.017
(D)	None of above		

2. Rate law of the above experiment is :
(A) $r = k\,[A]\,[B]$
(B) $r = k\,[A]^3\,[B]$
(C) $r = k\,[A]\,[B]^2$
(D) $r = k\,[A]^2\,[B]^0$

3. Rate constant of the above experiment is :
(A) 1.3×10^{-1}
(B) 2.6×10^{-2}
(C) 2.6×10^{-1}
(D) 1.3×10^{-2}

Comprehension # 6

The instantaneous rate of an elementary chemical reaction : aA + bB $\rightleftharpoons$ cC + dD can be given by : rate = $K_f[A]^a\,[B]^b - K_b\,[C]^c\,[D]^d$ where, K_f and K_b are rate constants for forward and backward reactions respectively for the reversible reaction. If the reaction is an irreversible one, the rate is expressed as : rate = $K[A]^a\,[B]^b$ where K is rate constant for the given irreversible reaction and (a + b) is order of reaction. It is also evident from the stoichiometry of reaction that rate of disappearance of A is $\frac{a}{b}$ times the rate of disappearance of B. The variation of rate constant K with temperature is expressed in terms of Arrhenius equation :

$K = Ae^{-E_a/RT}$ whereas the ratio $\frac{K_f}{K_b}$ is expressed in terms of van't Hoff isochore :

$\frac{K_f}{K_b} = Ae^{-\Delta H/RT}$, where E_a and ΔH are energy of activation and heat of reaction respectively.

1. For a chemical reaction aA → bB ;

$$\log\left[-\frac{d[A]}{dt}\right] = \log\left[\frac{d[B]}{dt}\right] + 0.3,$$

then the ratio of a and b is approximately :
(A) 3
(B) 0.3
(C) 2
(D) 0.5

2. The variation of K and $\frac{K_f}{K_b}$ with increase in temperature shows the following effects :

(i) For endothermic reaction K increase, $\frac{K_f}{K_b}$ also increases

(ii) For endothermic reaction K decreases, $\frac{K_f}{K_b}$ also decreases.

(iii) For exothermic reaction K and $\frac{K_f}{K_b}$ both increases.

(iv) For exothermic reaction K increases and $\frac{K_f}{K_b}$ decreases

(v) For exothermic reaction K and $\frac{K_f}{K_b}$ both decreases.

(A) i, iv **(B)** iii, v **(C)** ii, iii **(D)** ii, iii, v

3. For a gaseous phase I order reaction : $A(g) \longrightarrow B(g) + 2C(g)$ (rate constant $K = 10^{-2}$ $time^{-1}$), in a closed vessel of 2 litre containing 5 mole of A(g) at 27°C, which of the following is incorrect ?
(A) Rate of appearance of C(g) is 5×10^{-2} mol L^{-1} t^{-1}
(B) Rate of disappearance of A(g) is 6.15×10^{-3} atm t^{-1}
(C) Rate of disappearance of A(g) is 5.0×10^{-2} mol t^{-1}
(D) Rate of appearance of B(g) is 5×10^{-2} mol L^{-1} t^{-1}

4. For an elementary reaction $aA \longrightarrow$ product, the graph plotted between log $\left[\frac{-d[A]}{dt}\right]$ vs. time gives a straight line with intercept equal to 0.6 and showing an angle of 45° with origin, then :
(A) rate constant = 3.98 $time^{-1}$ and a = 1
(B) rate constant = 3.98 mol L^{-1} t^{-1} and a = 1
(C) rate constant = 1.99 $time^{-1}$ and a = 1
(D) rate constant = 1.99 mol^{-1} L^{1} t^{-1} and a = 2

Comprehension # 7

The thermal decomposition of N_2O_5 occurs as : $2N_2O_5 \longrightarrow 4NO_2 + O_2$

Experimental studies suggest that rate of decomposition of N_2O_5, rate of formation of NO_2 or rate of formation of O_2 all becomes double if concentration of N_2O_5 is doubled.

1. The correct mechanism for decomposition of N_2O_5 is :

(A) $N_2O_5 \xrightarrow{\text{Slow}} NO_2 + NO_3 ; N_2O_5 + NO_3 \xrightarrow{\text{Fast}} 3NO_2 + O_2$

(B) $N_2O_5 \xrightarrow{\text{Fast}} NO_2 + NO_3 ; N_2O_5 + NO_3 \xrightarrow{\text{Slow}} 3NO_2 + O_2$

(C) $N_2O_5 \xrightarrow{\text{Fast}} 2NO_2 + \frac{1}{2} O_2$

(D) $N_2O_5 \xrightarrow{\text{Slow}} NO + NO_2 + 2O_2 ; N_2O_5 + NO_2 \xrightarrow{\text{Fast}} 3NO_2 + \frac{1}{2} O_2$

2. If rate constants for decomposition of N_2O_5, formation of NO_2 and formation of O_2 are K_1, K_2 and K_3 respectively, then

(A) $K_1 = K_2 = K_3$
(B) $2K_1 = K_2 = 4K_3$
(C) $K_1 = 2K_2 = K_3$
(D) $K_1 = K_2 = 2K_3$

3. If rate of formation of O_2 is 16 g/hr, then rate of decomposition of N_2O_5 and rate of formation of NO_2 respectively is:

(A) can not be calculated without knowing rate constants

(B) 108 g/hr, 92 g/hr

(C) 32 g/hr, 64 g/hr

(D) 54 g/hr, 46 g/hr

4. The container of 2 litre contains 4 mole of N_2O_5. On heating to 100°C, N_2O_5 undergoes complete dissociation to NO_2 and O_2. Select the correct answers if rate constant for decomposition of N_2O_5 is 6.2×10^{-4} sec^{-1}.

1. The mole ratio before and after dissociation is 4 : 2.

2. Half life of N_2O_5 is 1117 sec and it is independent of temperature.

3. Time required to complete 40% of reaction is 824 sec.

4. If volume of container is doubled, the rate of decomposition becomes half of the initial rate :

(A) 1, 3, 4 **(B)** 1, 2, 3, 4 **(C)** 3, 4 **(D)** 2, 3, 4

Exercise # 4

[Subjective Type Questions]

1. Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volumes was left open. Due to this, some H_2O_2 decomposed. To determine the new volume strength after 6 hours, 10 mL of this solution was diluted to 100 mL. 10 mL of this diluted solution was titrated against 25 mL of 0.025M $KMnO_4$ solution under acidic conditions.

Calculate the rate constant for decomposition of H_2O_2. [$\ln \frac{20}{17.5} = 0.1335$]

2. A quantity of ethyl acetate is mixed with an excess of sodium hydroxide at 25ºC. 100 c.c. of the mixture is immediately titrated against 0.05 N Hydrochloric acid, of which 75 c.c. were required for neutralisation. After 30 minutes, 50 c.c. of the mixture required, similarly, 25 c.c. of the acid. When the original reaction of ester was complete 25 c.c. of the mixture required 6.25 c.c. of the acid. Calculate the second order velocity constant (at time = 0) of the reaction, using concentration in moles per litre and time in minutes. Reaction is first order each w.r.t. NaOH & ester. Indicator chosen for above titration is such that, it gives end point when hydrochloric acid reacts with NaOH only. ($\log 2 = 0.30, \log 3 = 0.48, \ln 10 = 2.3$)

3. A certain reactant B^{n+} is getting converted to $B^{(n+4)+}$ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing reagent which only reacts with B^{n+} and $B^{(n+4)+}$. In this process, it converts B^{n+} to $B^{(n-2)+}$ and $B^{(n+4)+}$ to $B^{(n-1)+}$. At t=0, the volume of the reagent consumed is 25 ml and at t = 10 min, the volume used up is 32 ml. Calculate the rate constant of the conversion of B^{n+} to $B^{(n+4)+}$ assuming it to be a first order reaction.

4. Decomposition of ammonia on platinum surface follow the change,

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

(a) What does $\frac{-d\,[NH_3]}{dt}$ denote ?

(b) What does $\frac{d\,[N_2]}{dt}$ and $\frac{d\,[H_2]}{dt}$ denote?

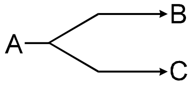
(c) If the decomposition is zero order then what are the rate of production of N_2 and H_2 if $k = 2.5 \times 10^{-4}\ Ms^{-1}$?

(d) If the rate obeys $-\frac{d\,[NH_3]}{dt} = \frac{k_1\,[NH_3]}{1+k_2[NH_3]}$, what will be the order for decomposition of NH_3 if (i) $[NH_3]$ is very very less and (ii) $[NH_3]$ is very very high K_1 and K_2 are constant.

5. A 1mL sample of a bacterial culture at 37^0C is taken, and diluted to 10 L. A 1mL sample of the diluted culture is spread on a culture plate. Ten minutes later, another 1mL sample taken from the original culture diluted and spread in the same way. The two plates are incubated for 24 hours. The first sample exhibits 48 colonies of bacteria, the second 72 colonies. If we assume that each colony originates with a single bacterium, what is the generation time (time required for doubling the population).

6. The acid catalysed hydrolysis of an organic compound A at 30^0C has a time for half change of 100 minutes, when carried out in a buffer solution at pH 5 and of 10 minutes, when carried out at pH 4. Both times of half change are independent of the initial concentration of A. If the rate of reaction is given by $\frac{-d[A]}{dt} = k[A]^a[H^+]^b$, what are the values of a and b?

7. An organic compound A decomposes by following two parallel first order mechanisms:



$\frac{k_1}{k_2} = \frac{1}{9}$ and $k_1 = 1.3 \times 10^{-5}\ sec^{-1}$.

Calculate the concentration ratio of C to A, if an experiment is allowed to start with only A for one hour.

8. The formation in water of *d*–potassium chromo–oxalate from its *l*–form is reversible reaction which is first order in both directions, the racemate being the equilibrium product. A polarimeter experiment at 22^{0}C showed that, after 506 sec, 12 mole % of the *l*–isomer was converted to the *d*–form. Find the rate constant for the forward and the reverse reactions.

9. For an isomerisation reaction $A \overset{\text{catalyst}}{\rightleftharpoons} B$ in gaseous phase, the equilibrium constant at 60°C is 3.60. Both forward and backward reactions are of first order. Starting with an initial pressure of P atm, of A, the pressure became 0.25 P atm in 40 minutes. Find the values of individual rate constants for the forward and backward reactions.

10. Experiment shows that the equilibrium constant of the reaction :

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

is 2.8 at room temperature, and the velocity constant of the forward reaction is 0.002. When a catalyst is added this velocity constant is increased to 0.0045. What is now the velocity constant of the backward reaction?

11. A 1st order chemical reaction was carried out for 1.0 hour in absence of a catalyst and 20% reaction was complete. A catalyst was then added and reaction was allowed to continue for next 30 min when 60% reaction was complete. A second catalyst was then added at this time and reaction was allowed to continue for further 10 min. when 90% reaction was complete. If activation energy of the original path was 80 kJ, determine activation energies of catalyzed pathways. Assume constant temperature throughout to be 300 K.

12. Derive an expression for the velocity of reaction :

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

With the help of following mechanism

$N_2O_5 \xrightarrow{K_a} NO_2 + NO_3$; $NO_3 + NO_2 \xrightarrow{K_{-a}} N_2O_5$

$NO_2 + NO_3 \xrightarrow{K_b} NO_2 + O_2 + NO$; $NO + NO_3 \xrightarrow{K_c} 2NO_2$

13. Mole percentage of A as a function of time in the following reversible first order reaction $A \rightleftharpoons B$ are :

Time (hr)	0	1	Infinity
Mole % of A	100	75	30

Determine mole percentage of A after four hour from the beginning.

14. The mean life of a first order reaction at 610 K is 127 hours. What fraction of the initial concentration will decompose in 42 hours at 600 K, given that the activation energy is 30 Kcal mol^{-1} ?

15. Two reaction (i) A → products (ii) B → products, follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310K. The half life for this reaction at 310K is 30 minutes. At temperature 310 K, B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300K.

16. Derive an expression for the velocity of reaction :

$$H_2\,(g) + Br_2\,(g) \longrightarrow 2HBr\,(g)$$

With the help of following mechanism

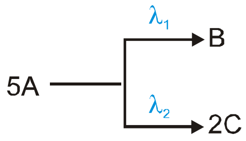
$Br_2 \xrightarrow{k_1} 2Br$; $Br + H_2 \xrightarrow{k_2} HBr + H$

$H + Br_2 \xrightarrow{k_3} HBr + Br$; $H + HBr \xrightarrow{k_4} H_2 + Br$; $Br + Br \xrightarrow{k_5} Br_2$

17. ${}_{84}Po^{210}$ decays with alpha to ${}_{82}Pb^{206}$ with half life of 138.4 days. If 1.0 gram of Po^{210} is placed in a sealed tube, how much helium will accumulate in 69.2 days? Express the answer in cm^3 at S.T.P.

18. The energy of activation for a reaction is 100 kJ mol^{-1}. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 20°C ; other things being equal ?

19. A follows parallel path I order reactions giving B and C as :



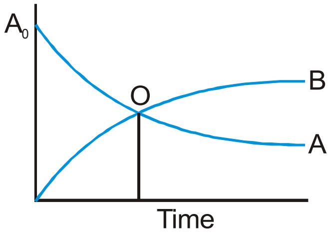
If initial concentration of A is 0.25 M calculate the concentration of C after 5 hrs. of reaction

Given : $\lambda_1 = 1.5 \times 10^{-5}$ sec^{-1} ; $\lambda_2 = 5 \times 10^{-6}$ sec^{-1}

20. Two reactants A and B separately shows two chemical reactions. Both reactions are made with same initial concentration of each reactant. Reactant A follows first order kinetics whereas reactant B follows second order kinetics. If both have same half lives, compare their rates (a) at the start of reaction (b) after the lapse of one half life.

21. Figure represents the variation of the concentrations of A and B with time for the reaction :

$A \longrightarrow nB$. Calculate the concentration of B at the point of intersection O.



22. The net rate of reaction for the change :

$$[Cu(NH_3)_4]^{2+} + H_2O \rightleftharpoons [Cu(NH_3)_3H_2O]^{2+} + NH_3 \text{ is,}$$

$$\frac{dx}{dt} = 2.0 \times 10^{-4} [Cu(NH_3)_4]^{2+} - 3.0 \times 10^{5} [Cu(NH_3)_3H_2O]^{2+}[NH_3]$$

Calculate :

(i) rate expression for forward and backward reaction.

(ii) the ratio of rate constants for forward and backward reaction.

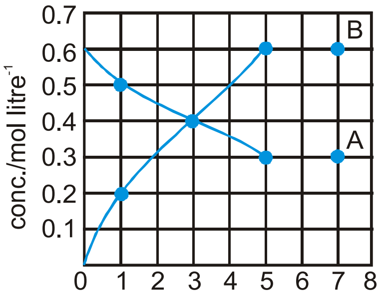
(iii) the direction of reaction in which the above reaction will be more predominant.

23. The catalytic decomposition of formic acid may take place in two ways :

(i) $HCOOH(g) \longrightarrow H_2O(g) + CO(g)$ **(ii)** $HCOOH(g) \longrightarrow H_2(g) + CO_2(g)$

The rate constant and activation energy for reaction (i) are 2.79×10^{-3} min^{-1} at 237°C and 12.0 kcal mol^{-1} respectively. These values for reaction (ii) are 1.52×10^{-4} min^{-1} at 237°C and 24.5 kcal mol^{-1} respectively. Find out the temperature at which equimolar quantities of H_2O, CO, CO_2 and H_2 are formed. (R = 2 cal) ?

24. The progress of the reaction, $A \rightleftharpoons nB$ with time is presented in the figure. Determine :



(i) the value of n **(ii)** the equilibrium constant K and **(iii)** the initial rate of conversion of A.

25. The reaction, $A + OH^- \longrightarrow$ Products, obeys rate law expression as, $\frac{-d[A]}{dt} = k[A][OH^-]$. If initial concentrations of [A] and [OH^-] are 0.002 M and 0.3 M respectively and if it takes 30 sec for 1% A to react at 25°C, calculate the rate constant for the reaction.

26. Catalytic decomposition of nitrous oxide by gold at 900°C at an initial pressure of 200 mm was 50% in 53 minute and 73% in 100 minute. (a) What is order of reaction ? (b) Calculate velocity constant. (c) How much will it decompose in 100 minutes at the same temperature but at an initial pressure of 600 mm ?

27. The gas phase decomposition of dimethyl ether follows first order kinetics,

$$CH_3OCH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

The reaction is carried out in a constant volume container at 500°C and has a half life of 14.5 minute. Initially only dimethyl ether is present at a pressure of 0.40 atmosphre. What is the total pressure of the system after 12 minute ? Assume ideal gas behaviour.

28. The half time of first order decomposition of nitramide is 2.1 hour at 15°C.

$$NH_2NO_2(aq) \longrightarrow N_2O(g) + H_2O(\ell).$$

If 6.2 g of NH_2NO_2 is allowed to decompose, calculate : (i) time taken for NH_2NO_2 to decomposition 99% (ii) volume of dry N_2O produced at this point measured at STP.

29. The reaction :

$$CH_3COF + H_2O \longrightarrow CH_3COOH + HF$$

has been studied under the following initial conditions :

Case-I	**Case-II**
$C^{\circ}_{H_2O} = 1.00\text{ M}$	$C^{\circ}_{H_2O} = 0.02\text{ M}$
$C^{\circ}_{CH_3COF} = 0.01\text{ M}$	$C^{\circ}_{CH_3COF} = 0.80\text{ M}$

Concentrations were monitored as a function of time and are given below :

	Case-I		**Case-II**
t/min	C_{CH_3COF} /M	t/min	C_{H_2O} /M
0	0.01000	0	0.0200
10	0.00857	10	0.0176
20	0.00735	20	0.0156
40	0.00540	40	0.0122

Determine the order of the reaction and the rate constant for the reaction.

30. Show that for a first order reaction, time required for 99.0% completion is twice for the time required for the completion of 90% of the reaction.

31. At 100°C, a gaseous reaction, $A \longrightarrow B + 2C$, is observed to be of I order. On starting with pure A, at the end of 14 minute, the total pressure was found to be 264 mm of Hg. After a long time the total pressure of the system was 450 mm of Hg. Calculate (a) initial pressure of A (b) rate constant of reaction (c) half life period of reaction.

32. The conversion of trypsinogen (A) and trypsin (B) is an autocatalytic reaction, $A \longrightarrow B$, where B catalyses the reaction. The rate equation is $\frac{-dx}{dt} = K \cdot x \cdot y$, where x and y are concentration of tripsinogen at time t. Integrate this equation for initial concentration of x_0 and y_0 for A and B. Show that, $Kt = \frac{2.303}{x_0 + y_0} \log \frac{y \cdot x_0}{x \cdot y_0}$.

33. The rate constant for the II order neutralization of 2-nitropropane by aqueous alkali obeys the equation

$$\log_{10} K = \frac{3163}{T} + 12$$

T is temperature in Kelvin.

Time and concentration were in minute and mol litre^{-1} respectively. Calculate half life at 43.3°C and for an initial concentration of 0.001 mol litre^{-1} for each of the reactant.

34. In the decomposition of H_2O_2 at 300 K, the energy of activation was found to be 18 kcal/mol while it decreases to 6 kcal/mol when the decomposition was carried out in the presence of a catalyst at 300 K. How many times is the catalysed reaction faster than uncatalysed one ?

35. The rate of decomposition of a substance increases by a factor 2.25 for 1.5 times increase in concentration of substance at same temperature. Find out order of reaction.

36. A substance A is mixed with equal quantities of the substance B and C. At the end of 1000 second, half of the amount of A has reacted. What fraction of A will be left unreacted at the end of 2000 second. If the reaction is (a) zero order with respect to A ? (b) II order with respect to A ?

37. Acetone on heating gives CO and other hydrocarbons at 600°C. The reaction obeys Ist order kinetics with respect to acetone concentration. The half life period is 81 sec. Calculate the time in which acetone taken in a container at 600° reduces its pressure from 0.5 atm to 0.4 atm.

38. The specific rate constant of the decomposition of N_2O_5 is 0.008 min^{-1}. The volume of O_2 collected after 20 minute is 16 mL. Find the volume that would be collected at the end of reaction. NO_2 formed is dissolved in CCl_4.

39. For a homogenous gaseous reaction, $A \longrightarrow B + C + D$, the initial pressure was P_0 while pressure after time t was P. Derive an expression for rate constant K in terms of P_0 and t.

40. In a II order reaction, when the concentration of both the reactants are equal, the reaction is completed 20% in 500 sec. How long it would take for the reaction to go to 60% completion ?

41. Half-life period for decomposition of NH_3 over tungsten wire are given below :

Initial Pressure in min	50	100	200
$T_{1/2}$	3.52	1.82	0.93

Calculate order of reaction.

42. A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives are 54.0 min for A and 18.0 min for B. If the concentrations of A and B are equal initially, how long will it take for the concentration of A to be four times that of B ?

43. Compounds A and B react to form C and D in a reaction that was found to be second-order overall and second-order in A. The rate constant at 30°C is 0.622 L mol^{-1} min^{-1}. What is the half-life of A when 4.10×10^{-2} M of A is mixed with excess B ?

44. Acetoacetic acid, CH_3COCH_2COOH, in acid solution decomposes to CO_2 and acetone by a first–order reaction. From the following data find the half–life time for this reaction at 37^0C.

A solution containing 6 mmol sodium acetoacetate was rapidly brought into about 0.2M HCl so that the total volume was 200ml. After 220 min. at 37^0C, a sample of 10 ml was taken out and immediately put into an excess of NaOH, which put an end to the decomposition. The acetone that had formed was blown away by bubbling air. The sample was again acidified and boiled; all the remaining acetoacetic acid was then transformed to acetone, which was distilled with water vapour. To this distillate, NaOH and 10.00 ml 50 mM I_2 solution were added, transforming all acetone to iodoform

$$CH_3COCH_3 + 3I_2 + 4OH^- \rightarrow CHI_3 + CH_3COO^- + 3I^- + 3H_2O$$

After acidification the remaining iodine was decolorize by 4.5 ml thiosulfate solution. Ten ml 50 mM I_2 solution was decolourized by 10 ml of the same thiosulfate solution. At pH = 0 to 3 the reaction rate is independent of pH.

45. A 22.4 litre flask contains 0.76 mm of ozone at 25°C. Calculate :

(i) the concentration of oxygen atom needed so that the reaction, $O + O_3 \rightarrow 2O_2$ having rate constant equal to 1.5×10^7 litre mol^{-1} sec^{-1} can proceed with a rate of 0.15 mol $litre^{-1}$ sec^{-1}.

(ii) the rate of formation of oxygen under this condition.

46. A vessel contains dimethyl ether at a pressure of 0.4 mm. Dimethyl ether decomposes as :

$CH_3OCH_3(g) \longrightarrow CH_4(g) + CO(g) + H_2(g)$. The rate constant of decomposition is 4.78×10^{-3} min^{-1}. Calculate the ratio of initial rate of diffusion to rate of diffusion after 4.5 hours of initiation of decomposition. Assume the composition of gas present and gas diffused to be same.

47. A certain reaction $A + B \longrightarrow$ Product is first-order w.r.t. each reactant with $k = 5.0 \times 10^{-3}$ M^{-1} s^{-1}. Calculate the concentration of A remaining after 100 s if the initial concentration of A was 0.1 M and that of B was 6.0 M. State any approximation made in obtaining your result.

Exercise # 5 Part # I [Previous Year Questions] [AIEEE/JEE-MAIN]

1. 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 : **[AIEEE- 2004]**

(A) 30 minutes **(B)** 15 minutes **(C)** 7.5 minutes **(D)** 60 minutes

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

(A) unit of k must be sec^{-1}

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

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

(D) value of k is independent of initial concentrations of A and B.

3. 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 : **[AIEEE- 2004]**

(A) 1.042 g **(B)** 2.084 g **(C)** 3.125 g **(D)** 4.167 g.

4. Consider an endothermic reaction $X \longrightarrow Y$ with the activation energies E_b and E_f for the backward and forward reaction, respectively. In general **[AIEEE- 2005]**

(A) $E_b < E_f$ **(B)** $\Delta H = \Delta U$ **(C)** $\Delta H < \Delta U$ **(D)** $\Delta H > \Delta U$

5. A reaction involving two different reactants can never be : **[AIEEE- 2005]**

(A) unimolecular reaction **(B)** first order reaction

(C) second order reaction **(D)** bimolecular reaction

6. 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 be **[AIEEE- 2006]**

(A) remain unchanged **(B)** tripled

(C) increased by a factor of 4 **(D)** doubled

7. The following mechanism has been proposed for the reaction of NO with Br_2 to form NOBr.

$$NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)\ ;\ NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g) \qquad \text{(slow step)}$$

If the second step is the rate determining step, the order of the reaction with respect to NO(g) is **[AIEEE- 2007]**

(A) 1 **(B)** 0 **(C)** 3 **(D)** 2

8. 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 catalyst will be (in kJ mol^{-1}). **[AIEEE- 2007]**

(A) 280 **(B)** 20 **(C)** 300 **(D)** 120

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

(A) 10 days **(B)** 100 days **(C)** 1000 days **(D)** 300 days

10. For a reaction $\frac{1}{2}A \longrightarrow 2B$, rate of disappearance of 'A' related to the rate of appearance of 'B' by the expression. **[AIEEE- 2008]**

(A) $-\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$ **(B)** $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$ **(C)** $-\frac{d[A]}{dt} = 4\frac{d[B]}{dt}$ **(D)** $-\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$

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

(A) 23.03 minutes **(B)** 46.06 minutes **(C)** 460.6 minutes **(D)** 230.3 minutes

12. 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? **[AIEEE - 2010]**

(A) 4 h **(B)** 0.5 h **(C)** 0.25 h **(D)** 1 h

13. Consider the reaction **[AIEEE - 2010]**

$$Cl_2\,(aq) + H_2S(aq) \longrightarrow S(s) + 2H^+\,(aq) + 2Cl^-\,(aq)$$

The rate equation for this reaction is, rate = k $[Cl_2][H_2S]$

Which of these mechanisms is/are consistent with this rate equation?

A. $Cl_2 + H_2S \longrightarrow H^+ + Cl^- + Cl^+ + HS^-$ (slow) ; $Cl^+ + HS^- \longrightarrow H^+ + Cl^- + S$ (fast)

B. $H_2S \Leftrightarrow H^+ + HS^-$ (fast equilibrium) ; $Cl_2 + HS^- \longrightarrow 2Cl^- + H^+ + S$ (slow)

(A) B only **(B)** Both A and B **(C)** Neither A nor B **(D)** A only

14. The rate of a chemical reaction doubles for every 10ºC rise of temperature. If the temperature is raised by 50ºC, the rate of the reaction increases by about : **[AIEEE - 2011]**

(A) 10 times **(B)** 24 times **(C)** 32 times **(D)** 64 times

15. A reactant **(A)** forms two products :

$A \xrightarrow{k_1} B$, 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 : **[AIEEE - 2011]**

(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)** $k_1 = 2k_2 e^{Ea_2/RT}$

16. For a first order reaction **(A)** $\rightarrow$ 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 : **[AIEEE - 2012]**

(A) 1.73×10^{-5} M/min **(B)** 3.47×10^{-4} M/min

(C) 3.47×10^{-5} M/min **(D)** 1.73×10^{-4} M/min

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

18. 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: **[JEE(Mains) - 2016]**

(A) 6.93×10^{-4} mol min^{-1} **(B)** 2.66 L min^{-1} at STP

(C) 1.34×10^{-2} mol min^{-1} **(D)** 6.93×10^{-2} mol min^{-1}

19. 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 In (k_2/k_1) is equal to : (R = 8.314 J $mol^{-1}K^{-1}$) **[JEE(Mains) - 2017]**

(A) 8 **(B)** 12 **(C)** 6 **(D)** 4

20. 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 :

[JEE(Mains) - 2018]

(A) 3 **(B)** 1 **(C)** 0 **(D)** 2

Part # II [Previous Year Questions][IIT-JEE ADVANCED]

1. Given $X \longrightarrow$ product (Taking 1st order reaction)

conc (mol/lit)	0.01	0.0025
time(min)	0	40

Initial rate of reaction is in mol /ℓ/min. **[JEE-2004]**

(A) 3.43×10^{-4} **(B)** 1.73×10^{-4} **(C)** 3.43×10^{-5} **(D)** 1.73×10^{-5}

2. Initial rates, r_0, of the $A + B \rightarrow P$ at different initial concentrations of A and B ($[A]_0$ and $[B]_0$) are given below:

$[A]_0$ (mol L^{-1})	$[B]_0$ (mol L^{-1})	r_0 (mol L^{-1} s^{-1})
0.1	0.1	0.05
0.2	0.1	0.10
0.1	0.2	0.05

(A) Write the rate equation.

(B) Calculate the rate constant of the reaction. **[JEE-2004]**

3. For a reaction $2X(g) \longrightarrow 3Y(g) + 2Z(g)$ the following data is obtained.

Time (min)	Px (mm of Hg) (Partial pressure of X)
0	800
100	400
200	200

Find order with respect to X, rate constant of the reaction, time taken for 75% completion and find the total pressure when partial pressure of X, Px = 700 mm of Hg. **[JEE-2005]**

Comprehension

Carbon–14 is used to determine the age of organic material. The procedure is based on the formation of ^{14}C by neutron capture in the upper atmosphere.

$$^{14}_{7}N + {}_0n^1 \longrightarrow {}^{14}_{6}C + {}_1p^1$$

^{14}C is absorbed by living organisms during photosynthesis. The ^{14}C content is constant in living organism, once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of ^{14}C in the dead being, falls due to the decay which C^{14} undergoes

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + \beta^-$$

The half life period of ^{14}C is 5770 years. The decay constant (λ) can be calculated by using the following formula

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

The comparison of the β^- activity of the dead matter with that of the carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method however, ceases to be accurate over periods longer than 30,000 years. The proportion of ^{14}C to ^{12}C in living matter is 1 : 10^{12}.

4. Which of the following option is correct? **[IIT-JEE 2006]**

(A) Rate of exchange of carbon between atmosphere and living is slower than decay of ^{14}C.
(B) Carbon dating can be used to find out the age of earth crust and rocks
(C) Rate of exchange of ^{14}C between atmosphere and living organism is so fast that an equilibrium is set up between the intake of ^{14}C by organism and its exponential decay.
(D) Carbon dating can not be used to determine concentration of ^{14}C in dead beings.

5. What should be the age of fossil for meaningful determination of its age? **[IIT-JEE 2006]**

(A) 6 years
(B) 6000 years
(C) 60,000 years
(D) It can be used to calculate any age

6. A nuclear explosion has taken place leading to increase in concentration of ^{14}C in nearby areas. ^{14}C concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be T_1 and T_2 at the places respectively then **[IIT-JEE 2006]**

(A) The age of the fossil will increase at the place where explosion has taken place and $T_1 - T_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$

(B) The age of the fossil will decrease at the place where explosion has taken place and $T_1 - T_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$

(C) The age of fossil will be determined to be same

(D) $\frac{T_1}{T_2} = \frac{C_1}{C_2}$

7. Consider a reaction aG + bH → Products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is : **[JEE-2007]**

(A) 0
(B) 1
(C) 2
(D) 3

8. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio $\left(\frac{k_1}{k_0}\right)$ of the rate constant for first order (k_1) and zero order (k_0) of the reaction is. **[JEE-2008]**

(A) 0.5 mol^{-1} dm^3
(B) 1.0 mol dm^{-3}
(C) 1.5 mol dm^{-3}
(D) 2.0 mol^{-1} dm^3

9. For a first order reaction A → P, the temperature (T) dependent rate constant (k) was found to follow the equation $\log k = -(2000)\frac{1}{T} + 6.0$. The pre-exponential factor A and the activation energy E_a, respectively, are : **[JEE-2009]**

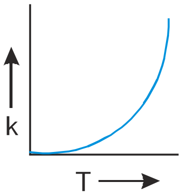
(A) $1.0 \times 10^6\ s^{-1}$ and 9.2 kJ mol^{-1}
(B) 6.0 s^{-1} and 16.6 kJ mol^{-1}
(C) $1.0 \times 10^6\ s^{-1}$ and 16.6 kJ mol^{-1}
(D) $1.0 \times 10^6\ s^{-1}$ and 38.3 kJ mol^{-1}

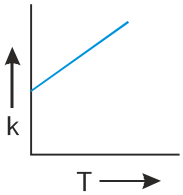
10. The concentration of R in the reaction $R \rightarrow P$ was measured as a function of time and the following data is obtained **[JEE-2010]**

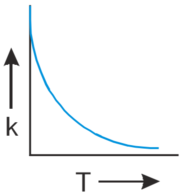
[R](molar)	1.0	0.75	0.40	0.10
t(min.)	0.0	0.05	0.12	0.18

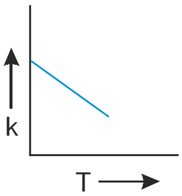
The order of the reaction is :

11. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is : **[JEE-2010]**

(A)


(B)


(C)


(D)


12. For the first order reaction $2N_2O_5\,(g) \rightarrow 4NO_2(g) + O_2\,(g)$ **[JEE-2011]**
(A) The concentration of the reaction decreases exponentially with time
(B) The half-life of the reaction decreases with increasing temperature
(C) The half-life of the reaction depends on the initial concentration of the reactant
(D) The reaction proceeds to 99.6% completion in eight half-life duration

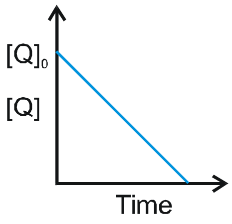
13. An organic compound undergoes first-order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\frac{[1_{t/8}]}{[t_{1/10}]}\times 10$?$(\log_{10}2 = 0.3)$

[JEE-2012]

14. In the reaction, $P + Q \longrightarrow R + S$

the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is :

[JEE(Advanced) 2013]



(A) 2 **(B)** 3
(C) 0 **(D)** 1

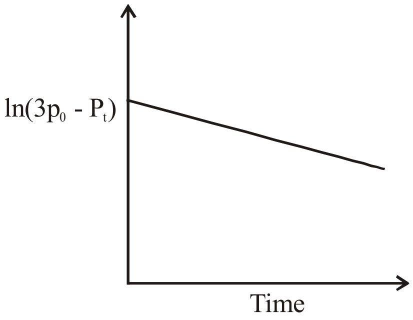
15. According to the Arrhenius equation, **[JEE(Advanced) 2016]**
(A) a high activation energy usually implies a fast reaction
(B) rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy
(C) higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant
(D) the pre – exponential factor is a measure of the rate at which collisions occur, irrespective of their energy.

16. In a bimolecular reaction, the steric factor P was experimentally determined to be 4.5. The correct option(s) among the following is(are) **[JEE(Advanced) 2017]**
(A) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation
(B) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally
(C) The activation energy of the reaction is unaffected by the value of the steric factor
(D) Since P = 4.5, the reaction will not proceed unless an effective catalyst is used

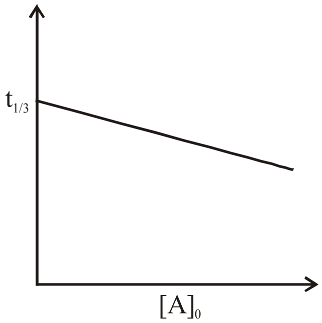
17. For a first order reaction $A(g) \rightarrow 2B(g) + C(g)$ at constant volume and 300 K, the total pressure at the beginning ($t = 0$) and at time t are P_o and P_t, respectively. Initially, only A is present with concentration $[A]_0$, and $t_{1/3}$ is the time required for the partial pressure of A to reach 1/3rd of its initial value. The correct option(s) is (are)

(Assume that all these gases behave as ideal gases) **[JEE(Advanced) 2018]**

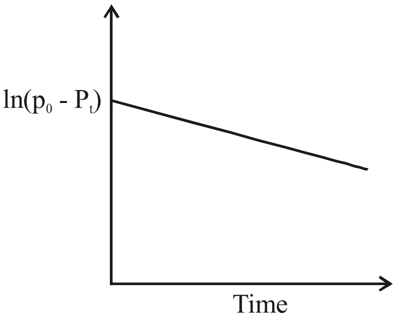
(A)



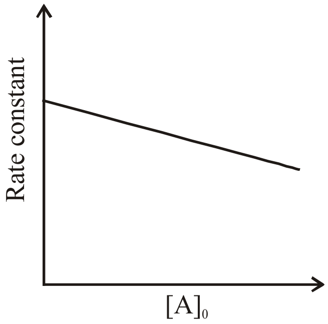
(B)



(C)



(D)



18. Consider the following reversible reaction **[JEE(Advanced) 2018]**

$$A(g) + B(g) \rightleftharpoons AB(g)$$

The activation energy of the backward reaction exceeds that of the forward reaction by 2 RT (in J mol^{-1}). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of ΔG° (in J mol^{-1}) for the reaction at 300 K is _______.

(Given : $\ln(2) = 0.7$, $RT = 2500$ J mol^{-1} at 300 K and G is the Gibbs energy)

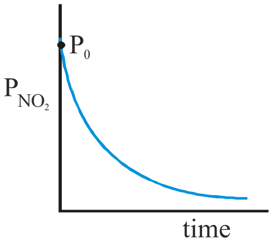
MOCK TEST

SECTION - I : STRAIGHT OBJECTIVE TYPE

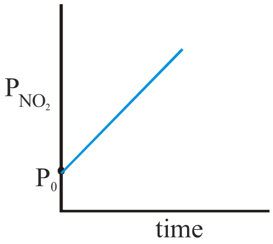
1. $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

When N_2O_5 decompose, its $t_{1/2}$ does not change with its changing pressure during the reaction. So which one is the correct representation for "pressure of NO_2" vs "time" during the reaction when initial $P_{N_2O_5}$ is equals to P_0.

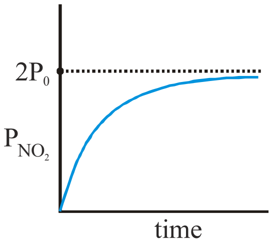
(A)



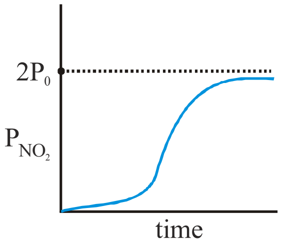
(B)



(C)



(D)



2. Choose the correct option :

(a) Antineutrino can be detected during the emission of :

(i) α-rays (ii) β-particles (iii) Protons (IV) X-rays

(b) Which has magic number of neutrons :

(i) $^{27}_{13}Al$ (ii) $^{209}_{83}Bi$ (iii) $^{238}_{92}U$ (iv) $^{56}_{26}Fe$

(c) $^{210}_{84}Po \longrightarrow ^{206}_{82}Pb + ^{4}_{2}He$. In this reaction predict the position of group of Po when lead is in the IVB group :

(i) II A (ii) IV B (iii) VIB (iv) VIA

(d) Which of the following can show γ-radiations :

(i) $^{81}_{37}Rb + ^{0}_{-1}e \longrightarrow ^{81}_{36}Kr + ...$ (ii) $^{11}_{6}C \longrightarrow ^{11}_{5}B + ...$

(iii) $^{11}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ...$ (iv) $^{60m}_{27}Co \longrightarrow ^{60}_{27}Co + ...$

(A) a – i, b – ii, c – iii, d – iv **(B)** a – ii, b – i, c – iii, d – iii

(C) a – ii, b – ii, c – iii, d – iv **(D)** a – ii, b – ii, c – iv, d – iv

3. In a hypothetical reaction

$$A\,(aq) \rightleftharpoons 2\,B(aq) + C\,(aq) \qquad (1^{st} \text{ order decomposition})$$

'A' is optically active (dextro-rotatory) while 'B' and 'C' are optically inactive but 'B' takes part in a titration reaction (fast reaction) with H_2O_2. Hence the progress of reaction can be monitored by measuring rotation of plane of plane polarised light or by measuring volume of H_2O_2 consumed in titration.

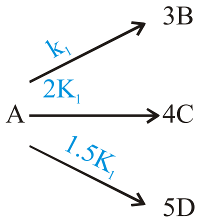
In an experiment the optical rotation was found to be $\theta = 30°$ at t 20 min and $\theta = 15°$ at $t = 50$ min. from start of the reaction. If the progress would have been monitored by titration method, volume of H_2O_2 consumed at $t = 30$ min. (from start) is 3d ml then volume of H_2O_2 consumed at $t = 90$ min will be :

(A) 60 ml **(B)** 45 ml **(C)** 52.5 ml **(D)** 90 ml

4. The elementary reaction $A + B \rightarrow$ products has $k = 2 \times 10^{-5}\ M^{-1}\ S^{-1}$ at a temperature of 27°C. Several experimental runs are carried out using stoichiometric proportion. The reaction has a temperature coefficient value of 2.0. At what temperature of should the reaction be carried out if inspite of halving the concentrations, the rate of reaction is desired to be 50% higher than a previous run. (Given $\dfrac{\ell n6}{\ell n2} = 2.585$).

(A) 47°C **(B)** 53°C **(C)** 57°C **(D)** 37°C

5.



All reactions are of 1st order

At time $t = t_1$ $(t_1 > 0)$

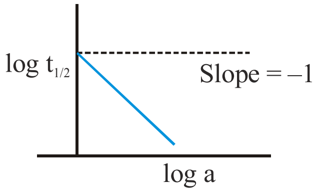
$\dfrac{[B]}{[C]} = \alpha$. Therefore at

time $t = t_2$ (where $t_2 \geq t_1$)

$\dfrac{[C]}{[D]} = \beta$ which of the following is correct.

(A) $\alpha > \beta$ **(B)** $\alpha = \beta$ **(C)** $\alpha\beta = 0.4$ **(D)** $\alpha + \beta = 0.4$

6. A graph between log $t_{1/2}$ and log a (abscissa) a being the initial concentration of A in the reaction For reaction $A \rightarrow$ Product, is the rate law is



(A) $\dfrac{-d[A]}{dt} = K$ **(B)** $\dfrac{-d[A]}{dt} = K[A]$ **(C)** $\dfrac{-d[A]}{dt} = K[A]^2$ **(D)** $\dfrac{-d[A]}{dt} = K[A]^3$

7. For the reaction $R - X + OH^- \rightarrow ROH + X^-$ The rate is given of Rate $= 5.0 \times 10^{-5}\ [R - X]\ [OH^-] + 0.20 \times 10^{-5}\ [R - X]$ what percentage of R – X Reaction by SN^2 mechanism when $[OH^-] = 1.0 \times 10^{-2}$ M

(A) 96.1 % **(B)** 3.9% **(C)** 80% **(D)** 20 %

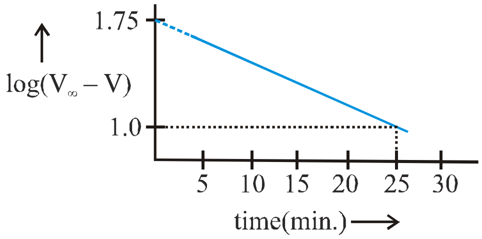
8. For a reaction the variation of the constant with temperature is given by the equation

$$\text{In}\, k_t = \text{In}\, k_0 + \frac{(\text{In}\,3)t}{10} \qquad (t \le 0°C)$$

The value of the temperature coefficient of the reaction is

(A) 0.1 **(B)** 1.0 **(C)** 10 **(D)** 3

9. The plot of log $(V_\infty - V)$ versus t (where V is the volume of nitrogen collected under constant temperature and pressure conditions) for the decomposition of $C_6H_5N_2Cl$ is given at 50°C with an amount of $C_6H_5N_2Cl$ equivalent to 58.3 cc N_2.



The rate constant for the reaction in hr^{-1} expressing your answer in a single significant digit is

(A) 1 **(B)** 2 **(C)** 4 **(D)** 8

10. The high temperature (≈ 1200 K) decomposition of $CH_3COOH(g)$ occurs as follows as per simultaneous 1st order reactions.

$$CH_3COOH \xrightarrow{k_1} CH_4 + CO_2$$

$$CH_3COOH \xrightarrow{k_2} CH_2CO + H_2O$$

What would be the % of CH_4 by mole in the product mixture (excluding CH_3COOH)?

(A) $\frac{50k_1}{(k_1+k_2)}$ **(B)** $\frac{100k_1}{(k_1+k_2)}$ **(C)** $\frac{200k_1}{(k_1+k_2)}$ **(D)** it depends on time

11. The inversion of cane sugar proceeds with half life of 600 minute at pH = 5 for any concentration of sugar, However at pH = 6, the half life changes to 60 minute, The rate law expression for sugar inversion can be written as

(A) $r = k\,[\text{sugar}]^2\,[H^+]^0$ **(B)** $r = k\,[\text{sugar}]^1[H^+]^0$ **(C)** $r = k\,[\text{sugar}]^2\,[H^+]^1$ **(D)** $r = k[\text{sugar}]^0[H^+]^{-1}$

12. A hypothetical reaction :

$A_2 + B_2 \longrightarrow$ 2AB Follows mechanism as given below :

$A_2 \underset{}{\overset{k_c}{\rightleftharpoons}} A + A$ .... (fast) (K_c – is equilibrium constant)

$A + B_2 \overset{k_1}{\rightleftharpoons} AB + B$ .... (slow) (k_1 – rate constant)

$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AB$ .... (fast) (k_2, k_1 – are rate constant)

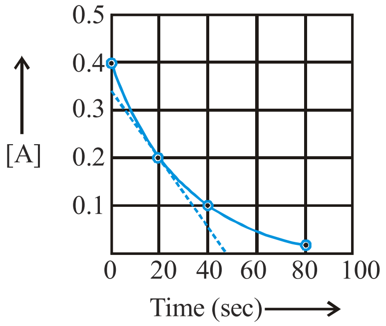
The order of overall reaction is :

(A) 2.5 **(B)** 1 **(C)** 3/2 **(D)** Zero

13. For the system $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$, $A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C$ which was started with only A the equilibrium concentration $[A]_{eq}$ is correctly related to $[B]_{eq}$ and $[C]_{eq}$ as :

(A) $\frac{k_{-1}[B]_{eq} + k_{-2}[C]_{eq}}{(k_1+k_2)}$ **(B)** $\frac{k_{-1}[B]_{eq} - k_{-2}[C]_{eq}}{(k_1-k_2)}$ **(C)** $\frac{k_{-1}[B]_{eq} + k_{-2}[C]_{eq}}{(k_1-k_2)}$ **(D)** $\frac{k_{-1}[B]_{eq} - k_{-2}[C]_{eq}}{(k_1+k_2)}$

14. A certain reaction A → B follows the given concentration (Molarity) – time graph. Which of the following statement is true?



(A) The reaction is second order with respect to A

(B) The rate for this reaction at 40 second will be approximately 3.5×10^{-3} M s^{-1}

(C) The rate for this reaction at 80 second will be 1.75×10^{-3} M s^{-1}

(D) The [B] will be 0.25 M at t = 60 second

SECTION - II : MULTIPLE CORRECT ANSWER TYPE

15. For the consecutive reaction $A \xrightarrow{k_1(\text{time}^{-1})} B \xrightarrow{k_2(\text{time}^{-1})} C$ following curves were obtained depending upon the relative values of k_1 & k_2

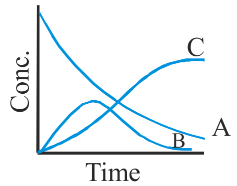


Figure 1

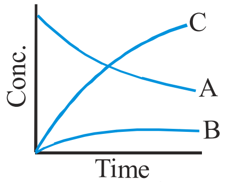


Figure 2

Now which of the following is the correct match

(A) figure 1 – ($k_1 < k_2$)

(B) figure 2 – ($k_1 < k_2$)

(C) figure 2 – ($k_1 >> k_2$)

(C) figure 1 – ($k_1 >> k_2$)

16. The reaction $2NO + Br_2 \longrightarrow 2NOBr$ follows the mechanism :

(A) $NO + Br_2 \xrightleftharpoons{\text{Fast}} NOBr_2$

(B) $NOBr_2 + NO \xrightleftharpoons{\text{Slow}} 2NOBr$

Which of the following is/are true regarding this :

(A) The order of the reaction with respect to NO is two.

(B) The molecularity of the steps **(A)** and **(B)** are two each.

(C) The molecularity of the overall reaction is three.

(D) The overall order of the reaction is three

17. The polarimeter readings in an experiment to measure the rate of inversion of cane sugar (1st order reaction) were as follows

time (min)	:	0	30	∞
angle (degree)	:	30	20	– 15

Identify the **true** statement(s) log 2 = 0.3, log 3 = 0.48, log 7 = 0.84, $\log_e 10 = 2.3$

(A) The half life of the reaction is 75 min

(B) The solution is optically inactive at 120 min.

(C) the equimolar mixture of the products is dextroroatory

(D) The angle would be 7.5° at half time

18. Identify the true statement(s)

(A) A catalyst is chemically unchanged at the end of a reaction

(B) A catalyst may appear in the kinetic rate equation of the reaction

(C) A catalyst will not affect the composition of an equilibrium mixture

(D) A catalyst cannot cause a non-spontaneous ($\Delta G > 0$) reaction to proceed

19. Rate of a chemical reaction $2A(g) \longrightarrow B(g)$ is defined as

$$\text{'}r_B\text{'} = \frac{1}{V}\frac{dn_B}{dt}$$

Where n_B = number of moles of B formed and C_B = concentration of B then which of the following relation is correct

(A) $r_B = \frac{dC_B}{dt} + \frac{C_B}{V}\frac{dV}{dt}$ (If volume V is not constant)

(B) $r_B = \frac{dC_B}{dt}$ (If volume V is constant)

(C) $r_B = \frac{dC_B}{dt} - \frac{C_B}{V}\frac{dV}{dt}$ (If volume V is not constant)

(D) $r_B = \frac{dC_B}{dt} - \frac{C_B}{V}\frac{dV}{dt}$ (If volume V is not constant)

SECTION - III : ASSERTION AND REASON TYPE

20. **Statement -1 :** If the order reaction is zero than degree of dissociation will be independent upon initial concentration.

Statement - 2 : The degree of dissociation of Zero order reaction is given by $\alpha = \frac{kt}{c_0}$

(A) Statement - 1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement - 1.

(B) Statement - 1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1.

(C) Statement-1 is True, Statement-2 is False.

(D) Statement-1 is False, Statement-2 is True.

21. **Statement-1 :** For $A + 2B \longrightarrow C$ (rate = $K[A]^1[B]^0$, the half life time of reaction is only defined when conc of A and B are in stoichiometric ratio

Statement - 2 : For above given order half life of reaction is directly proportional to conc of A and not to conc of B due to its zero order.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

22. **Statement-1 :** Many reactions occurring on solid surface are zero order reactions.

Statement-2 : $N_2O(g) \xrightarrow{Au} N2(g) + 1/2O_2$; rate = $k[N_2O]^0 = k$ = constant is a zero order reaction.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(C) Statement-1 is True, Statement-2 is False

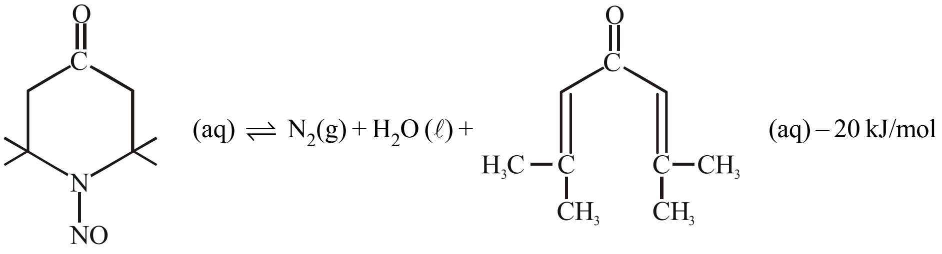
(D) Statement-1 is False, Statement-2 is True

SECTION - IV : COMPREHENSION TYPE

Read the following comprehensions carefully and answer the questions.

Comprehension # 1

Consider the inter conversion of nitrosotriacetoamine into nitrogen phorone and water.



The reaction is 1^{st} order in each direction, with an equilibrium constant of 10^4, the activation energy for the forward reaction is 57.45 kJ/mol. Assuming arrhenius pre exponential factor of $10^{12}\ s^{-1}$.

23. What is the expected forward constant at 300K, if we initiate this reaction starting with only reactant

(A) 10^2 **(B)** 10^6 **(C)** 10^8 **(D)** 10^4

24. If the change in entropy of the reaction is 0.07 KJ. $K^{-1}\ mol^{-1}$ at 1 atm pressure. Calculate up to which temperature the reaction would not be spontaneous. (For forward reaction)

(A) $T < 258.7$ K **(B)** $T > 250$ K **(C)** $T < 340.2$ K **(D)** $T > 200$K

25. Calculate Kp of the reaction at 300 K

(A) $2.4 \times 10^4\ atm^{-1}$ **(B)** 10^4 atm **(C)** 24.6×10^4 atm **(D)** $2.82 \times 10^2\ atm^{-1}$

Comprehension # 2

Reactions Tending To Equilibrium

Not all chemical reactions proceed to a stage at which the concentrations of the reactants become vanishingly small. Here we consider the kinetics of such reactions.

Let a reaction be represented in general terms by the scheme

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

where k_1 and k_{-1} represent the rate constant for the forwards and reverse reactions, respectively. The equilibrium constant for this reaction may be written as

$$K = [B]_\infty / [A]_\infty = k_1/k_{-1} \qquad ...(1)$$

where the subscript ∞ refers to a time t, sufficiently long to establish equilibrium at the given temperature.

The initial concentration of species A is $[A]_0$, and that of B is $[B]_0$. After a time t, let the concentration of species A be $[A]_t$ and that of B be $[B]_t$. The total rate of change of $[A]_t$ is given by

$$d[A]_t/dt = -k_1[A]_t + k_{-1}[B]_t$$

If, as is usual, $[B]_0$ is initially zero, it follows from a mass balance that at any time t, $[B]_t = [A]_0 - [A]_t$, where

$$d[A]_t/dt = -k_1[A]_t + k_{-1}([A]_0 - [A]_t) \qquad \text{or} \qquad d[A]_t/dt = -(k_1 + k_{-1})\left([A]_t - \frac{k_{-1}}{k_1 + k_{-1}}[A]_0\right) \qquad ...(2)$$

Now, from **(1)** we have $[B]_\infty / [A]_\infty = ([A]_0 - [A]_\infty) / [A]_\infty = k_1 / k_{-1}$, or $[A]_\infty = [A]_0\, k_{-1} / (k_1 + k_{-1})$ Introducing this result into **(2)**, we obtain

$$d[A]_t/dt = -(k_1 + k_{-1})([A]_t - [A]_\infty)$$

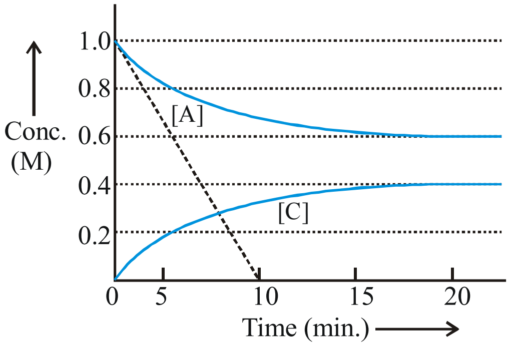
Integrating

$$\text{In}(A)_t - [A]_\infty) = -(k_1 + k_{-1})t + f$$

For $t = 0$, $f = \text{In}([A]_0 - [A]_\infty)$; hence,

$$\text{In}\left(\frac{[A]_t - [A]_\infty}{[A]_0 - [A]_\infty}\right) = -(k_1 + k_{-1})t$$

26. For the reaction $A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C$ (having both 1st order reactions), the concentration as a function of time are given for a certain experimental run along with a tangent to the graph at the origin. The ratio of the magnitude of the slopes of the graph of [A] and [C] at the origin would be



(A) 1 **(B)** $\frac{3}{4}$ **(C)** $\frac{4}{3}$ **(D)** None of these

27. At what time is the rate of change of concentration of A equal to rate of change of concentration of C in magnitude?

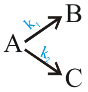
(A) t = 0 only **(B)** t ≥ equilibrium only

(C) t = 10 only **(D)** at all times

28. What is the K_C of the reaction $2C \rightleftharpoons 2A$?

(A) $\frac{2}{3}$ **(B)** $\frac{3}{2}$ **(C)** 1 **(D)** None of these

Comprehension # 5

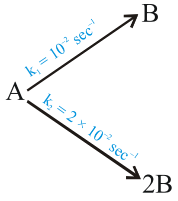
For first order parallel path reaction 

$[A]_t = [A]_0\, e^{-(k1+k2)t}$.

$$[B]_t = \frac{[A]_0 k_1}{k_1 + k_2}[1 - e^{-(k_1+k_2)^t}] \quad ; \quad [C]_t = \frac{[A]_0 k_2}{k_1 + k_2}\ [1 - e{-(k1+k2)t}]$$

two calculate the rate constant of first order reaction.

$$k = \frac{1}{t}\ln\frac{[A]_0}{[A]_t}.$$

29. 

If initial concentration of 'A' is 1M, the conc. of 'A' after 33.33 second is equal to –

(A) $\frac{1}{e}$ **(B)** $\frac{2}{e}$ **(C)** $\frac{1}{e^2}$ **(D)** none of these

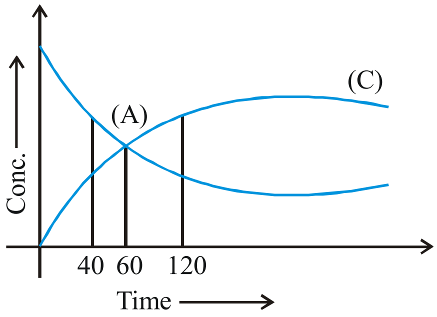
30. $A \longrightarrow B + C$ is a first order reaction

time	t	∞
mole of reagent	a	b

If A, B and C react with reagent and have 'n' factor in the ratio of 1 : 2 : 3 with reactant then the value of 'k' is –

(A) $k = \frac{1}{t}\ \ln\ \frac{b}{b-a}$ **(B)** $k = \frac{1}{t}\ \ln\ \frac{4b}{b-a}$ **(C)** $k = \frac{1}{t}\ \ln\ \frac{4b}{5(b-a)}$ **(D)** $k = \frac{1}{t}\ \ln\ \frac{4a}{5(b-a)}$

31. $A \longrightarrow nC$

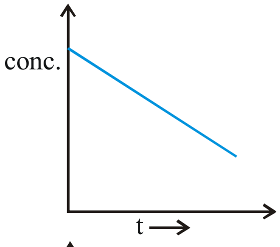
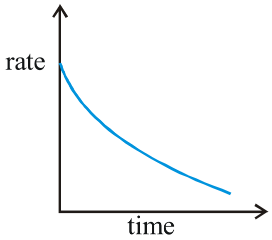


If half life of **(A)** is 20 sec. then $\frac{1}{n}$ is

(A) 7 **(B)** $\frac{1}{7}$ **(C)** $\frac{7}{8}$ **(D)** $\frac{1}{8}$

SECTION - V : MATRIX - MATCH TYPE

32. Match Matrix

(A) Ester + NaOH $\longrightarrow$ Alcohol + Salt	**(p)** $k = Ae^{-Ea/RT}$
(B) $2H_2O_2 \longrightarrow 2H_2O + O_2$	**(q)** 
(C) $2NH_3 \xrightarrow{Au} N_2 + 3H_2$	**(r)** 
(D) Sucrose + $H_2O \longrightarrow$ Glucose + Fructose	**(s)** $t_{1/2}$ = x min at a constant temperature any time of the reaction.

33. For A + B $\longrightarrow$ C in column = II the graphs given can be from any of these four types.

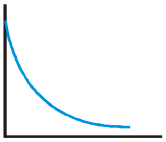
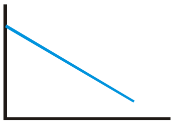
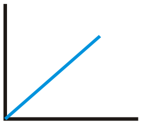
(A) $-\frac{dA}{dt}$ Vs time (x axis)

(B) $t_{1/2}$ Vs initial conc. (x axis)

(B) $\left(\frac{C_0 - C_t}{C_t}\right)$ Vs time (x axis)

(D) Conc. Vs time (x axis)

Match the graphs in Column - II for the given order of reactions in Column - I.

Column - I	**Column - II**
(A) Ist order	**(p)** 
(B) Zero order	**(q)** 
(C) Second order	**(r)** 
(D) Pseudo first order	**(s)** 

34. Match the following :

Column - I	**Column - II**
(A) Constant boiling mixture	**(p)** 2nd order reaction
(B) K_f	**(q)** Azeotrope
(C) $\frac{t_3}{4} = 2\frac{t_1}{2}$ $(A \rightarrow B$, single run)	**(r)** 1st order reaction
(D) $\frac{t_1}{2}(1^{st}):\frac{t_1}{2}(2^{nd}):\frac{t_1}{2}(3^{rd})$: : 1 : 2 : 4 (For the same run	**(s)** Solvent

SECTION - VI : SUBJECTIVE TYPE

35. The rate constant of 1st order decomposition reaction of an organic compound (X) into another organic compound Y and an inorganic compound (gas) (Z) may be given by :

$$\log_{10} k\,(\sec^{-1}) = 12.37 - \frac{1.25 \times 10^4}{T(\text{in kelvin})}$$

Find the activation energy and rate constant at 750 K and indicate your answer as the product of Ea (in Joules mol^{-1}) and rate constant (in unit $\sec^{-1}$) and fill the answer as a nearest whole number.
Take R = 8.3 $JK^{-1}mol^{-1}$, {antilog (–4.3) = 5×10^{-5}}

36. For the reaction A $\longrightarrow$ production, the following data is given for a particular run.

time (min.) :	0	5	15	35
$\frac{1}{[A]}(M^{-1})$:	1	2	4	8

Determine the order of the reaction.

37. Surface catalysed reactions that are inhibited by the products obey the rate equation (in same cases) $\frac{dx}{dt} = \frac{K(a-x)}{1+bx}$ where a is the initial concentration of the reaction and K and b are constants. Intergrate this equation. Derive an expression for $t_{1/2}$. x is the concentration of products an any time t and the reaction is A $\longrightarrow$ B.

38. **(A)** The decomposition of HI to yield H_2 and I_2 at 508°C has a half-life of 135 minutes when $P_{HI} = 0.1$ atm (initial) which comes down to one-tenth of that value when the initial pressure is 1 ati. Calculate the rate constant.

(B) The viscosity of water changes by about 2% per degree at 25°C. What is the activation energy for the process?

39. Decomposition of H_2O_2 (Ist order)

$$H_2O_2(aq) \longrightarrow H_2O(\ell) + \frac{1}{2}O_2(g)$$

Can be monitored by titration method by pressure measurement. It

Time (min)	t = 0	30	∞
Pressure (mm of hg)	200	375	400

While when progress of same reaction was monitored by titration method, the volume of titrant consumed after 10 min was found to be 20 ml. Then complete the following table.

Time (min)	t = 0	10	30
Pressure (mm of Hg)	200	(B)	(C)
Volume of $KMnO_4$ consumed (ml)	(A)	20	(D)

ANSWER KEY

EXERCISE - 1

1. B **2.** B **3.** A **4.** B **5.** D **6.** C **7.** D **8.** A **9.** A **10.** A **11.** B **12.** B **13.** C

14. C **15.** D **16.** B **17.** A **18.** D **19.** C **20.** D **21.** C **22.** C **23.** C **24.** D **25.** B **26.** B

27. C **28.** B **29.** B **30.** B **31.** D **32.** C **33.** A **34.** C **35.** B **36.** B **37.** B **38.** B **39.** D

40. A **41.** B **42.** B **43.** B **44.** B **45.** D **46.** B **47.** C **48.** B **49.** B **50.** B **51.** B **52.** D

53. A **54.** B **55.** A **56.** B **57.** C **58.** C **59.** C **60.** C **61.** D **62.** A **63.** D **64.** A **65.** B

66. B **67.** D **68.** A **69.** A **70.** C **71.** C **72.** C **73.** B **74.** B **75.** C **76.** B **77.** A **78.** C

79. C **80.** C **81.** B **82.** A **83.** A **84.** B **85.** B **86.** B **87.** A

EXERCISE - 2 : PART # I

1. B, C **2.** B, C **3.** A, B **4.** A, B, D **5.** A, B, D **6.** A, B, C **7.** C, D **8.** B, C **9.** A, B, C

10. B, C **11.** A, B, C, D **12.** B, C, D **13.** A, B, C **14.** B, C **15.** A, D **16.** D **17.** C **18.** A **19.** D

20. A **21.** D **22.** B **23.** B **24.** D **25.** B **26.** D **27.** B **28.** B **29.** A **30.** C **31.** A **32.** A

33. D **34.** A **35.** C **36.** A **37.** C **38.** C **39.** B **40.** C **41.** A **42.** C **43.** B **44.** A **45.** C

46. A **47.** B **48.** A **49.** A **50.** D **51.** D **52.** C **53.** B **54.** D **55.** B **56.** D **57.** B **58.** B

59. A **60.** B **61.** C **62.** C **63.** C **64.** C **65.** D **66.** B, D **67.** A, B, C **68.** A, D **69.** A, B

70. A, B, C **71.** B, D **72.** A, B **73.** A, B, C **74.** A, B, C, D **75.** A, D

PART # II

1. B **2.** D **3.** C **4.** B **5.** A **6.** A **7.** A **8.** A **9.** B **10.** C **11.** C

EXERCISE - 3 : PART # I

1. A → p, q, r, s, B → q, r, s, C → p, q, r, s, D → p, r, s

2. A → r, B → s, C → q, D → p

3. A → r, B → s, C → p, D → q

4. A → r, B-t, C → p, D → q, E → v, F → s, G → u

PART # II

Comprehension # 1 : **1.** A **2.** C **3.** A

Comprehension # 2 : **1.** A **2.** D **3.** B

Comprehension # 3 : **1.** C **2.** B **3.** B **4.** B

Comprehension # 4 : **1.** A **2.** A **3.** D

Comprehension # 5 : **1.** A **2.** C **3.** C

Comprehension # 6 : **1.** C **2.** A **3.** D **4.** A

Comprehension # 7 : **1.** A **2.** B **3.** B **4.** C

EXERCISE - 5 : PART # I

1. A **2.** D **3.** C **4.** A **5.** A **6.** C **7.** D **8.** B **9.** B **10.** A **11.** B **12.** C **13.** D

14. C **15.** C **16.** B **17.** A **18.** A **19.** D **20.** D

PART # II

1. A **2.** A $R_0 = k[A_0]$, B 0.5 sec^{-1}. **3.** 950 mm of Hg **4.** C **5.** B **6.** A **7.** D **8.** A **9.** D **10.** 0
11. A **12.** A,B,D **13.** 9 **14.** D **15.** B, C, D **16.** B, C **17.** A, D **18.** –8500 J/mole

MOCK TEST

1. C **2.** C **3.** C **4.** B **5.** C **6.** C **7.** D **8.** D **9.** C **10.** A **11.** B **12.** C **13.** A

14. B **15.** B, C **16.** A, B, D **17.** A, B, D **18.** A, B, C, D **19.** A,B **20.** D **21.** C **22.** B **23.** B

24. A **25.** C **26.** A **27.** D **28.** D **29.** A **30.** C **31.** A

32. A → p, r ; B → p, r, s ; C → q ; D → p, r, s **33.** A → p, q ; B → p, r, s ; C → s ; D → p, q

34. A → q, B → s, C → r, D → p