SOLVED PROBLEMS

SUBJECTIVE

Problem 1 :

Rate of a reaction $A + B \rightarrow$ Products; is given below as a function of different initial concentrations of A and B

[A] mol/litre	[B] mol litre ⁻¹	Initial rate mol litre ⁻¹ time ⁻¹
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005
D	1 0.1 .1 1.1	

Determine the order of the reaction with respect to A and with respect to B. What is the half life of A in the reaction ?

Solution :

Let order with respect to A is m and with respect to B is 'n'. Rate = $K[A]^m [B]^n$

$0.005 = K [0.01]^m [0.01]^n$	(i)
$0.010 = K [0.02]^{m} [0.01]^{n}$	(ii)
$0.005 = K[0.01]^{m} [0.02]^{n}$	(iii)
Dividing Eq. (i) by (ii), we get	

Dividing Eq. (1) by (11), we get $1 \quad [1]^m$

0.005	0.01	_	1_		
$\overline{0.010} =$	$\left\lfloor \overline{0.02} \right\rfloor$	\Rightarrow	$\frac{1}{2}$	$\left\lfloor \frac{1}{2} \right\rfloor$	∴ m=

Thus, order with respect to A is one. Dividing Eq. (i) by (ii), we get

$$\frac{0.005}{0.005} = \left[\frac{0.01}{0.02}\right]^n \qquad \Rightarrow \qquad 1 = \left[\frac{1}{2}\right]^n \qquad \therefore n = 0$$

Thus, order with respect to B is zero. Substituting the values of m and n in Eq. (i), we get

$$0.005 = K [0.01]^1 [0.01]^0$$

$$\frac{0.005}{0.01} = 0.5$$

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 $t_{1/2}$ (Half life period) $= \frac{0.693}{K} = \frac{0.693}{0.5} = 1.386$ time

Problem 2 :

The decomposition of Cl_2O_7 at 440K in the gas phase to Cl_2 and O_2 is a first order reaction.

- (i) After 55 seconds at 400 K the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm., calculate that rate constant.
- (ii) Calculate the pressure of Cl_2O_7 after 100 sec. of decomposition at this temperature.

Solution :

(i) In the present equation we may apply the formula

$$K = \frac{2.303}{t} \log \frac{p_0}{p_t} = \frac{2.303}{55} \log \frac{0.062}{0.044} = 6.2364 \times 10^{-3} \text{ sec}^{-1}$$

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(ii) Pressure after 100 sec may be calculated as

$$6.2364 \times 10^{-3} = \frac{2.303}{100} \log \frac{0.062}{p_t}$$

 $p_t = 0.0332 atm$

Problem 3 :

Rate law for the following reaction; is

Ester +
$$H^+ \Longrightarrow Acid + Alcohol;$$
 is $\frac{dx}{dt} = K [ester]^1 [H^+]^0$

What would be the effect on the rate if

- (i) Concentration of ester is doubled ?
- (ii) Concentration of H^+ ion is doubled ?

Solution:

The rate law expression in this question, suggests that concentration of acid is nothing to play with velocity.

- (i) When concentration of ester is doubled; velocity of the reaction will become double.
- (ii) When concentration of H^+ ion is doubled velocity will be unaffected.

Problem 4 :

The reaction $2A + B + C \rightarrow D + 2E$; is found to be first order in A; second order in B and zero order in C.

- (i) Give the rate law for the above reaction in the form of a differential equation.
- (ii) What is the effect on the rate of increasing the concentration of A, B and C two times ?

Solution :

- (i) The rate law according to given information may be given as, $\frac{dx}{dt} = K[A]^{1}[B]^{2}[C]^{0}$
- (ii) When concentration of A, B and C are doubled then rate will be

$$\frac{dx}{dt} = K[2A][2B]^{2}[C]^{0} = 8K[A][B]^{2}[C]^{0}$$

i.e., rate becomes 8 fold, the original rate.

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Problem 5:

At 27°C it was observed, during a reaction of hydrogenation that the pressure of H_2 gas decreases from 2 atm to 1.1 atm in 75 min. Calculate the rate of reaction (molarity/sec). Given (R = 0.082/litre atom K^{-1} mole⁻¹)

Solution:

Rate =
$$\frac{\text{Decrease in pressure}}{\text{Time duration}} = \frac{2-1.1}{75} = 0.012 \text{ atm/min}$$

Rate in atm/sec = $\frac{0.012}{60} = 2 \times 10^{-4} \text{ atm/sec.}$
Answer is required in molarity per second
 $\therefore \text{ PV} = \text{nRT}$

$$\frac{P}{RT} = \frac{n}{V}$$
$$\frac{P/\sec}{RT} = \left(\frac{n}{V}\right)/\sec$$

 $\left(\frac{n}{V}\right)$ / sec = molarity per second

$$\frac{2 \times 10^{-4}}{0.0821 \times 300} = \left(\frac{n}{V}\right) / \sec \frac{n}{V}$$

 8.12×10^{-6} . Rate in molarity/sec = (n/V)/sec

Problem 6 :

In presence of an acid N-chloro acetanilide changes slowly into p-chloro acetanilide. Former substance liberated iodine from KI and not the later and hence progress of reaction can be measured by titrating iodine liberated with $Na_2S_2O_3$ solution, the results obtained were as follows :

Time (hours) 0 1 2 4 6 8 3.7 *45* 32 22.5 11.3 2.9 (a-x)i.e., hyposhow that reaction is uniomlecular and find out the fraction of N-chloroacetanilide decomposed after three hours.

Solution :

The present reaction is :



Let us apply the kinetics of first order reaction.

After 1 hour	$K = \frac{2.303}{1} \log \left\{ \frac{45}{32} \right\} = 0.34098 \text{ hour}^{-1}$
After 2 hours	$\mathrm{K} = \frac{2.303}{2} \log \left\{ \frac{45}{22.5} \right\} = 0.34660 \text{ hour}^{-1}$
After 4 hours	$\mathrm{K} = \frac{2.303}{4} \log \left\{ \frac{45}{11.3} \right\} = 0.3455 \text{ hour}^{-1}$
After 6 hours	$\mathrm{K} = \frac{2.303}{6} \log \left\{ \frac{45}{3.7} \right\} = 0.4164 \text{ hour}^{-1}$
After 8 hours	$\mathrm{K} = \frac{2.303}{8} \log \left\{ \frac{45}{2.9} \right\} = 0.3428 \text{ hour}^{-1}$
Average value of cons	$tant = 0.3584 \text{ hours}^{-1}$
\mathbf{C}^{\prime}	1 1

Since, on applying first order kinetics, we get almost same values of rate constant after different time intervals, hence, the reaction is of first order.

Let us see the fraction decomposed after 3 hours.

$$K = \frac{2.303}{t} \log\left\{\frac{a}{a-x}\right\}$$
$$0.3584 = \frac{2.303}{3} \log\frac{a}{a-x}$$

$$\therefore \frac{a}{a-x} = 2.98$$

$$\therefore \frac{a-x}{a} = 0.3412$$

$$1 - \frac{x}{a} = 0.3412$$

$$\therefore \frac{x}{a} = 0.658 \text{ [fraction decomposed]}$$

Problem 7 :

For the decomposition of dimethyl ether, A in the Arrhenius equation $K = Ae^{-E/RT}$ has a value of 1.26 $\times 10^{13}$ and E_a value of 58.5 kcal. Calculate half life period for first order decomposition at 527°C.

Solution :

Taking logarithm of Arrhenius equation $K = Ae^{-E/RT}$ we get $\log K = \log A - \frac{E}{2.303RT}$... (i) Given $A = 1.26 \times 10^{13}$ E = 58.5 kcal T = 527 + 273 = 800 K Substituting these value in Eq. (i), we get $\log K = \log (1.26 \times 10^{13}) - \frac{58.5 \times 10^2}{2.303 \times 1.987 \times 800} = 13.1003 - 15.9799 = -2.8796$ $K = 1.3194 \times 10^{-3}$ sec⁻¹ $t_{1/2} = \frac{0.693}{1.3194} \times 10^3$ sec = 525 sec **Problem 8 :** For the reaction , $2NQ(g) + H(g) \longrightarrow NQ(g) + HQ(g)$ at 900 K, the following data are obtained

$2NO(g) + H_2(g) -$	$\longrightarrow N_2 O(g) + H_2 O(g)$ at	900 K, the following data are obtain	ed:
Initial pressure	Initial pressure	Rate	
of NO (atm)	of H ₂ (atm)	(atm min ⁻¹)	
0.150	0.400	0.020	
0.075	0.400	0.005	
0.150	0.200	0.010	
Find the rate law	and the value of rate c	onstant.	

Solution:

Let order with respect to NO(g) is 'm' and order with respect to $H_2(g)$ is 'n'

Then, Rate = $K[P_{NO}]^{m}[P_{H_{2}}]^{n}$... (1) $0.020 = K [0.15]^{m} [0.40]^{n}$... (2) $0.005 = K [0.075]^{m} [0.40]^{n}$... (3) $0.010 = K [0.15]^{m} [0.2]^{n}$... (4) Dividing Eq. (2) by (3), we get

 $\frac{0.020}{0.005} = \left(\frac{0.15}{0.075}\right)^{\mathrm{m}}$

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m = 2

Dividing Eq. (2) by (4), we get $\frac{0.020}{0.010} = \left(\frac{0.4}{0.2}\right)^n$

n = 1

Rate = $[P_{NO}]^2 [P_{H_2}]^1$ Substituting the values of m, n in Eq. (2), we get $0.020 = K (0.15)^2 [0.40]$ $K = 2.22 \text{ atm}^{-2} \text{min}^{-1}$

Problem 9:

10 gram atoms of an α -active radio isotope are disintegrating in a sealed container. In one hour the helium gas collected at STP is 11.2 cm³. Calculate the half-life of the radio-isotope.

Solution :

No. of atoms of helium is 11.2 cc at NTP = $\frac{11.2}{22400} \times 6.02 \times 10^{23} = 3.01 \times 10^{20}$ atoms

Since, helium atom corresponds to α -particle. Thus, Rate of disintegration = 3.01 $\times 10^{20}$ per hour.

We know, Rate = Rate constant \times concentration in atom $3.01 \times 10^{20} = K \times 10 \times 6.02 \ 10^{23}$ $K = 0.05 \times 10^{-3} \text{ hour}^{-1}$

$$T_{1/2} = \frac{0.693}{K} = \frac{0.693}{0.05 \times 10^{-3}} = 13860$$
 hours

$$T_{1/2} = \frac{13860}{24 \times 365} = 1.58 \text{ years}$$

Problem 10:

A carbon radio isotope $_{Z}X^{A}$ (half life 10 days) decays to give $_{Z-2}Y^{A-4}$. If 1.00 gm atom of $_{Z}X^{A}$ is kept in a sealed tube, how much helium will accumulate in 20 days? Express the result in cm³ at STP.

Solution :

Initial concentration (N_0) of radio-isotope is 1 gm atom. Concentration remained after 20 days may be calculated as

$$\mathbf{N}_{t} = \mathbf{N}_{0} \left(\frac{1}{2}\right)^{t}$$

where $n = n_0$ of half lives $= 20/10 = 2 = 1\left(\frac{1}{2}\right)^2 = \frac{1}{4}$

Concentration decayed to α -particles = $1 - \frac{1}{4} = \frac{3}{4}$ gm atom. An α -particle takes 2 electron from air and from helium gas. Thus,

Helium formed $=\frac{3}{4}$ gm atom $=\frac{3}{4} \times 22400$ cc =16800 cc

Problem 11:

Radioactive decay is a first order process. Radioactive carbon wood sample decays with a half life of 5770 years. What is the rate constant in (years)⁻¹ for the decay? What fraction would remain after 11540 years?

Solution :

$$K = \frac{0.693}{T_{1/2}} = \frac{0.693}{5770} = 1.201 \times 10^{-4} \text{ year}^{-1}$$
$$K = \frac{2.303}{t} \log \frac{N_0}{N_t}$$
$$1.201 \times 10^{-4} = \frac{2.303}{11540} \log \frac{N_0}{N_t}$$
$$4.002 = \frac{N_0}{N_t}$$
$$\frac{N_t}{N_0} \text{ (Remaining fraction)} = \frac{1}{4.002}$$

Problem 11:

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A sample of ${}_{53}I^{131}$, as iodide ion, was administered to a patient in a carrier consisting of 0.10 mg of stable iodide ion. After 4.00 days, 67.7% of the initial radioactivity was detected in the thyroid gland of the patient. What mass of the stable iodide ion had migrated to the thyroid gland? Given $T_{1/2}I^{131} = 8$ days.

Solution :

We know,

$$\frac{0.693}{T_{1/2}} = \frac{2.303}{t} \log_{10} \left[\frac{N_0}{N} \right]$$
$$\frac{0.693}{8} = \frac{2.303}{4} \log_{10} \left[\frac{N_0}{N} \right]$$
$$\frac{N}{N_0} = 0.707$$

 \Rightarrow 70.7 % of initial activity is present. Given that 67.7% activity is migrated to thyroid gland.

Thus, weight of I- migrated to thyroid gland may be calculated as

$$\frac{67.7}{70.7} \times 100 = 95.75\%$$

i.e, $0.1 \times \frac{95.75}{100} = 0.09575 \text{ mg}$

OBJECTIVE

Problem 1 :

If a reaction $A + B \longrightarrow C$ is exothermic to the extent of 30 kJ/mol and the forward reaction has an activation energy 70 kJ/mol, the activation energy for the reverse reaction is

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



By seeing the curve, activation energy for backward reaction = 100 kJ

Problem 2 :

The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} \text{ s}^{-1}$, 104.4 kJ mol⁻¹ and $6.0 \times 10^{14} \text{ s}^{-1}$ respectively the value of the rate constant as $T \longrightarrow \infty$ is :

(A) $2.0 \times 10^{18} \, \text{s}^{-1}$ (B) $6.0 \times 10^{14} \, \text{s}^{-1}$ (C) ∞ (D) $3.6 \times 10^{30} \, \text{s}^{-1}$ Solution : (B) $K = A e^{-Ea/RT}$ When $T \longrightarrow \infty$ $K \longrightarrow A$ $A = 6 \times 10^{14} \, \text{s}^{-1}$

Problem 3 :

The inversion of cane sugar proceeds with half-life of 500 minute at pH 5 for any concentration of sugar. However if pH = 6, the half-life changes to 50 minute. The rate law expression for the sugar inversion can be written as
(A) $r = K[sugar]^2[H]^6$ (B) $r = K[sugar]^1[H]^6$

(1)		
(C) r =	=K[sugar] ^ø [H ⁺] ⁶	(D) $r = K[sugar]^0[H^+]^1$

Solution : (B)

Since $t_{1/2}$ does not depends upon the sugar concentration means it is first order respect to sugar concentration. $t_{1/2} \propto [sugar]^1$.

$$t_{1/2} \times a^{n-1} = k$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{[H^+]_1^{1-n}}{[H^+]_2^{1-n}}$$

$$\frac{500}{50} = \left(\frac{10^{-5}}{10^{-6}}\right)^{1-1}$$

$$10 = (10)^{1-n}$$
Hence $n = 0$

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Problem 4 :

Two substances A and B are present such that $[A_0] = 4[B_0]$ and half-life of A is 5 minute and that of B is 15 minute. 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 minute (B) 10 minute (C) 5 minute (D) 12 minute Solution: (A)

Amount of A left in n_1 halves = $\left(\frac{1}{2}\right)^{n_1} [A_0]$

Amount of B left in n_2 halves = $\left(\frac{1}{2}\right)^{n_2} [B_0]$

At the end, according to the question

$$\frac{[A^{0}]}{2^{n_{1}}} = \frac{[B_{0}]}{2^{n_{2}}} \implies \frac{4}{2^{n_{1}}} = \frac{1}{2^{n_{2}}}, \ \left[[A_{0}] = 4[B_{0}]\right]$$
$$\therefore \frac{2^{n_{1}}}{2^{n_{2}}} = 4 \Longrightarrow 2^{n_{1}-n_{2}} = (2)^{2} \therefore n_{1} - n_{2} = 2$$
$$\therefore n_{2} = (n_{1} - 2) \qquad \dots (1)$$

Also $t = n_1' t_{1/2(A)} t = n_2 \times t_{1/2(B)}$

(Let concentration of both become equal after time t)

Problem 5:

 Fill in the blank

 ${}^{235}_{92}U + {}^{I}_{\theta}n \longrightarrow ? + {}^{92}_{36}Kr + 3{}^{I}_{\theta}n$

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

 Solution:
 (A)
 ${}^{92} + 0 = Z + 36 + 0 \Rightarrow Z = 56$ ${}^{235}_{235} + 1 \longrightarrow A + 92 + 3$ ${}^{\cdot}_{\cdot}$ A = 144
 Missing nuclide is ${}^{141}_{56}Ba$

Problem 6 :

The rate of a reaction increases 4-fold when concentration of reactant is increased 16 times. If the rate of reaction is 4×10^{-6} mole $L^{-1} S^{-1}$ mole L^{-1} when concentration of the reactant is 4×10^{-4} , the rate constant of the reaction will be (A) 2×10^{-4} mole^{1/2} $L^{-1/2} S^{-1}$ (B) $1 \times 10^{-2} S^{-1}$ (C) 2×10^{-4} mole^{-1/2}, $L^{1/2} S^{-1}$ (D) 25 mole⁻¹ L min⁻¹ ion : (A)

Solution : (A)

Rate $\propto \sqrt{\text{concentration}}$, Rate = $k\sqrt{\text{concentration}}$

k =
$$\frac{\text{Rate}}{(\text{concen})^{1/2}} = \frac{4 \times 10^{-6}}{(4 \times 10^{-4})^{1/2}} = \frac{4 \times 10^{-6}}{2 \times 10^{-2}} = 2 \times 10^{-4} \text{ mole}^{1/2} \text{ L}^{-1/2} \text{ S}^{-1}$$

Problem 7 :

A catalyst lowers the activation energy of a reaction from 20 kJ mole⁻¹ to 10 kJ mole⁻¹. The temperature at which the uncatalysed reaction will have the same rate as that of the catalysed at 27 °C is

(A) $-123 \,^{\circ}C$ (B) $327 \,^{\circ}C$ (C) $327 \,^{\circ}C$ (D) $+ 23 \,^{\circ}C$ Solution : (B) $\frac{E'a}{T_1} = \frac{E_a}{T_2} = \frac{10}{300} = \frac{20}{T_2} \qquad \therefore \qquad T_2 = 600 \text{ K} = 327^{\circ} \text{ C}$

Problem 8 :

The reaction, $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A and B are $P_A = 0.60$ and $P_B = 0.80$ atm. When $P_C = 0.2$ atm the rate of reaction relative to the initial rate is

(A) 1/48 **(B)** 1/24 (C) 9/16 (D)1/6 Solution : (D) $R_1 = K[A][B]^2 = K[0.6][0.80]^2$ After reaction $2B \longrightarrow$ С D А ++0.6 - 0.20.8 - 0.40.2 0.2 0.4 0.4 0.2 0.2 $\frac{R_2}{R_1} = \frac{K(0.4)(0.4)^2}{(0.6)(0.8)^2} = \frac{1}{6}$

Problem 9 :

Thermal decomposition of a compound is of first order. If 50 % of a sample of the compound is decomposed in 120 minutes, show how long will it take for 90 % of the compound to decompose?

(A) 399 min (B) 410 min (C) 250 min (D) 120 min Solution : (A)

$$K = \frac{0.6932}{120} \qquad \dots (1)$$
$$K = \frac{2.303}{t} \log \frac{a}{0.10a} = \frac{2.303}{t} \log 10 \qquad \dots (2)$$
Equating (1) and (2)
$$\frac{0.6932}{120} = \frac{2.303}{t}$$

t = 399 minutes

Problem 10 :

If concentration are measured in mole/litre and time in minutes, the unit for the rate constant of a 3rd order reaction are

(A) mol lit⁻¹min⁻¹ (B) lit² mol⁻² min⁻¹ (C) lit mol⁻¹min⁻¹ (D) min⁻¹ **Solution :** (B) $K = [conc.]^{1-n} min^{-1}$

For 3^{rd} order reaction = $[mole/litre]^{1-3} min^{-1} = lit^2.mole^{-2}min^{-1}$

Problem 11 :

What is the activation energy for the decomposition of N_2O_5 as

$$N_2 O_5 \Longrightarrow 2NO_2 + \frac{1}{2}O_2$$

If the values of the rate constants are 3.45×10^{-5} and 6.9×10^{-3} at $27^{\circ}C$ and $67^{\circ}C$ respectively.

(A) $102 \times 10^2 kJ$ (B) 488.5 kJ (C) 112 kJ (D) 112.5 kJSolution : (D)

$$\log \frac{K_2}{K_1} = \frac{Ea}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$
$$\log \frac{6.9 \times 10^{-3}}{3.45 \times 10^{-5}} = \frac{Ea}{2.303 \times 8.31} \left[\frac{40}{300 \times 400} \right]$$
$$E_2 = 112.5 \text{ kJ}$$

Problem 12:

Half life period for a first order reaction is 20 minutes. How much time is required to change the concentration of the reactants from 0.08 M to 0.01M

(A) 20 minutes (B) 60 minutes (C) 40 minutes (D) 50 minutes Solution : (B)

> $K = \frac{2.303}{t} \log \frac{a}{a - x}$ $\frac{0.6932}{20} = \frac{2.303}{t} \log \frac{0.08}{0.01} = \frac{2.303}{t} \log 8 = \frac{2.303 \times 3 \times \log 2}{t}$ $\frac{1}{20} = \frac{3}{t}$ t = 60 minutes

Problem 13 :

The kinetic datas for the reaction: $2A + B_2 \longrightarrow 2AB$ are as given below: [A]**[B**,**]** Rate mol L^{-1} mol L⁻¹ mol L^{-1} min⁻¹ 2.5×10^{-3} 0.5 1.0 1.0 1.0 5.0×10^{-3} 1 × 10⁻² 0.5 2.0 Hence the order of reaction w.r.t. A and B, are, respectively, (D) 2 and 2 **(B)** 2 and 1 (C) 1 and 1 (A) 1 and 2 Solution : (A) $2.5 \times 10^{-3} = K[0.5]^{\alpha} [1.0]^{\beta}$...(1) $5 \times 10^{-3} = K[1.0]^{\alpha} [1.0]^{\beta}$...(2) $1 \times 10^{-2} = K[0.5]^{\alpha} [2.0]^{\beta}$...(3) Dividing equation (1) and (2) $\frac{1}{2} = \left\lceil \frac{1}{2} \right\rceil^{\alpha}$ hence $\alpha = 1$ Dividing equation (1) and (3)

$$\frac{2.5 \times 10^{-3}}{1 \times 10^{-2}} = \left(\frac{1.0}{2.0}\right)^{\beta}$$
$$\frac{1}{4} = \left(\frac{1}{2}\right)^{\beta}$$
$$\beta = 2$$

Problem 14 :

For the first order reaction $A_{(g)} \longrightarrow 2B_{(g)} + C_{(g)}$, the initial pressure is $P_A = 90$ mm Hg, the pressure after 10 minutes is found to be 180 mm Hg. The rate constant of the reaction *is* : (A) $1.15 \times 10^{-3} \text{ sec}^{-1}$ (B) $2.3 \times 10^{-3} \text{ sec}^{-1}$ (D) $6 \times 10^{-3} \text{ sec}^{-1}$ (C) $3.45 \times 10^{-3} \text{ sec}^{-1}$ Solution : (A) \rightarrow 2B + С А Ρ 0 0 $\mathbf{P} - \mathbf{x}$ 2x Х At equilibrium

180 = P - x + 2x + x 180 = 90 + 2x 2x = 90, x = 45 $K = \frac{2.303}{t} \log \frac{P}{P - x} = \frac{2.303}{10} \log \frac{90}{90 - 45} = \frac{2.303}{10} \log 2 = \frac{0.6932}{10}$ $= 0.6932 = \frac{0.06932}{60} = 1.1555 \times 10^{-3} \text{ sec}^{-1}$

ASSIGNMENTS

OBJECTIVE QUESTIONS

Level – I

- The rate of the simple reaction $2NO + O_2 \longrightarrow 2NO_2$, when the volume of the reaction vessel Q.1 is doubled-(A) will grow eight times of its initial rate (B) rate reduce to one-eights of its initial rate (C) will grow four times of its initial rate (D) reduce to one-fourth of its initial rate The rate expression for the reaction $A(g) + B(g) \rightarrow C(g)$ is rate = $KC_A^2C_B^{4}$. What changes in Q.2 the initial concentration of A and B will cause the rate of reaction increase by a factor of eight (A) $C_A \times 2; C_B \times 2$ (B) $C_A \times 2; C_B \times 4$ (C) $C_A \times 1; C_B \times 4$ (D) $C_A \times 4; C_B \times 1$ Given that k is the rate constant for some order of any reaction at temperature T, then the value Q.3 of T $\xrightarrow{\lim} \infty \log k$, (where A is the Arrhenius constant) is – (A) A/2.303(B)A(C) 2.303A $(D) \log A$ According to the Arrhenius equation a straight line is to be obtained by plotting the logarithm of **Q.4** the rate constant of a chemical reaction (log k) against -(A)T $(B) \log T$ (C) 1/T (D) $\log 1/T$ Select the rate law that corresponds to the data shown for the following reaction : Q.5 $A + B \longrightarrow C$ Extp. No. **[B]**₀ initial rate $[\mathbf{A}]_{0}$ 1. 0.012 0.035 0.10 0.024 0.070 0.80 2. 3. 0.024 0.035 0.10 0.80 4. 1.012 0.070 (C) rate = $k[A][B]^3$ (A) rate = $k[B]^3$ (B) rate = $k[B]^4$ (D) rate = $k[A]^2[B]^2$ **Q.6** If in the fermentation of sugar in an enzymatic solution that is 0.12 M, the concentration of the
- Q.6 If in 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 10h to 0.03 M in 20 h, what is the order of the reaction : (A) 1 (B) 2 (C) 3 (D) 0
- Q.7 Which of the following curves represents a Ist order reaction :



Q.8 Rate constant of a reaction with a virus is 3.3×10^{-4} s⁻¹. Time required for the virus to become 75% to activate is :

(A) 35 min (B) 70 min (C) 105 min (D) 175 min

Q.9	Inversion of a sugar follows first order rate equation which can be followed by noting the change in rotation of the plane of polarization of light in the polarimeter. Of r_{∞} , r_t and r_0 are the rotation at $t \longrightarrow \infty$, $t = t$ and $t = 0$, then first order reaction can be written as –						
	(A) $k = \frac{1}{t} ln \frac{r_t - r_{\infty}}{r_0 - r_{\infty}}$	(B) $k = \frac{1}{t} ln \frac{r_0 - r_\infty}{r_t - r_\infty}$	(C) k = $\frac{1}{t} \ln \frac{r_0}{r_t}$	(D) k = $\frac{1}{t} \ln \frac{r_{\infty} - r_t}{r_{\infty} - r_0}$			
Q.10	The half life period c is 10 minutes. In wha concentration :	of a first order reaction t period of time is the co	$, A \longrightarrow Product$ oncentration of A is red	uced to 10% of the original			
	(A) 26 min	(B) 33 min	(C) 71 min	(D) 90 min			
Q.11	For the reaction B +	$2D \rightarrow 3T, -\frac{dC_B}{dt} =$	$kC_BC_D^2$. The expressi	on for, $-\frac{dC_D}{dt}$ will be :			
	(A) $2k C_B C_D^2$	(B) $\frac{1}{2} k C_B C_D^2$	(C) 4k $C_B C_D^2$	(D) $\frac{1}{4} k C_B C_D^2$			
Q.12	For a given reaction of to 0.6 M. The time re (A) more than 20 min (C) equal to 20 minut	of first order, it takes 20 equired for the concent nutes tes	minutes for the concert tration to drop from 0.4 (B) less than 20 minu (D) infinity	ntration to drop from 1.0 M 6 M to 0.36 M will be : ntes			
Q.13	Time required to proportional to : (A) a^{n+1}	decompose half of th (B) a ⁿ⁻¹	e substance for nth o (C) a ⁿ⁻²	rder reaction is inversely (D) a ⁿ			
Q.14	$A \longrightarrow B, \Delta H = -1$ (A) 40 kj mol ⁻¹	$\begin{array}{l} 0 \text{ kJ mol}^{-1}, \text{ E}_{a} = 50 \text{ kj} \\ \text{ (B) } 50 \text{ kj mol}^{-1} \end{array}$	mol^{-1} , then E_a of B (C) - 50 kj mol^{-1}	$\longrightarrow A \text{ will be :}$ (D) 60 kj mol ⁻¹			
Q.15	If for any reaction, t The order is :	he rate constant is equ	al to the rate of the rea	ction at all concentration.			
	(A) 0	(B) 2	(C) 1	(D) 3			
Q.16	For a given reaction t with negative slope	the concentration of the The order of the reaction of the reac	e reactant plotted again	ist time gave a straight line			
	(A) 3	(B) 2	(C) 1	(D) 0			
Q.17	What is the order of a chemical reaction $A + 2B \xrightarrow{k} C$. If the rate of formation of C increases by a factor of 2.82 on doubling the concentration of A and increases by a factor of 9 on tripling the concentration of B.						
	(A) 7/2	(B) 7/4	(C) 5/2	(D) 5/4			
Q.18	 When a β-particle is emitted by the atom of a radioactive element, the new species formed possesses: (A) same atomic mass and atomic number less by one unit (B) same atomic mass and atomic number less by two units (C) same atomic mass and atomic number higher by one unit (D) same atomic mass and atomic number higher by two units 						
Q.19	The number of α - and	β -particle emitted in the	the nuclear reaction $\frac{228}{90}$]	Th $\longrightarrow {}^{212}_{83}$ Bi are :			
	(Α) 8α, 1β	(B) 4α , 7β	(C) 3α, 7β	(D) 4α, 1β			

Q.20 A radioactive element A on disintegration gives two elements B and C., If B is helium and C is the element of atomic number 90 and atomic mass 234, the element A is :

(A)
$${}^{238}_{92}$$
 U (B) ${}^{234}_{88}$ Ra (C) ${}^{234}_{90}$ Sc (D) ${}^{234}_{91}$ Pa

- Q.21 The number of α -particles emitted per second by 1 g of ²²⁶ Ra is 3.7 × 10¹⁰. The decay constant is (A) $1.39 \times 10^{-11} \sec^{-1}$ (B) $13.9 \times 10^{-11} \sec^{-1}$ (C) $139 \times 10^{-10} \sec^{-1}$ (D) $13.9 \times 10^{-10} \sec^{-1}$
- Q.22One curie of activity is equivalent to :
 $(A) 3.7 \times 10^{17}$ disintegrations per sec
 $(C) 3.7 \times 10^{14}$ disintegrations per sec(B) 3.7×10^{10} disintegrations per sec
 $(D) 3.7 \times 10^{3}$ disintegrations per sec
- Q.23 Radioactivity of a radioactive element remains 1/10 of the original radioactivity after 2.303 seconds. The half life period is :
 (A) 2.303 (B) 0.2303 (C) 0.693 (D) 0.0693
- Q.24The half life periods of four isotopes are given below :
(i) 7.6 years(ii) 4000 years, (iii) 6000 years (iv) 3.2×10^5 years
Which of the above isotopes is most stable ?
(A) iv(B) iii(C) ii(D) i
- Q.25 Which of the following transformations is not correct?
 - (A) ${}^{75}_{33}As + {}^{4}_{2}He \longrightarrow {}^{78}_{35}Br + {}^{1}_{0}n$ (B) ${}^{7}_{3}Li + {}^{1}_{1}H \longrightarrow {}^{7}_{4}Be + {}^{1}_{0}n$ (C) ${}^{45}_{21}Sc + {}^{1}_{0}n \longrightarrow {}^{45}_{20}Ca + {}^{1}_{0}n$ (D) ${}^{209}_{83}Bi + {}^{2}_{1}H \longrightarrow {}^{210}_{84}Po + {}^{1}_{0}n$
- **Q.26** A sample of rock from moon contains equal number of atoms of uranium and lead $(t_{1/2} \text{ for } U = 4.5 \times 10^9 \text{ years})$. The age of the rock would be : (A) 9.0 × 10⁹ years (B) 4.5 × 10⁹ years (C) 13.5 × 10⁹ years (D) 2.25 × 10⁹ years

Level – II

- Q.1 The rate of reaction becomes 2 times for every 10°C rise in temperature. How the rate of reaction will increase when temperature is increased from 30°C to 80°C :
 (A) 16 (B) 32 (C) 64 (D) 128
- **Q.2** For the consecutive unimolecular-type first order reaction A $\xrightarrow{k_1}$ R $\xrightarrow{k_2}$ S, the concentration of component R, C_R at any time t is given by :

$$C_{R} = C_{AO} K_{1} \left[\frac{e^{-k_{1}t}}{(k_{2} - k_{1})} + \frac{e^{-k_{2}t}}{(k_{1} - k_{2})} \right]$$

if $C_A = C_{AO}, C_R = C_{RO} = 0$ at t = 0

the time at which the maximum concentration of R occurs is :

(A)
$$t_{\max} = \frac{k_2 - k_1}{\ln(k_2 / k_1)}$$
 (B) $t_{\max} = \frac{\ln(k_2 / k_1)}{k_2 - k_1}$ (C) $t_{\max} = \frac{e^{k_2 / k_1}}{k_2 - k_1}$ (D) $t_{\max} = \frac{e^{k_2 - k_1}}{k_2 - k_1}$

Q.3A consecutive reaction A $__{k_1}$ B $__{k_2}$ C is characterised by –(A) maxima in the concentration of A
(C) maxima in the concentration of C(B) maxima in the concentration of B
(D) high exothermicity

- Q.4 For the chemical reaction A + B + C __k → D, it was found that the rate of the reaction doubled when the concentration of B was doubled, that the rate of reaction doubled when the concentration of both A and B were doubled, and quadrupled when the concentration of both B and C were doubled. The order of the reaction is :

 (A) 2
 (B) 3
 (C) 4
 (D) 6
- **Q.5** A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as :

A
$$k_1 = 1.26 \times 10^{-4} \text{s}^{-1}$$
 and $k_2 = 3.8 \times 10^{-5} \text{s}^{-1}$

 The percentage distributions of B and C are :

 (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

Q.6 For a gas reaction at T(K) the rate is given by $-\frac{dp_A}{dt} = k'p_A^2 atm/hr$. If the rate equation is

expressed as $:-r_A = -\frac{1}{V} \frac{dN_A}{dt} = kC_A^2$, mol/(litre-hr), the rate constant k is given by – (A) k = k' (B) k = k' RT (C) k = k'/RT (D) k = k'(RT)^2 where R = ideal gas law constant, cal/g mol K.

Q.7 The activation energies of two reactions are E_{a1} and E_{a2} with $E_{a1} > E_{a2}$. If the temperature of the reacting system is increased from T_1 to T_2 predict which of the following alternative is correct

(A)
$$\frac{K'_1}{K_1} = \frac{K'_2}{K_2}$$
 (B) $\frac{K'_1}{K_1} > \frac{K'_2}{K_2}$ (C) $\frac{K'_1}{K_1} < \frac{K'_2}{K_2}$ (D) $\frac{K'_1}{K_1} < 2\frac{K'_2}{K_2}$

Q.8 The reaction $v_1A + v_2B \rightarrow products$ is first order with respect to A and zero-order with respect to B. If the reaction is started with $[A_0]$ and $[B_0]$, the integrated rate expression of this reaction would be –

(A)
$$\lambda n \frac{[A]_0}{[A]_0 - x} = k_1 t$$

(B) $\lambda n \frac{[A]_0}{[A]_0 - v_1 x} = v_1 k_1 t$
(C) $\lambda n \frac{[A]_0}{[A]_0 - v_1 x} = k_1 t$
(D) $\lambda n \frac{[A]_0}{[A]_0 - v_1 x} = -v_1 k_1 t$

Q.9 When the mechanism of reaction is not known, one often attempts to fit the data with an nth order rate equation of the form

$$-\mathbf{r}_{A} = -\frac{\mathrm{d}\mathbf{C}_{A}}{\mathrm{d}t} = \mathbf{k}\mathbf{C}_{A}^{n}$$

for $n \neq 1$, the integration of this equation yields –

- (A) $C_A^{l+n} C_{A_0}^{l+n} = (l+n)kt$ (B) $C_A^{l-n} C_{A_0}^{l-n} = (l-n)kt$ (C) $C_A^{l-n} - C_{A_0}^{l-n} = (n-1)kt$ (D) $C_A^{l-n} - C_{A_0}^{l-n} = kt/(n-1)$
- Q.10 For the chemical reaction $A \rightarrow$ products, the rate of disappearance of A is given by :

$$-r_{A} = -\frac{dC_{A}}{dt} = k_{1}C_{A}/(1+k_{2}C_{A})$$

At low C_A the reaction is of the first-order with rate constant : (A) k_1/k_2 (B) k_1 (C) $k_1.k_2$ (D) $k_1/(k_1+k_2)$

Q.11 A first order homogeneous reaction of the type X → Y → Z (consecutive reaction) is carried out in a CSTR. Which of the following curves respectively show the variation of the concentration of X, Y and Z with time –
(A) I, II, II
(B) III, II, I
(C) III, I, II
(D) II, III, I

Q.12 For the consecutive unimolecular-type first order reaction A $\xrightarrow{k_1}$ R $\xrightarrow{k_2}$ S, the concentration of component A, C_A at any time t is given by –

(A)
$$C_A = C_{A_0} e^{(k_1 + k_2)t}$$
 (B) $C_A = C_{A_0} e^{-(k_1 + k_2)t}$ (C) $C_A = C_{A_0} e^{-k_1 t}$ (D) $C_A = C_{A_0} e^{k_1 t}$

Q.13 The energy of activation for a reaction is 100 kJ/mol. Presence of a catalyst lowers the energy of activation by 75%. The ratio of k_{cat}/k_{uncat} (T = 298 K) – (A) 23.4 × 10¹⁵ (B) 2.34 × 10¹³ (C) 1.324 × 10⁵ (D) 3.25 × 10⁶

Q.14 For a certain reaction of order n, the time for half change, $t_{1/2}$, is given by $t_{1/2} = \frac{[2 - \sqrt{2}]}{k} \times C_0^{1/2}$ where k is the rate constant and C₀ is the initial concentration what is n :

Q.15 In the Lindemann theory of unimolecular reactions, it is shown that the apparent rate constant for such a reaction is $k_{app} = \frac{k_{a}C}{1 + \alpha C}$ where C is the concentration of the reactant, k_1 and α are constants. Calculate the value of C for which k_{app} has 90% of its limiting value at C tending to infinitely large values, given $\alpha = 9 \times 10^5$. (A) 10⁻⁶ mol/litre (B) 10⁻⁴ mol/litre (C) 10⁻⁵ mol/litre (D) 5 × 10⁻⁵ mol/litre

Q.16 Given that for a reaction of order n the integrated form of the rate equation is

 $k = \frac{1}{t(n-1)} \left\lfloor \frac{1}{C^{n-1}} - \frac{1}{C_0^{n-1}} \right\rfloor$ where C₀ and C are the values of the reactant concentration at the

start and after time t . What is the relationship between $t_{3/4}$ and $t_{1/2}$ where $t_{3/4}$ is the time required for C to become $1/4 C_0$:

(A) $t_{3/4} = t_{\frac{1}{2}} [2^{n-1} + 1]$ (B) $t_{3/4} = t_{\frac{1}{2}} [2^{n-1} - 1]$ (B) $t_{3/4} = t_{\frac{1}{2}} [2^{n-1} - 1]$ (D) $t_{3/4} = t_{\frac{1}{2}} [2^{n+1} + 1]$

Q.17 Rate constant of a reaction is 0.0693 min⁻¹. Starting with 10 mol, rate of the reaction after 10 min is:
(A) 0.693 mol min⁻¹
(B) 0.0693 × 2 mol min⁻¹

(C) $0.0693 \times 5 \text{ mol min}^{-1}$ (D) $0.0693 \times (5)^2 \text{ mol min}^{-1}$

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

- Q.19 Which of the following statements is not correct?
 - (A) Law of mass action and rate law expressions are same for single step reactions
 - (B) Molecularity of the slowest elementary step of a complex reaction gives molecularity of 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.
- **Q.20** Which of the following are correct?
 - (A) total collision rate ∞ mean speed ∞ absolute temperature
 - (B) total collision rate $\propto \frac{1}{\text{mean speed}} \propto \frac{1}{\text{absolute temperature}}$
 - (C) total collision rate ∞ mean speed ∞ (absolute temperature)^{1/2}
 - (D) total collision rate ∞ (mean speed)² ∞ (absolute temperature)³
- Q.21 The rate equation for an autocatalytic reaction,

$$A + R \xrightarrow{k} R + R$$
 is $-r_A = -\frac{dC_A}{dt} = k C_A C_R$.

The rate of disappearance of reactant A is maximum where : (A) $C_A = 2 C_R$ (B) $C_A = C_R$ (C) $C_A = C_R/2$ (D) $C_A = (C_R)^{1/2}$

Q.22 The decomposition of a gaseous substance A to yield gaseous products, A (g) → 2 B (g) + C (g) follows first order kinetics. If the total pressure at the start of an experiment & 9 minutes after the start are 169 mm and 221 mm, what is the rate constant?
(A) 0.6804 min⁻¹ (B) 0.3024 min⁻¹ (C) 0.4536 min⁻¹ (D) 0.3780 min⁻¹

Q.23The decay constant of 226 Ra is 1.37×10^{-11} sec $^{-1}$. A sample of $_{226}$ Ra having an activity of 1.5 milli curie will contain atoms.(A) 4.05×10^{18} (B) 3.7×10^{17} (C) 2.05×10^{15} (D) 4.7×10^{10}

(A) they have the same difference of neutrons and protons or same isotopic number

(B) nuclide and its decay product after α -emission are isodiaphers

(C) $_{z}A^{m} \longrightarrow_{z-2}B^{m-4} + _{2}He^{4}$ 'A' and 'B' are isodiaphers

(D) all correct

Q.25 A radioactive element decays as

$$X \xrightarrow{\alpha \text{ decay}} Y \xrightarrow{(-2\beta)\beta \text{ decay}} Z$$

which of the following statements about this decay process is incorrect?

(A) after two hours, less than 10% of the initial X is left

(B) maximum amount of Y present at any time before 30 min is less than 50% of the initial amount of X.

(C) atomic number of X and Z are same

(D) the mass number of Y is greater than \boldsymbol{X}

Q.26 Among the following nuclides, the highest tendency to decay by (β^+) emission is – (A) Cu⁵⁹ (B) ⁶³Cu (C) ⁶⁷Cu (D) ⁶⁸Cu

Level – III

- **Q.1** Which of the following statement are correct?
 - (A) The order of a reaction is the sum of the components of all the concentration terms in the rate equation.
 - (B) The order of a reaction with respect to one reactant is the ratio of the change of logarithm of the rate of the reaction to the change in the logarithm of the concentration of the particular reactant, keeping the concentration all other reactants constant
 - (C) Orders of reactions can be whole numbers of fractional numbers.
 - (D) The order of a reaction can only be determined from the stoichiometric equation for the reaction.
- Q.2 Which of the following statements are correct?
 - (A) The rate of the reaction involving the conversion of ortho-hydrogen to parahydrogen is

$$-\frac{d[H_2]}{dt} = k[H_2]^{3/2}$$

- (B) The rate of the reaction involving the thermal decomposition of acetaldehyde is $k[CH_3CHO]^{3/2}$
- (C) In the formation of phosgene gas from CO and Cl_2 , the rate of the reaction is $k[CO][Cl_2]^{1/2}$
- (D) In the decomposition of H_2O_2 , the rate of the reaction is $k[H_2O_2]$.

Q.3Which of the following isomerization reactions is of the first order ?(A) cyclopropane \rightarrow propane(B) cis-but-2-ene \rightarrow trans-but-2-ene(C) vinyl allyl ether \rightarrow pent-4-enal(D) CH₃NC \rightarrow CH₃CN

- **Q.4** Which of the following reactions is of the first order ?
 - (A) The decomposition of ammonium nitrate in an aqueous solution
 - (B) The inversion of cane-sugar in the presence of an acid
 - (C) The acidic hydrolysis of ethyl acetate
 - (D) All radioactive decays.
- Q.5 Which of the following are examples of unimolecular reactions?

(A)
$$O_3 \rightarrow O_2 + O$$

(B) $CH_2 - CH_2 \longrightarrow CH_3CH = CH_2$
(C) $NO + O_3 \rightarrow NO_2 + O_2$
(D) $O + NO + N_2 \rightarrow + NO_2 + N_2$

Q.6 The calculation of the pre-exponential factor is based on the

- (A) idea that, for a reaction to take place, the reactant species must come together
- (B) Calculation of the molecularity of the reaction
- (C) idea that the reactant species must come together, leading to the formation of the transition state which then transforms into the products

CII

- (D) calculation of the order of the reaction
- Q.7 Which of the following are examples of pseudo-unimolecular reactions?

(A)
$$CH_3CO_2C_2H_5 + H_2O \xrightarrow{H^+} CH_3CO_2H + C_2H_5OH$$

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

(glu cose) (fructose)

- (C) $CH_3COCl + H2O \longrightarrow CH_3CO_2H + HCl$
- (D) $CH_3CO_2C_2H_5 + H_2O \xrightarrow{OH^-} CH_3CO_2H + C_2H_5OH$

- Q.8 In which of the following ways does an activated complex differ from an ordinary molecule ?
 - (A) It is quite unstable and has no independent existence.
 - (B) ΔH°_{f} is probably positive
 - (C) The system has a greater vibrational character.
 - (D) The system has no vibrational character.
- Q.9 The basic theory behind Arrhenius's equation is that
 - (A) the number of effective collisions is proportional to the number of molecules above a certain threshold energy
 - (B) as the temperature increases, so does the number of molecules with energies exceeding the threshold energy.
 - (C) the rate constant is function of temperature.
 - (D) the activation energy and pre-exponential factor are always temperature-independent

Q.10 In arrhenius's equation, $k = A \exp\left(-\frac{E_a}{RT}\right)$. A may be termed as the rate constant at

- (A) very low temperature(B) very high temperature(C) zero activation energy(D) the boiling temperature of the reaction mixture
- Q.11 Which of the following statements are correct about half-life 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% reaction is thrice of 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

Q.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)
$$\frac{\mathrm{dx}}{\mathrm{dt}} = k[Zn]^0[\mathrm{H}^+]^2$$
 (B) $\left(\frac{\mathrm{dx}}{\mathrm{dt}}\right) = k[Zn][\mathrm{H}^+]^2$

- (C) rate is not affected if concentration of zinc is made four times and that of H^+ ions is halved.
- (D) rate becomes four times if concentration of H⁺ ion is doubled at constant Zn concentration,.
- **Q.13**. In which of the following case, E_a of the backward reaction is greater than that of the forward reaction?

(A)
$$A + 10 \text{ kcal} \longrightarrow B$$
, $E_a = 50 \text{ kcal}$
(C) $A + 40 \text{ kcal} \longrightarrow B$, $E_a = 10 \text{ kcal}$

(B)
$$A + 20 \text{ kcal} \longrightarrow B, E_a = 40 \text{ kcal}$$

(D) A-40 kcal \longrightarrow B, $E_a = 20$ kcal

Q.14
$$A \longrightarrow B + C$$

(g) (g) (g)
 $-d[A]$

 $\frac{d_{\rm L}A_{\rm J}}{dt} = k[A]$

At the starting 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) $\frac{2.303}{10}\log\frac{100}{120}$



Which of the following statements are correct?

- (A) it is unimolecular nucleophilic substitution reaction S_{N^1} if I or II is formed.
- (B) it is bimolecular nucleophilic substituton reaction S_{N^2} if I or II is formed.
- (C) it is S_{N^1} if I and its enantiomer are formed so that mixture is racemic.
- (D) it is S_{N^2} if II is formed.
- **Q.16** The reaction, $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ Initial pressure of A and B are respectively $p_A = 0.60$ atm, $p_B = 0.80$ atm. When $p_C = 0.20$ atm, the rate of the reaction relative to the initial rate, is

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

Q.17 Rate constant k varies with temperature by eqn:

$\log k (\min^{-1}) = 5 - \frac{2000 \text{ K}}{\text{T}}.$	We can conclude
(A) pre-expontial factor A is 5	(B) E_a is 2000 kcal
(C) pre-exponential factor A is 10^5	(D) E^{i} is 9.212 kcal.

Q.18 The rate law for the dimerisation of NO_2 is

$$\frac{-\mathrm{d}[\mathrm{NO}_2]}{\mathrm{d}t} = \mathrm{k} \ [\mathrm{NO}_2]^2$$

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(D) none

Q.19 For a reaction for which the activation energies of the forward and reverse directions are equal in value:

(A) the stoichiometry is the mechanism	(B) $\Delta H = 0$
(C) $\Delta S = 0$	(D) the order is zero.

Q.20 A reaction is catalysed by H⁺ ion. In presence of H_A, rate constant is 2×10^{-3} min⁻¹ and in presence of H_B rate constant is 1×10^{-3} min⁻¹ HA and HB both being stronge acids, we may conclude.

(A) Equilibrium constant is 2

- (B) H_A is stronger than HB
- (C) relative strength of HA and HB is 2
- (D) HA is weaker than HB and relative strength is 0.5

Level – IV

Instruction: From Question (1 to 6) match the items under Column (A) with items under Column (B). Select the correct answer from the sets (A), (B), (C) and (D). Match the following

1.	Matc	Match the following							
		Column A		Column B					
	(i)	Half life of first order reaction	(a)	Active mass					
	(ii)	Arrhenius equation	(b)	$k = Ae^{-E_a/RT}$					
	(iii)	Molar concentration	(c)	$t_{1/2} = \frac{0.693}{k}$					
	(iv)	Half life period of zero order reaction	(d)	$\frac{a}{2k}$					
	(A) i-	·b, ii-a, iii-d, iv-c	(B) i-a, ii-c, i	ii-b, iv-d					
	(C) i-	c, ii-b, iii-a, iv-d	(D) i-c, ii-b, i	ii-d, iv-a					
2.	Mate	h the following							
		Column A		Column B					

- (i) Rate of reaction (a) Mol L⁻¹ time⁻¹ $\Delta[A]$ dx (ii) (b) dt Λt (iii) Unit of rate of reacton (c) Average rate of reaction (A) i-c, ii-a, iii-b (B) i-a, ii-b, iii-c (A) i-a, ii-c, iii-b (D) i-b, ii-c, iii-a
- 3. Match the following

Column A

- Zero order reaction (i)
- First order reation (ii)
- (iii) Second order reaction
- (iv) Instantaneous rate
- Temperature coefficient (v)
- (vi) Rate equation for third order reaction
- (vii) Acidic hydrolysis of ester
- (A) i-e, ii-f, iii-g, iv-c, v-a, vi-d, vii-b
- (C) i-e, ii-g, iii-f, iv-d, v-a, vi-c, vii-b

Column B

- k_{t+10} (a) k_t dx (b) dt
- $-\frac{\mathrm{d}x}{\mathrm{d}t} = \mathrm{k}[\mathrm{A}]^2[\mathrm{B}]$ (c)
- $H_2 + Cl_2 \xrightarrow{hv} 2HCl$ (d)
- $\tilde{CH}_{3}COOCH_{3} + NaOH \rightarrow$ (e)
 - $CH_{3}COONa + CH_{3}OH$
- $2H_2O_2 \rightarrow H_2O + O_2$ (f)
- Pseudo-unimolecular reaction (g)
- (B) i-d, ii-f, iii-e, iv-b, v-a, vi-c, vii-g
- (D) i-b, ii-c, iii-a, iv-d, v-f, vi-g, vii-e

4.	Match	the following						
		Column I	Column II Rate reaction					
		order				reaction	1	
	(i)	Zero			(a)	$k_2 = -\frac{1}{a}$	$\frac{x}{t(a-x)}$	
	(ii)	One			(b)	$k_0 = \frac{2}{3}$	$\frac{x}{t}$	
	(iii)	Two			(c)	$k_3 = -\frac{1}{t}$	$\frac{x(2a-2a^2)}{x(2a-2a^2)}$	$(-x)^{2}$
	(iv)	Three			(d)	$k_1 = \frac{2}{2}$	$\frac{.303}{t}\log$	$\frac{a}{a-x}$
	(A) i-l (C) i-c	b, ii-d, iii-a, iv-c c, ii-a, iii-b, iv-d			(B) i-d, ii-b, (D) i-a, ii-b,	iii-c, iv- iii-c, iv	-a -d	
5.	Match	the following						
	Column I Order		Column II Value of t _{0.5}			Column III Unit of K		
	(i)	Zero	(a)	$t_{0.5} = -$	$\frac{0.693}{k_1}$		(A) 1.r	nole ⁻¹ time ⁻¹
	(ii)	One	(b)	$t_{0.5} = -$	$\frac{A}{2k_0}$		(B) tin	ne ⁻¹
	(iii)	Two	(c)	t _{0.5} = -	$\frac{3}{2k_3a^2}$		(C) l ² .1	mole ² time ⁻¹
	(iv)	Three	(d)	t _{0.5} = -	$\frac{1}{k_{2a}}$		(D) mo	ol l ⁻¹ time ⁻¹
	(A) i-b,D, ii-a,B, iii-d,A iv-c-C (C) i-c,C, ii-b,A, iii-a,B iv-d-D		c-C d-D		(B) i-a,A, ii- (A) i-d,B, ii-	•c,B, iii-b •c,C, iii-b	o,C iv-o o,D iv-a	l-D a-A
6.	Match	the following						
		column I		Colun	nn II			Column II
	(i)	$N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_1$	2	(a)	Order $= 3$,		(A)	molecularity $= 2$
	(11)	$N_2O_2 \rightarrow N_2O + \frac{1}{2}O$	2	(b)	Order = 2 ,		(B)	molecularity = 3
	(Ш) (iv)	$2\Pi \rightarrow \Pi_2 + I_2$ $2NO + O \rightarrow 2NO$		(c) (d)	Order = 1, Order = 1		(\mathbf{U})	molecularity = 1
	(A) i - s	$2100 + O_2 \rightarrow 210O_2$	d.B	(u)	(B) i-d A ii-	c.B. iii-b	C iv-	1 D
	(C) i-0	c,C, ii-d,D, iii-a,B, iv-	b,A		*(D) i-d.C. ii	-c,D, iii-	b,A, iv	-, ∕-a,B
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OBJECTIVE QUESTION ANSWERS

Level–I						
1. B	2. B	3. D	4. C	5. A	6. A	
7. B	8. B	9. B	10. B	11. A	12. B	
13. B	14. D	15. A	16. C	17. A	18. C	
19. D	20. A	21. A	22. B	23. C	24. A	
25. C	26. B					

Level-II

1. B	2. B	3. B	4. A	5. B	6. B
7. B	8. B	9. C	10. B	11. B	12. C
13. B	14. D	15. C	16. A	17. C	18. D
19. D	20. C	21. B	22. B	23. A	24. D
25. D	26. C				

Level-III

1. ABC	2. ABCD	3. ABCD	4. ABCD	5. AB	6. AC
7. ABC	8. AC	9. ABC	10. BC	11. ABCD	12. BCD
13. D	14. C	15. CD	16. C	17. CD	18. B
19. B	20. BC				
		Leve	el–IV		
1. C	2. D	3. B	4. A	5. A	6. D