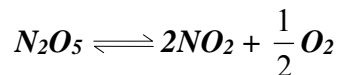


## Solved Problems

### Objective

**Problem 1:** What is the activation energy for the decomposition of  $N_2O_5$  as



If the values of the rate constants are  $3.45 \times 10^{-5}$  and  $6.9 \times 10^{-3}$  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 kJ

**Solution:**

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{6.9 \times 10^{-3}}{3.45 \times 10^{-5}} = \frac{E_a}{2.303 \times 8.31} \left[ \frac{40}{300 \times 400} \right]$$

$E_a = 112.5$  kJ  
 $\therefore$  (d)

**Problem 2:** 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:**

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

$$\frac{0.6932}{20} = \frac{2.303}{t} \log \frac{0.08}{0.01} = \frac{2.303}{t} \log 8 = \frac{2.303 \times 3 \times \log 2}{t}$$

$$\frac{1}{20} = \frac{3}{t}$$

$t = 60$  minutes  
 $\therefore$  (b)

**Problem 3:** The kinetic datas for the reaction:  $2A + B_2 \longrightarrow 2AB$  are as given below:

[A]	[B <sub>2</sub> ]	Rate
mol L <sup>-1</sup>	mol L <sup>-1</sup>	mol L <sup>-1</sup> min <sup>-1</sup>
0.5	1.0	$2.5 \times 10^{-3}$
1.0	1.0	$5.0 \times 10^{-3}$
0.5	2.0	$1 \times 10^{-2}$

Hence the order of reaction w.r.t. A and B<sub>2</sub> are, respectively,

- (a) 1 and 2 (b) 2 and 1  
(c) 1 and 1 (d) 2 and 2

**Solution:**  $2.5 \times 10^{-3} = K[0.5]^\alpha [1.0]^\beta \quad \dots(1)$

$5 \times 10^{-3} = K[1.0]^\alpha [1.0]^\beta \quad \dots(2)$

$1 \times 10^{-2} = K[0.5]^\alpha [2.0]^\beta \quad \dots(3)$

Dividing equation (1) and (2)

$$\frac{1}{2} = \left[ \frac{1}{2} \right]^\alpha$$

hence  $\alpha = 1$

Dividing equation (1) and (3)

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

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

$\beta = 2 \therefore$  (a)

**Problem 4:** For the first order reaction  $A_{(g)} \rightarrow 2B_{(g)} + C_{(g)}$ , 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)  $2.3 \times 10^{-3} \text{ sec}^{-1}$

(c)  $3.45 \times 10^{-3} \text{ sec}^{-1}$

(d)  $6 \times 10^{-3} \text{ sec}^{-1}$

**Solution:**  $A \rightarrow 2B + C$

P      0      0

P - x    2x    x

At equilibrium

$180 = P - x + 2x + x$

$180 = 90 + 2x$

$2x = 90, x = 45$

$$K = \frac{2.303}{t} \log \frac{P}{P-x} = \frac{2.303}{10} \log \frac{90}{90-45} = \frac{2.303}{10} \log 2 = \frac{0.6932}{10}$$

$$= 0.6932 = \frac{0.06932}{60} = 1.1555 \times 10^{-3} \text{ sec}^{-1}$$

$\therefore$  (a)

**Problem 5:** In the reaction  $2N_2O_5 \longrightarrow 4NO_2 + O_2$ ,  $+\frac{d[NO_2]}{dt}$  at any time  $t$  was found to be

$2.4 \times 10^{-4} \text{ mole L}^{-1} \text{ min}^{-1}$  with rate constant  $4.4 \times 10^{-4} \text{ min}^{-1}$ . Hence  $-\frac{d[N_2O_5]}{dt}$

at the same time  $t$  and the corresponding rate constant of the reactions respectively would be

(a)  $1.2 \times 10^{-4} \text{ mole L}^{-1} \text{ min}^{-1}$  and  $2.2 \times 10^{-4} \text{ min}^{-1}$

(b)  $1.2 \times 10^{-4} \text{ mole L}^{-1} \text{ min}^{-1}$  and  $8.8 \times 10^{-4} \text{ min}^{-1}$

(c)  $4.8 \times 10^{-4} \text{ mole L}^{-1} \text{ min}^{-1}$  and  $2.2 \times 10^{-4} \text{ min}^{-1}$

(d)  $2.4 \times 10^{-4} \text{ mole L}^{-1} \text{ min}^{-1}$  and  $4.4 \times 10^{-4} \text{ min}^{-1}$

**Solution:** For 4 moles of  $\text{NO}_2$  formed, 2 moles of  $\text{N}_2\text{O}_5$  consumed in a given time interval, so the rate consumption of  $\text{N}_2\text{O}_5$  must be half of the rate of formation of  $\text{NO}_2$ . Rate constants w.r.t. these two rates will also have the same relationship. So, the choice (A) is the correct answer.

**Problem 6:** The reaction  $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$ , follows the kinetics  $\text{Rate} \propto [\text{N}_2] [\text{O}_2]$   
 The order of reactions when both  $\text{N}_2$  and  $\text{O}_2$  are in small amount,  $\text{N}_2$  is in large excess as compared to  $\text{O}_2$  and both  $\text{N}_2$  and  $\text{O}_2$  are in large excess are  
 (a) 2,1 and 2 (b) 2,1, and 1  
 (c) 2,1 and 0 (d) 1,1, and 0

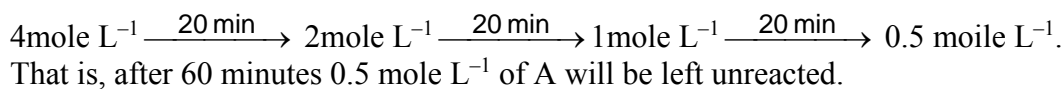
**Solutions:** When both  $\text{N}_2$  and  $\text{O}_2$  are in small amount or in large excess, the rate law obeyed will be  
 $\text{Rate} \propto [\text{N}_2] [\text{O}_2] \therefore \text{order} = 1 + 1 = 2$   
 When  $\text{N}_2$  is in large excess as compared to  $\text{O}_2$ , the rate law will reduce to  
 $\text{Rate} \propto [\text{O}_2] \therefore \text{order w.r.t. } \text{O}_2 = 1$   
 Order w.r.t.  $\text{N}_2 = 0$   
 Overall order =  $1 + 0 = 1$   
 So, choice (A) is the correct answer.

**Problem 7:** The reaction :  $2\text{NO} + 2\text{H}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$  has been assigned to follow following mechanism.  
 I.  $\text{NO} + \text{NO} \rightleftharpoons \text{N}_2\text{O}_2$  (fast)  
 II.  $\text{N}_2\text{O}_2 + \text{H}_2 \longrightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$  (slow)  
 III.  $\text{N}_2\text{O} + \text{H}_2 \longrightarrow \text{N}_2 + \text{H}_2\text{O}$  (fast)  
 The rate constant of step II is  $1.2 \times 10^{-4} \text{ mole}^{-1} \text{ L. min}^{-1}$  while equilibrium constant of step I is  $1.4 \times 10^{-2}$ . What is the rate of reaction when concentration of  $\text{NO}$  and  $\text{H}_2$  each is  $0.5 \text{ mole L}^{-1}$   
 (a)  $2.1 \times 10^{-7} \text{ mole L}^{-1} \text{ min}^{-1}$  (b)  $3.2 \times 10^{-6} \text{ mole L}^{-1} \text{ min}^{-1}$   
 (c)  $3.5 \times 10^{-4} \text{ mole L}^{-1} \text{ min}^{-1}$  (d) none of these

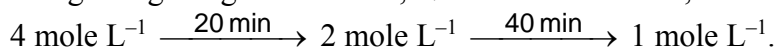
**Solution:**  $k_{\text{obs}} = k \cdot k_c = 1.2 \times 10^{-1} \times 1.4 \times 10^{-2} = 1.68 \times 10^{-6} \text{ mole}^{-1} \text{ L min}^{-1}$   
 $\text{Rate} = k_{\text{obs}} [\text{NO}]^2 [\text{H}_2]$   
 $= 1.68 \times 10^{-6} \times 0.5^2 \times 0.5$   
 $= 2.1 \times 10^{-7} \text{ mole L}^{-1} \text{ min}^{-1}$   
 So, answer must be choice (a)

**Problem 8:** A first order reaction :  $\text{A} \longrightarrow \text{Products}$  and a second order reaction :  $2\text{R} \longrightarrow \text{Products}$  both have half - time of 20 minutes when they are carried out taking  $4 \text{ mole L}^{-1}$  of their respective reactants. Number of mole per litre of A and R remaining unreacted after 60 minutes from the start of the reaction, respectively will be.  
 (a) 1 and 0.5 (b) 0.5 and negligible  
 (c) 0.5 and 1 (d) 1 and 0.25

**Solution:** In the case of first order reaction  $t_{1/2}$  will remain constant independent of initial concentration so.



In the case of second order reaction  $t_{1/2}$  is inversely proportional to initial concentration of reactant i.e.,  $t_{1/2}$  will go on doubling as concentration of reactant will go on getting half. That is,  $t_{1/2}$  will be constant, so.



That is, after 60 minutes, the concentration of R remaining unreacted will be 1 mole  $\text{L}^{-1}$ . Note that  $t_{1/2} a = 20 \times 4 = 40 \times 2 = 80 \text{ mole L}^{-1} \text{ min}$ , a constant.

$\therefore$  (b)

**Problem 9:** In a reaction carried out at 500 K, 0.001% of the total number of collisions are effective. The energy of activation of the reaction is approx.

- (a) 15.8 K cal  $\text{mole}^{-1}$                       (b) 11.5 K cal  $\text{mole}^{-1}$   
 (c) 12.8 K cal  $\text{mole}^{-1}$                       (d) zero

**Solution:**  $e^{-E_a/2 \times 50} = 10^{-5} \therefore E_a = 11.5 \text{ K cal}$   
 $\therefore$  Option (b) is the correct choice.

**Problem 10:** The catalyst decrease the  $E_a$  from 100  $\text{kJ mol}^{-1}$  to 80  $\text{kJ mol}^{-1}$ . At what temperature the rate of reaction in the absence of catalyst at 500 K will be equal to rate reaction in presence of catalyst.

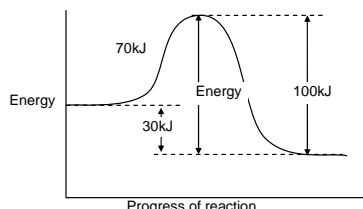
- (a) 400 K                                      (b) 200 K  
 (c) 625 K                                      (d) None of these

**Solution:**  $\frac{-E_a}{RT} = -\frac{E'_a}{RT'}$ ,  $\frac{100}{500} = \frac{80}{T'}$ ,  
 $\therefore T' = 400\text{K}$   
 $\therefore$  (a)

**Problem 11:** If a reaction  $A + B \rightarrow C$  is exothermic to the extent of 30  $\text{kJ/mol}$  and the forward reaction has an activation energy 70  $\text{kJ/mol}$ , the activation energy for the reverse reaction is

- (a) 30  $\text{kJ/mol}$                               (b) 40  $\text{kJ/mol}$   
 (c) 70  $\text{kJ/mol}$                               (d) 100  $\text{kJ/mol}$

**Solution:**



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

$\therefore$  (d)

**Problem 12:** The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are  $3.0 \times 10^{-4} \text{ s}^{-1}$ ,  $104.4 \text{ kJ mol}^{-1}$  and  $6.0 \times 10^{14} \text{ s}^{-1}$  respectively the value of the rate constant as  $T \rightarrow \infty$  is

- (a)  $2.0 \times 10^{18} \text{ s}^{-1}$  (b)  $6.0 \times 10^{14} \text{ s}^{-1}$   
 (c)  $\infty$  (d)  $3.6 \times 10^{30} \text{ s}^{-1}$

**Solution:**  $K = Ae^{-E_a/RT}$   
 When  $T \rightarrow \infty$   
 $K \rightarrow A$   
 $A = 6 \times 10^{14} \text{ s}^{-1}$   
 $\therefore$  (b)

**Problem 13:** 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)  $r = K[\text{sugar}]^2[\text{H}]^6$  (b)  $r = K[\text{sugar}]^1[\text{H}]^0$   
 (c)  $r = K[\text{sugar}]^0[\text{H}^+]^6$  (d)  $r = K[\text{sugar}]^0[\text{H}^+]^1$

**Solution:** Since  $t_{1/2}$  does not depend upon the sugar concentration means it is first order respect to sugar concentration.  $t_{1/2} \propto [\text{sugar}]^1$ .  
 $t_{1/2} \times a^{n-1} = k$

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

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

$$10 = (10)^{1-n}, \text{ Hence } n = 0. \therefore \text{(b)}$$

**Problem 14:** 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:** 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

$$\frac{[A^0]}{2^{n_1}} = \frac{[B_0]}{2^{n_2}} \Rightarrow \frac{4}{2^{n_1}} = \frac{1}{2^{n_2}}, \quad [[A_0] = 4[B_0]]$$

$$\therefore \frac{2^{n_1}}{2^{n_2}} = 4 \Rightarrow 2^{n_1-n_2} = (2)^2 \therefore n_1 - n_2 = 2$$

$$\therefore n_2 = (n_1 - 2) \quad \dots(1)$$

$$\text{Also } t = n_1 \cdot t_{1/2(A)} \quad t = n_2 \times t_{1/2(B)}$$

(Let concentration of both become equal after time t)

$$\sqrt{\frac{n_1 \cdot t_{1/2(A)}}{n_2 \cdot t_{1/2(B)}} = 1} \Rightarrow \frac{n_1 \cdot 5}{n_2 \cdot 15} = 1 \Rightarrow \frac{n_1}{n_2} = 3 \quad \dots(2)$$

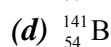
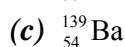
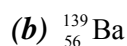
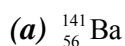
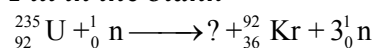
For equation (1) and (2)

$$n_1 = 3, n_2 = 1$$

$$t = 3 \times 5 = 15 \text{ minute}$$

$\therefore$  (a)

**Problem 15:** *Fill in the blank*



**Solution:**  $92 + 0 = Z + 36 + 0 \Rightarrow Z = 56$

$$235 + 1 \longrightarrow A + 92 + 3$$

$$\therefore A = 144$$

Missing nuclide is  ${}_{56}^{141}\text{Ba}$

$\therefore$  (a)

**Problem 16:** *The rate of a reaction increases 4-fold when concentration of reactant is increased 16 times. If the rate of reaction is  $4 \times 10^{-6} \text{ mole L}^{-1} \text{ S}^{-1}$  when concentration of the reactant is  $4 \times 10^{-4}$ , the rate constant of the reaction will be*

(a)  $2 \times 10^{-4} \text{ mole}^{1/2} \text{ L}^{-1/2} \text{ S}^{-1}$

(b)  $1 \times 10^{-2} \text{ S}^{-1}$

(c)  $2 \times 10^{-4} \text{ mole}^{-1/2}, \text{ L}^{1/2} \text{ S}^{-1}$

(d)  $25 \text{ mole}^{-1} \text{ L min}^{-1}$

**Solution:** Rate  $\propto \sqrt{\text{concn}}$ , Rate =  $k\sqrt{\text{concn}}$

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

$\therefore$  (a)

**Problem 17:** *A catalyst lowers the activation energy of a reaction from  $20 \text{ kJ mole}^{-1}$  to  $10 \text{ kJ mole}^{-1}$ . The temperature at which the uncatalysed reaction will have the same rate as that of the catalysed at  $27^\circ \text{C}$  is*

(a)  $-123^\circ \text{C}$

(b)  $327^\circ \text{C}$

(c)  $327^\circ \text{C}$

(d)  $+23^\circ \text{C}$

**Solution:**  $\frac{E'_a}{T_1} = \frac{E_a}{T_2} = \frac{10}{300} = \frac{20}{T_2}$

$$\therefore T_2 = 600 \text{ K} = 327^\circ \text{C}$$

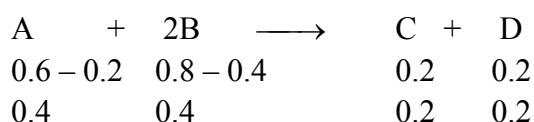
$\therefore$  (b)

**Problem 18:** 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:**  $R_1 = K[A][B] = K[0.6][0.80]^2$

After reaction



$$\frac{R_2}{R_1} = \frac{K(0.4)(0.4)^2}{(0.6)(0.8)^2} = \frac{1}{6}$$

$\therefore$  (d)

**Problem 19:** Thermal decomposition of a compound is of first order. If 50% of a sample of the compound is decomposed in 120 minute show long will it take for 90% of the compound to decompose?

- (a) 399 min (b) 410 min  
(c) 250 min (d) 120 min

**Solution:**  $K = \frac{0.6932}{120} \dots(1)$

$$\begin{aligned} K &= \frac{2.303}{t} \log \frac{a}{0.10a} \\ &= \frac{2.303}{t} \log 10 \dots(2) \end{aligned}$$

Equating (1) and (2)

$$\frac{0.6932}{120} = \frac{2.303}{t}$$

$$t = 399 \text{ minutes}$$

$\therefore$  (a)

**Problem 20:** If concentration are measured in mole/litre and time in minutes, the unit for the rate constant of a 3<sup>rd</sup> order reaction are

- (a)  $\text{mol lit}^{-1} \text{min}^{-1}$  (b)  $\text{lit}^2 \text{mol}^{-2} \text{min}^{-1}$   
(c)  $\text{lit mol}^{-1} \text{min}^{-1}$  (d)  $\text{min}^{-1}$

**Solution:**  $K = [\text{conc.}]^{1-n} \text{min}^{-1}$

For 3<sup>rd</sup> order reaction

$$= [\text{mole/litre}]^{1-3} \text{min}^{-1} = \text{lit}^2 \cdot \text{mole}^{-2} \text{min}^{-1}$$

$\therefore$  (b)

**Subjective**

**Problem 1:** *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)<sup>-1</sup> for the decay? What fraction would remain after 11540 years?*

**Solution:**

$$K = \frac{0.693}{T_{1/2}} = \frac{0.693}{5770} = 1.201 \times 10^{-4} \text{ year}^{-1}$$

$$K = \frac{2.303}{t} \log \frac{N_0}{N_t}$$

$$1.201 \times 10^{-4} = \frac{2.303}{11540} \log \frac{N_0}{N_t}$$

$$4.002 = \frac{N_0}{N_t} \therefore \frac{N_t}{N_0} \text{ (Remaining fraction)} = \frac{1}{4.002}$$

**Problem 2:** *A sample of  $^{131}_{53}\text{I}$ , 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  $T_{1/2} \text{ } ^{131}\text{I} = 8 \text{ days}$ .*

**Solution:** We know,

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

$$\frac{0.693}{8} = \frac{2.303}{4} \log_{10} \left[ \frac{N_0}{N} \right]$$

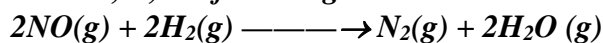
$$\frac{N}{N_0} = 0.707$$

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

Thus, weight of  $\text{I}^-$  migrated to thyroid gland may be calculated as

$$\frac{67.7}{70.7} \times 100 = 95.75\% \text{ i.e., } 0.1 \times \frac{95.75}{100} = 0.09575 \text{ mg}$$

**Problem 3:** *At 1100, K, the following data were obtained on the homogeneous reaction:*



	$[\text{NO}]$ (mole $\text{dm}^{-3}$ )	$[\text{H}_2]$ (mole $\text{dm}^{-3}$ )	Rate, $r$ (mole $\text{dm}^{-3} \text{ s}^{-1}$ )
1)	$5 \times 10^{-3}$	$2.5 \times 10^{-3}$	$3 \times 10^{-5}$
2)	$15 \times 10^{-3}$	$2.5 \times 10^{-3}$	$9 \times 10^{-5}$
3)	$15 \times 10^{-3}$	$10 \times 10^{-3}$	$3.6 \times 10^{-5}$

- Calculate the order of the reaction with respect to NO, with respect to  $\text{H}_2$  and the overall reaction order.
- Write the rate law expression for the reaction.
- Calculate the rate constant of the reaction.
- What will be the initial rate of the reaction if  $[\text{NO}] = [\text{H}_2] = 8 \times 10^3$  mole  $\text{dm}^{-3}$ ?



- Solution:** i) Let the rate  $r$  be equal to  $r = k[\text{NO}]^a [\text{H}_2]^b$   
 where  $a$  and  $b$  are the order with respect to  $\text{NO}$  and  $\text{H}_2$   
 Dividing (1) by (2)  

$$\frac{3 \times 10^{-5}}{9 \times 10^{-5}} = \left( \frac{5 \times 10^{-3}}{15 \times 10^{-3}} \right)^a \left( \frac{2.5 \times 10^{-3}}{2.5 \times 10^{-3}} \right)^b \Rightarrow \frac{1}{3} = \left( \frac{1}{3} \right)^a \quad \therefore a=1$$
  
 Dividing (2) by (3)  

$$\frac{9 \times 10^{-5}}{3.6 \times 10^{-5}} = \left( \frac{2.5 \times 10^{-3}}{10 \times 10^{-3}} \right)^b \quad 0.25 = (0.25)^b \quad \therefore b=1$$
  
 ii)  $r = k[\text{NO}] [\text{H}_2]$   
 iii)  $k = \frac{(3 \times 10^{-5})}{(5 \times 10^{-3})(2.5 \times 10^{-3})} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 2.4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$   
 iv) Initial rate =  $(2.4)(8 \times 10^{-3})(8 \times 10^{-3}) \text{ mol dm}^{-3} \text{ s}^{-1}$   
 $= 1.536 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$

**Problem 4:** *The inactivation of a viral preparation in a chemical bath is found to be a first order reaction (a) calculate the rate constant for the viral inactivation if in the beginning 1.5 % of the virus is inactivated per minute. Also calculate the time required for (b) 50% inactivation and (c) 80% inactivation of the virus.*

- Solution:** a) The rate law for the first - order reaction is  

$$-\frac{d[\text{A}]}{dt} = k_1 [\text{A}] \text{ or } k_1 = \frac{1}{[\text{A}]} \times \frac{d[\text{A}]}{dt}$$
  
 For a small finite change.  

$$k_1 = -\frac{1}{[\text{A}]} \frac{\Delta[\text{A}]}{\Delta t} \Rightarrow \left( \frac{\Delta[\text{A}]}{[\text{A}]} \right) / \Delta t = 1.5\% \text{ per minute}$$
  

$$k_1 = \frac{0.015}{60\text{s}} = 2.5 \times 10^{-4} \text{ s}^{-1}$$
  
 b)  $t_{1/2} = \frac{0.693}{k_1} = \frac{0.693}{2.5 \times 10^{-4} \text{ s}^{-1}} = 2.77 \times 10^3 \text{ s} = 46 \text{ min}$   
 c)  $t = \frac{2.303}{k_1} \log \frac{100}{100-80} = 6.44 \times 10^3 \text{ s} = 10.7 \text{ min}$

**Problem 5:** *5 ml of ethylacetate was added to a flask containing 100 ml of 0.1 N HCl placed in a thermostat maintained at 30°C. 5 ml of the reaction mixture was withdrawn at different intervals of time and after chilling, titrated against a standard alkali. The following data were obtained :*

<i>Time (minutes)</i>	<i>0</i>	<i>75</i>	<i>119</i>	<i>183</i>	<i><math>\infty</math></i>
<i>ml of alkali used</i>	<i>9.62</i>	<i>12.10</i>	<i>13.10</i>	<i>14.75</i>	<i>21.05</i>

*Show that hydrolysis of ethyl acetate is a first order reaction.*

**Solution:** The hydrolysis of ethyl acetate will be a first order reaction if the above data confirm to the equation.

$$k_1 = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

Where  $V_0$ ,  $V_t$  and  $V_\infty$  represent the volumes of alkali used at the commencement of the reaction, after time  $t$  and at the end of the reaction respectively, Hence

$$V_\infty - V_0 = 21.05 - 9.62 = 11.43$$

$$\text{Time} \quad V_\infty - V_t \quad \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_0 - V_t} = k_1$$

$$75 \text{ min} \quad 21.05 - 12.10 = 8.95 \quad \frac{2.303}{75} \log \frac{11.43}{8.95} = 0.003259 \text{ min}^{-1}$$

$$119 \text{ min} \quad 21.05 - 13.10 = 7.95 \quad \frac{2.303}{119} \log \frac{11.43}{7.95} = 0.003264 \text{ min}^{-1}$$

$$83 \text{ min} \quad 21.05 - 14.75 = 6.30 \quad \frac{2.303}{183} \log \frac{11.43}{6.30} = 0.003254 \text{ min}^{-1}$$

A constant value of  $k$  shows that hydrolysis of ethyl acetate is a first order reaction

**Problem 6:** *Rate of a reaction  $A + B \rightarrow \text{Products}$ ; is given below as a function of different initial concentrations of A and B*

<i>[A] mol/litre</i>	<i>[B] mol litre<sup>-1</sup></i>	<i>Initial rate mol litre<sup>-1</sup> time<sup>-1</sup></i>
<i>0.01</i>	<i>0.01</i>	<i>0.005</i>
<i>0.02</i>	<i>0.01</i>	<i>0.010</i>
<i>0.01</i>	<i>0.02</i>	<i>0.005</i>

*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  $n$ .

$$\text{Rate} = K[A]^m [B]^n$$

$$0.005 = K [0.01]^m [0.01]^n \quad \dots \text{ (i)}$$

$$0.010 = K [0.02]^m [0.01]^n \quad \dots \text{ (ii)}$$

$$0.005 = K [0.01]^m [0.02]^n \quad \dots \text{ (iii)}$$

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

$$\frac{0.005}{0.010} = \left[ \frac{0.01}{0.02} \right]^m$$

$$\frac{1}{2} = \left[ \frac{1}{2} \right]^m \quad \therefore m = 1$$

Thus, order with respect to A is one.

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

$$\frac{0.005}{0.005} = \left[ \frac{0.01}{0.02} \right]^n$$

$$1 = \left[ \frac{1}{2} \right]^n \quad \therefore n = 0$$

Thus, order with respect to B is zero.

Substituting the values of m and n in Eq. (i), we get

$$0.005 = K [0.01]^1 [0.01]^0 \quad \therefore \frac{0.005}{0.01} = 0.5$$

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

**Problem 7:** *The decomposition of  $\text{Cl}_2\text{O}_7$  at 440K in the gas phase to  $\text{Cl}_2$  and  $\text{O}_2$  is a first order reaction.*

i) *After 55 seconds at 400 K the pressure of  $\text{Cl}_2\text{O}_7$  falls from 0.062 to 0.044 atm., calculate that rate constant.*

ii) *Calculate the pressure of  $\text{Cl}_2\text{O}_7$  after 100 sec. of decomposition at this temperature.*

**Solution:** i) In the present equation we may apply the formula

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

ii) Pressure after 100 sec may be calculated as

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

$$p_t = 0.0332 \text{ atm}$$

**Problem 8:** *Rate law for the following reaction; is*  
*Ester +  $\text{H}^+ \rightleftharpoons$  Acid + Alcohol; is*

$$\frac{dx}{dt} = K [\text{ester}]^1 [\text{H}^+]^0$$

*What would be the effect on the rate if*

i) *Concentration of ester is doubled?*

ii) *Concentration of  $\text{H}^+$  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  $\text{H}^+$  ion is doubled velocity will be unaffected.

**Problem 9:** *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

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

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

**Problem 10:** At 27°C it was observed, during a reaction of hydrogenation that the pressure of H<sub>2</sub> gas decreases from 2 atm to 1.1 atm in 75 min. Calculate the rate of reaction (molarity/sec). Given (R = 0.082/litre atm K<sup>-1</sup> mole<sup>-1</sup>)

**Solution:** Rate =  $\frac{\text{Decrease in pressure}}{\text{Time duration}}$

$$= \frac{2 - 1.1}{75} = 0.012 \text{ atm/min}$$

$$\text{Rate in atm/sec} = \frac{0.012}{60} = 2 \times 10^{-4} \text{ atm/sec.}$$

Answer is required in molarity per second

$$\therefore PV = nRT$$

$$\frac{P}{RT} = \frac{n}{V}$$

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

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

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

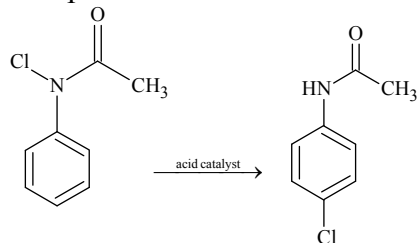
$$8.12 \times 10^{-6} \text{ . Rate in molarity/sec} = (n/V)/\text{sec}$$

**Problem 11:** 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<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, the results obtained were as follows :

Time (hours)	0	1	2	4	6	8
(a-x) i.e., hypo	45	32	22.5	11.3	3.7	2.9

show that reaction is unimolecular 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.

$$\text{After 1 hours} \quad K = \frac{2.303}{1} \log \left\{ \frac{45}{32} \right\} = 0.34098 \text{ hour}^{-1}$$

$$\text{After 2 hours} \quad K = \frac{2.303}{2} \log \left\{ \frac{45}{22.5} \right\} = 0.34660 \text{ hour}^{-1}$$

$$\text{After 4 hours} \quad K = \frac{2.303}{4} \log \left\{ \frac{45}{11.3} \right\} = 0.3455 \text{ hour}^{-1}$$

$$\text{After 6 hours} \quad K = \frac{2.303}{6} \log \left\{ \frac{45}{3.7} \right\} = 0.4164 \text{ hour}^{-1}$$

$$\text{After 8 hours} \quad K = \frac{2.303}{8} \log \left\{ \frac{45}{2.9} \right\} = 0.3428 \text{ hour}^{-1}$$

Average value of constant =  $0.3584 \text{ hours}^{-1}$

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.

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

$$0.3584 = \frac{2.303}{3} \log \frac{a}{a-x}$$

$$\therefore \frac{a}{a-x} = 2.98 \quad \therefore \frac{a-x}{a} = 0.3412$$

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

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

**Problem 12:** 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  $58.5 \text{ kcal}$ . Calculate half life period for first order decomposition at  $527^\circ\text{C}$ .

**Solution:** Taking logarithm of Arrhenius equation

$$K = Ae^{-E/RT} \text{ we get}$$

$$\log K = \log A - \frac{E}{2.303RT} \quad \dots \text{ (i)}$$

$$\text{Given } A = 1.26 \times 10^{13}$$

$$E = 58.5 \text{ kcal}$$

$$T = 527 + 273 = 800 \text{ K}$$

Substituting these value in Eq. (i), we get

$$\log K = \log (1.26 \times 10^{13}) - \frac{58.5 \times 10^2}{2.303 \times 1.987 \times 800}$$

$$= 13.1003 - 15.9799 = -2.8796$$

$$K = 1.3194 \times 10^{-3} \text{ sec}^{-1}$$

$$t_{1/2} = \frac{0.693}{1.3194} \times 10^3 \text{ sec} = 525 \text{ sec}$$

**Problem 13:** For the reaction —

$2\text{NO}(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{g})$  at 900 K, the following data are obtained :

Initial pressure of NO (atm)	Initial pressure of H <sub>2</sub> (atm)	Rate (atm min <sup>-1</sup> )
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 constant.

**Solution:** Let order with respect to NO(g) is 'm' and order with respect to H<sub>2</sub>(g) is 'n'

$$\text{Then, Rate} = K[\text{P}_{\text{NO}}]^m[\text{P}_{\text{H}_2}]^n \quad \dots (1)$$

$$0.020 = K [0.15]^m [0.40]^n \quad \dots (2)$$

$$0.005 = K [0.075]^m [0.40]^n \quad \dots (3)$$

$$0.010 = K [0.15]^m [0.2]^n \quad \dots (4)$$

Dividing Eq. (2) by (3), we get

$$\frac{0.020}{0.005} = \left(\frac{0.15}{0.075}\right)^m, m = 2$$

Dividing Eq. (2) by (4), we get

$$\frac{0.020}{0.010} = \left(\frac{0.4}{0.2}\right)^n, n = 1$$

$$\text{Rate} = [\text{P}_{\text{NO}}]^2[\text{P}_{\text{H}_2}]^1$$

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 14:** 10 gram atoms of an  $\alpha$ -active radio isotope are disintegrating in a sealed container. In one hour the helium gas collected at STP is 11.2 cm<sup>3</sup>. Calculate the half-life of the radio-isotope.

**Solution:** No. of atoms of helium is 11.2 cc at NTP

$$= \frac{11.2}{22400} \times 6.02 \times 10^{23} = 3.01 \times 10^{20} \text{ atoms}$$

Since, helium atom corresponds to  $\alpha$ -particle. Thus, Rate of disintegration

$$= 3.01 \times 10^{20} \text{ per hour.}$$

We know, Rate = Rate constant  $\times$  concentration in atom

$$3.01 \times 10^{20} = K \times 10 \times 6.02 \times 10^{23}$$

$$K = 0.05 \times 10^{-3} \text{ hour}^{-1}$$

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

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

**Problem 15:** 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  $\text{cm}^3$  at STP.

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

$$N_t = N_0 \left( \frac{1}{2} \right)^n$$

$$\text{where } n = \text{no of half lives} = 20/10 = 2 = 1 \left( \frac{1}{2} \right)^2 = \frac{1}{4}$$

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

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

## Assignments (New Pattern)

### SECTION - I

### Single Choice Questions

1. For a hypothetical reaction  
 $A + B \longrightarrow \text{Product}$ , the rate law is  
 $r = k [B] [A]^0$ , the order of reaction is  
 (a) 0 (b) 1  
 (c) 2 (d) 3.
  
2. A hypothetical reaction  $A_2 + B_2 \longrightarrow 2AB$  follows the mechanism as given below:  
 $A_2 \longrightarrow A + A$  (fast)  
 $A + B_2 \longrightarrow AB + B$  (slow)  
 $A + B \longrightarrow AB$  (fast)  
 The order of the overall reaction is  
 (a) 2 (b) 1  
 (c)  $1 \frac{1}{2}$  (d) 0.
  
3. 99% of a first order reaction was completed in 32 min. When will 99.9% of the reaction complete ?  
 (a) 24 min (b) 8 min  
 (c) 4 min (d) 48 min
  
4. A gaseous reaction  $A_2(g) \longrightarrow B(g) + \frac{1}{2} C(g)$ . Shows increase in pressure from 100 mm to 120 mm in 5 minutes. The rate of disappearance of  $A_2$  is  
 (a)  $4 \text{ mm min}^{-1}$  (b)  $8 \text{ mm min}^{-1}$   
 (c)  $16 \text{ mm min}^{-1}$  (d)  $2 \text{ mm min}^{-1}$ .
  
5. In the formation of sulphur trioxide by the contact process.  
 $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$   
 The rate of reaction is expressed as  
 $-\frac{d(\text{O}_2)}{dt} = 2.5 \times 10^{-4} \text{ mole}^{-1}\text{L}^{-1} \text{ sec}^{-1}$   
 The rate of disappearance of ( $\text{SO}_2$ ) will be  
 (a)  $5.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$  (b)  $-2.25 \times 10^4 \text{ mol L}^{-1} \text{ s}^{-1}$   
 (c)  $3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$  (d)  $50.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ .
  
6. The half life period for catalytic decomposition of  $\text{AB}_3$  at 50 mm in found to be 4 hrs and at 100 mm it is 2.0 hrs. The order of reaction is  
 (a) 3 (b) 1  
 (c) 2 (d) 0



7. For a reaction  
 $X(g) \rightarrow Y(g) + Z(g)$   
 The half-life period is 10 min. In what period of time would be concentration of X be reduced to 10% of original concentration ?  
 (a) 20 min. (b) 33 min  
 (c) 15 min (d) 25 min.
8. For the reaction  $2NH_3 \longrightarrow N_2 + 3H_2$   

$$-\frac{d[NH_3]}{dt} = k_1[NH_3], \quad \frac{d[N_2]}{dt} = k_2[NH_3], \quad \frac{d[H_2]}{dt} = k_3[NH_3]$$
  
 Then relation between  $k_1$ ,  $k_2$  and  $k_3$  is:  
 (a)  $1.5k_1 = 3k_2 = k_3$  (b)  $2k_1 = k_2 = 3k_3$   
 (c)  $k_1 = k_2 = k_3$  (d)  $k_1 = 3k_2 = 2k_3$
9. The rate of the reaction  $A + B_2 \longrightarrow AB + B$  is directly proportional to the concentration of A and independent of concentration of  $B_2$ , hence, rate law is:  
 (a)  $k[A][B_2]$  (b)  $k[A]^2[B_2]$   
 (c)  $k[A]$  (d)  $k[B_2]$
10.  $A \rightarrow \text{Product}$ ,  $[A]_0 = 2M$ . After 10 minutes reaction is 10% completed. If  $-\frac{d[A]}{dt} = k[A]$  then  $T_{50}$  is approximately:  
 (a) 0.693 min (b) 69.3 min  
 (c) 66.0 min (d) 0.0693 min
11. The decomposition of nitrogen pentoxide can be represented as  

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$
  
 The rate of the reaction can be expressed as  
 (a)  $-\frac{d[N_2O_5]}{dt} = 2\frac{d[NO_2]}{dt} = \frac{1}{2}\frac{d[O_2]}{dt} = k[N_2O_5]$   
 (b)  $\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt} = k[N_2O_5]$   
 (c)  $-\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = 2\frac{d[O_2]}{dt} = k[N_2O_5]$   
 (d)  $-\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = \frac{1}{2}\frac{d[O_2]}{dt} = k[N_2O_5]$
12. The rate constant for the reaction  
 $2N_2O_5 \longrightarrow 4NO_2 + O_2$   
 is  $3 \times 10^{-5} s^{-1}$ . If the rate at a given time is  $2.40 \times 10^{-5} \text{ mol L}^{-1} s^{-1}$ , then concentration of  $N_2O_5$  at that time is:  
 (a) 1.4 (b) 1.2  
 (c) 0.04 (d) 0.8

13. Calculate the half-life of the first-order reaction  
 $\text{C}_2\text{H}_4\text{O}(\text{g}) \longrightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$   
if the initial pressure of  $\text{C}_2\text{H}_4\text{O}(\text{g})$  is 80 mm and the total pressure at the end of 20 minutes is 120 mm.  
(a) 40 min (b) 120 min  
(c) 20 min (d) 80 min
14. 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:  
(a) 10 min (b) 20 min  
(c) 30 min (d) 40 min
15. Rate of formation of  $\text{SO}_3$  in the following reaction  
 $2\text{SO}_2 + \text{O}_2 \longrightarrow 2\text{SO}_3$   
is  $100 \text{ g min}^{-1}$ . Hence, rate of disappearance of  $\text{O}_2$  is:  
(a)  $50 \text{ g min}^{-1}$  (b)  $100 \text{ g min}^{-1}$   
(c)  $200 \text{ g min}^{-1}$  (d)  $40 \text{ g min}^{-1}$
16. In the first order reaction the concentration of reactant decreases from 2 M to 0.50 M in 20 minutes. The value of specific rate is  
(a) 69.32 (b) 6.932  
(c) 0.6932 (d) 0.06932
17. For a chemical reaction  $\text{A} \longrightarrow \text{B}$ , the rate of reaction increases by a factor of 1.837 when the concentration of A is increased by 1.5 times. The order of reaction with respect to A is  
(a) 1 (b) 1.5  
(c) 2 (d) -1
18. Rate of the chemical reaction :  $n\text{A} \longrightarrow \text{products}$ , is doubled when the concentration of A is increased four times. If the half time of the reaction at any temperature is 16 min. then time required for 75% of the reaction to complete is  
(a) 24.0 min. (b) 27.3 min.  
(c) 48 min. (d) 49.4 min.
19. For a first order reaction the ratio of  $t_{0.75}$  to  $t_{0.50}$  would be  
(a) 4 : 3 (b) 3 : 2  
(c) 2 : 1 (d) 1 : 2
20. Two substances A( $t_{1/2} = 5 \text{ min.}$ ) and B( $t_{1/2} = 15 \text{ min.}$ ) are taken in such way that initially  $[\text{A}]_0 = 4[\text{B}]_0$ . The time after which both the concentrations will be equal is  
(a) 5 min. (b) 15 min.  
(c) 20 min (d) Concentrations can never be equal
21. Two substances A( $t_{1/2} = 5 \text{ min.}$ ) and B( $t_{1/2} = 15 \text{ min.}$ ) are taken in such way that initially  $[\text{A}] = 4[\text{B}]$ . The time after which both the concentrations will be equal is  
(a) 5 min. (b) 15 min.  
(c) 20 min. (d) concentrations can never be equal

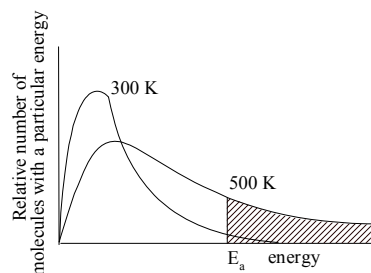
22. The time elapsed of a certain reaction between 33% and 67 % completion of a first order reaction is 30 minutes. What is the time needed for 25% completion?  
 (a) 150.5 minutes (b) 125 minutes  
 (c) 180.5 minutes (d) 165.5 minutes
23. The rate constant of a reaction is  $6.93 \times 10^{-3} \text{ min}^{-1}$ . If initial concentration of the reactant is 2.0 M, the rate after 100 minutes  
 (a)  $6.93 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$  (b)  $6.93 \times 10^{-5} \text{ mol L}^{-1} \text{ min}^{-1}$   
 (c)  $6.93 \times 10^{-3} \times 2 \text{ mol L}^{-1} \text{ min}^{-1}$  (d)  $6.93 \times 10^{-3} \times 0.5 \text{ mol L}^{-1} \text{ min}^{-1}$
24. For the first order reaction  $\text{C}_2\text{H}_4\text{O}_{(g)} \rightarrow \text{CH}_4_{(g)} + \text{CO}_{(g)}$ , the initial pressure of  $\text{C}_2\text{H}_4\text{O}_{(g)}$  is 80 torr and total pressure at the end of 20 minutes is 120 torr. The time needed for 75% decomposition of  $\text{C}_2\text{H}_4\text{O}$  would be  
 (a) 20 minutes (b) 40 minutes  
 (c) 80 minutes (d) 120 minutes
25. The rate constant of a reaction at  $27^\circ\text{C}$  is  $2.3 \times 10^{-3} \text{ min}^{-1}$  and at this temperature 0.001 % of the reactant molecules are able to cross over the energy barrier existing between the reactants and the products. What can the maximum value of rate constant be achieved on raising the temperature ?  
 (a)  $23.0 \text{ min}^{-1}$  (b)  $2.3 \times 10^{-2}$   
 (c)  $115.0 \text{ min}^{-1}$  (d)  $230.0 \text{ min}^{-1}$

**SECTION – II****May be more than one choice**

1. Which of the following statements 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 concentrations of all other reactants constant.  
 (c) Orders of reactions can be whole numbers or fractional numbers.  
 (d) The order of a reaction can only be determined from the stoichiometric equation for the reaction.
2. Which of the following statements are correct?  
 (a) The rate of the reaction involving the conversion of ortho-hydrogen to parahydrogen is  $-\frac{d[\text{H}_2]}{dt} = k[\text{H}_2]^{3/2}$   
 (b) The rate of the reaction involving the thermal decomposition of acetaldehyde is  $k[\text{CH}_3\text{CHO}]^{3/2}$   
 (c) In the formation of phosgene gas from CO and  $\text{Cl}_2$ , the rate of the reaction is  $k[\text{CO}][\text{Cl}_2]^{1/2}$   
 (d) In the decomposition of  $\text{H}_2\text{O}_2$ , the rate of the reaction is  $k[\text{H}_2\text{O}_2]$

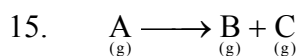
3. Which of the following isomerization reactions is of the first order?
- cyclopropane  $\longrightarrow$  propane
  - cis-but-2-ene  $\longrightarrow$  trans-but-2-ene
  - vinyl allyl ether  $\longrightarrow$  pent-4-enal
  - $\text{CH}_3\text{NC} \longrightarrow \text{CH}_3\text{CN}$
4. Which of the following reactions is of the first order?
- The decomposition of ammonium nitrate in an aqueous solution
  - The inversion of cane-sugar in the presence of an acid
  - The acidic hydrolysis of ethyl acetate
  - All radioactive decays
5. Which of the following are examples of unimolecular reactions?
- $\text{O}_3 \longrightarrow \text{O}_2 + \text{O}$
  - $$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{H}_2\text{C} - \text{CH}_2 \end{array} \longrightarrow \text{H}_3\text{C} - \text{CH} = \text{CH}_2$$
  - $\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$
  - $\text{O} + \text{NO} + \text{N}_2 \longrightarrow \text{NO}_2 + \text{N}_2$
6. The calculation of the pre-exponential factor is based on the
- idea that, for a reaction to take place, the reactant species must come together
  - calculation of the molecularity of the reaction
  - idea that the reactant species must come together, leading to the formation of the transition state which then transforms into the products
  - calculation of the order of the reaction
7. Which of the following are examples of pseudo-unimolecular reactions?
- $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{CO}_2\text{H} + \text{C}_2\text{H}_5\text{OH}$
  - $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \underset{\text{(glucose)}}{\text{C}_6\text{H}_{12}\text{O}_6} + \underset{\text{(fructose)}}{\text{C}_6\text{H}_{12}\text{O}_6}$
  - $\text{CH}_3\text{COCl} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CO}_2\text{H} + \text{HCl}$
  - $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{OH}^-} \text{CH}_3\text{CO}_2\text{H} + \text{C}_2\text{H}_5\text{OH}$
8. In which of the following ways does an activated complex differ from an ordinary molecule?
- It is quite unstable and has no independent existence
  - $\Delta H_f^\circ$  is probably positive
  - The system has a greater vibrational character
  - The system has no vibrational character
9. The basic theory behind Arrhenius's equation is that
- the number of effective collisions is proportional to the number of molecules above a certain threshold energy
  - as the temperature increases, so does the number of molecules with energies exceeding the threshold energy
  - the rate constant is a function of temperature
  - the activation energy and pre-exponential factor are always temperature-independent

10. The distribution of molecular kinetic energy at two temperatures is as shown in the following graph.



- Which of the following conclusions are correct?
- (a) The number of molecules with energy  $E_a$  or greater is proportional to the shaded area for each temperature
- (b) The number of molecules with energy  $E_a$  or less is proportional to the shaded area for each temperature.
- (c) The number of molecules with energy  $E_a$  is the mean of all temperatures
- (d) The graph follows the Maxwell-Boltzmann energy distribution law.
11. 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
12. 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  $0.0693 \text{ min}^{-1}$
13.  $\text{Zn} + 2\text{H}^+ \longrightarrow \text{Zn}^{2+} + \text{H}_2$   
 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)  $\frac{dx}{dt} = k[\text{Zn}]^0[\text{H}^+]^2$
- (b)  $\left(\frac{dx}{dt}\right) = k[\text{Zn}][\text{H}^+]^2$
- (c) rate is not affected if concentration of zinc is made four times and that of  $\text{H}^+$  ion is halved.
- (d) rate becomes four times if concentration of  $\text{H}^+$  ion is doubled at constant Zn concentration.

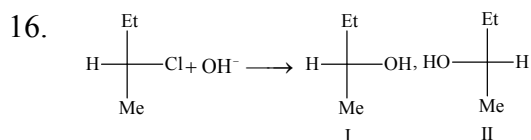
14. In which of the following case,  $E_a$  of the backward reaction is greater than that of the forward reaction?



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

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

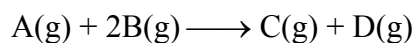
(a)  $\frac{2.303}{10} \log \frac{120}{100}$       (b)  $\frac{2.303}{10} \log \frac{100}{20}$   
 (c)  $\frac{2.303}{10} \log \frac{100}{80}$       (d)  $\frac{2.303}{10} \log \frac{100}{120}$



Which of the following statements are correct?

- (a) it is unimolecular nucleophilic substitution reaction  $S_N1$  if I or II is formed.  
 (b) it is bimolecular nucleophilic substitution reaction  $S_N2$  if I or II is formed  
 (c) it is  $S_N1$  if I and its enantiomer are formed so that mixture is racemic  
 (d) it is  $S_N2$  if II is formed

17. The reaction



Initial pressure of A and B are respectively  $p_A = 0.60 \text{ atm}$ ,  $p_B = 0.80 \text{ atm}$ . when  $p_C = 0.20 \text{ atm}$ , the rate of the reaction, relative to the initial rate, is:

(a)  $\frac{1}{48}$       (b)  $\frac{1}{24}$   
 (c)  $\frac{1}{6}$       (d)  $\frac{1}{4}$

18. Rate constant  $k$  varies with temperature by eqn:

$$\log k (\text{min}^{-1}) = 5 - \frac{2000 \text{ K}}{T}$$

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

19. The rate law for the dimerisation of  $\text{NO}_2$  is  $\frac{-d[\text{NO}_2]}{dt} = k[\text{NO}_2]^2$

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 of these

20. 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
21. A reaction is catalysed by  $H^+$  ion. In presence of HA, rate constant is  $2 \times 10^{-3} \text{ min}^{-1}$  and in presence of HB rate constant is  $1 \times 10^{-3} \text{ min}^{-1}$ , HA and HB both being strong acids, we may conclude:
- (a) equilibrium constant is 2  
(b) HA 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
22. The rate law for the reaction  
 $RCl + NaOH \longrightarrow ROH + NaCl$   
Is given by: rate =  $k [RCl]$ . The rate of this reaction
- (a) is doubled by doubling the concentration of NaOH  
(b) is halved by reducing the concentration of RCl by one half  
(c) is increased by increasing the temperature of the reaction  
(d) is unaffected by change in temperature
23. For a first order reaction
- (a) The degree of dissociation is equal to  $1 - e^{-kt}$   
(b) A plot of reciprocal of concentration of reactant vs. time gives a straight line  
(c) The time taken for the completion of 75% of reaction is thrice  $t_{1/2}$  of the reaction  
(d) The pre-exponential factor in the Arrhenius equation has the dimensions of  $\text{time}^{-1}$
24. Which of the following statements are correct?
- (a) A plot of  $\log K_p$  versus  $1/T$  is linear  
(b) A plot of  $\log [X]$  versus time is linear for a first order reaction  $X \longrightarrow P$   
(c) A plot of  $\log P$  versus  $1/T$  is linear at constant volume  
(d) A plot of  $P$  versus  $1/V$  is linear at constant temperature
25. Taking the reaction,  $A + 2B \longrightarrow \text{Products}$ , to be of second order, which of the following are the correct rate law expressions?
- (a)  $\frac{dx}{dt} = k[A][B]$       (b)  $\frac{dx}{dt} = k[A][B]^2$   
(c)  $\frac{dx}{dt} = k[A]^2$       (d)  $\frac{dx}{dt} = k_1[A] + k_2[B]^2$

✎ **Write-up I**

Arrhenius studied the effect of temperature on the rate of a reaction and postulated that rate constant varies with temperature exponentially as  $k = Ae^{-E_a/RT}$ . For most of the reactions, it was found that the temperature coefficient of the reaction lies between 2 to 3. The method is generally used for finding the activation energy of a reaction. Keeping temperature constant, the effect of catalyst on the activation energy has also been studied by studying how much the rate of reaction changes in the presence of catalyst. In most of the cases, it is observed that catalyst lowers the activation energy barrier and increases the rate of reaction.

- The pre-exponential factor in the Arrhenus equation of a second order reaction has the units  
 (a)  $\text{mol L}^{-1} \text{s}^{-1}$  (b)  $\text{L mol}^{-1} \text{s}^{-1}$   
 (c)  $\text{s}^{-1}$  (d) dimensionless
- If the rate of reaction grows 15.6 times on increasing the temperature by 30 K, the temperature coefficient of the reaction will be nearly  
 (a) 2 (b) 2.5  
 (c) 3.0 (d) 3.5
- If 'x' is the fraction of molecules having energy greater than  $E_a$ , it will be given by  
 (a)  $x = -\frac{E_a}{RT}$  (b)  $\ln x = -\frac{E_a}{RT}$   
 (c)  $x = e^{E_a/RT}$  (d) None of these

✎ **Write-up II**

The rate of reaction between the reactants A and B were studied starting with different initial concentrations. The following data were obtained:

[A], mol lit <sup>-1</sup>	[B], mol lit <sup>-1</sup>	Initial rate, mol lit <sup>-1</sup> s <sup>-1</sup> at 300 K	320 K
$2.5 \times 10^{-4}$	$3.0 \times 10^{-5}$	$5.0 \times 10^{-4}$	$2.0 \times 10^{-3}$
$5.0 \times 10^{-4}$	$6.0 \times 10^{-5}$	$4.0 \times 10^{-3}$	—
$1.0 \times 10^{-3}$	$6.0 \times 10^{-5}$	$1.6 \times 10^{-2}$	—

- The order of reaction with respect to A and B are respectively  
 (a) 1, 1 (b) 1, 2  
 (c) 2, 1 (d) 2, 0
- The rate constant of the reaction at 300 K when concentrations are in  $\text{mol L}^{-1}$  and time in seconds will be  
 (a)  $2.67 \times 10^8$  (b)  $1.33 \times 10^5$   
 (c)  $1.6 \times 10^4$  (d)  $2.22 \times 10^9$



6. The pre-exponential factor will be of the order of  
 (a)  $10^8$  (b)  $10^{12}$   
 (c)  $10^{15}$  (d)  $10^{18}$

✎ **Write-up III**

Consider a reaction  $A \rightarrow B$

$\frac{dx}{dt} \propto C_A$  where  $C_A$  is molar concentration,  $\frac{dx}{dt} = KC_A$  where K rate const

Units of rate constant = (unit of concentration) $^{1-n} \times \text{times}^{-1}$

Where n is order of reaction

7. For the reaction  $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$   
 $\frac{-d[\text{NH}_3]}{dt} = K_1[\text{NH}_3]$ ,  $\frac{d[\text{N}_2]}{dt} = K_2[\text{NH}_3]$ ,  $\frac{d[\text{H}_2]}{dt} = K_3[\text{NH}_3]$ . Then the relation between  $K_1$ ,  $K_2$  and  $K_3$  is =  
 (a)  $1.5 K_1 = 3K_2 = K_3$  (b)  $2K_1 = K_2 = 3K_3$   
 (c)  $K_1 = K_2 = K_3$  (d)  $K_1 = 3K_2 = 2K_3$
8.  $A + B \rightarrow \text{product}$ ,  $\frac{dx}{dt} = K[A]^a[B]^b$  if  
 $\frac{dx}{dt} = K$ , then the order is:  
 (a) 4 (b) 2  
 (c) 1 (d) 0
9. For the first order reaction  $A \rightarrow \text{product}$ , the half life is 200s. The rate constant of the reaction is:  
 (a)  $3.46 \times 10^{-2} \text{ s}^{-1}$  (b)  $3.46 \times 10^{-3} \text{ s}^{-1}$   
 (c)  $3.46 \times 10^{-4} \text{ s}^{-1}$  (d)  $3.75 \times 10^{-5} \text{ s}^{-1}$

✎ **Write-up IV**

Rate of forward reaction decreases and that of backward reaction increases with passage of time. The rate of reaction increases considerable with an increase in temperature.

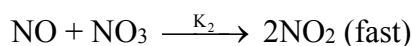
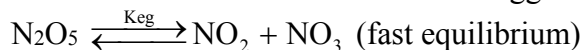
10. The rate of a chemical reaction generally increases rapidly even for small temperature increase because of rapid increase in the  
 (a) collision frequency (b) fraction of molecules  
 (c) activation energy (d) average kinetic energy of molecules
11. The temperature coefficient of a reaction is:  
 (a) ratio of rate constants at two temperatures differing by  $1^\circ\text{C}$   
 (b) ratio of rate constants at temperature  $35^\circ\text{C}$  and  $25^\circ\text{C}$   
 (c) ratio of rate constants at temperature  $30^\circ\text{C}$  and  $25^\circ\text{C}$   
 (d) specific reaction rate at  $25^\circ$

12. The specific rate constant of a first order reaction depends on  
 (a) concentration of the reactants (b) concentration of products  
 (c) times (d) temperature

✎ **Write-up V**

The rate law for the decomposition of gaseous  $\text{N}_2\text{O}_5$  is  $\text{N}_2\text{O}_5 \longrightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$ . A

reaction mechanism which has been suggested



13. In 20 minutes of 80% of  $\text{N}_2\text{O}_5$  is decomposed find rate constant  
 (a) 0.08 (b) 0.05  
 (c) 0.12 (d) 0.2
14. At the equilibrium state  $\text{N}_2\text{O}_5$ ,  $\text{NO}_2$  and  $\text{NO}_3$  concentrations are 0.2, 0.4 and 0.4 M respectively. Find  $K_1$   
 (a) 0.1 (b) 0.2  
 (c) 1 (d) 2
15. When graph is plotted between  $t_{1/2}$  Vs initial concentration then slope is  
 (a) 0 (b)  $\infty$   
 (c)  $>0$  (d)  $<0$

**SECTION – IV**

**Subjective Questions**

**LEVEL – I**

- A radioactive isotope has an initial activity of  $2 \times 10^6$  disintegration / min. After 4 days its activity is  $9 \times 10^5$  dis/min. Find out the activity after 40 days.
- While studying the decomposition of  $\text{N}_2\text{O}_5(\text{g})$  it is observed that a plot of logarithm of its partial pressure versus time is linear. What kinetic parameter can be obtained from this.
- The first order reaction has  $k = 1.5 \times 10^6$  per second at  $200^\circ\text{C}$ . If the reaction is allowed to run for 10 hours, what percentage of the initial concentration would have changed in the product? What is the half-life period of this reaction?
- Substance A reacts according to first order rate law with  $k = 5.0 \times 10^{-5} \text{ s}^{-1}$ .  
 a) If the initial concentration of A is 1.0 M what is the initial rate?  
 b) What is the rate after 1.0 hour.

5. From the following data for the reaction between A and B

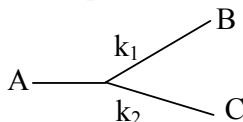
[A], mol lit <sup>-1</sup>	[B], mol lit <sup>-1</sup>	Initial rate mol lit <sup>-1</sup> s <sup>-1</sup> , at	
		300 K	320 K
$2.5 \times 10^{-4}$	$3.0 \times 10^{-5}$	$5.0 \times 10^{-4}$	$2.0 \times 10^{-3}$
$5.0 \times 10^{-4}$	$6.0 \times 10^{-5}$	$4.0 \times 10^{-3}$	—
$1.0 \times 10^{-3}$	$6.0 \times 10^{-5}$	$1.6 \times 10^{-2}$	—

Calculate the following

- The order w.r.t. A and w.r.t. B
  - The rate constant at 300 K
  - The energy of activation
  - The pre-exponential factor
6. For the reaction  $2\text{NO} + \text{Cl}_2 \longrightarrow 2\text{NOCl}$ , it was found that on doubling concentration of both reactants the rate increases eight fold. But on doubling the concentration of chlorine alone, rate only doubles. What is the overall order.
7. For the reaction:  
 $2\text{A} + \text{B} + \text{C} \longrightarrow \text{A}_2\text{B} + \text{C}$   
the rate =  $k[\text{A}][\text{B}]^2$  with  $k = 2 \times 10^{-6} \text{ M}^{-2}\text{s}^{-1}$ . Calculate the initial rate of the reaction when  $[\text{A}] = 0.1 \text{ M}$ ,  $[\text{B}] = 0.2 \text{ M}$  and  $[\text{C}] = 0.8 \text{ M}$ . If the rate of reverse reaction is negligible then calculate the rate of reaction after  $[\text{A}]$  is reduced to  $0.06 \text{ M}$ .
8. In a pseudo first order hydrolysis of ester in water the following results were obtained:
- |           |      |      |      |       |
|-----------|------|------|------|-------|
| t/s       | 0    | 30   | 60   | 90    |
| [ester]/M | 0.55 | 0.31 | 0.17 | 0.085 |
- Calculate the average rate of reaction between the time interval 30 to 60 seconds.
  - Calculate the pseudo first order rate constant for the hydrolysis of ester.
9. Calculate the half life of a first order reaction from their rate constants given below:  
a)  $200 \text{ s}^{-1}$ ; b)  $2 \text{ min}^{-1}$ ; c)  $4 \text{ year}^{-1}$
10. The rate constant for a first order reaction is  $60 \text{ s}^{-1}$ . How much time will it take to reduce the initial concentration of the reactant to its  $1/16^{\text{th}}$  value?

### LEVEL - II

1. A certain organic compound A decomposes by two parallel first order mechanisms.



If  $k_1 : k_2 = 1:9$  and  $k_1 = 1.3 \times 10^{-5} \text{ s}^{-1}$ . Calculate the concentration ratio of C to A if an experiment is started with only A and allowed to run for one hour.

2.  ${}^{210}_{84}\text{Po}$  decays with  $\alpha$  particle to  ${}^{206}_{82}\text{Pb}$  with a half life of 138.4 days. If  $1.0 \text{ g}$  of  ${}^{210}_{84}\text{Po}$  is placed in a sealed tube, how much helium will accumulate in 69.2 days. Express the answer in  $\text{cm}^3$  at STP.

3. At 380°C, the half-life period for the first order decomposition of H<sub>2</sub>O<sub>2</sub> is 360 min. the energy of activation of the reaction is 200 kJ mol<sup>-1</sup>, Calculate the time required for 75% decomposition at 450°C.
4. The rate constant of a reaction is  $1.5 \times 10^7 \text{ s}^{-1}$  at 50°C and  $4.5 \times 10^7 \text{ s}^{-1}$  at 100°C. Evaluate the Arrhenius parameters A and E<sub>a</sub>.
5. For a reaction:  
 $A + B + C \rightarrow \text{product}$ ,  
 The rate of the reaction is given by  
 $\text{Rate} = K[A]^l[B]^m[C]^n$   
 From the following data determine
- The order with respect to A
  - The order with respect to B
  - The order with respect to C
  - The over all order
  - Rate constant

	Initial concentrations (mole dm <sup>-3</sup> )			Initial rate (mole dm <sup>-3</sup> s <sup>-1</sup> )
	[A]	[B]	[C]	
a)	0.010	0.005	0.010	$5.0 \times 10^{-5}$
b)	0.010	0.005	0.015	$5.0 \times 10^{-5}$
c)	0.010	0.010	0.010	$2.5 \times 10^{-5}$
d)	0.020	0.005	0.010	$14 \times 10^{-5}$

6. A drug is known to be ineffective after it has decomposed to the extent of 30%. The original concentration of a sample was 500 units/ml. When analysed 20 months later, the concentration was found to be 420 units / ml. Assuming that the decomposition is of first order, what will be the expiration time of the drug sample. What is the half life of the drug.
7. The decomposition of formic acid on a gold surface follows first order kinetics and specific rate constants are  $5.5 \times 10^{-4} \text{ s}^{-1}$  and  $9.2 \times 10^{-3} \text{ s}^{-1}$  at 140°C and 185°C respectively. Calculate energy of activation.
8. Bicyclohexane was found to undergo two parallel first order rearrangements. At 730 K, the first order rate constant for the formation of cyclohexane was measured as  $1.26 \times 10^4 \text{ s}^{-1}$ , and for the formation of methyl cyclopentene the rate constant was  $3.8 \times 10^5 \text{ s}^{-1}$ . What is the percentage distribution of the rearrangement products ?
9. Two reactions proceed at 25°C at the same rate, the temperature coefficient of the rate of the first reaction is 2.0 and of the second, 2.5. Find the ratio of rates of these reactions at 95°C.
10. Decomposition of diazobenzene chloride was followed at constant temperature by measuring the volume of nitrogen evolved at suitable intervals. Following readings were observed.
- |                        |   |    |    |    |     |
|------------------------|---|----|----|----|-----|
| Time                   | 0 | 20 | 55 | 70 | ∞   |
| Vol. of N <sub>2</sub> | 0 | 10 | 25 | 33 | 162 |
- Calculate order of the reaction.

**LEVEL – III (Judge yourself at JEE level)**

- 1 g atm of  $\text{Ra}^{226}$  is placed in an evacuated tube of volume 5 litre. Assuming that each  ${}_{88}\text{Ra}^{226}$  nucleus is an  $\alpha$ -emitter and all the contents are present in tube, calculate the total pressure of gases and partial pressure of He collected in tube at  $27^\circ\text{C}$  after the end of 800 years.  $t_{1/2}$  of Ra is 1600 year. Neglect volume occupied by undecayed Ra.
- A solution contains 1 milli-curie of L-phenyl alanine  $\text{C}^{14}$  (uniformly labeled) in 2.0 mL solution. The activity of labeled sample is given as 150 milli-curie/milli-mole. Calculate:
  - The concentration of sample in the solution in mole/litre.
  - The activity of the solution in terms of counting per minute/mL at a counting efficiency of 80%.
- Two reactions (I)  $\text{A} \rightarrow \text{Products}$  (II)  $\text{B} \rightarrow \text{Products}$  follow first order kinetics. The rate of the reaction (I) is doubled when temperature is raised from 300K to 310K. The half life for this reaction at 310 K is 30 minute. At the same temperature 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 reaction (II) at 300K.
- A solution contains a mixture of isotopes of  $\text{X}^{\text{A}_1}$  ( $t_{1/2} = 14$  days) and  $\text{X}^{\text{A}_2}$  ( $t_{1/2} = 25$  days). Total activity is 1 curie at  $t = 0$ . The activity reduces by 50% in 20 days. Find :
  - The initial activities of  $\text{X}^{\text{A}_1}$  and  $\text{X}^{\text{A}_2}$ .
  - The ratio of their initial no. of nuclei.
- The rate of decomposition for methyl nitrite and ethyl nitrite can be given in terms of rate constant (in  $\text{sec}^{-1}$ )  $\text{K}_1$  and  $\text{K}_2$  respectively. The energy of activations for the two reactions are  $152.30 \text{ kJ mol}^{-1}$  and  $157.7 \text{ kJ mol}^{-1}$  as well as frequency factors are  $10^{13}$  and  $10^{14}$  respectively for the decomposition of methyl and ethyl nitrite. Calculate the temperature at which rate constant will be same for the two reactions.
- A given sample of milk turns sour at room temperature ( $20^\circ\text{C}$ ) in 64 hours. In a refrigerator at  $3^\circ\text{C}$ , milk can be stored three times as long before it sours. Estimate
  - The activation energy for souring of milk,
  - How long it take milk to sour at  $40^\circ\text{C}$  ?
- A 22.4 litre flask contains 0.76 mm of ozone at  $25^\circ\text{C}$ . Calculate:
  - the concentration of oxygen atoms needed so that the reaction  $\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$  having rate constant equal to  $1.5 \times 10^7 \text{ litre mol}^{-1} \text{ sec}^{-1}$  can proceed with a rate of  $0.15 \text{ mol litre}^{-1} \text{ sec}^{-1}$ .
  - the rate of formation of oxygen under this condition.
- Decomposition of  $\text{H}_2\text{O}_2$  is a first order reaction. A solution of  $\text{H}_2\text{O}_2$  labelled as 20 volumes was left open. due to this some  $\text{H}_2\text{O}_2$  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 0.025 M  $\text{KMnO}_4$  acidified solution. Calculate the rate constant for decomposition of  $\text{H}_2\text{O}_2$ .

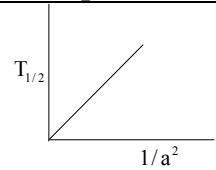
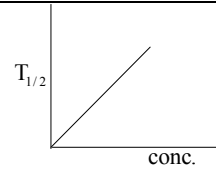
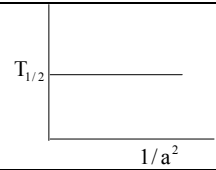
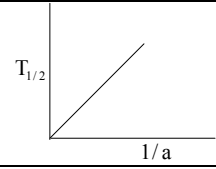
9.  $^{238}_{92}\text{U}$  is radioactive and it emits  $\alpha$  and  $\beta$  particles to form  $^{206}_{82}\text{Pb}$ . Calculate the number of  $\alpha$  and  $\beta$  particles emitted in this conversion. An ore of  $^{238}_{92}\text{U}$  is found to contain  $^{238}_{92}\text{U}$  and  $^{206}_{82}\text{Pb}$  in the weight ratio of 1:0.1. The half-life period of  $^{238}_{92}\text{U}$  is  $4.5 \times 10^9$  years. Calculate the age of the ore.
10.  $^{64}\text{Cu}$  (half-life = 12.8h) decays by  $\beta^-$  emission (38%),  $\beta^+$  emission (19%) and electron capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes.

**SECTION - V****Miscellaneous Questions**

1. Match List - I with List - II and select the correct answer using the codes given below the lists.

List - I		List - II	
(a)	Collision theory	1.	$\text{Mol L}^{-1}\text{s}^{-1}$
(b)	Zero order reaction	2.	Bimolecular reaction
(c)	Photochemical reaction	3.	Fractional
(d)	Intercept (in Arrhenius plot)	4.	In A
(e)	Order of reaction	5.	Zero order reaction

2. List - I (order of reaction)                      List - II (plots of  $T_{1/2}$  vs conc.)

(A) zero	1.	
(B) First	2.	
(C) Second	3.	
(D) Third	4.	

**Codes**

	(A)	(B)	(C)	(d)
(a)	2	3	1	4
(b)	3	2	1	4
(c)	2	3	4	1
(d)	3	2	4	1

The following questions (3 to 7) consists of two statements, one labelled as **ASSERTION (A)** and **REASON (R)**. Use the following key to choose the correct appropriate answer.

- (a) If both (A) and (R) are correct, and (R) is the correct explanation of (A).  
 (b) If both (A) and (R) are correct, but (R) is not the correct explanation of (A).  
 (c) If (A) is correct, but (R) is incorrect.  
 (d) If (A) is incorrect, but (R) is correct.

ASSERTION (A)	REASON (R)
3. In the reaction, $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ , the rate of reaction is different in terms of $\text{N}_2$ , $\text{H}_2$ and $\text{NH}_3$	Rate of reaction is equal to the rate of disappearance of a reactant or rate of formation of a product
4. Both $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$ and $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$ have the same order of reaction.	Both reactions proceed by the same mechanism.
5. Order of a reaction can be fractional but molecularity is never fractional.	Order of a reaction does not depend upon the stoichiometric coefficients of the balanced equation.
6. For a first order reaction, the concentration of the reactant decreases exponentially with time.	Rate of reaction at any time depends upon the concentration of the reactant at that time.
7. The rate constant of a pseudo-unimolecular reaction has the units of a second order reaction.	A pseudo-unimolecular reaction is a reaction of second order in which one of the reactant is present in large excess.

## Answers to Assignments

### SECTION - I

- |        |         |         |         |         |
|--------|---------|---------|---------|---------|
| 1. (b) | 6. (c)  | 11. (d) | 16. (d) | 21. (b) |
| 2. (c) | 7. (b)  | 12. (d) | 17. (b) | 22. (b) |
| 3. (d) | 8. (a)  | 13. (c) | 18. (b) | 23. (a) |
| 4. (b) | 9. (c)  | 14. (c) | 19. (c) | 24. (b) |
| 5. (a) | 10. (c) | 15. (d) | 20. (b) | 25. (d) |

### SECTION - II

- |                 |                  |               |                   |
|-----------------|------------------|---------------|-------------------|
| 1. (a, b, c)    | 7. (a, b, c)     | 13. (b, c, d) | 20. (b)           |
| 2. (a, b, c, d) | 8. (a, c)        | 14. (d)       | 21. (b, c)        |
| 3. (a, b, c, d) | 9. (a, b, c)     | 15. (c)       | 22. (b, c)        |
| 4. (a, b, c, d) | 10. (a, d)       | 16. (c, d)    | 23. (a), (b)      |
| 5. (a, b)       | 11. (b, c)       | 17. (c)       | 24. (a), (b), (d) |
| 6. (a, c)       | 12. (a, b, c, d) | 18. (c, d)    | 25. (a), (c)      |
|                 |                  | 19. (b)       |                   |

### SECTION - III

- |        |        |         |         |
|--------|--------|---------|---------|
| 1. (b) | 5. (a) | 9. (b)  | 13. (a) |
| 2. (a) | 6. (d) | 10. (b) | 14. (a) |
| 3. (b) | 7. (b) | 11. (b) | 15. (a) |
| 4. (c) | 8. (d) | 12. (d) |         |

### SECTION - IV

#### LEVEL - I

- 699.31 dis/min
- intercept =  $\log P^0$ ; slope =  $-k/2.303$
- $t_{1/2} = 128.33$  hr.
- (a)  $5.0 \times 10^{-5} \text{ mol S}^{-1}$ ; (b)  $4.117 \times 10^{-5} \text{ S}^{-1}$
- (i) order with respect to A = 2  
order with respect to B = 1  
(ii)  $k = 2.667 \times 10^8 \text{ mol}^{-2} \text{ lit}^2 \text{ S}^{-1}$   
(iii)  $55327 \text{ J mol}^{-1}$   
(iv)  $A = 1.143 \times 10^{18} \text{ mol}^{-2} \text{ S}^{-1}$
- 3
- i)  $8.0 \times 10^{-9} \text{ M}^{-2} \text{ s}^{-1}$ ; ii)  $3.89 \times 10^{-9} \text{ M}^{-2} \text{ s}^{-1}$
- i)  $4.67 \times 10^{-3} \text{ M s}^{-1}$ ; ii)  $1.92 \times 10^{-2} \text{ s}^{-1}$
- a)  $3.47 \times 10^{-3}$  seconds; (b) 0.35 minutes; (c) 0.173 years
- $4.6 \times 10^{-2}$  seconds



**LEVEL – II**

- 0.537
- $31.25 \text{ cm}^3$
- 20.33 min
- $E_a = 2.2 \times 10^4 \text{ J mol}^{-1}$   
 $A = 5.4 \times 10^{10}$
- (i)  $3/2$ , (ii)  $-1$ , (iii)  $0$ , (iv)  $\frac{1}{2}$ , (v)  $2.5 \times 10^{-4} (\text{mol dm}^{-3})^{1/2} \text{ S}^{-1}$
- 40.9 months, 79.49 months
- $E = 2.37 \times 10^4 \text{ cal/mole}$
- 23%.
- 5 times
- First

**LEVEL – III**

- 2.887 atm, 1.443 atm
- (a) 0.3669 Ci, 0.6331 Ci (b) 0.3245
- (i)  $2.45 \times 10^{-4}$ , (ii)  $0.30 \text{ mol L}^{-1}\text{t}^{-1}$
- $0.022 \text{ hr}^{-1}$
- $7.097 \times 10^8 \text{ years}$

**SECTION - V**

- (a)  $-2$ , (b)  $-1$ , (c)  $-5$ , (d)  $-4$ , (e)  $-3$
- (c)
- (d)
- (d)
- (a)
- (b)
- (a)

