

## 2. CHEMICAL KINETICS

### SYNOPSIS

#### I. INTRODUCTION, RATE OF REACTION, FACTORS INFLUENCING RATE, SPECIFIC RATE

- \* Rate of appearance or Disappearance of a Substance C

$$(i) \text{Average} \left( \pm \frac{\Delta[C]}{\Delta t} \right) \quad (ii) \text{Instantaneous} \left( \pm \frac{\Delta[C]}{\Delta t} \right)$$

- \* Expressions of the rate : For a general reaction :  $aA + bB \longrightarrow cC + dD$

$$\text{Rate of disappearance of A} = -\frac{d[A]}{dt}; \quad \text{Rate of disappearance of B} = -\frac{d[B]}{dt}$$

$$\text{Rate of appearance of C} = \frac{d[C]}{dt} \quad \text{& Rate of appearance of D} = \frac{d[D]}{dt}$$

The positive sign shows that concentrations of C and D increases with time and the negative sign indicates that concentrations of A and B decreases with time

$$\text{Instantaneous rate of reaction : } -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

$$\text{Average rate of reaction : } -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

- \* Units of Rate of Reaction :  $\text{mol L}^{-1} \text{ s}^{-1}$  or  $\text{mol L}^{-1} \text{ min}^{-1}$  (concentration time $^{-1}$ ).

**Rate Law and Rate constant :** Rate  $\propto [A]^a \cdot [B]^b$  or Rate =  $k[A]^a [B]^b$

The constant of proportionality, k is known as the rate constant (specific reaction rate) and may be defined as the rate at unit concentrations of the reactants.

- \* k depends on the temperature and is independent of the concentration of the reactants/products.
- \* At a fixed temperature, k is a constant and is a characteristic of the reaction. Larger value of k indicates fast reaction and small k indicates slow reactions.

#### II. ORDER MOLECULARITY AND HALF-LIFE

**Molecularity :** It is always a whole number (not zero) and never a fraction. Its value does not exceed 3 & it has no meaning for a complex reaction.

**Order of Reaction :**  $aA + bB \longrightarrow cC$

Rate of reaction =  $k[A]^m [B]^n$

Order of reaction =  $m + n$  and the order w.r.t. A, B are m, n respectively.

- \* The order of reaction is obtained from the experimentally determined rate and may be zero, integral or a fraction. In a multi-step complex reaction, the order of the reaction can be determined with the help of slowest step, which is called rate determining step.
- \* In elementary reaction stoichiometric coefficient of reactants is equal to order of reaction :

$$m + n = a + b$$

- \* Some useful relationships between times for different fractions of reaction of first order reaction.

$$t_{3/4} \text{ or } t_{75\%} = 2t_{1/2}$$
$$t_{87.5\%} = 3t_{1/2}$$

\* Amount of the substance left after n half-lives =  $\frac{A_0}{2^n}$

Number of half-lives =  $\frac{t}{t_{1/2}}$ ; t = total time;  $t_{1/2}$  = half-life time

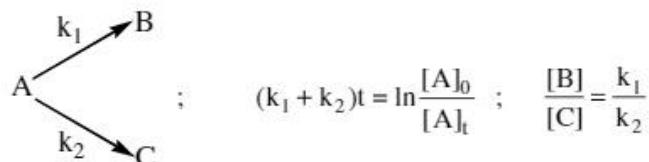
\* **n<sup>th</sup> Order Reaction :** A → product

$$k \cdot t = \frac{1}{n-1} \left\{ \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right\} \quad [n \neq 1, n = \text{order}]; \quad t_{1/2} = \frac{1}{k(n-1)} \left[ \frac{2^{n-1} - 1}{a^{n-1}} \right]$$

\* **Reversible reaction** A  $\xrightleftharpoons[k_b]{k_f}$  B

$$(k_f + k_b) = \frac{1}{t} \ln \left( \frac{x_{eq}}{x_{eq} - x} \right); \quad \text{At equilibrium } k_{eq} = \frac{k_f}{k_b} = \frac{[B]}{[A]} = \frac{x_{eq}}{a - x_{eq}}$$

\* **Parallel/Side Reactions**



$$\% \text{ Yield of B} = \frac{k_1}{k_1 + k_2} \times 100 \quad \text{and} \quad \% \text{ Yield of C} = \frac{k_2}{k_1 + k_2} \times 100$$

\* **Series/Consecutive Reactions :** A  $\xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C}$

$$t_{max} = \frac{1}{k_1 - k_2} \ln \left( \frac{k_1}{k_2} \right)$$

\* **Temperature coefficient ( $\mu$ )** =  $\frac{k_{T+10}}{k_T}$

\* For general chemical reactions with rise in temperature by 10°C, the rate constant is nearly doubled.

### III. THEORIES OF CHEMICAL KINETICS

**Arrhenius Equation :**  $k = Ae^{-E_a/RT}$

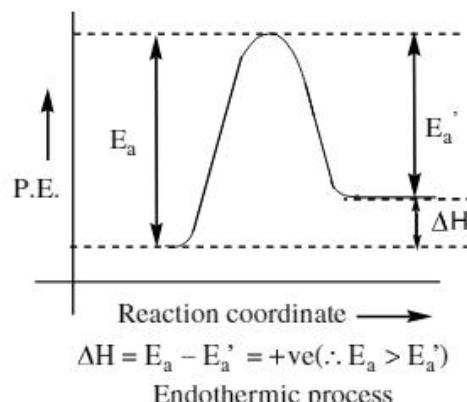
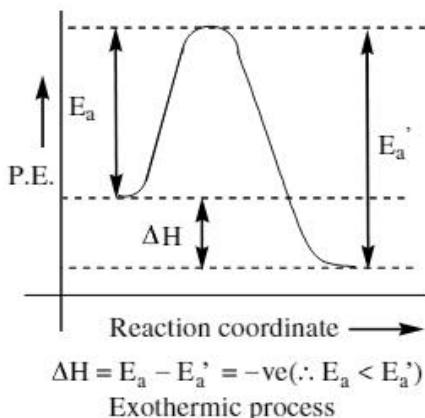
where k = Rate constant, A = Pre-exponential factor, T = Temperature in kelvin, E<sub>a</sub> = Activation Energy

The factor  $e^{-E_a/RT}$  represents fraction of molecules that have kinetic energy greater than E<sub>a</sub>

**Logarithmic expression**

$$\log_{10} \left( \frac{k_2}{k_1} \right) = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

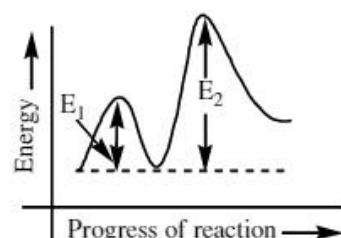
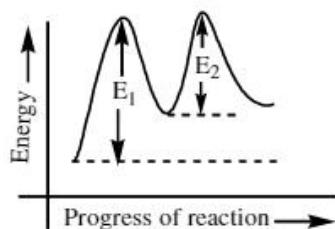
Energy profile for exothermic process and endothermic process :



Threshold Energy = Activation Energy + Energy possessed by reactant molecules.

**Activation energy diagram for two step endothermic reaction :**

- (A) (i) I step-Slow      (ii) II step-Fast  
 (B) (i) Rapid equilibrium (ii) Slow



**Factors affecting reaction rates :** Concentration of reactants and reaction temperature, Besides these, presence of catalyst and surface area (if a reactant or a catalyst is a solid) exposure to radiation also affect the reaction rates.

### LECTURE SHEET

#### EXERCISE-I

(Introduction, Rate of reaction, Factors influencing rate, Specific rate)

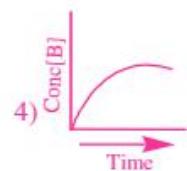
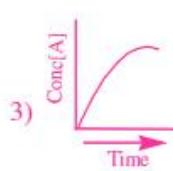
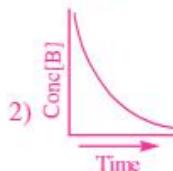
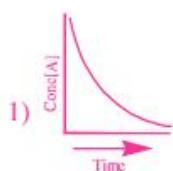
#### LEVEL-I (MAIN)

##### Straight Objective Type Questions

1. For  $\frac{1}{2}X_2 + Y_2 \rightarrow XY_2$ , relative rates of species is given as

- 1) Rate =  $\frac{-d[X_2]}{dt} = \frac{-d[Y_2]}{dt} = +\frac{d[XY_2]}{dt}$   
 2) Rate =  $-2\frac{d[X_2]}{dt} = \frac{-d[Y_2]}{dt} = +\frac{d[XY_2]}{dt}$   
 3) Rate =  $\frac{-1}{2}\frac{d[X_2]}{dt} = \frac{-d[Y_2]}{dt} = +\frac{d[XY_2]}{dt}$   
 4) Rate =  $-\frac{1}{2}\frac{d[X_2]}{dt} = \frac{+d[Y_2]}{dt} = +\frac{d[XY_2]}{dt}$

2. For the reaction  $A \rightarrow B$ ; following curves represent conc. vs time



The correct curves are

- 1) 1, 2 only      2) 2, 3 only      3) 1, 4 only      4) 3, 4 only
3. For  $N_2 + 3H_2 \rightarrow 2NH_3$ , rates of disappearance of  $N_2$  and  $H_2$  and rate of appearance of  $NH_3$  respectively are a, b and c, then
- 1)  $a > b > c$       2)  $a < c < b$       3)  $a = b > c$       4)  $a = b = c$
4. The reaction  $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+}$  products is a/an \_\_\_\_\_ process

A) Instantaneous      B) Spontaneous      C) Moderately slow

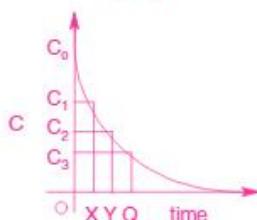
Then correct statement(s) is/are

- 1) A & C      2) B & C      3) A only      4) C only
5. From the graph the value  $\frac{\Delta C}{\Delta t}$  and the value of rate of reaction at X respectively are called
- 1) Average rate and instantaneous rate  
2) Instantaneous rate and average rate  
3) Average rate only  
4) Instantaneous rate only
6. In the following reaction, how is the rate of appearance of the underlined product related to the rate of disappearance of the underlined reactant?



$$1) \frac{d[\underline{Br}_2]}{dt} = -\frac{5}{3} \frac{d[Br^-]}{dt} \quad 2) \frac{d[\underline{Br}_2]}{dt} = -\frac{d[Br^-]}{dt} \quad 3) \frac{d[\underline{Br}_2]}{dt} = -\frac{d[Br^-]}{dt} \quad 4) \frac{d[\underline{Br}_2]}{dt} = -\frac{3}{5} \frac{d[Br^-]}{dt}$$

7. From the graph.



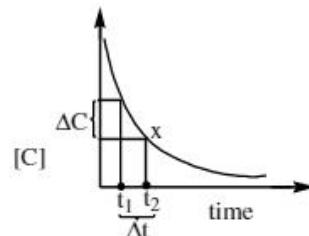
X = 10 min;

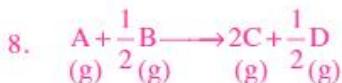
Y = 20 min;

Q = 30 min

Now, correct relationship is

- 1)  $\frac{C_0 - C_1}{X} = \frac{C_1 - C_2}{Y} = \frac{C_2 - C_3}{Q}$
- 2)  $\frac{C_2 - C_3}{Q} > \frac{C_1 - C_2}{Y} > \frac{C_0 - C_1}{X}$
- 3)  $\frac{C_0 - C_1}{X} > \frac{C_1 - C_2}{Y - X} > \frac{C_2 - C_3}{Q - Y}$
- 4)  $\frac{C_1 - C_3}{Q - X} = \frac{C_0 - C_2}{Y}$

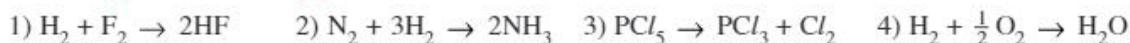




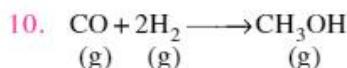
The rate of disappearance of 'B' is 'x'. What is the rate of appearance of 'C' ?

- 1)  $3x$       2)  $x/2$       3)  $2x$       4)  $4x$

9. In which of the following cases, rate of disappearance of any reactant at a given instant equals to rate of appearance of any product



#### Numerical Value Type Questions



In the above reaction Hydrogen disappears at the rate of 0.2 gm/sec. What is the rate of appearance of methanol (gm/sec) at that moment?

11. In the reaction  $2A + B \rightarrow 2C + D$ , 5 mol/lt of 'A' are allowed to react with 3 mol/lt of B. After 5 seconds the concentration of 'A' was found to be 4 molar. What is the rate of reaction in terms of A?

12. For  $3A \rightarrow xB$ ,  $\frac{d[B]}{dt}$  is found to be  $2/3$ rd of  $\frac{d[A]}{dt}$ . Then, the value of x is

#### LEVEL-II (ADVANCED)

#### Straight Objective Type Questions

1. For the reaction  $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$ ; Given  $\frac{-d[N_2O_5]}{dt} = K_1[N_2O_5]$ ,  $\frac{d[NO_2]}{dt} = K_2[N_2O_5]$  and  $\frac{d[O_2]}{dt} = K_3[N_2O_5]$ . The relation in between  $K_1$ ,  $K_2$  and  $K_3$  is :

- a)  $2K_1 = K_2 = 4K_3$     b)  $K_1 = K_2 = K_3$     c)  $2K_1 = 4K_2 = K_3$     d) None of these

2. Hydrogenation of vegetable ghee at  $25^{\circ}C$  reduces pressure of  $H_2$  from 2 atm to 1.2 atm in 50 minute. The rate of reaction in terms of molarity per second is

- a)  $1.06 \times 10^{-6}$     b)  $1.06 \times 10^{-5}$     c)  $1.06 \times 10^{-7}$     d)  $1.06 \times 10^{-9}$

#### More than One correct answer Type Questions

3. Which of the following statements is (are) true for the given reaction,  $4A + B \rightleftharpoons 2C + 2D$ ?
- a) The rate of disappearance of B is one fourth the rate of disappearance of A
  - b) The rate of appearance of C is half the rate of disappearance of B
  - c) The rates of formation of C and D are equal
  - d) The rate of formation of D is half the rate of disappearance of A
4. The rate equation for the decomposition of  $N_2O_5$  in  $CCl_4$  is, rate =  $K[N_2O_5]$ , where  $K = 6.3 \times 10^{-4} s^{-1}$  at 320 K. What would be the initial rate of decomposition of  $N_2O_5$  in a 0.10 M solution of  $N_2O_5$ ?
- a)  $6.3 \times 10^{-6} \text{ mol litre}^{-1} s^{-1}$
  - b)  $0.63 \times 10^{-6} \text{ mol litre}^{-1} s^{-1}$
  - c)  $6.3 \times 10^{-5} \text{ mol litre}^{-1} s^{-1}$
  - d)  $0.63 \times 10^{-4} \text{ mol litre}^{-1} s^{-1}$

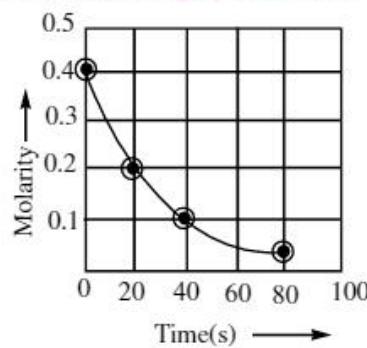
5. Select the correct statement(s).
- The rate of reaction decreases with decrease in temperature
  - The rate of reaction depends on nature of reactants
  - As time proceeds concentration of reactants decreases
  - As time proceeds concentration of products increases
6.  $\text{SO}_2$  reacts with  $\text{O}_2$  as follows  $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ , the rate of disappearance of  $\text{SO}_2$  is  $2.4 \times 10^{-4}$  mole lit $^{-1}$  min $^{-1}$ . Then
- Rate of reaction is  $1.2 \times 10^{-4}$  mole lit $^{-1}$  min $^{-1}$
  - Rate of appearance of  $\text{SO}_3$  is  $2.4 \times 10^{-4}$  mole lit $^{-1}$  min $^{-1}$
  - Rate of disappearance of  $\text{O}_2$  is  $1.2 \times 10^{-4}$  mole lit $^{-1}$  min $^{-1}$
  - Rate of reaction is twice the rate of disappearance of  $\text{SO}_3$

#### Linked Comprehension Type Questions

##### Passage-I:

$$\text{For the reaction : } aA + bB \longrightarrow cC + dD ; \text{ Rate} = \frac{dx}{dt} = \frac{-1}{a} \frac{d[A]}{dt} = \frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

7. The 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, the rate of disappearance of  $\text{O}_2$  is
- $2\text{ g min}^{-1}$
  - $20\text{ g min}^{-1}$
  - $200\text{ g min}^{-1}$
  - $50\text{ g min}^{-1}$
8. A reaction follows the given concentration-time graph. The rate for this reaction at 20 s will be



- a)  $4 \times 10^{-3}\text{ Ms}^{-1}$       b)  $1 \times 10^{-2}\text{ Ms}^{-1}$       c)  $2 \times 10^{-2}\text{ Ms}^{-1}$       d)  $7 \times 10^{-3}\text{ Ms}^{-1}$

9. In the following reaction :  $x\text{A} \longrightarrow y\text{B}$

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

Where negative sign indicates rate of disappearance of the reactant. Thus  $x : y$  is

- a) 1 : 2      b) 2 : 1      c) 3 : 1      d) 3 : 10

#### Integer Type Questions

10. For a chemical reaction  $a\text{A} \rightarrow b\text{B}$ ,  $\log \left[ -\frac{d[\text{A}]}{dt} \right] = \log \left[ \frac{d[\text{B}]}{dt} \right] + 0.6$  then find the approximate ratio of a and b
11. In a gaseous phase reaction,  $\text{A}_2(\text{g}) \rightarrow \text{B}(\text{g}) + (1/2)\text{C}(\text{g})$ , the increase in pressure from 100 mm to 120 mm is noticed in 5 minute. The rate of disappearance of  $\text{A}_2$  in  $\text{mm min}^{-1}$  is :

## EXERCISE-II

(Order, molecularity and Half-life)

## LEVEL-I (MAIN)

Straight Objective Type Questions

- For an elementary reaction,  $2A + B \rightarrow C + D$ , the active mass of B is kept constant but that of A is tripled. The rate of reaction will
  - decrease by 3 times
  - increase by 9 times
  - increase by 3 times
  - decrease by 6 times
- For a chemical reaction  $Y_2 + 2Z \rightarrow$  Product, rate controlling step is  $Y + 1/2 Z \rightarrow Q$ . If the concentration of Z is doubled, the rate of reaction will
  - Remain the same
  - Become four times
  - Become 1.414 times
  - Become double
- In a reaction  $A \rightarrow B$ , when the concentration of reactant is made 8 times, the rate got doubled. The order of reaction is
  - $1/3$
  - 1
  - $1/2$
  - 2
- The initial rates for gaseous reaction  $A + 3B \rightarrow AB_3$  are given below

[A] (M)	[B] (M)	Rate(M sec <sup>-1</sup> )
0.1	0.1	0.002
0.2	0.1	0.002
0.3	0.2	0.008
0.4	0.3	0.018

Order of reaction is

- zero
  - three
  - one
  - two
- If the initial concentration is reduced to  $1/4^{\text{th}}$  of the initial value of a zero order reaction, the half life of the reaction
    - remains constant
    - Becomes  $1/4^{\text{th}}$
    - becomes double
    - Becomes fourfold
  - If  $\frac{dx}{dt} = k[H_3O^+]^n$  and rate becomes 100 times when pH changes from 2 to 1. Hence order of reaction is
    - 1
    - 2
    - 3
    - 0
  - The initial concentration of cane sugar in presence of an acid was reduced from 0.20 to 0.10M in 5 hours and to 0.05M in 10 hours, value of K ? (in hr<sup>-1</sup>)
    - 0.693
    - 1.386
    - 0.1386
    - 3.465
  - 50% completion of a first order reaction takes place in 16 minutes. Then fraction that would react in 32 minutes from the beginning
    - $1/2$
    - $1/4$
    - $1/8$
    - $3/4$

9. Consider the order of a reaction. Choose the incorrect statement(s).
- Order of a reaction may be zero, integer or fractional
  - Overall order of the reaction never be negative.
  - The order of an elementary step is always equal to its molecularity.
  - For the chemical equation  $2\text{NH}_3 \xrightarrow{\text{Au}} \text{N}_2 + 3\text{H}_2$  the order of reaction is 4.
10. For a first order reaction, the half-life is 50 sec. Identify the correct statement from the following.
- the reaction is almost complete in 500 sec
  - the same quantity of reactant is consumed for every 50 sec of the reaction
  - quantity of reactant remaining after 100 sec is half of what remains after 50 sec
  - All the above three
11. For a first order reaction, if the time taken for completion of 50% of the reaction is 't' second, the time required for completion of 99.9% of the reaction is:
- $10t$
  - $5t$
  - $100t$
  - $2t$
12. In case of first order reactions
- $t_{3/4} = 2t_{1/2}$
  - $t_{7/8} = 3t_{1/2}$
  - $t_{99.9} = 10t_{1/2}$
  - All
13. The kinetic datas for the reaction:  $2\text{A} + \text{B}_2 \rightarrow 2\text{AB}$  are as given below:
- | [A]<br>mol L <sup>-1</sup> | [B]<br>mol L <sup>-1</sup> | Rate<br>mol L <sup>-1</sup> min <sup>-1</sup> |
|----------------------------|----------------------------|---|
| 2                          | 1.0                        | $2.5 \times 10^{-3}$                          |
| 1.0                        | 1.0                        | $5.0 \times 10^{-3}$                          |
| 2                          | 2.0                        | $1 \times 10^{-2}$                            |
- Hence the order of reaction w.r.t. A and B<sub>2</sub> are, respectively,
- 1 and 2
  - 2 and 1
  - 1 and 1
  - 2 and 2
14. The rate law of a reaction,  $\text{A} + \text{B} \rightarrow \text{Product}$  is rate =  $K[\text{A}]^n(\text{B})^m$ . On doubling the concentration of A and halving the concentration of B, the ratio of new rate to the earlier rate of reaction will be
- $n - m$
  - $2^{n-m}$
  - $\frac{1}{2^{m+n}}$
  - $m + n$
15. Consider a reaction;  $a\text{G} + b\text{H} \rightarrow \text{products}$ . When concentration of both the reactants G and H is doubled, the rate increase by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is:
- 0
  - 1
  - 2
  - 3
16. In a first order reaction, the concentration of reactant decreases from  $800 \text{ mol/dm}^3$  to  $50 \text{ mol/dm}^3$  in  $2 \times 10^4 \text{ sec}$ . The rate constant in  $\text{sec}^{-1}$  is: [ $\log 2 = 0.3$ ]
- $2 \times 10^4$
  - $3.45 \times 10^{-5}$
  - $1.386 \times 10^{-4}$
  - $2 \times 10^{-4}$
17. A reaction involving two different reactants can never be:
- Unimolecular reaction
  - I order reaction
  - II order reaction
  - Bi-molecular reaction

18. The rate equation for the reaction;  $2A+B \rightarrow C$  is rate =  $K[A][B]$ . The correct statement about this is:
- $K$  is independent of  $[A]$  and  $[B]$
  - $t_{1/2}$  with respect to  $A$  is dependent on initial concentration of  $A$
  - Unit of  $K$  is  $\text{sec}^{-1}$
  - Rate of formation of  $C$  is twice the rate of disappearance of  $A$
19. The half life period of pyruvic acid in the presence of an amino transferase enzyme (which converts it to alanine) was found to be 221 sec. How long will it take for the concentration of pyruvic acid to fall to 1/64 of its initial value in this first order reaction?
- 1200 sec
  - 2440 sec
  - 663 sec
  - 1326 sec

**Numerical Value Type Questions**

20. For the reaction  $2A + B \rightarrow \text{Products}$ , it is found that doubling the concentration of both reactants increases the rate by a factor of 8. But doubling the concentration of  $B$  alone, only doubles the rate. What is the order of the reaction w.r.t to  $A$  ?
21. Based on the following data for a reaction what is its order ( $A \rightarrow \text{products}$ )
- | Conc. A      | 2M | 0.2M | 0.02M | 0.00     |
|--------------|----|------|-------|----------|
| Time in min. | 0  | 10   | 20    | $\infty$ |
22. In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is \_\_\_ min.
23. Rate constant of a reaction with a virus is  $3.3 \times 10^{-4} \text{ s}^{-1}$ . Time (min) required for the virus to become 75% inactivated is: (Assume virus growth cannot take place simultaneously)

**LEVEL-II (ADVANCED)****Straight Objective Type Questions**

1. In a first order reaction, 20% reaction is completed in 24 minutes. The percentage of reactant remaining after 48 minutes is
- 60
  - 64
  - 81
  - 80
2. The concentration of the reactant A in the reaction  $A \rightarrow B$  at different times are given below:

Concentration (M)	Time (seconds)
0.069	0
0.052	17
0.035	34
0.018	51

The rate constant of the reaction according to the correct order of reaction is

- $0.001 \text{ M}^{-2}\text{s}^{-1}$
  - $0.001 \text{ M}^{-2}\text{s}^{-1}$
  - $0.001 \text{ s}^{-1}$
  - $0.001 \text{ Ms}^{-1}$
3. For a first order reaction with half-life of 150 seconds, the time taken for the concentration of the reactant to fall from  $M/10$  to  $M/100$  will be approximately
- 1500 s
  - 500 s
  - 900 s
  - 600 s

4. For a first order reaction  $A \rightarrow B$ , the reaction rate at reactant concentration of 0.01 M is found to be  $2.0 \times 10^{-5}$  mol L<sup>-1</sup> s<sup>-1</sup>. The half life period of the reaction is  
 a) 220s                    b) 30 s                    c) 374 s                    d) 347 s
5. For a first order reaction at 27°C, the ratio of time required for 75% completion to 25% completion of reaction is :  
 a) 3.0                    b) 2.303                    c) 4.8                            d) 0.477
6. Two first order reaction have halflives in 1:2 ratio. After two halflives of first reaction. What is the ratio of their rates of reactions ? (Initial concentrations same)  
 a) 1 : 2                    b) 1 : 3                    c) 1 : 4                            d) 1 : 1
7. A reaction  $2A \longrightarrow 3B$  takes place according to first order kinetics the time in which the concentration of reactant and product become equal is ( $K = 4.6 \times 10^{-2}$  min<sup>-1</sup>,  $\log 5 = 0.7$ ,  $\log 3 = 0.48$ ,  $\log 2 = 0.3$ )  
 a) 11 min                    b) 15 min                    c) 9 min                            d) 25 min
8. Heptene decomposes according to following reaction  $C_7H_{14} \xrightarrow{\Delta} 2C_2H_4 + C_3H_6$ . Rate constant was found to be  $1 \times 10^{-4}$  sec<sup>-1</sup>. In what time molar ratio of heptene to ethene in the reaction mixture will attain the value 1? [ $\log 2 = 0.3010$ ,  $\log 3 = 0.4771$ ]  
 a) 68 min                    b) 4055 min                    c) 1736 min                    d) 228 min
9. The initial rate of a reaction if its rate constant is  $10^{-3}$  min<sup>-1</sup> when the initial concentration of reactant is 0.2 mol dm<sup>-3</sup> and also percent amount of reactant converted into products in 200 minutes are respectively.  
 a)  $2 \times 10^{-4}$  mol dm<sup>-3</sup> min<sup>-1</sup>, 81.97%                    b)  $2 \times 10^{-4}$  mol dm<sup>-3</sup> min<sup>-1</sup>, 18.03%  
 c)  $2 \times 10^{-4}$  mol dm<sup>-3</sup> min<sup>-1</sup>, 76%                            d)  $2 \times 10^{-4}$  mol dm<sup>-3</sup> min<sup>-1</sup>, 24%

**More than One correct answer Type Questions**

10. Which of the following statements are correct?  
 a) Time required for 75% completion is 1.5 times of half-life for zero order reaction.  
 b) Time needed for a definite fraction of 1<sup>st</sup> order reaction does not vary with the initial concentration.  
 c) Time for 25% reaction is one-third of half life in second order process.  
 d) Rate of 1<sup>st</sup> order reaction gets doubled if the conc of the reactant is increased to a two fold value.
11. For a reaction,  $A + B \rightarrow$  products, the rate of reactions is increased by 8 times when the concentration of A & B are doubled. The rate of reaction is doubled when the concentration of A alone is doubled. Then  
 a) Order of reaction with respect to A is 1                    b) Order of reaction with respect to B is 2  
 c) Rate =  $K[A][B]^2$     d) Units of rate constant are mole<sup>-2</sup> lit<sup>2</sup> time<sup>-1</sup>
12. For a reaction  $A \rightarrow$  products, the rate of reaction is increased by 8 times when the concentration of A is doubled then  
 a) order of the reaction is 4                                    b) order of the reaction is 3  
 c) units of rate constant are mole<sup>-2</sup> lit<sup>2</sup> time<sup>-1</sup>                    d) rate =  $K[A]^3$
13. In case of zero order reactions  
 a)  $t_{1/2} = 2t_{1/4}$                     b)  $t_{3/4} = 3t_{1/2}$                     c)  $t_{\infty} = 2t_{1/2}$                     d)  $t_{90\%} = 3t_{50\%}$

14. Identify incorrect statements
- Molecularity is not always an integral quantity
  - Molecularity can be defined for elementary reactions only
  - Order of reaction does not exceed three
  - Molecularity became zero
15. Hydrolysis of an ester is catalysed by  $H^+$  ion. Using equimolar concentrations of two acids HX and HY both being strong acids. The rate constants of the reaction are found to be  $3 \times 10^{-3} \text{ min}^{-1}$  &  $5 \times 10^{-3} \text{ min}^{-1}$  respectively at a fixed temperature. It can be concluded that.
- Rate const may be taken as the measure of degree of ionization of one acid used as catalyst.
  - HX is a stronger acid than HY, their relative strength being 1.7
  - HX is a weaker acid than HY.
  - HX is a stronger base than HY.
16.  $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$
- 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
- $\frac{dx}{dt} = k[Zn]^0[H^+]^2$
  - $\left( \frac{dx}{dt} \right) = k[Zn][H^+]^2$
  - rate is not affected if concentration of zinc is made four times and that of  $H^+$  ion is halved.
  - rate becomes four times if concentration of  $H^+$  ion is doubled at constant Zn concentration.
17. The rate law for the reaction :  $RCI + NaOH \rightarrow ROH + NaCl$ . Is given by : rate =  $k [RCI]$ . The rate of this reaction
- is doubled by doubling the concentration of NaOH
  - is halved by reducing the concentration of RCI by one half
  - is increased by increasing the temperature of the reaction
  - is unaffected by change in temperature

#### Linked Comprehension Type Questions

Passage-I :

Consider the reaction represented by the equation :  $CH_3Cl(g) + H_2O(g) \rightarrow CH_3OH(g) + HCl(g)$   
These kinetic data were obtained for the given reaction concentrations :

Initial conc (M)		Initial rate of disappearance of $CH_3Cl(Ms^{-1})$
$[CH_3Cl]$	$[H_2O]$	
0.2	0.2	1
0.4	0.2	2
0.4	0.4	8

18. The rate law for the reaction will be
- $r = k [CH_3Cl][H_2O]$
  - $r = k [CH_3Cl]^2[H_2O]$
  - $r = k [CH_3Cl] [H_2O]^2$
  - $r = k [CH_3Cl]^2[H_2O]^4$

19. Overall order of the reaction will be

- a) 0      b) 1      c) 2      d) 3

20. If  $H_2O$  is taken in large excess, the order of the reaction will be

- a) 1      b) 0      c) 3      d) 2

Passage-II :

The following data were observed for the following reaction at  $25^\circ C$ .



Set	Initial concentration (M)		time (t) (min)	Final concentration (M)
	[A] <sub>0</sub>	[B] <sub>0</sub>		
I	0.10	0.05	25	0.0033
II	0.10	0.10	15	0.0039
III	0.20	0.10	7.5	0.0077

21. Rates  $\frac{d[C]}{dt}$  in sets I, II and III are respectively, (in  $M\ min^{-1}$ ) :

- | I                        | II                    | III                   |
|--------------------------|-----------------------|-----------------------|
| a) $1.30 \times 10^{-4}$ | $2.6 \times 10^{-4}$  | $1.02 \times 10^{-3}$ |
| b) 0.033                 | 0.0039                | 0.0077                |
| c) $0.02 \times 10^{-4}$ | $0.04 \times 10^{-4}$ | 0.017                 |
| d) None of above         |                       |                       |

22. Rate constants of the above experiment is (in  $L^2M^{-2}\ min^{-1}$ )

- a)  $2.6 \times 10^{-2}$       b)  $2.6 \times 10^{-1}$       c)  $2.6 \times 10^{-4}$       d)  $1.3 \times 10^{-2}$

23. Rate law of the above experiment is

- a)  $k[A]^2[B]$       b)  $k[A][B]$       c)  $k[A][B]^2$       d)  $k[A]^2[B]^2$

Matrix Matching Type Questions

24. **Column-I**

- A) Molecularity of a reaction
  - B) Order of a reaction
  - C) The dissociation of  $H_2O_2$  (aq)
  - D)  $H_{2(g)} + Cl_{2(g)} \xrightarrow{h\nu} 2HCl$
- p) 0,1 possible
  - q) 1,2 possible
  - r) First order
  - s) Zero order
  - t) Always only +ve integer
  - u)  $t_{1/2}$  independent on initial concentration

**Column-II**

25. **Column-I (Half-life)**

- A)  $t_{1/2} = \text{constant}$
  - B)  $t_{1/2} \propto a$
  - C)  $t_{1/2} \propto p^{-1}$
  - D)  $t_{1/2} \propto 1/a$
- p) First order
  - q) Pseudo first order
  - r) Zero order
  - s) Second order

**Column-II (Order)**

## 26. Column-I (Reaction)

- A)  $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$   
 B)  $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$   
 C)  $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$   
 D)  $\text{H}_2\text{O}_2 + 2\text{I}^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + \text{I}_2$

## Column-II (Units of K)

- p)  $\text{S}^{-1}$   
 q)  $\text{min}^{-1}$   
 r)  $\text{L.mole}^{-1} \text{ min}^{-1}$   
 s)  $\text{L.mole}^{-1} \text{ S}^{-1}$

## 27. Column-I

- A) Decomposition of  $\text{SO}_2\text{Cl}_2$   
 B)  $\text{RCOOR} + \text{NaOH} \rightarrow \text{RCOONa} + \text{ROH}$   
 C) Decomposition of  $\text{N}_2\text{O}_5$   
 D)  $\text{RCOOR} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{RCOOH} + \text{ROH}$

## Column-II

- p) First order reaction  
 q) Units of rate constant  $\text{sec}^{-1}$   
 r) Half life is independent of initial conc  
 s) Pseudo unimolecular reaction  
 t) Units of rate of reaction are  $\text{M}^{-1} \cdot \text{time}^{-1}$

## 28. Column-I

## Linear plots (with non zero slope)

- A)  $\ln\left[\frac{d[A]}{dt}\right] \text{ vs. } \ln[A]$   
 B)  $\log k \text{ vs. } \frac{1}{T}$   
 C)  $\log t_{1/2} \text{ vs. } \log[A]_0$   
 D)  $\frac{-d[A]}{dt} \text{ vs. } [A]^2$

## Column-II

## (Order)

- p) 2  
 q)  $\frac{1}{2}$   
 r) 0  
 s) 1

Integer Type Questions

29. The concentration of R in the reaction  $\text{R} \rightarrow \text{P}$  was measured as a function of time and the following data is obtained :

[R] (molar)	1.0	0.75	0.40	0.10
t(min.)	0.0	0.05	0.12	0.18

The order of the reaction is

30. Half-life period of the decomposition of a compound is 20 minutes. If the initial concentration is doubled, the half-life period is reduced to 10 mins. What is the order of the reaction?
31. For the first order reaction  $t_{99.99\%} = xt_{90\%}$  then, find the value of  $x$ .
32. For a reaction, the graph drawn between  $t_{1/2}$  and 'a' gives a straight line passing through the origin with the slope  $2 \times 10^2 \text{ mole}^{-1} \cdot \text{lit} \cdot \text{min}$ . If the initial concentration of the reactant is 1M, then the half life period is  $\text{_____} \times 10^2 \text{ min}$ .
33. For hypothetical chemical reaction  $\text{A} \rightarrow \text{I}$ , it is found that the reaction is third order in A. What happens to the rate of reaction when the concentration of A is doubled? Rate increases by  $x$  times. Then  $x$  value is
34. The conversion of molecules of A to B follows second order kinetics. Doubling the concentration of 'A' will increase the rate of formation of 'B' by a factor of ?

## EXERCISE-III

(Theories of Chemical Kinetics)

## LEVEL-I (MAIN)

Straight Objective Type Questions

1. For the reaction  $A + B \rightleftharpoons C + D$ , the forward reaction is exothermic. The activation energy of formation of A + B is \_\_\_\_ that for the formation of C + D  
 1) equal to                    2) less than                    3) greater than                    4) double
2. The minimum energy required for molecules to enter into chemical reaction is called  
 1) Kinetic energy            2) Potential energy            3) Threshold energy            4) Activation energy
3. Wrong statement among the following is  
 1) effective collisions are more if activation energy is less  
 2) zero order reaction proceeds at a constant rate independent of concentration or time  
 3) reactions with highest rate constant values have lowest activation energies  
 4) if initial concentration increases half life decreases in zero order
4. The population of activated molecules can be increased by  
 1) increase in temperature                    2) using a catalyst  
 3) increase of concentration of reactants                    4) All
5. Collision theory satisfactorily explains  
 1) First order reaction                    2) Zero order reaction  
 3) Bimolecular reaction                    4) Any order reaction
6. An endothermic reaction  $A \rightarrow B$  has an activation energy as  $x\text{KJ.mol}^{-1}$  of A. If energy change of the reaction is  $y\text{KJ}$ , the activation energy of the reverse reaction is  
 1)  $-x$                     2)  $x - y$                     3)  $x + y$                     4)  $y - x$
7. Which of the following explains the increase of reaction rate by a catalyst ?  
 1) Catalyst provides the necessary energy to the colliding molecules to cross the barrier  
 2) Catalyst decreases the rate of backward reaction so that the rate of forward reaction increases  
 3) Catalyst decreases the enthalpy change of the reaction  
 4) Catalyst provides an alternative path of lower activation energy
8. In a reaction, threshold energy is equal to  
 1) activation energy                    2) normal energy of the reactants  
 3) activation energy + energy of reactants                    4) activation energy – energy of reactants
9. For reaction  $A \rightarrow B$ , the rate constant  $k_1 = A_1 e^{-E_{a1}/RT}$  and for the reaction  $P \rightarrow Q$ , the rate constant  $k_2 = A_2 e^{-E_{a2}/RT}$ . If  $A_1 = 10^8$ ,  $A_2 = 10^{10}$  and  $E_{a1} = 600$ ,  $E_{a2} = 1200$ , then the temperature at which  $k_1 = k_2$  is  
 1)  $\frac{600}{R}\text{K}$                     2)  $\frac{300 \times 4.606}{R}\text{K}$                     3)  $\frac{600}{4.606R}\text{K}$                     4)  $\frac{4.606}{600R}\text{K}$

10. If a reaction  $A + B \rightarrow C$  is exothermic to the extent of 30 KJ/mol and the forward reaction has an activation energy of 70 KJ/mol, the activation energy for the reverse reaction is  
 1) 30 KJ/mol      2) 40KJ/mol      3) 70KJ/mol      4) 100KJ/mol
11. Unit of frequency factor A in :  $K = Ae^{-E_a/RT}$  is :  
 1) time<sup>-1</sup>      2) mole litre<sup>-1</sup>time<sup>-1</sup>  
 3) litre mol<sup>-1</sup>t<sup>-1</sup>      4) dependent of order of reaction
12. For the decomposition of  $N_2O_5(g)$ , it is given that:  $2N_2O_5(g) \rightarrow 4NO_{2(g)} + O_{2(g)}$ . Activation energy  $E_a$ ,  $N_2O_5(g) \rightarrow 2NO_{2(g)} + \frac{1}{2}O_{2(g)}$ ; Activating energy  $E'_a$ ,  
 1)  $E_a = E'_a$       2)  $E_a > E'_a$       3)  $E_a < E'_a$       4)  $E_a = 2E'_a$
13. Effective collision are those in which molecules must:  
 1) Have energy equal to or greater than the threeshold energy  
 2) Have proper orientation  
 3) Acquire the energy of activation  
 4) All of these
14. The activation energy of a reaction is zero. The rate constant of the reaction:  
 1) Increases with increase of temperature      2) Decreases with decrease of temperature  
 3) Decreases with increase of temperature      4) Independent of temperature
15. Which reaction characteristics are changing by the addition of a catalyst to a reaction at constant temperature  
 1) Activation energy      2) Equilibrium constant  
 3) Reaction entropy      4) Reaction enthalpy
16. For a first order reaction  $A \rightarrow P$ , the temperature (T) dependent rate constant (K) was found to follow the equation  $\log k = - (2000) \frac{1}{T} + 6.0$ . The pre-exponential factor A and the activation energy  $E_a$ , respectively, are  
 1)  $1 \times 10^6 s^{-1}$  & 9.2KJ mol<sup>-1</sup>      2)  $6s^{-1}$  & 16.6KJ mol<sup>-1</sup>  
 3)  $1 \times 10^6 s^{-1}$  & 16.6 KJ mol<sup>-1</sup>      4)  $1 \times 10^6 s^{-1}$  & 38.3 KJ mol<sup>-1</sup>
17. The activation energy of a reaction is 58.3 kJ/mole. The ratio of the rate constants at 305K and 300K is about ( $R = 8.3 Jk^{-1}mol^{-1}$ ) (Antilog 0.1667 = 1.468)  
 1) 1.25      2) 1.75      3) 1.5      4) 2.0
18. For  $X \rightarrow Y$ ,  $\frac{k_{t+10}}{k_t} = 3$ . If the rate constant at 300 K is 'Q' min<sup>-1</sup>, at what temperature rate constant becomes '9Q' min<sup>-1</sup>?  
 1) 47°C      2) 320°C      3) 280 K      4)  $\sqrt{9 \times 300}$  K
19. For  $N_2O_5(\text{in } CCl_4) \rightarrow 2NO_2 + \frac{1}{2}O_2$ ,  $K = 6 \times 10^{-4}s^{-1}$  at 350K and  $K = 1.2 \times 10^{-3}s^{-1}$  at 360 K. Then, when temperature is changed to 380 K, value of K (in s<sup>-1</sup>)  
 1)  $1.2 \times 10^{-3}$       2)  $2.4 \times 10^{-3}$       3)  $4.8 \times 10^{-4}$       4)  $4.8 \times 10^{-3}$

## **Numerical Value Type Questions**

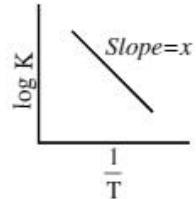
20. For the reaction, following data is given :  
 $A \rightarrow B; K_1 = 10^{15} \exp\left(\frac{-2000}{T}\right)$ ;  $C \rightarrow D; K_2 = 10^{14} \exp\left(\frac{-1000}{T}\right)$ . The temperature at which  $K_1 = K_2$  is

21. At  $52^{\circ}\text{C}$  the activation energy  $E_{\text{a(b)}}$  for a reaction is  $2 \times 10^{-2}$  k.cal and enthalpy of reaction at same temperature is 0.12 k.cal. Calculate % of reactant molecules which crossover the energy barrier.

22. The rate of a chemical reaction doubles for every  $10^{\circ}\text{C}$  rise in temperature. If the temperature is increased by  $60^{\circ}\text{C}$ , the rate of reaction increases by about \_\_\_\_\_ times.

LEVEL-II (ADVANCED)

### **Straight Objective Type Questions**



- a)  $\frac{-E_a}{2.303}$       b)  $\frac{-E_a}{2.303R}$   
 c)  $\frac{-2.303}{E_a \cdot R}$       d)  $\frac{-2.303R}{E_a}$

7. The effect of temperature on a reaction rate for which  $E_a$  is zero is given by  
 a) with increase of temperature rate increases      b) with increase of temperature rate decreases  
 c) rate is independent of temperature      d) reaction never occurs
8. A first order reaction is 50% completed in 20 minutes at  $27^\circ\text{C}$  and in 5 minutes at  $47^\circ\text{C}$ . The energy of activation of the reaction is :  
 a) 43.85 kJ/mol      b) 55.14 kJ/mol      c) 11.97 kJ/mol      d) 6.65 kJ/mol
9. A first order reaction is 12.5% completed in 20 minutes at 300 K. When same reaction is carried out at 315 K, it is 12.5% complete in 2.5 minute. What is the activation energy of reaction (in k cal/mol)? [Given:  $R = 2 \text{ cal/mol}$  and  $\ln 2 = 0.7$ ]  
 a) 35.38      b) 26.46      c) 17.69      d) 26.56

***More than One correct answer Type Questions***

10. Arrhenius equation may be represented as  
 a)  $\ln \frac{A}{k} = \frac{E_a}{RT}$       b)  $\frac{d \ln k}{dT} = \frac{E_a}{RT}$   
 c)  $\log A = \log k + \frac{E_a}{2.303 RT}$       d)  $\log \left( -\frac{E_a}{RT} \right) = \frac{k}{A}$
11. Which of the following is correct for Arrhenius equation  $k = Ae^{-E_a/RT}$   
 a)  $k$  is the rate of reaction at zero concentration of reactants  
 b)  $A$  may be termed as the rate constant at very high temperature  
 c)  $A$  may be termed as the rate constant at zero activation energy  
 d)  $E_a$  is the activation energy of reactants
12. Which of the following statements are correct about the Arrhenius equation?  
 a) The Arrhenius constant becomes equal to rate constant at a very high temperature  
 b) When  $E_a$  is zero, rate is independent of temperature  
 c)  $e^{-E_a/RT}$  represents the fraction of molecules having energy more than threshold energy  
 d) Positive catalyst increases  $E_a$  of the reaction
13. Pick out the correct Statements.  
 a) Activated complex is an unstable intermediate with maximum energy and normal bonds  
 b) Acitvated complex is an unstable intermediate with maximum energy and fractional bond orders  
 c) Transition state cannot exist independently, it has greater vibrationl character than unstable intermediate  
 d) Transition state is a state in which bonds are half broken and half formed
14. In Arrhenius equation  
 a) The Arrhenius constant has units of rate of reaction  
 b) The Arrhenius constant has the units of rate constant of reaction  
 c) If  $E_a$  is high, rate of reaction is slow  
 d) If  $E_a$  is high, rate of reaction is high

Linked Comprehension Type QuestionsPassage-I :

For a chemical reaction,  $A \rightarrow \text{products}$ , the following equation is found to be followed,

$$\log K = 16.398 - \frac{2800}{T}$$

15. Arrhenius factor for the reaction is \_\_\_\_\_  
 a)  $2.5 \times 10^{16}$       b)  $5 \times 10^{16}$       c)  $7.5 \times 10^{16}$       d)  $4 \times 10^{16}$
16. Activation energy of the reaction is \_\_\_\_\_ K.Cal  
 a) 128.13      b) 12.767      c) 12813      d) 1.2813
17. At  $27^{\circ}\text{C}$  the rate constant of the reaction is \_\_\_\_\_  
 a)  $1.16 \times 10^5$       b)  $1.16 \times 10^6$       c)  $1.321 \times 10^7$       d)  $1.16 \times 10^7$

Passage-II :

Arrhenius studied the effect of temperature on the rate of a reaction and postulated that rate constant varies with temperature exponentially as  $k = A e^{-E_a/RT}$ . 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.

18. The pre-exponential factor in the Arrhenius equation of a second order reaction has the units  
 a) mol L<sup>-1</sup> s<sup>-1</sup>      b) L mol<sup>-1</sup> s<sup>-1</sup>      c) s<sup>-1</sup>      d) dimensionless
19. Which of the following plot will be linear?  
 a) In k versus T with -ve slope      b) k versus 1/T with -ve slope  
 c) In k versus 1/T with -ve slope      d) In k versus 1/T with + ve slope
20. 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

Passage-III :

A certain endothermic reaction :  $A \rightarrow \text{Product}$   $\Delta H = +\text{ve}$  proceeds in a sequence of three elementary steps with the rate constants  $K_1$ ,  $K_2$  and  $K_3$  and each one having energy of activation  $E_1$ ,  $E_2$  and  $E_3$  respectively at  $25^{\circ}\text{C}$ . The observed rate constant for the reaction is equal to  $K_3 \sqrt{\frac{K_1}{K_2}}$ .  $A_1$ ,  $A_2$  and  $A_3$  are Arrhenius parameters respectively.

21. The observed energy of activation for the reaction is  
 a)  $\frac{2E_1 - E_2 + 2E_3}{2}$       b)  $\frac{E_2 - E_1 - 2E_3}{2}$       c)  $\sqrt{\frac{E_1 E_3}{E_2}}$       d)  $\frac{E_1 - E_2 + E_3}{2}$
22. The observed Arrhenius parameter for the reaction is  
 a)  $\frac{2A_1 - A_2 + 2A_3}{2}$       b)  $\sqrt{\frac{A_1}{A_2}} \cdot A_3$       c)  $A_1 A_2 A_3$       d)  $\frac{A_1 \cdot A_3}{A_2}$

23. Presence of a catalyst decreases the energy of activation of each path by half the value of  $E_1$ . Assuming the other factors same, the observed energy of activation would be

a)  $E_3 - \frac{E_2}{2}$

b)  $2E_3 - E_2$

c)  $E_2 - \frac{E_3}{2}$

d)  $\frac{E_1}{2} + \frac{E_2}{2} + E_3$

#### Matrix Matching Type Questions

24. **Column-I**

A) Decomposition of  $H_2O_2$

B)  $\frac{k_{308K}}{k_{298K}}$

C) Arrhenius equation

D)  $t_{99.9\%}$

**Column-II**

p) Ten halflives

q) 1<sup>st</sup> order

r) Temperature coefficient

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

t) 2 to 3

25. **Column-I**

A)  $e^{-E_a/RT}$

B) A

C)  $\frac{-k}{2.303}$

D)  $t_{1/2} = \frac{a}{2k}$

**Column-II**

p)  $\tan\theta, \theta > \frac{\pi}{2}$

q) Boltzmanns factor

r) Zero order reation

s) Arrhenius factor

#### Integer Type Questions

26. The energy of activation for a reaction is 100 kJ/mol at 57°C. Presence of catalyst lower activation energy by 25%. The rate of reaction is increased by 10<sup>x</sup>, the value of x is
27. The rate of reaction becomes two times for every 10°C rise in temperature. If the rate of reaction increases by 32 times when the temperature is increased from 30°C to (10x)°C. Then x =
28. A first order chemical reaction. A → P is occurring at 500 K. If the same reaction is to be carried out in presence of a catalyst, temperature of 400 K is required to be maintained in order to maintain the same rate of reaction. If the catalyst lowers the activation energy by 30 kJ, then what would

#### EXERCISE-IV

(1<sup>st</sup> order, Parallel, Sequential, Eqm reactions, reaction mechanism)

**LEVEL-I (MAIN)**

#### Straight Objective Type Questions

1. In the reversible reaction :  $2NO_2 \rightleftharpoons N_2O_4$  the rate of disappearance of  $NO_2$  is equal to
- 1)  $\frac{2k_1}{k_2}[NO_2]^2$
- 2)  $2k_1[NO_2]^2 - 2k_2[N_2O_4]$
- 3)  $2k_1[NO_2]^2 - k_2[N_2O_4]$
- 4)  $(2k_1 - k_2)[NO_2]$

2. Benzene diazonium chloride (A) decomposes into chlorobenzene (B) and N<sub>2</sub>(g) in first-order reaction. Volumes of N<sub>2</sub> collected after 5 min and at the complete decomposition of A are 10 mL and 50 mL respectively. The rate constant for the reaction is  
 1) 0.446 min<sup>-1</sup>      2) 0.0446 min<sup>-1</sup>      3) 0.223 min<sup>-1</sup>      4) 0.112 min<sup>-1</sup>
3. For a reaction A<sub>(g)</sub> → B<sub>(g)</sub> + C<sub>(g)</sub> + D<sub>(g)</sub> at 750K the rate constant is  $2.3 \times 10^{-3}$  min<sup>-1</sup>. Starting with a pressure of 400 mm of Hg at this temperature in a closed container, how many minutes would it take for the pressure in the container to become 760 mm Hg. ( $\log 11 = 1.041$ )  
 1) 360      2) 460      3) 260      4) 160
4. Consider the following reactions A + B ⇌<sub>k<sub>1</sub></sub> C, C + B →<sub>k<sub>2</sub></sub> D. If  $\frac{d[C]}{dt} = 0$  (i.e., steady state). Then  $\frac{-d[A]}{dt}$  is equal to  
 1)  $\frac{k_1[A][B]}{k_{-1} + k_2[B]}$       2)  $\frac{k_1 k_2[A][B]^2}{k_{-1} + k_2[B]}$       3)  $\frac{2k_1 k_2[A][B]}{k_{-1} + k_2[B]}$       4)  $\frac{k_1 k_2[A]^2[B]}{k_{-1} + k_2[B]}$
5. The inversion of cane sugar proceeds with half-life of 500 minutes at P<sub>H</sub> = 5 for any concentration of sugar. However if P<sub>H</sub> = 6; the half life changed to a 50 minutes. The rate law expression for sugar inversion can be written as  
 1)  $r = k[\text{sugar}]^2[\text{H}^+]^0$       2)  $r = k[\text{sugar}]^1[\text{H}^+]^0$   
 3)  $r = k[\text{sugar}]^1[\text{H}^+]^1$       4)  $r = k[\text{sugar}]^0[\text{H}^+]^1$

**Numerical Value Type Questions**

6. A reactant 'A' decomposes to produce two different products simultaneously, but at different rate as shown below:



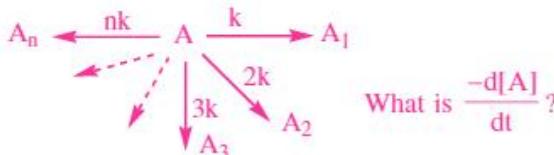
The order of reaction is unity for both reaction and their respective rate constants K<sub>1</sub> & K<sub>2</sub> are  $1.2 \times 10^{-2}$  &  $3 \times 10^{-2}$  per second, respectively. The activation energy for overall reaction (KJ/mol) (if the activation energy for individual reactions E<sub>1</sub> and E<sub>2</sub> are 180 & 200 KJ/mol respectively) is

**LEVEL-II (ADVANCED)****Single Correct Answer type Questions**

1. Which integrated equation is correct for the reaction given below? A(g) → B(g) + C(g) + D(g)  
 P<sub>i</sub> → initial pressure ; P<sub>t</sub> → total pressure
- a)  $k = \frac{2.302}{t} \log_{10} \left[ \frac{P_i}{P_t} \right]$       b)  $k = \frac{2.302}{t} \log_{10} \left[ \frac{P_t}{P_i} \right]$   
 c)  $k = \frac{2.302}{t} \log_{10} \left[ \frac{2P_t}{3P - P_t} \right]$       d)  $k = \frac{2.302}{t} \log_{10} \left[ \frac{3P_t}{2P - 3P_t} \right]$
2. For the formation of phosgene from CO(g) and chlorine (g) as, CO(g) + Cl<sub>2</sub>(g) → COCl<sub>2</sub>(g) the possible mechanism is Cl<sub>2</sub> ⇌ 2Cl (fast); Cl + CO ⇌ COCl (fast) ; COCl + Cl<sub>2</sub> → COCl<sub>2</sub> + Cl (slow). The rate law expression can be written as  
 a) Rate = k [CO] [Cl<sub>2</sub>]      b) Rate = k [CO]<sup>1/2</sup> [Cl<sub>2</sub>]  
 c) Rate = k [CO] [Cl<sub>2</sub>]<sup>3/2</sup>      d) Rate = k [CO] [Cl<sub>2</sub>]<sup>1/2</sup>

3. For any elementary reaction  $2A \xrightleftharpoons[k_2]{k_1} B$ , the rate of disappearance of A is equal to  
 a)  $\frac{2k_1}{k_2}[A]^2$       b)  $-2k_1[A]^2 + 2k_2[B]$       c)  $2k_1[A]^2 - 2k_2[B]$       d)  $(2k_1 - k_2)[A]$

4. Mechanism of the reaction is :



- a)  $\frac{n(n+1)}{2}k[A]$       b)  $k[A]$       c)  $nk[A]$       d)  $\frac{2}{n(n+1)}k[A]$
5. Mechaism of the reaction is  $A_2 \xrightleftharpoons[k_1]{k_2} 2A$ ;  $A + B \xrightarrow{k_2} C$ ;  $A_2 + C \xrightarrow{k} D + A$ . What is  $\frac{-d[A_2]}{dt}$ ?  
 a)  $k_1[A_2] - k_{-1}[A]^2 + k[A_2][C]$       b)  $2k_1[A]^2 - k_1[A_2] + k_2[A][B] - k[A_2][C]$   
 c)  $k_2[A][B] - k[A_2][C]$       d)  $l[A_2][C]$

#### Linked Comprehension Type Questions

##### Passage-I :

Consider the reaction  $2A \longrightarrow 4B + C$ ;

optically active A, decomposes into B and C, which are also optically active, if rotation per mole of A is  $10^\circ$ , B is  $30^\circ$  and C is  $-40^\circ$  respectively. After 10 sec the rotation of mixture was  $25^\circ$  and at infinite time was  $30^\circ$ . [Degree of dissociation is fraction dissociated per mole]

6. Rate constant of reaction is

a)  $\frac{1}{10} \ln \frac{9}{2}$       b)  $\frac{1}{10} \ln \frac{3}{2}$       c)  $\frac{1}{10} \ln \frac{4}{9}$       d)  $\frac{1}{10} \ln \frac{2}{9}$

7. Degree of dissociation of A at 10 sec is

a)  $\alpha = \frac{7}{9}$       b)  $\alpha = \frac{3}{4}$       c)  $\alpha = \frac{7}{12}$       d)  $\alpha = \frac{12}{9}$

8. Degree of dissociation of A at 20 sec is

a)  $\alpha = \frac{77}{81}$       b)  $\alpha = \frac{81}{77}$       c)  $\alpha = \frac{3}{4}$       d)  $\alpha = \frac{6}{13}$

##### Passage-II :

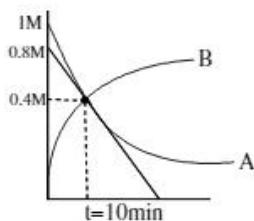
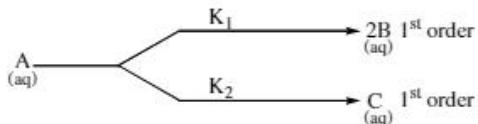
Elementary unimolecular reactions have first order rate laws, elementary bimolecular reactions have second order rate laws. A rate law is often derived from a proposed mechanism by imposing the steady state approximation or by assuming that there is a pre-equilibrium. A proposed mechanism must be consistent with the experimental rate law.

9. The molecularity of the elementary reaction  $C_2N_2 \rightarrow 2CN$  is :

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

10. In a gas-phase reaction, a reaction takes place only if the reactant molecules get \_\_\_\_\_ during the molecular collisions give products.

a) threshold energy      b) activation energy      c) both a & b      d) heat of reaction

Passage-III :

11. What is the half life of the given reaction?  
 a) 8min      b) 7.5min      c) 3.5min      d) 10min
12. What is the ratio of the rate constants  $K_1$  and  $K_2$ ?  
 a) 2 : 3      b) 1 : 3      c) 2 : 5      d) 1 : 2
13. What is the ratio of concentrations of 'B', 'C' at any stage of the reaction?  
 a) 1      b) 2      c) 3      d) 4

Integer Type Questions

14. A tiny spherical ball of water soluble solute is dropped in 1 litre of water. Mass of ball is  $1/7$  gm and mol mass of solute is 125. Decrease in surface area due to dissolution follows 1st order of half life period 1 sec. and after 2 sec. molarity of solution is  $10^{-x}$ . Find the value of  $x$ .
15. A chemical reaction occurs in three paths having rate constants  $k_1$ ,  $k_2$  &  $k_3$  respectively. If  $E_{a1}$ ,  $E_{a2}$  and  $E_{a3}$  are 4, 5 & 8 kJ respectively and overall rate constant  $k = \frac{k_1 k_3}{k_2}$ . Assuming  $A_{av} = \frac{A_1 A_3}{A_2}$ , the overall energy of activation in kJ is \_\_\_\_

**KEY SHEET (LECTURE SHEET)****EXERCISE-I**

<b>LEVEL-I</b>	1) 2	2) 3	3) 2	4) 1	5) 1	6) 4	7) 3	8) 4
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9) 3	10) 1.6	11) 0.1	12) 2
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<b>LEVEL-II</b>	1) a	2) b	3) acd	4) cd	5) abcd	6) abc	7) b	8) d
-----------------	------	------	--------	-------	---------	--------	------	------

9) b	10) 4	11) 8
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**EXERCISE-II**

<b>LEVEL-I</b>	1) 2	2) 3	3) 1	4) 1	5) 2	6) 2	7) 3	8) 4
----------------	------	------	------	------	------	------	------	------

9) 4	10) 3	11) 1	12) 4	13) 1	14) 2	15) 4	16) 3
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17) 1	18) 1	19) 4	20) 2	21) 0	22) 30	23) 70
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<b>LEVEL-II</b>	1) b	2) d	3) b	4) d	5) c	6) d	7) a	8) a
-----------------	------	------	------	------	------	------	------	------

9) b	10) abcd	11) abcd	12) bcd	13) ac	14) ac	15) ac	16) bcd
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17) bcd	18) c	19) d	20) a	21) a	22) b	23) a
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24) A-qt; B-pq; C-ru; D-s	25) A-pq; B-r; C-s; D-s
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26) A-pq; B-rs; C-pq; D-rs	27) A-pq; B-t; C-r; D-s
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28) A-pqs; B-pqr; C-pqr; D-p	29) 0	30) 2	31) 4
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32) 2	33) 8	34) 4
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**EXERCISE-III****LEVEL-I**

- 1) 3    2) 4    3) 4    4) 4    5) 3    6) 2    7) 4    8) 3  
 9) 3    10) 4    11) 4    12) 1    13) 4    14) 4    15) 1    16) 4  
 17) 3    18) 1    19) 4    20) 434.22    21) 80.6    22) 64

**LEVEL-II**

- 1) d    2) b    3) b    4) c    5) c    6) b    7) c    8) b  
 9) b    10) ac    11) bcd    12) abc    13) bd    14) bc    15) a    16) b  
 17) d    18) b    19) c    20) b    21) d    22) b    23) a  
 24) A-q; B-rst; C-rs; D-p    25) A-q; B-s; C-p; D-r    26) 4    27) 8  
 28) 6

**EXERCISE-IV****LEVEL-I**

- 1) 2    2) 2    3) 3    4) 2    5) 2    6) 194.7

**LEVEL-II**

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

**PRACTICE SHEET****EXERCISE-I**

(Introduction, rate of reactions Factors influencing rate, specific rate)

**LEVEL-I (MAIN)****Straight Objective Type Questions**

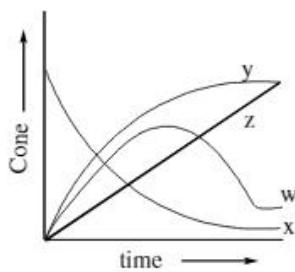
- Which of the following reactions occurs at measurable rate?
  - reaction between  $\text{H}^+$  and  $\text{OH}^-$  ions in aqueous solution
  - reaction between  $\text{AgNO}_3$  and  $\text{NaCl}$  aqueous solutions
  - hydrolysis of methyl acetate
  - reaction between hydrogen and oxygen gases at room temperature
- Which of the following reaction is spontaneous at room temperature?
 

1) $\text{I}_2 + \text{H}_2\text{O} \rightarrow \text{HI} + \text{HIO}$	2) $2\text{H}_2 + \text{O}_2 \xrightarrow{\text{Pt}} 2\text{H}_2\text{O}$
3) $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$	4) $2\text{HCl} \rightarrow \text{H}_2 + \text{Cl}_2$
- The rate of a chemical reaction
 

1) increases as the reaction proceeds	2) decreases as the reaction proceeds
3) may increase or decrease during the reaction	4) remains constant as the reaction proceeds
- The chemical reaction occurring between covalent molecules involves
 

1) breaking of existing bonds	2) formation of new bonds
3) evolution of heat energy	4) 1& 2

5. For a hypothetical reaction;  $A \rightarrow L$  the rate expression is, rate =  $-\frac{dC_A}{dt}$
- negative sign represents that rate is negative
  - negative sign pertains to the decrease in the concentrations of reactant
  - negative sign indicates the attractive forces between reactants
  - all of the above are correct
6. The specific rate constant of a reaction depends on the
- concentration of the reactant
  - time
  - temperature
  - concentration of the product
7. The variation of the concentration of the products with time is given by the curve :



- X
  - Y
  - Z
  - W
8. Observe the following reaction  $A_{(g)} + 3B_{(g)} \rightarrow 2C_{(g)}$ . The rate of this reaction  $\left[ -\frac{d[A]}{dt} \right]$  is  $3 \times 10^{-3}$  mole lit $^{-1}$  min $^{-1}$ . What is the value of  $-\frac{d[B]}{dt}$  in mole lit $^{-1}$  min $^{-1}$  ?
- $3 \times 10^{-3}$
  - $9 \times 10^{-3}$
  - $10^{-3}$
  - $1.5 \times 10^{-3}$
9.  $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$  Rate law is expressed as  
(excess) (glucose) (fructose)
- $r = K [C_{12}H_{22}O_{11}] [H_2O]$
  - $r = K[C_{12}H_{22}O_{11}]$
  - $r = K[H_2O]$
  - $r = K[C_{12}H_{22}O_{11}][H_2O]^2$

#### Numerical Value Type Questions

10. For the reaction  $N_2 + 3H_2 \rightarrow 2NH_3$ , the rate  $\frac{d[NH_3]}{dt} = 2 \times 10^{-4} \text{ Ms}^{-1}$ . Therefore the rate  $-\frac{d[N_2]}{dt}$  is given as  $10^x$ ,  $x = \underline{\hspace{2cm}}$
11. For the reaction  $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ , the rate of reaction with respect to  $NH_3$  is  $2 \times 10^{-3} \text{ Ms}^{-1}$ . Then the rate of the reaction with respect to oxygen is  $\underline{\hspace{2cm}} \times 10^{-3} \text{ Ms}^{-1}$

#### LEVEL-II (ADVANCED)

#### Straight Objective Type Questions

1. For the reaction  $X + 3Y \rightarrow Z$ , which form of differential rate law is incorrect?
- $dX/dt = dY/3dt$
  - $3dZ/dt = -dY/dt$
  - $dZ/dt = -dX/dt$
  - $-dx/dt = dZ/dt$

2. Which statement is incorrect?
- Positive catalyst increase the rate of reaction
  - During the course of the reaction, specific reaction rate remains constant
  - rate constant always increases with rise in temperature whether the reaction is endothermic or exothermic
  - negative catalyst increase the rate of reaction

***More than One correct answer Type Questions***

3. For a gaseous reaction :  $A(g) \rightarrow B(g)$ , the rate expression may be given as
- $-\frac{d[A]}{dt} = k[A]^n$
  - $-\frac{1}{V} \frac{dn_A}{dt} = k[A]^n$
  - $-\frac{1}{RT} \frac{dP_A}{dt} = k[A]^n$
  - $-\frac{dP_A}{dt} = k[P_A]^n$
4. Which of the following statement is incorrect?
- For reaction  $xX \rightarrow yY$ ; Rate =  $\frac{1}{x} \frac{dx}{dt} = \frac{dy}{dt}$
  - The parameter, rate constant, and specific reaction rate have different meaning
  - For any reaction the value of specific reaction rate is independent of the initial concentration of reactants.
  - $E_a = E_R + E_{\text{Threshold}}$
5. In acidic medium, the rate of reaction between  $\text{BrO}_3^-$  and  $\text{Br}^-$  is given by the expression
- $$-\frac{d[\text{BrO}_3^-]}{dt} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$
- The rate constant of the reaction depends upon the concentration of  $\text{H}^+$  ions
  - The rate of reaction is independent of the concentration of the acid added
  - Doubling the concentration of  $\text{H}^+$  ions will increase the reaction rate by 4 times
  - The change in pH of the solution will affect the rate of reaction

***Linked Comprehension Type Questions***

***Passage-I :***

The thermal decomposition of  $\text{N}_2\text{O}_5$  occurs as :  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$

Experimental studies suggest that rate of decomposition of  $\text{N}_2\text{O}_5$ , rate of formation of  $\text{NO}_2$  or rate of formation of  $\text{O}_2$  all becomes double if concentration of  $\text{N}_2\text{O}_5$  is doubled.

6. The correct mechanism for the decomposition of  $\text{N}_2\text{O}_5$  is :
- $\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$ ;  $\text{N}_2\text{O}_5 + \text{NO}_3 \rightarrow 3\text{NO}_2 + \text{O}_2$
  - $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \text{O}$ ;  $\text{N}_2\text{O}_5 + \text{O} \rightarrow 3\text{NO}_2 + \text{O}_2$
  - $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$
  - $\text{N}_2\text{O}_5 \rightarrow \text{NO} + \text{NO}_2 + 2\text{O}_2$ ;  $\text{N}_2\text{O}_5 + \text{NO}_2 \rightarrow 3\text{NO}_2 + \frac{1}{2}\text{O}_2$
7. If rate constant for decomposition of  $\text{N}_2\text{O}_5$ , formation of  $\text{NO}_2$  and formation of  $\text{O}_2$  are  $k_1, k_2$  and  $k_3$  respectively, then :
- $k_1 = k_2 = k_3$
  - $2k_1 = k_2 = 4k_3$
  - $k_1 = 2k_2 = k_3$
  - $k_1 = k_2 = 2k_3$
8. If rate of formation of  $\text{O}_2$  is 16g/hr, then rate of decomposition of  $\text{N}_2\text{O}_5$  and rate of formation of  $\text{NO}_2$  respectively is :
- cannot be calculated without knowing rate constants
  - 108g/hr, 92g/hr
  - 35g/hr, 64g/hr
  - 54g/hr, 46g/hr

Integer Type Questions

9. For the reaction  $\text{NO}_2 + \text{CO} \rightarrow \text{CO}_2 + \text{NO}$ , the experimental rate expression is  $-\frac{dc}{dt} = k[\text{NO}_2]^2$ . Find the number of molecules of CO involved in the slowest step.

 EXERCISE-II

(Order, molecularity and half life)

 LEVEL-I (MAIN)Straight Objective Type Questions

1. Which of the following is correct?
  - 1) Molecularity of a reaction is always same as the order of reaction
  - 2) In some cases molecularity of the reaction is same as the order of reaction
  - 3) Molecularity of the reaction is always more than order of reaction
  - 4) Molecularity never be equal to order
2. The rate equation for the reaction  $2\text{A} + \text{B} \rightarrow \text{C}$  is found to be : rate =  $K[\text{A}]^2[\text{B}]$ . The correct statement in relation to this reaction is
  - 1) units of k must be  $\text{sec}^{-1}$
  - 2) value of k is independent of the initial concentrations of A and B
  - 3) rate of formation of C is twice the rate of disappearance of A
  - 4)  $t_{1/2}$  is a constant
3. If the rate for the chemical reaction is expressed as Rate =  $K [\text{A}]^{[B]}_n$ , then
 

1) order of reaction is one	2) order of reaction is n
3) order of reaction is $1 + n$	4) order of reaction is $1 - n$
4. Which of the following statements is correct regarding order of reaction
  - 1) first order reaction should be bimolecular
  - 2) order of reaction must be positive
  - 3) order depends upon stoichiometry
  - 4) order is determined by experimental results
5. If the rate of gaseous reaction is independent of pressure, the order of reaction is
 

1) 0	2) 1	3) 2	4) 3
------	------	------	------
6. For the reaction  $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ , the rate expression is, rate =  $K [\text{H}_2] [\text{Br}_2]^{1/2}$  which statement is true about this reaction
 

1) The reaction is of second order	2) Order of the reaction is $3/2$
3) The unit of K is $\text{sec}^{-1}$	4) Molecularity of the reaction is 2
7. For the following elementary step  $(\text{CH}_3)_3\text{CBr}_{(\text{aq})} \rightarrow (\text{CH}_3)_2\text{C}^+_{(\text{aq})} + \text{Br}^-_{(\text{aq})}$  the molecularity is
 

1) Zero	2) 1	3) 2	4) fractional
---------	------	------	---------------
8. The units of rate constant for the reaction obeying rate expression,  $r = k[\text{A}][\text{B}]^{2/3}$  is
 

1) $\text{mole}^{-2/3} \text{lit}^{2/3} \text{time}^{-1}$	2) $\text{mole}^{2/3} \text{lit}^{-2/3} \text{time}^{-1}$
3) $\text{mole}^{-5/3} \text{lit}^{5/3} \text{time}^{-1}$	4) $\text{mole}^{2/3} \text{lit}^{2/3} \text{time}^{-1}$

9. Two gases 'A' and 'B' are in a container. The experimental rate law for the reaction between them has been found to be rate =  $k[A]^2[B]$ . Predict the effect on the rate of the reaction when the partial pressure of each reactant is doubled :
- the rate is doubled
  - rate becomes four times
  - the rate becomes six times
  - the rate becomes eight times
10. In the following sequence of reactions  $M \xrightarrow{K_1} N \xrightarrow{K_2} O \xrightarrow{K_3} P : K_1 < K_2 < K_3$ , then the rate determining step is
- $M \rightarrow N$
  - $N \rightarrow O$
  - $O \rightarrow P$
  - $M \rightarrow P$
11. Taking the reaction  $x + 2y \rightarrow$  products to be of second order, which of the following is/are the rate law expression/s for the reaction
- $\frac{dx}{dt} = K[x][y]$
  - $\frac{dx}{dt} = K[x][y]^2$
  - $\frac{dx}{dt} = K[x]^2$
  - $\frac{dx}{dt} = K[x] + K[y]^2$
- Then the correct answers can be
- I only
  - I and III only
  - I and II only
  - I and IV only
12. \_\_\_\_\_ of a reaction cannot be determined experimentally.
- Order
  - Rate
  - Rate constant
  - Molecularity
13. The rate expression for the reaction  $A_{(g)} + B_{(g)} \rightarrow C_{(g)}$  is rate =  $kC_A^2 C_B^{1/2}$ . What changes in the initial concentrations of A and B will cause the rate of reaction to increase by a factor of eight?
- $C_A \times 2; C_B \times 2$
  - $C_A \times 2; C_B \times 4$
  - $C_A \times 1; C_B \times 4$
  - $C_A \times 4; C_B \times 1$
14. For a reaction  $pA + qB \rightarrow$  products, the rate law expression is  $r = k[A]^l [B]^m$  then
- $(p + q) = (l + m)$
  - $(p + q) > (l + m)$
  - $(p + q)$  may or may not be equal to  $(l + m)$
  - $(p + q) \neq (l + m)$
15. For  $H_2 + Cl_2 \xrightarrow{X} 2 HCl$ , rate law is given by  $R = K$ . Then, X is
- Pt
  - Ni
  - $h\nu$
  - Water
16. If both  $\frac{dc}{dt}$  & specific rate have same units, then rate law is
- $R = K[A]^2$
  - $R = K[A]^{1/2}$
  - $R = K[A]^{-2}$
  - $R = K$
17. Which of the following relation is correct for a first order reaction? ( $k$  = rate constant;  $r$  = rate of reaction ;  $c$  = conc. of reactant)
- $k = r \times c^2$
  - $k = r \times c$
  - $k = \frac{c}{r}$
  - $k = \frac{r}{c}$
18. The half life for a given reaction was doubled as the initial concentration of the reactant was doubled. The order of the reaction is
- Zero
  - 1st
  - 2nd
  - 3rd

19. For the reaction  $aA + bB \rightarrow$  products, the rate law is given by rate =  $K[A]^m[B]^n$ , when the concentration of A is doubled and that of B is halved then the ratio of the new rate with respect the earlier one will be

- 1)  $n - 1$       2)  $m + n$       3)  $2^{-(m+n)}$       4)  $2^{m-n}$

20. Half lives of decomposition of  $\text{NH}_3$  on the surface of a catalyst for different initial pressure are given as

P(torr)	200	300	500
$t_{1/2}(\text{min})$	10	15	25

The order of the reaction is

- 1) 2      2) 1      3) 0      4) 0.5

21. At 500 K, the half life period of a gaseous reaction at an initial pressure of 80KPa is 350 Sec. When the pressure is 40 KPa, the half life period is 175 Sec. The order of the reaction is

- 1) Zero      2) 1      3) 2      4) 3

#### Numerical Value Type Questions

22. For  $A + B \rightarrow C + D$ , when [A] alone is doubled, rate gets doubled. But, when [B] alone is increased by 9 times, rate gets tripled. Then, order of reaction is

23. Decomposition of  $\text{NH}_3$  on gold surface follows zero order kinetics. If rate constant K is  $5 \times 10^{-4} \text{ M-s}^{-1}$ , rate of formation of  $\text{N}_2$  will be  $\text{_____} \times 10^{-4}$

24. In a zero order reaction, 47.5% of the reactant remains at the end of 2.5 hours. The percentage amount of reactant consumed in one hour is

25. Some pure organic solvent (density = 2 gm/cc and mol. mass = 100) evaporates with rate constant  $2 \times 10^2 \text{ mol lit.}^{-1} \text{ min}^{-1}$ . Time (sec) required for complete evaporation of 1 drop (0.1 ml) of it will be

#### LEVEL-II (ADVANCED)

#### Straight Objective Type Questions

- Identify the reaction order from the following rate constant  $K = 2.3 \times 10^{-5} \text{ lt/mole/sec}$ 
  - 1<sup>st</sup> order
  - 2<sup>nd</sup> order
  - 3<sup>rd</sup> order
  - None of these
- For a first order reaction,  $(A) \rightarrow$  products, the concentration of A changes from 0.1 M to 0.025M in 40 minutes. The rate of reaction when the concentration of A is 0.01 M, is :
  - $3.47 \times 10^{-4} \text{ M/min}$
  - $3.47 \times 10^{-5} \text{ M/min}$
  - $1.73 \times 10^{-4} \text{ M/min}$
  - $1.73 \times 10^{-5} \text{ M/min}$
- The time needed for the completion of  $2/3$  of a 1st order reaction, when rate constant is  $4.771 \times 10^{-2} \text{ min}^{-1}$  is
  - 23.03 min
  - 2.303 min
  - 6.93 min
  - 69.3 min

4. The half-life of a first order reaction is 100 seconds. What is the time required for 90% completion of the reaction ?  
 a) 100 sec.      b) 200 sec.      c) 333 sec.      d) 500 sec.
5. Initial concentration of the reactant is 1.0M. The concentration becomes 0.9M, 0.8M and 0.7M in 2 hours, 4 hours and 6 hours respectively. Then the order of reaction is  
 a) 2      b) 1      c) zero      d) 3
6. Half-life periods for a reaction at initial concentration of 0.1M and 0.01M are 5 and 50 minutes respectively. Then the order of reaction is  
 a) zero      b) 1      c) 2      d) 3
7. For a first order reaction  $t_{0.75}$  is 138.6 sec. Its specific rate constant is (in  $s^{-1}$ )  
 a)  $10^{-2}$       b)  $10^{-4}$       c)  $10^{-5}$       d)  $10^{-6}$
8. A first order reaction is half-completed in 45 minutes. How long does it need for 99.9% of the reaction to be completed ?  
 a) 20 hours      b) 10 hours      c)  $7 \frac{1}{2}$  hours      d) 5 hours
9. Consider the following reaction  $\text{CH}_3\text{Cl}(\text{aq}) + \text{OH}^- (\text{aq}) \rightarrow \text{CH}_3\text{OH}(\text{aq}) + \text{Cl}^- (\text{aq})$ . The following data are given

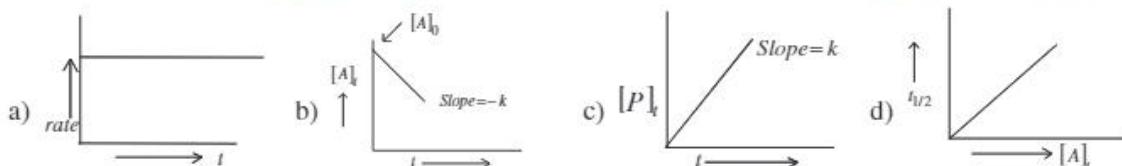
$[\text{CH}_3\text{Cl}]$	$[\text{OH}^-]$	Initial rate for $\text{CH}_3\text{OH}$ formations (moles/L min)
0.2	0.1	$1 \times 10^{-5}$
0.4	0.1	$2 \times 10^{-5}$
0.4	0.2	$4 \times 10^{-5}$

If  $K_C$  is  $1 \times 10^{10}$ , what is the specific reaction rate for substitution of  $\text{OH}^-$  by  $\text{Cl}^-$  from methyl alcohol.

- a)  $1 \times 10^{-14}$       b)  $5 \times 10^{-14}$       c)  $1 \times 10^{14}$       d)  $5 \times 10^{-6}$

#### More than One correct answer Type Questions

10. Which of the following graphs represents zero order if  $A \rightarrow P$  At  $t = 0 \Rightarrow [A]_0$  At  $t = t \Rightarrow [A]_t$



11. Which of the following is/are examples of pseudo unimolecular reactions?

- a)  $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{CO}_2\text{H} + \text{C}_2\text{H}_5\text{OH}$
- b)  $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$
- c)  $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$  glucose fructose
- d)  $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{OH}^-} \text{CH}_3\text{CO}_2\text{H} + \text{C}_2\text{H}_5\text{OH}$

12. Select the correct statements.
- Every substance that appears in the rate law of reaction must be a reactant or product in that reaction
  - If we know the rate law of a reaction, we can deduce its mechanism
  - If the reaction has rate  $r = K[A][B]^{3/2}$  then reaction may be elementary
  - A zero order reaction must be a complex reaction.
13. It is observed that only 0.39% of the original radioactive sample remains undecayed after eight hours. Hence:
- the half-life of that substance is 1hr
  - the mean life of the substance is  $\frac{1}{\log_2} \text{ hr}$
  - decay constant of the substance is  $(\log_e 2) \text{ hour}^{-1}$
  - if the number of radioactive nuclei of this substance at a given instant is  $10^8$  then the number left after 30 min would be  $\sqrt{2} \times 10^9$
14. Which of the following are true for the first order reaction
- $t_{3/4} = 2t_{1/2}$
  - $t_{15/16} = 4t_{1/2}$
  - $t_{15/16} = 3t_{3/4}$
  - $t_{7/8} = 2t_{3/4}$
15. For a reaction  $X \rightarrow Y$ , the rate law is Rate =  $k[A]^{1/2}$ . Which of the following statements are correct
- Half life of the reaction is inversely proportional to the initial concentration.
  - Half life of the reaction is directly proportional to the square root of the initial concentration.
  - The rate constant of the reaction is constant at a particular temperature for this reaction.
  - On increasing the concentration of the reactant 9 times ,the rate of reaction increases by 3 times
16.  $2\text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}$   
If the reaction is second order with respect to NO and first order with respect to  $\text{O}_2$ , the rate of reaction will
- On decreasing the volume to half the rate of reaction increases to 8 times of its initial value
  - On increasing the conc. of reactant to two times the rate of reaction increases to 8 times of its initial value
  - If pressure is doubled the rate of reaction increases eight times of its initial value
  - If pressure is doubled the rate of reaction increases 16 times of its initial value
17. Which of the following statements are correct for the first order reaction?
- Half life is independent of initial concentration
  - Half life is dependent upon temperature
  - For reaction  $A \rightarrow B$  the degree of dissociation increases with time and becomes maximum at infinite time
  - Rate constant of the reaction is dependent upon the temperature
18. 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

Linked Comprehension Type QuestionsPassage-I :

Suppose bacteria are placed in a flask containing nutrients for the bacteria so that they can multiply. A study at 35°C gave the following results.

Time (minutes)	0	15	30	45	60
Number of bacteria	100	200	400	800	1600

Then

19. This multiplication of bacteria follows a  
 a) Zero order reaction   b) 1<sup>st</sup> order reaction   c) 2<sup>nd</sup> order reaction   d) 3<sup>rd</sup> order reaction
20. The rate of the reaction initially is  
 a) 4.62 bacteria per minute   b) 23.1 bacteria per minute  
 c) 23.1 bacteria per sec   d) 0.231 bacteria per sec
21. The expression used for calculating the rate constant value in this experiment is  
 a)  $k = \frac{2.303}{t} \log \frac{a}{a-x}$    b)  $k = -\frac{2.303}{t} \log \frac{a}{a-x}$   
 c)  $k = -\frac{0.693}{t}$    d)  $k = -\frac{2.303}{t} \log \frac{a}{a+x}$

Passage-II :

The reaction of the reactive fragment OH<sup>-</sup> with H<sub>2</sub>S :  $4OH^{-}(g) + H_2S(g) \rightarrow SO_2(g) + 2H_2O(g) + 4e^-$  was studied at a particular temperature.

[OH <sup>-</sup> ]	[H <sub>2</sub> S]	Rate of disappearance of H <sub>2</sub> S mol L <sup>-1</sup> s <sup>-1</sup>
$1.3 \times 10^{-8}$	$2.1 \times 10^{-8}$	$1.4 \times 10^{-6}$
$3.9 \times 10^{-8}$	$2.1 \times 10^{-8}$	$4.2 \times 10^{-6}$
$3.9 \times 10^{-8}$	$4.2 \times 10^{-8}$	$8.4 \times 10^{-6}$

22. What is the rate law expression for the reaction?  
 a)  $r = k[OH^{-}]^2 [H_2S]$    b)  $r = k[OH^{-}][H_2S]^2$    c)  $r = k[OH^{-}]^{-1} [H_2S]$    d)  $r = k[OH^{-}][H_2S]$
23. What is the rate constant of the reaction at the given temperature?  
 a)  $5.1 \times 10^9 M^{-1}s^{-1}$    b)  $2.8 \times 10^{15} M^{-1}s^{-1}$    c)  $1.5 \times 10^{10} M^{-1}s^{-1}$    d)  $3.9 \times 10^{17} M^{-2}s^{-1}$
24. What is the rate, mol L<sup>-1</sup>s<sup>-1</sup>, at the instant when [OH] =  $1.7 \times 10^{-8}$  M and [H<sub>2</sub>S] =  $1.0 \times 10^{-8}$  M?  
 a)  $8.7 \times 10^{-6}$    b)  $8.7 \times 10^{-8}$    c)  $8.7 \times 10^{-7}$    d)  $1.15 \times 10^6$

Integer Type Questions

25. For a reaction, A → products, initially 8M of A is taken. In 20 minutes the concentration of A is reduced to 4M. In next 10 minutes the concentration of A is reduced to 2M. Report the order of the reaction.
26. For a reaction, A → products, the graph drawn between rate of reaction vs (a-x) gives a straight line with the slope 0.0693 min<sup>-1</sup>. Initial concentration of the reactant is 0.4 M After 20 minutes the rate of the reaction is calculated as  $6.93 \times 10^{-x}$ . Report the value of x?

27. If the concentration of reactant increases four-fold then rate of reaction is increased 16 times. If the rate of reaction is  $4 \times 10^{-6} \text{ mol L}^{-1} \text{s}^{-1}$  when the concentration of the reactant is  $4 \times 10^{-4} \text{ mol L}^{-1}$ . The rate constant of the reaction will be K. Then K-15 value is
28. At some temperature, the rate constant for the decomposition of HI on a gold surface is  $0.08 \text{ M s}^{-1}$ . The reaction is  $2\text{HI} \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ . The time taken for the concentration of HI to drop from  $1.50 \text{ M}$  to  $0.06 \text{ M}$  is \_\_\_\_\_ (sec).
29. The rate of a first order reaction at  $20 \text{ min}$  is  $0.55 \text{ mol L}^{-1} \text{ min}^{-1}$  and  $0.055 \text{ mol L}^{-1}$  at  $40 \text{ min}$  after initiation. Find half life the reaction in minutes
30. Consider reactions :



Concentrations of A and B are observed after equal intervals of time. These values are

$$\text{For A : C, } \frac{\text{C}}{\text{x}}, \frac{\text{C}}{\text{x}^2}, \frac{\text{C}}{\text{x}^3} \dots \dots$$

And for B : C,  $(\text{C} - \text{y}), (\text{C} - 2\text{y}), (\text{C} - 3\text{y}) \dots \dots$

Hence value of  $(n + m)$  will be

### EXERCISE-III

*(Theory of Chemical Kinetics)*

#### LEVEL-I (MAIN)

##### Straight Objective Type Questions

- At  $300\text{K}$  rate constant for  $\text{A} \rightarrow \text{products}$  at  $t = 50 \text{ min}$  is  $0.02 \text{ s}^{-1}$ , then rate constant at  $t = 75 \text{ min}$  &  $310 \text{ K}$  will be (in  $\text{s}^{-1}$ )
  - $\frac{0.04}{25}$
  - $0.04 \times 25$
  - $0.04$
  - $\left( \frac{0.02}{25} \right)$
- The rate constant of a first order reaction at  $27^\circ\text{C}$  is  $10^{-3} \text{ min}^{-1}$ . The 'temperature coefficient' of this reaction is 2. What is the rate constant (in  $\text{min}^{-1}$ ) at  $17^\circ\text{C}$  for this reaction?
  - $10^{-3}$
  - $5 \times 10^{-4}$
  - $2 \times 10^{-3}$
  - $10^{-2}$
- By what fraction the  $E_a$  should be decreased in order to increase the rate by 10 times at  $300\text{K}$  (initial  $E_a = 8.314 \text{ kJ/mol}$ ) by use of a catalyst?
  - 0.79
  - 0.84
  - 0.76
  - 0.69
- The rate constants of a reaction at  $500 \text{ k}$  and  $700\text{k}$  are  $0.02 \text{ sec}^{-1}$  and  $0.07 \text{ sec}^{-1}$  respectively. Calculate the value of  $E_a$ 
  - $18230.8\text{J}$
  - $190.83\text{J}$
  - $185.02\text{J}$
  - $172.02\text{J}$
- The temperature coefficient of most of the reactions lies between
  - 1 & 3
  - 2 & 3
  - 1 & 4
  - 2 & 4
- For a reaction,  $\frac{K_{(t+10)}}{K_{(t)}} = x$ . When temperature is increased from  $10^\circ\text{C}$  to  $100^\circ\text{C}$ , rate constant (K) increased by a factor of 512. Then, value of x is
  - 1.5
  - 2.5
  - 3
  - 2

7. A catalyst accelerates the reaction, because
- it brings the reactants closer
  - it lowers the activation energy
  - it changes the heat of reaction
  - it increases the activation energy
8. Which of the following parameters of a chemical reaction are increased when a catalyst is used ?
- Rate & activation energy
  - Rate constant & enthalpy
  - Enthalpy & time duration
  - Rate & Rate constant
9. The value of activation energy for a chemical reaction primarily depends on
- temperature
  - nature of the reacting species
  - the collision frequency
  - concentration of the reacting species
10. Increase of temperature will increase the reaction rate due to
- increase of number of effective collisions
  - increase of mean free path
  - increase of number of molecules
  - increase of number of collisions
11. The rate constants of a reaction at 300K & 280K respectively are  $K_1$  &  $K_2$ . Then
- $K_1 = 20K_2$
  - $K_2 = 4K_1$
  - $K_1 = 4K_2$
  - $K_1 = 0.5 K_2$
12. The rate of the reaction at  $40^{\circ}\text{C}$  is 5 units, then the rate of same reaction at  $80^{\circ}\text{C}$  is (nearly)
- 10 units
  - 40 units
  - 20 units
  - 80 units
13. At  $227^{\circ}\text{C}$ , in the presence of a catalyst the activation energy of a reaction decreases by 4.606 Kcal. Then the rate of the reaction will be increased by
- 2 times
  - 10 times
  - 100 times
  - 1000 times
14. The activation energy of a reaction which doubles the rate when the temperature is raised from 300K to 310K.
- 50.6 KJ/mole
  - 53.6 KJ/mole
  - 63.6 KJ/mole
  - 40.6KJ/mole
15. For the formation of  $\text{SO}_3$  in the following reaction
- $$2\text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightarrow 2\text{SO}_{3(\text{g})}; E_a = \text{activation energy}$$
- $$\text{SO}_{2(\text{g})} + \frac{1}{2}\text{O}_{2(\text{g})} \rightarrow \text{SO}_{3(\text{g})}; E_a^I = \text{activation energy}$$
- Then the correct selection is
- $E_a > E_a^I$
  - $E_a < E_a^I$
  - $E_a = E_a^I$
  - $E_a^I = E_a^{\frac{1}{2}}$
16. In a reaction at  $27^{\circ}\text{C}$ ,  $10^{-3}$  % reactant molecule manage to cross over the transition state barrier. The energy of these molecules in excess of average value will be ;  $R = 2\text{cal/mole}$
- 6.91K.cal/mole
  - 3K Cal/mole
  - 4.15K.Cal/mole
  - 5.10K.Cal/mole
17. At  $227^{\circ}\text{C}$ , the presence of a catalyst causes the activation energy of a reaction to decrease by 4.606K.cal. The rate of the reaction will be increased by
- 2 times
  - 10 times
  - 100 times
  - 1000 times
18. The activation energy of a reaction can be determined by
- changing the concentration of reactants
  - evaluating rate constant at standard temperature
  - evaluating rate constants at two different temperatures
  - by doubling conc. of reactants

19. According to collision theory of reaction rates, the activation energy is
- the energy gained by the molecule on colliding with other molecules
  - the energy that molecule should possess in order to undergo reaction
  - the energy it should possess so that it can enter into an effective collision
  - the energy it has to acquire so that it can enter into an effective collision
20. For a reaction  $A \rightarrow B$  with activation energy  $E_a$  and rate constant  $k = Ae^{-E_a/RT}$ . The rate of the reaction (Rate =  $k[A]$ ) increases by increasing the temperature because
- activation energy decreases with increase in temperature
  - the factor  $-E_a / RT$  increases
  - less number of collision take place
  - the value of  $[A]$  increases

#### Numerical Value Type Questions

21. An endothermic reaction  $A \rightarrow B$  has an activation energy 15 kcal/mole and the heat of reaction is 5 kcal/mole. The activation energy of the reaction  $B \rightarrow A$  is \_\_\_\_\_ kcal/mole.
22. For a gaseous reaction, following data is given,  
 $A \rightarrow B, k_1 = 10^{15}e^{-2000/T}$ ;  $C \rightarrow D, k_2 = 10^{14}e^{-1000/T}$
23. The energies of activation for forward and reverse reactions for  $A_2 + B_2 \rightarrow 2AB$  are 280 kJ mol<sup>-1</sup> and 400 kJ mol<sup>-1</sup> respectively. The presence of catalyst lowers the activation energy of both forward as well as reverse reactions by 100 kJ mol<sup>-1</sup>. The enthalpy change of the reaction  $A_2 + B_2 \rightarrow 2AB$  in the presence of catalyst will be (in kJ mol<sup>-1</sup>)
24. The rate constant for the first order decomposition of a reaction is given by  
 $\log K(S^{-1}) = 14.34 - \frac{1.25 \times 10^4 K}{T}$ . Then the activation energy of the reaction is \_\_\_\_\_ kJ/mole.

#### **LEVEL-II (ADVANCED)**

#### Straight Objective Type Questions

1. The rate of a reaction triples when temperature changes from 20°C to 50°C. Calculate the energy of activation for the reaction ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )
- 28.811 Kg/mole
  - 28.811 J/mole
  - 2.881 J/mole
  - 0.288 KJ/mole
2. The rate constant, activation energy, and Arrhenius parameter of a chemical reaction are  $3.0 \times 10^{-4} \text{ s}^{-1}$ , 104.4 kJ mol<sup>-1</sup>, and  $6.0 \times 10^{14} \text{ s}^{-1}$ , respectively. The value of rate constant at  $T \rightarrow \infty$  is
- $2.0 \times 10^8 \text{ s}^{-1}$
  - $6.0 \times 10^{14} \text{ s}^{-1}$
  - $3.6 \times 10^{30} \text{ s}^{-1}$
  - None of these
3. A certain reaction proceeds in a sequence of three elementary steps with the rate constant  $k_1$ ,  $k_2$  and  $k_3$ . If the observed rate constant of the reaction expressed as  $k(\text{obs}) = \left[ \frac{k_1}{k_2} \right]^{1/2} \times k_3$ , the observed energy of activation of the reaction is
- $\frac{1}{2} \left[ \frac{E_1}{E_2} \right] + E_3$
  - $\frac{E_3 + E_1}{2}$
  - $E_3 \left[ \frac{E_1}{E_2} \right]^{1/2}$
  - $E_3 + \frac{1}{2} [E_1 - E_2]$

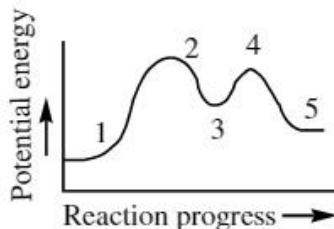
4. In general the rate of a given reaction can be increased by all the factors except
- Increasing the temperature
  - Increasing the concentration of reactants
  - Increasing the activation energy
  - Using a positive catalyst
5. The rate constant of a reaction is  $1.5 \times 10^{-4} \text{ s}^{-1}$  at  $27^\circ\text{C}$  and  $3 \times 10^{-4} \text{ s}^{-1}$  at  $127^\circ\text{C}$ . The  $E_a$  is
- $16.58 \text{ cal}$
  - $3.326 \times 10^3 \text{ cal}$
  - $8.314 \times 10^3 \text{ cal}$
  - $2.255 \times 10^3 \text{ cal}$

***More than One correct answer Type Questions***

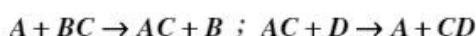
6. The rate constant of a reaction is given by  $k = 2.1 \times 10^{10} \exp(-2700/RT)$ . It means that
- $\log k$  versus  $1/T$  will be a straight line with slope =  $\frac{-2700}{2.303R}$
  - $\log k$  versus  $1/T$  will be a straight line with intercept on  $\log k$  axis =  $2.1 \times 10^{10}$
  - The number of effective collisions are  $2.1 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1}$
  - Half life of the reaction increases with increases of temperature
7. Rate constant  $k$  varies with temperature by equation  $\log k (\text{min}^{-1}) = \log 5 - \frac{2000 \text{ kcal}}{RT \times 2.303}$ . We can conclude that
- The pre exponential factor  $A$  is  $10^5$
  - $E_a$  is  $2000 \text{ kcal}$
  - $E_a$  is  $9.12 \text{ kcal}$
  - The pre-exponential factor  $A$  is  $5$
8. According to the collision theory, most molecular collisions do not lead to reaction. Which of the following is/are necessary for collisions to successfully lead to reaction?
- The total kinetic energy of the collision must be greater than some minimum value
  - A catalyst must be present at the collision
  - The colliding particles must be properly oriented in space when they collide
  - None of the above
9. In Arrhenius equation  $k = A \exp\left(-\frac{E_a}{RT}\right)$ ,  $A$  may be termed as the rate constant at
- Very low temperature
  - Very high temperature
  - Zero activation energy
  - The boiling temperature of the reaction mixture

***Linked Comprehension Type Questions***

***Passage-I :***



Consider a reaction that occurs by the following mechanism;



The potential energy profile for this reaction is as shown in the adjacent diagram

10. The rate law for the overall reaction, is  
 a) rate =  $k[BC][D]$   
 b) rate =  $k[AC][D]$   
 c) rate =  $k[A][BC]$   
 d) the rate law cannot be predicted
11. In the potential energy profile, the intermediate species corresponding to point 3, is  
 a) AC  
 b) D—A—C  
 c) B  
 d) A—B—C
12. In the potential energy profile, the first transition state peak-2 represents the  
 a) energy of A—C  
 b) sum total energy of A—B—C and D  
 c) energy of only A—B—C  
 d) sum total energy of B—C and D

**Passage-II :**

According to the collision theory, only the effective collisions among the reacting species result in the products. In order that the collisions may be effective, the reacting species must have energy equal to or more than a certain minimum energy called threshold energy ( $E^\circ$ ). Extra energy which has been supplied to the reactants to make collisions effective is known as activation energy ( $E_a$ ). This is related to reaction rate with the help of Arrhenius equation.

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

The equation also helps in calculating the activation energy for a reaction at a specific temperature. In general, the rate of reaction is inversely proportional to the activation energy required.

13. The plot of  $\log k$  Vs  $1/T$  helps to calculate  
 a) Energy of activations  
 b) Rate constant of the reaction  
 c) Order of reaction  
 d) Energy of activation as well as the frequency factor
14. An increase in reaction rate with rise in temperature is due to  
 a) an increase in number of collisions  
 b) an increase in the number of activated molecules  
 c) lowering the activation energy  
 d) shortening of mean free path
15. The chemical reactions in which the reactants require high amount of activation energy are generally  
 a) slow  
 b) fast  
 c) instantaneous  
 d) spontaneous

**Matrix Matching Type Questions**

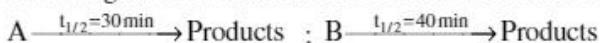
- |                             |   |
|-----------------------------|---|
| 16. <b>Column-I</b>         | <b>Column-II</b>                        |
| A) $e^{-E_a/RT}$            | p) $\tan\theta, \theta > \frac{\pi}{2}$ |
| B) A                        | q) Boltzmanns factor                    |
| C) $\frac{-k}{2.303}$       | r) Zero order reaction                  |
| D) $t_{1/2} = \frac{a}{2k}$ | s) Arrhenius factor                     |

**Integer Type Questions**

17. In a reaction the following equation holds good as per chemical kinetics is viewed.

$$\log k = 4 - \frac{4000}{2.303RT}. \text{ The frequency factor is } 10^x. \text{ What is } x.$$

18. The rate of reaction becomes two times for every  $10^{\circ}\text{C}$  rise in temperature. If the rate of reaction increases by 32 times when the temperature is increased from  $30^{\circ}\text{C}$  to  $(10x)^{\circ}\text{C}$ . Then  $x =$
19. If the activation energy is decreased by  $(5x)\%$  by using a catalyst (300K) to achieve the same effect as of increasing the temperature from 300K - 400K in a reaction, then find  $x$ .
20. If the rate of reaction increases by 27 times, when temperature is increased by 30 K, then temperature coefficient of the reaction is
21. Following are two first order reactions with their half times given at  $25^{\circ}\text{C}$ .



The temperature coefficients of their reaction rates are 3 and 2, respectively, between  $25^{\circ}\text{C}$  and  $35^{\circ}\text{C}$ . If the above two reactions are carried out taking 0.4 M of each reactant but at different temperatures:  $25^{\circ}\text{C}$  for the first order reaction and  $35^{\circ}\text{C}$  for the second order reaction, find the ratio of the concentrations of A and B after an hour.

### EXERCISE-IV

*(1<sup>st</sup> order, Parallel, Sequential, Eqm reactions, reaction mechanism)*

#### LEVEL-I (MAIN)

##### *Straight Objective Type Questions*

1. For the first order decomposition of  $\text{C}_2\text{H}_4\text{O}_{(g)} \rightarrow \text{CH}_{4(g)} + \text{CO}_{(g)}$  the initial pressure of  $\text{C}_2\text{H}_4\text{O}_{(g)}$  is 80 torr and the total pressure at the end of 20 min is 120 torr. The time needed for 75% decomposition of  $\text{C}_2\text{H}_4\text{O}$  would be

- 1) 20 min      2) 40 min      3) 80 min      4) 120 min

2. The reaction:  $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$  has been assigned to follow following mechanism.

- I)  $\text{NO} + \text{NO} \rightleftharpoons \text{N}_2\text{O}_2$  (fast)  
 II)  $\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$  (slow)  
 III)  $\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$  (fast)

The rate constant of step II is  $1.2 \times 10^{-4}$  mole  $\text{L}^{-1} \cdot \text{min}^{-1}$  while equilibrium constant of step I is  $1.4 \times 10^{-2}$ . What is the rate of reaction when concentration of NO and  $\text{H}_2$  each is 0.5 mole  $\text{L}^{-1}$

- 1)  $2.1 \times 10^{-7}$  mole  $\text{L}^{-1} \cdot \text{min}^{-1}$       2)  $3.2 \times 10^{-6}$  mole  $\text{L}^{-1} \cdot \text{min}^{-1}$   
 3)  $3.5 \times 10^{-4}$  mole  $\text{L}^{-1} \cdot \text{min}^{-1}$       4) none of these

3. For the first order reaction  $\text{A}_{(g)} \rightarrow 2\text{B}_{(g)} + \text{C}_{(g)}$ , 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

- 1)  $1.15 \times 10^{-3} \text{ sec}^{-1}$       2)  $2.3 \times 10^{-3} \text{ sec}^{-1}$       3)  $3.45 \times 10^{-3} \text{ sec}^{-1}$       4)  $6 \times 10^{-3} \text{ sec}^{-1}$

4.  $2\text{A}(g) + \text{B}(g) \rightleftharpoons 3\text{C}(g) + \text{D}(g) ; \Delta H_{\text{reaction}}^{\circ} = +\text{ve}$

- I)  $r_f = k_f [\text{A}]^2 [\text{B}]$  and  $r_b = k_b [\text{C}]^3 [\text{D}]$   
 II) If temperature is increased then reaction shift in forwarded direction.

III)  $K_{\text{eq(P)}} = \frac{(\text{n}_c)^3 (\text{n}_D)}{(\text{n}_A)^2 (\text{n}_B)} \times \left( \frac{P_T}{n_T} \right)^{\Delta n}$  ;  $\Delta n = 1$

IV) On adding inert gas at constant pressure reaction shifts in forward direction

- 1) only I & II are correct      2) All are correct  
 3) only II & III are correct      4) II, III & IV are correct

5. Nitrogen monoxide, NO, reacts with hydrogen, H<sub>2</sub>, according to the following equation:



If the mechanism for this reaction were,



Which of the following rate laws would we expect to obtain experimentally?

$$1) \text{Rate} = k[\text{H}_2\text{O}_2][\text{H}_2] \quad 2) \text{Rate} = k[\text{NO}]^2[\text{H}_2] \quad 3) \text{Rate} = k[\text{NO}]^2[\text{H}_2]^2 \quad 4) \text{Rate} = k \frac{[\text{NO}]^2[\text{H}_2]^2}{[\text{N}_2]}$$

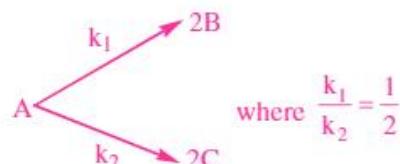
## *Numerical Value Type Questions*

6. The reaction, sucrose  $\xrightarrow{H^+}$  glucose + fructose, takes place at certain temperature while volume of solution is maintained at 1 lt. At time zero, the initial rotation of the mixture is  $34^\circ$ . After 30 minutes the total rotation of solution is  $19^\circ$  and after a very long time, the total rotation is  $-11^\circ C$ . Find the time (min) when the solution would be optically inactive?

LEVEL-II (ADVANCED)

### **Straight Objective Type Questions**

1. For a hypothetical elementary reaction (both  $k_1$  and  $k_2$  first order rate constants)



Initially only two moles of 'A' are present. Then total number of moles of A, B and C at the end of 50% reaction are

- a) 2                      b) 3                      c) 1                      d) 4

2. Calculate the rate constant of first order reaction:  $\text{CH}_3\text{CHO(g)} \xrightarrow{\text{Heat}} \text{CH}_4\text{(g)} + \text{CO(g)}$ . If the initial pressure of  $\text{CH}_3\text{CHO}$  is 80 mm Hg and the total pressure at the end of 20 minutes is 120 mm Hg.

a)  $3.465 \times 10^{-2}$       b)  $34.65 \text{ min}^{-1}$       c)  $3.465 \text{ min}^{-1}$       d)  $0.3465 \text{ min}^{-1}$

3. Consider the following reactions :

I)  $\text{A} + \text{B} \xrightleftharpoons[k_{-1}]{k_1} \text{C}$       II)  $\text{C} + \text{B} \xrightleftharpoons{k_2} \text{D}$ .

Then  $k_1[\text{A}][\text{B}] - k_{-1}[\text{C}] - k_2[\text{C}][\text{B}]$  is equal to

a)  $\frac{-d[\text{A}]}{dt}$       b)  $\frac{-d[\text{B}]}{dt}$       c)  $\frac{d[\text{C}]}{dt}$       d)  $\frac{-d[\text{D}]}{dt}$

4. The mechanism of the reaction  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$  is  $\text{NO} + \text{NO} \xrightleftharpoons[k_{-1}]{k_1} \text{N}_2\text{O}_2$  (fast);  $\text{N}_2\text{O}_2 + \text{O}_2 \xrightleftharpoons{k_2} 2\text{NO}_2$  (slow)

The rate constant of the reaction is

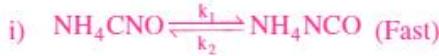
a)  $k_2$       b)  $k_2 k_1 (k_{-1})$       c)  $k_2 k_1$       d)  $k_2 \left( \frac{k_1}{k_{-1}} \right)$

5. A reaction takes place in three steps : the rate constant are  $k_1$ ,  $k_2$  and  $k_3$ . The overall rate constant  $k = k_1 k_3 / k_4$ . If the energies of activation are 40, 30 and 20 kJ mol<sup>-1</sup>, the overall energy of activation is (assuming A to be constant for all)

a) 10                    b) 15                    c) 30                    d) 60

### **More than One correct answer Type Questions**

6. The rate expression for the reaction :  $\text{NH}_4\text{CNO} \rightleftharpoons \text{NH}_2\text{CONH}_2$  can be derived from the mechanism:



Which of the following statement(s) is/are correct about the rate expression ?

$$a) \frac{d_{\text{[urea]}}}{dt} = \frac{k_1 k_3}{k_2} [\text{NH}_4\text{CNO}]$$

$$b) \frac{d_{[urea]}}{dt} = \frac{k_1 k_3}{k_2 k_4} [NH_4NCO]$$

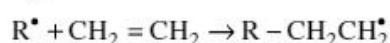
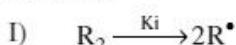
$$c) \frac{d_{[urea]}}{dt} = k[NH_4CNO]$$

$$d) \frac{d_{\text{[urea]}}}{dt} = \frac{k_1 \times k_2}{k_3 \times k_4} [\text{NH}_4\text{NCO}]$$

### **Linked Comprehension Type Questions**

### *Passage-I :*

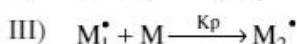
*Kinetics usually plays an important role in industrial process, since the product must be manufactured in minimum time under the most economical conditions. Consider the synthesis of polythene which a polymer of ethylene and made by joining many units of ethylene molecules (called monomer, M) together a process called polymerization mechanism involves first heating initiator.*



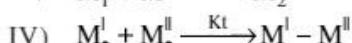
$K_i$  = rate constant of initiator



(M = monomer)



Propagation  $K_p$  = rate constant for propagation.



$M^{\cdot}$  &  $M''^{\cdot}$  are radicals of different length.  $K_t$  = rate constant for termination.

7. The initiator frequently used for polymerization process is benzoyl peroxide  $(C_6H_5CO)_2O_2$   
 $(C_6H_5CO)_2O_2 \longrightarrow 2C_6H_5COO^\bullet$ ;  $R_2 \longrightarrow 2R^\bullet$

This is a first order reaction and half life of benzoyl peroxide at 100°C is 19.8 min. The rate constant of reaction is

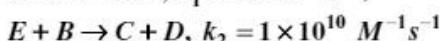
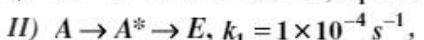
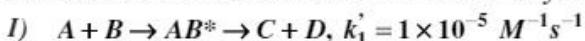
8. If the half life of the benzoyl peroxide is 7.30hrs or 438 min at 70°C, what is the activation energy (in KJ/mol) for the decomposition of benzoyl peroxide?

a)  $1 \times 10^4$ KJ/mole      b) 200KJ/mole  
 c) 110KJ/mole      d) 160KJ/mole

9. What condition would favour the growth of long high-molar-mass polyethylene?
- Low concentration of initiator  $R_2$
  - High concentration of ethylene
  - Low concentration of radical fragment  $M^\cdot$  &  $M^{\ddot{}}$
- a) i only      b) ii only      c) i, ii only      d) i, ii and iii

***Passage-II :***

For the overall reaction between A and B to yield C and D, two mechanisms are proposed :



(species with \* are short-lived)

10. Rate of reaction for mechanism I when concentration of each is 0.1M, is:
- a)  $1 \times 10^{-7} Ms^{-1}$       b)  $1 \times 10^{-6} Ms^{-1}$       c)  $1 \times 10^{-5} Ms^{-1}$       d)  $1 \times 10^{-4} Ms^{-1}$
11. Rate of reaction for mechanism II when concentration of each 1 M is:
- a)  $1 \times 10^{-4} Ms^{-1}$       b)  $1 \times 10^{10} Ms^{-1}$       c)  $1 \times 10^{-5} Ms^{-1}$       d)  $1 \times 10^{-10} Ms^{-1}$
12. At what concentration of B, rates of two mechanism are equal ?
- a) 1M      b) 5M      c) 7M      d) 10M

***Passage-III :***

The instantaneous rate of an elementary chemical reaction:  $aA + bB \rightleftharpoons cC + dD$  can be given by:  $\text{rate} = K_f[A]^a[B]^b - K_b[C]^c[D]^d$  where,  $K_f$  and  $K_b$  are rate constants for forward and backward reactions respectively for the reversible reaction. If the reaction is an irreversible one, the rate is expressed as;  $\text{rate} = K[A]^a[B]^b$  where  $K$  is rate constant for the given irreversible reaction and  $(a+b)$  is order of reaction. It is also evident from the stoichiometry of reaction that rate of disappearance of A is  $a/b$  times the rate of disappearance of B. The variation of rate constant  $K$  with temperature is expressed in terms of Arrhenius equation:  $K = Ae^{-E_a/RT}$  whereas the ratio  $\frac{K_f}{K_b}$  is expressed in terms of Van't Hoff isochore:  $\frac{K_f}{K_b} = Ae^{-\Delta H/RT}$ , where  $E_a$  and  $\Delta H$  are energy of activation and heat of reaction respectively.

13. For a gaseous phase-I order reaction:  $A(g) \rightarrow B(g) + 2C(g)$  (rate constant  $K = 10^{-2}\text{time}^{-1}$ ), in a closed vessel of 2 litre containing 5 mole of A (g) at  $27^\circ\text{C}$ , which of the following is correct?
- a) Rate of appearance of C (g) is  $5 \times 10^{-2}$ , mol  $\text{L}^{-1}\text{t}^{-1}$   
 b) Rate of disappearance of A (g) is  $6.15 \times 10^{-3}$  atm $\text{t}^{-1}$   
 c) Rate of disappearance of A (g) is  $5.0 \times 10^{-2}$  mol  $\text{t}^{-1}$   
 d) Rate of appearance of B (g) is  $5 \times 10^{-2}$  mol $\text{L}^{-1}\text{t}^{-1}$
14. For an elementary reaction  $aA \rightarrow \text{product}$ , the graph plotted between  $\log \frac{[-d[A]]}{dt}$  vs  $\log[A]_t$  gives a straight line with intercept equal to 0.6 and showing an angle of  $45^\circ$  then :
- a) rate constant = 4 time $^{-1}$  and  $a = 1$   
 b) rate constant = 4 mol  $\text{L}^{-1} \text{t}^{-1}$  and  $a = 1$   
 c) rate constant = 1.99 time $^{-1}$  and  $a = 1$   
 d) rate constant = 1.99 mol $^{-1} \text{ L}^{-1}$  and  $a = 2$

*Matrix Matching Type Questions*

15. Assume that all forward reaction are of first order and all backward reactions to be elementary process  $P_0$  = initial pressure of  $A_{(g)}$  and  $P_T$  is total pressure of system at time t.

**Column-I**

- A)  $2A(g) \rightleftharpoons B(g) + 2C(g)$   
 B)  $2A(g) \rightleftharpoons 4B(g) + C(g)$   
 C)  $4A(g) \rightleftharpoons 5B(g) + C(g)$   
 D)  $2A(g) \rightleftharpoons 3B(g) + 2C(g)$

**Column-II**

- p)  $K_f \times t = \ell n \frac{P_0}{3P_0 - 2P_T}$   
 q) Order of backward reaction is 3.  
 r)  $K_f \times t = \ell n \frac{3P_0}{5P_0 - 2P_T}$   
 s) Order of backward reaction is 5.  
 t) Order of forward reaction is 6

*Integer Type Questions*

16. A reaction  $X_{2(g)} \rightarrow Z(g) + \frac{1}{2} Y_{(g)}$  exhibits an increase in pressure from 150 mm to 170 in 10 min. The rate of disappearance of  $X_2$  in mm per min is

**KEY SHEET (PRACTICE SHEET)****EXERCISE-I**

<b>LEVEL-I</b>	1) 3	2) 2	3) 2	4) 4	5) 2	6) 3	7) 2	8) 2
	9) 2	10) -4	11) 2					
<b>LEVEL-II</b>	1) d	2) d	3) abcd	4) abd	5) cd	6) a	7) b	8) b
	9) 0							

**EXERCISE-II**

<b>LEVEL-I</b>	1) 2	2) 2	3) 3	4) 4	5) 1	6) 2	7) 2	8) 1
	9) 4	10) 1	11) 2	12) 4	13) 2	14) 3	15) 3	16) 4
	17) 4	18) 1	19) 4	20) 3	21) 1	22) 1.5	23) 5	24) 21
	25) 6							
<b>LEVEL-II</b>	1) b	2) a	3) a	4) c	5) c	6) c	7) a	8) c
	9) b	10) abcd	11) ab	12) bd	13) abc	14) ab	15) bcd	16) abc
	17) abd	18) abcd	19) b	20) a	21) d	22) d	23) a	24) c
	25) 0	26) 3	27) 5	28) 9	29) 6	30) 1		

**EXERCISE-III**

<b>LEVEL-I</b>	1) 3	2) 2	3) 4	4) 1	5) 2	6) 4	7) 2	8) 4
	9) 2	10) 1	11) 3	12) 4	13) 3	14) 2	15) 3	16) 1
	17) 3	18) 3	19) 4	20) 2	21) 10	22) 434.2	23) -120	24) 239

**LEVEL-II**

- 1) a      2) b      3) d      4) c      5) a      6) ab      7) ab      8) ac  
 9) bc      10) c      11) a      12) c      13) d      14) b      15) a  
 16) A-q; B-s; C-p; D-r      17) 4      18) 8      19) 5      20) 3      21) 2

**EXERCISE-IV****LEVEL-I**

- 1) 2      2) 1      3) 1      4) 3      5) 4      6) 103.7

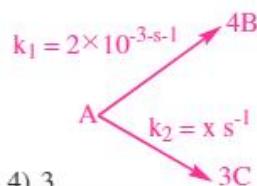
**LEVEL-II**

- 1) c      2) a      3) c      4) d      5) c      6) ac      7) b      8) c  
 9) d      10) a      11) a      12) d      13) a      14) a  
 15) A-pq; B-rs; C-p; D-rs      16) 4

**ADDITIONAL PRACTICE EXERCISE****LEVEL-I (MAIN)*****Straight Objective Type Questions***

- The reaction  $A(g) + 2B(g) \rightarrow C_{(g)} + D_{(g)}$  is an elementary process. In an experiment, the initial pressure of A and B are atm  $P_A = 0.6$  and  $P_B = 0.8$  atm. When  $P_C = 0.2$  Atm, the rate of the reaction relative to the initial rate is  
 1) 1/48      2) 1/24      3) 9/16      4) 1/6
- In a reaction A products, the rate is doubled when the concentration of A is increased 4 times. If 50% of the reaction occurs in 1414 sec, how long would it takes for the completion of 75% reaction.  
 1) 4242 sec      2) 2825 sec      3) 2414 sec      4) 2121 sec
- A mixture of compounds A and B undergo first order decomposition. The half-lives are 54.0 min and 18.0 min respectively. If both the concentrations of A and B are equal initially, the time taken for the concentration of A to be four times that of B is.  
 1) 18 min      2) 54 min      3)  $\frac{54 - 18}{2}$  min      4)  $\frac{54 + 18}{2}$  min
- Decomposition of dimethyl ether is a first order reaction  $CH_3OCH_3(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$ . Half life period is 14.5 minutes. Initially the pressure of ether is 0.4 atm. The total pressure of system after 29 minutes is  
 1) 0.1 atm      2) 0.3 atm      3) 0.7 atm      4) 1 atm
- A second order chemical reaction has a half-life of 60hrs at 300K when the initial concentration of reactant is 0.5M. If the same reaction is carried out with 1.0M initial concentration at 300K, what time would be required to reduce the concentration of reactant to 0.25M ?  
 1) 60 hr      2) 30 hr      3) 90 hr      4) 180 hr
- For the following parallel chain reaction what will be the value of overall half life of A in minutes?  

$$\left( \text{given that, } \frac{[B]_t}{[C]_t} = \frac{16}{9} \right)$$
 1) 3.3      2) 6.3      3) 3.6      4) 3



7. A reactant (A) forms two products :



If  $E_{a_2} = 2E_{a_1}$ , then  $k_1$  and  $k_2$  will be related as [Assume frequency factor  $A_1 = A_2$ ]

$$1) k_2 = k_1 e^{E_{a_1}/RT} \quad 2) k_2 = k_1 e^{E_{a_2}/RT} \quad 3) k_1 = Ak_2 e^{E_{a_1}/RT} \quad 4) k_1 = 2k_2 e^{E_{a_2}/RT}$$

8. For a particular reaction, with initial concentrations of the reactants as  $A_1$  and  $A_2$ , the half life periods are  $t_1$  and  $t_2$  respectively. The order of the reaction ( $n$ ) is given by:

$$1) n = \frac{\log(t_1/t_2)}{\log(A_2/A_1)} \quad 2) n = \frac{t_1}{A_1} \times \frac{A_2}{t_2} \quad 3) n = 1 + \frac{\log(t_1/t_2)}{\log(A_2/A_1)} \quad 4) \text{None of these}$$

9. The rate constant of a reaction is  $0.0693 \text{ min}^{-1}$  starting with 10moles, the rate of reaction after 10min is

$$1) 0.693 \frac{\text{mole}}{\text{min}} \quad 2) 0.0693 \times 5 \frac{\text{mole}}{\text{min}} \quad 3) 0.0693 \times 10 \frac{\text{mole}}{\text{min}} \quad 4) 0.0693$$

10. At  $25^\circ\text{C}$  the rate constant for the reaction  $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_4\text{OH}$  is  $4 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$

Then the rate constant for the transfer of proton from water to  $\text{NH}_3$  is ( $K_b \text{NH}_4\text{OH} = 1.8 \times 10^{-5}$ )

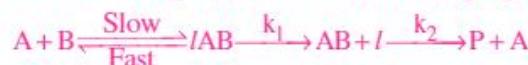
$$1) 7.2 \times 10^5 \text{ s}^{-1} \quad 2) 5.2 \times 10^5 \text{ s}^{-1} \quad 3) 2.7 \times 10^5 \text{ s}^{-1} \quad 4) 10.2 \times 10^5 \text{ s}^{-1}$$

## LEVEL-II

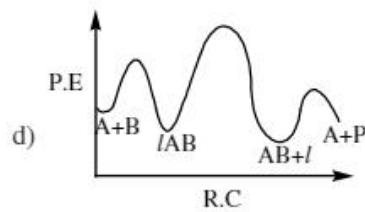
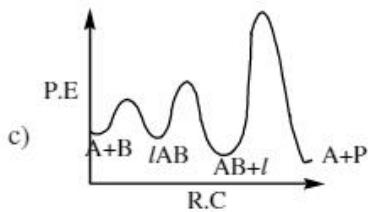
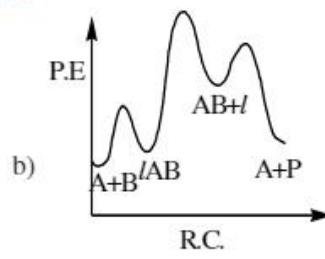
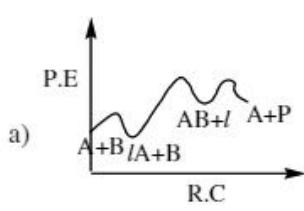
### LECTURE SHEET (ADVANCED)

#### Straight Objective Type Questions

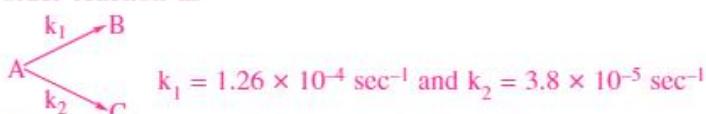
1. The following mechanism has been proposed for the exothermic catalyzed complex reaction



If  $k_1$  is much smaller than  $k_2$ , the most suitable qualitative plot of potential energy (P.E) versus reaction co-ordinate (R.C) for the above reaction.



2. The reaction  $2A(g) + B_2(g) \rightarrow 2AB(g)$  is second order in A and first order in  $B_2$ . When 10 mole of A and 4 mol  $B_2$  are taken in vessel of volume  $2\text{dm}^3$  together and the initial rate is  $2 \times 10^{-3}$  mole  $\text{dm}^{-3}\text{s}^{-1}$ . What will be the rate when half quantity of the  $B_2$  has reacted?
- $4.3 \times 10^{-3}$  mol  $\text{dm}^{-3}\text{s}^{-1}$
  - $3.6 \times 10^{-4}$  mol  $\text{dm}^{-3}\text{s}^{-1}$
  - $3.6 \times 10^{-3}$  mol  $\text{dm}^{-3}\text{s}^{-1}$
  - $3.2 \times 10^{-3}$  mol  $\text{dm}^{-3}\text{s}^{-1}$
3. A first order reaction is 50% complete in 200 hrs at  $27^\circ\text{C}$  & in 20 hrs at  $27^\circ\text{C}$  in presence of catalyst. The decrease in activation energy caused by catalyst is nearly
- 5.7 kJ
  - 7.5 kJ
  - 6.7 kJ
  - 7.6 kJ
4. At  $380^\circ\text{C}$ , half life period for the first order decomposition of  $H_2O_2$  is 360 min. The energy of activation of the reaction is  $200 \text{ kJ mol}^{-1}$ . Calculate the time required for 75% decomposition at  $450^\circ\text{C}$  if half life for decomposition of  $H_2O_2$  is 10.17 min at  $450^\circ\text{C}$ .
- 20.34 min
  - 40.8 min
  - 10.2 min
  - none of these
5. A substance undergoes first order decomposition. The decomposition follows two parallel first order reaction as



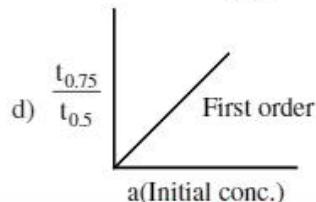
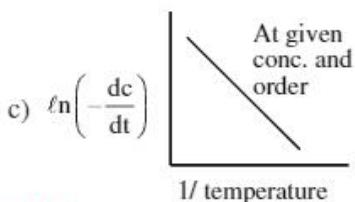
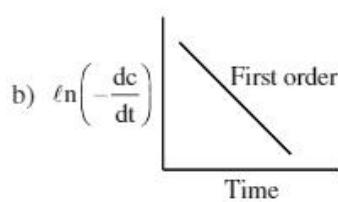
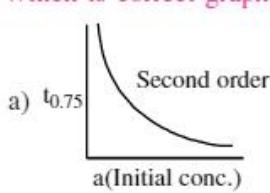
Thus the percentage distribution of B and C are

- 80% B and 20% C
- 76.83% B and 23.17% C
- 90% B and 10% C
- 60% B and 40% C

### PRACTICE SHEET (ADVANCED)

#### More than one Correct Answer Type Questions

1. Which of the following statements are correct? Where  $[A]$  = concentration at any time t.
- The slope of straight-line plot of  $\log[A]$  versus t for a first-order reaction is  $-k$
  - The stoichiometry of a reaction tells nothing about the order of the reaction unless it is an elementary step
  - Half-life period for a zero-order reaction is directly proportional to the initial concentration of the reacting species
  - For a given reaction, the rate constant is found to be  $k = 1.6 \times 10^{-2} \text{ min}^{-1} \text{ mol L}^{-1}$ . The reaction is of second order
2. Which is correct graph?



3. From the following kinetic data given for the reaction of A and B

[A]	[B]	Initial rate (mol L <sup>-1</sup> S <sup>-1</sup> )
0.01M	0.02M	$2 \times 10^{-4}$
0.02M	0.02M	$4 \times 10^{-4}$
0.02M	0.04M	$8 \times 10^{-4}$

Which of the following observations are correct?

- a) Rate law of the reaction is rate =  $k[A]^1[B]^1$
- b) Rate constant of the reaction is
- c) Rate of reaction is quadrupled on doubling the concentrations of both the reactants.
- d) A and B are wrong.



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

a)  $\frac{dx}{dt} = k[Zn]^0[H^{\oplus}]^2$

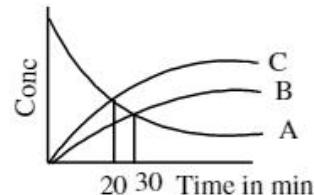
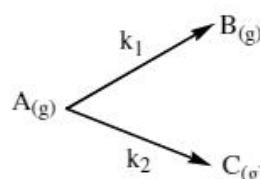
b)  $\frac{dx}{dt} = k[Zn][H^{\oplus}]^2$

- c) Rate is not affected if the concentration of zinc is made four times and that of  $H^{\oplus}$  ion is halved
- d) Rate becomes four times if the concentration of  $H^{\oplus}$  ion is doubled at constant Zn concentration

#### Linked Comprehension Type Questions

##### Passage-I :

Consider a first order parallel gas phase reaction. The concentration of reactants and products change according to the graph given. Also given that  $K_1 : K_2 = 1 : 2$ ,  $\log 5 = 0.7$  and  $\log 2 = 0.3$



5. The half life of the overall reaction is
- a) 30min
  - b) 15min
  - c) 10min
  - d) 20min
6. Identify the correct statement
- a) The ratio of concentration of B to C is 3 : 2 after 30 min
  - b) The half life for the formation of B less than C
  - c) At 20<sup>th</sup> minute the conc of B is one fifth of the initial conc of A
  - d) At 30<sup>th</sup> minute  $[A]_t = 2C + B$
7. If the activation energy of individual reactions are  $Ea_1$  and  $Ea_2$ . The activation energy for the overall reaction is
- a)  $Ea = \frac{Ea_1 + Ea_2}{2}$
  - b)  $Ea = \frac{Ea_1 + 2Ea_2}{2}$
  - c)  $Ea = \frac{2Ea_1 + Ea_2}{3}$
  - d)  $Ea = \frac{Ea_1 + 2Ea_2}{3}$

Passage-II :

Time (in min)	0	100	200
Partial pressure of x (in mm of Hg)	800	400	200

Assume ideal gas condition.

8. order of reaction is

a) zero                    b) 2                    c)  $\frac{1}{2}$                     d) 1

9. Value of rate constant is

a)  $2 \times 10^{-3}$             b)  $3.45 \times 10^{-3}$             c)  $6.93 \times 10^{-3}$             d)  $4.5 \times 10^{-1}$ 

10. Time taken for 75% completion of reaction

a) 100 min                b) 200 min                c) 150 min                d) 43 min

Matrix Matching Type Questions11. **Column-I**

- A) First order reaction  
 B) Second order reaction  
 C) Zero order reaction  
 D)  $t_{1/2}$  varies inversely to the concentration of reactants.

**Column-II**

- p)  $C_0 = 0.1\text{M}$ ,  $t_{1/2} = 25\text{min}$   
 $C_0 = 0.05\text{M}$ ,  $t_{1/2} = 12.5 \text{ min}$   
 q)  $C_0 = 0.1\text{M}$ ,  $t_{1/2} = 12\text{min}$   
 $C_0 = 0.05\text{M}$ ,  $t_{1/2} = 24\text{min}$   
 r) Radioactive decay  
 s)  $C_0 = 0.1\text{M}$ ,  $t_{1/2} = 8\text{min}$   
 $C_0 = 0.05\text{M}$ ,  $t_{1/2} = 24\text{min}$

**KEY SHEET (ADDITIONAL PRACTICE EXERCISE)****LEVEL-I (MAIN)**

1) 4      2) 3      3) 2      4) 4      5) 3      6) 1      7) 1      8) 3      9) 2      10) 1

**LEVEL-II****LECTURE SHEET (ADVANCED)**

1) b      2) b      3) a      4) a      5) b

**PRACTICE SHEET (ADVANCED)**

1) bc      2) abc      3) ac      4) bcd      5) b      6) c      7) a      8) d      9) c      10) b

11) A-rs; B-q; C-p; D-q

