

## CHEMICAL KINETICS – II PUC

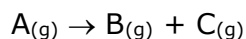
- Nitrogen dioxide ( $\text{NO}_2$ ) dissociates into nitric oxide (NO) and oxygen ( $\text{O}_2$ ) as follows:  
 $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$ . If the rate of decrease of concentration of  $\text{NO}_2$  is  $6.0 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$ . What will be the rate of increase of concentration of  $\text{O}_2$ ?  
a)  $3 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$     b)  $6 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$   
c)  $1 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$     d)  $1.5 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$
- The rate of formation of a dimer in a second order dimerisation reaction is  $9.1 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$  at  $0.01 \text{ mol L}^{-1}$  monomer concentration. What will be the rate constant for the reaction?  
a)  $9.1 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$     b)  $9.2 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$   
c)  $3 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$     d)  $27.3 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$
- The rate law for a reaction,  $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$  is given by the expression  $k [\text{A}]$ . The rate of reaction will be  
a) doubled on doubling the concentration of B  
b) halved on reducing the concentration of A to half  
c) decreased on increasing the temperature of the reaction  
d) unaffected by any change in concentration or temperature.
- The rate of the reaction:  
 $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$  is given by the equation,  
Rate =  $k [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{NaOH}]$ .  
If concentration is expressed in mol/L, the units of k are  
a)  $\text{mol}^{-2} \text{ L}^2 \text{ s}^{-1}$     b)  $\text{mol L}^{-1} \text{ s}^{-1}$     c)  $\text{L mol}^{-1} \text{ s}^{-1}$     d)  $\text{s}^{-1}$
- A first order reaction is 20% complete in 10 minutes. What the specific rate constant for the reaction?  
a)  $0.0970 \text{ min}^{-1}$     b)  $0.009 \text{ min}^{-1}$     c)  $0.0223 \text{ min}^{-1}$     d)  $2.223 \text{ min}^{-1}$
- The decomposition of a substance follows first order kinetics. If its concentration is reduced to  $1/8$  of its initial value in 12 minutes, the rate constant of the decomposition system is  
a)  $\left(\frac{2.303}{12} \log \frac{1}{8}\right) \text{ min}^{-1}$     b)  $\left(\frac{2.303}{12} \log 8\right) \text{ min}^{-1}$   
c)  $\left(\frac{0.693}{12}\right) \text{ min}^{-1}$     d)  $\left(\frac{1}{12} \log 8\right) \text{ min}^{-1}$
- The decomposition of dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) follows first order rate law. What will be the rate constant from the given data?  
At  $t = 800 \text{ s}$ ,  $[\text{N}_2\text{O}_5] = 1.45 \text{ mol L}^{-1}$   
At  $t = 1600 \text{ s}$ ,  $[\text{N}_2\text{O}_5] = 0.88 \text{ mol L}^{-1}$   
a)  $3.12 \times 10^{-4} \text{ s}^{-1}$     b)  $6.24 \times 10^{-4} \text{ s}^{-1}$     c)  $2.84 \times 10^{-4} \text{ s}^{-1}$     d)  $8.14 \times 10^{-4} \text{ s}^{-1}$
- The temperature dependence of the rate of a chemical reaction can be explained by Arrhenius equation which is  
a)  $k = \text{Ae}^{E_a/RT}$     b)  $k = \text{Ae}^{-E_a/RT}$     c)  $k = \text{Ae} \times \frac{E_a}{RT}$     d)  $k = \text{Ae} \times \frac{RT}{E_a}$

9. Rate of a general reaction  $A + B \rightarrow$  products can be expressed as follows on the basis of collision theory.  $\text{Rate} = Z_{AB} e^{-E_a/RT}$ .

Which of the following statements is not correct for the above expression?

- a) Z is collision frequency and is equal to number of collisions per second per unit volume of the reaction mixture.
- b)  $e^{-E_a/RT}$  is the fraction of molecules with kinetic energy equal to or greater than  $E_a$ .
- c)  $E_a$  is activation energy of the reaction.
- d) All the molecules which collide with one other are effective collisions.

10. Consider a first order gas phase decomposition reaction given below:

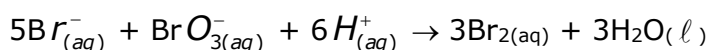


The initial pressure of the system before decomposition of A was  $p_i$ . After lapse of time 't', total pressure of the system increased by x units and became 'p<sub>t</sub>'

The rate constant k for the reaction is given as .....

- a)  $k = \frac{2.303}{t} \log \frac{p_i}{p_i - x}$
- b)  $k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$
- c)  $k = \frac{2.303}{t} \log \frac{p_i}{2p_i + p_t}$
- d)  $k = \frac{2.303}{t} \log \frac{p_i}{p_i + x}$

11. Which of the following expressions is correct for the rate of reaction given below?



- a)  $\frac{\Delta[Br^-]}{\Delta t} = 5 \frac{\Delta[H^+]}{\Delta t}$
- b)  $\frac{\Delta[Br^-]}{\Delta t} = \frac{6}{5} \frac{\Delta[H^+]}{\Delta t}$
- c)  $\frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6} \frac{\Delta[H^+]}{\Delta t}$
- d)  $\frac{\Delta[Br^-]}{\Delta t} = 6 \frac{\Delta[H^+]}{\Delta t}$

12. In the reaction  $2A + B \rightarrow A_2B$ , if the concentration of A is doubled and of B is halved, then the rate of the reaction will:

- a) increase by two times
- b) decrease by two times
- c) increase by four times
- d) remain the same

13. The thermal decomposition of a compound is of first order. If a sample of the compound decompose 50% in 120 min. What time will it take to undergo 90% decomposition?

- a) nearly 400 min
- b) nearly 45 min
- c) nearly 480 min
- d) nearly 240 min

14. Which of the following expression is correct for second order reactions? ( $C_0$  refers to initial concentration of reactant)?

- a)  $t_{1/2} \propto C_0$
- b)  $t_{1/2} \propto C_0^0$
- c)  $t_{1/2} \propto C_0^{-1}$
- d)  $t_{1/2} \propto C_0^{-2}$

15. The time taken for the completion of 3/4 of a first order reaction is:

- a)  $(2.303/k) \log 3/4$
- b)  $(2.303/k) \log 4$
- c)  $(2.303/k) \log 1/4$
- d)  $(2.303/0.75) \log k$

16. Which of the following statement about the catalyst is true?
- A catalyst accelerates the rate of reaction by bringing down the energy of activation
  - A catalyst does not participate in reaction mechanism
  - A catalyst makes the reaction more feasible by making  $\Delta G$  more negative
  - A catalyst makes equilibrium constant more favourable for forward reaction

17. In the sequence of reaction:  $A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$   
 $k_3 > k_2 > k_1$  then the rate determining step of the reaction is:

- $A \rightarrow B$
- $B \rightarrow C$
- $C \rightarrow D$
- $A \rightarrow D$

18. In a second order reaction when the concentration of both reactant are equal. The reactions are completed in 500 s. How long will it take for the reaction to go to 60% completion?

- 1000 s
- 300 s
- 3000 s
- 2000 s

19. A reaction proceeds in 3 steps. The first stage is a fast second order reaction. The second stage is slow and of first order. The third stage is fast again and is a third order reaction. The overall order of the reaction is:

- zero order
- first order
- second order
- third order

20. During the kinetic study of the reaction  $2A + B \rightarrow C + D$ , following results were obtained

Run	[A]/mol L <sup>-1</sup>	[B]/mol L <sup>-1</sup>	Initial rate of formation of D/mol L <sup>-1</sup> min <sup>-1</sup>
I	0.1	0.1	$6.0 \times 10^{-3}$
II	0.3	0.2	$7.2 \times 10^{-2}$
III	0.3	0.4	$2.88 \times 10^{-1}$
IV	0.4	0.1	$2.40 \times 10^{-2}$

Based on the above data which one of the following is correct?

- rate =  $k [A] [B]^2$
- rate =  $k [A]^2 [B]$
- rate =  $k [A] [B]$
- rate =  $k [A]^2 [B]^2$

21. The rate constant is numerically the same for three reactions of first, second and third order respectively. Which one of the following is true for rate of these three reactions if concentration of the reactant is same and greater than 1 M?

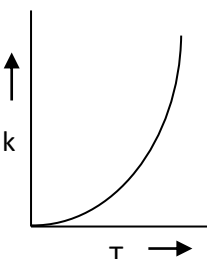
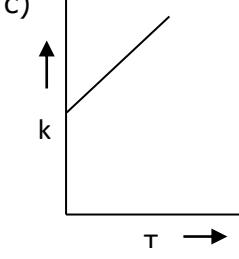
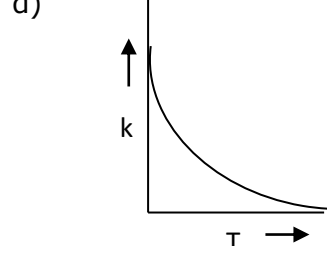
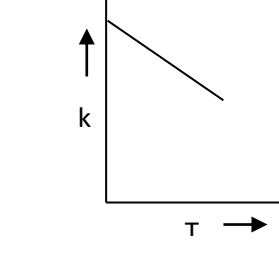
- $r_1 = r_2 = r_3$
- $r_1 > r_2 > r_3$
- $r_1 < r_2 < r_3$
- There can be no definite order

22. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25<sup>o</sup> C are  $3.0 \times 10^{-4} \text{ s}^{-1}$ , 104.4 kJ mol<sup>-1</sup> and  $6.0 \times 10^{14} \text{ s}^{-1}$ , 104.4 kJ mol<sup>-1</sup> and  $6.0 \times 10^4 \text{ s}^{-1}$  respectively. The value of the rate constant at  $T \rightarrow \infty$  is

- $2.0 \times 10^{18} \text{ s}^{-1}$
- $6.0 \times 10^{14} \text{ s}^{-1}$
- infinity
- $3.6 \times 10^{30} \text{ s}^{-1}$

23. The concentration of a reactant X decreases from 0.1 M to 0.005 M in 40 min. If the reaction follows first order kinetics, the rate of the reaction when the concentration of X is 0.01 M will be

- $1.73 \times 10^4 \text{ M min}^{-1}$
- $3.47 \times 10^{-4} \text{ M min}^{-1}$
- $3.47 \times 10^{-5} \text{ M min}^{-1}$
- $7.5 \times 10^{-4} \text{ M min}^{-1}$

24. Decomposition of a compound is known to be a first order reaction. Three fourths of the compound taken is decomposed at the end of two hours. The quantity left over at the end of the next three hours will be about
- a) 1 percent                      b) 2 percent                      c) 3 percent                      d) 4 percent
25. A first order reaction is 50% complete in 30 minutes at 27<sup>o</sup> C and in 10 minutes at 47<sup>o</sup> C. The energy of activation of the reaction is
- a) 43.84 kJ mol<sup>-1</sup>                      b) 34.84 kJ mol<sup>-1</sup>                      c) 84.00 kJ mol<sup>-1</sup>                      d) 30.00 kJ mol<sup>-1</sup>
26. For the reactions  $A + B \rightarrow C$ , it is found that doubling the concentration of A increases the rate 4 times, and doubling the concentration of B doubles the reaction rate. What is the overall order of the reaction?
- a) 4                                      b) 3/2                                      c) 3                                      d) 1
27. 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) 10 hours                      b) 20 hours                      c) 5 hours                      d)  $7\frac{1}{2}$  hours
28. When two reactants A and B are mixed to give products C and D, the reaction quotient Q at the initial stages of the reaction
- a) is zero                                      b) decreases with time  
c) is independent of time                      d) increases with time
29. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is
- a)                       b)                       c)                       d) 
30. When temperature of a reaction mixture is changed from T<sub>1</sub> to T<sub>2</sub>, half life is found to decrease. Thus,
- a) T<sub>2</sub> > T<sub>1</sub> and the reaction is endothermic  
b) T<sub>2</sub> > T<sub>1</sub> and the reaction is exothermic  
c) T<sub>1</sub> > T<sub>2</sub> and the reaction is endothermic  
d) T<sub>2</sub> > T<sub>1</sub> and the reaction can be endothermic or exothermic.
31. The reaction  $A \rightarrow B$  follows first order kinetics. The time taken for 0.8 mole of A to produce 0.6 mole of B is 1 hour. What is the time taken for conversion of 0.9 mole of A to produce 0.675 mole of B?
- a) 1 hour                                      b) 0.5 hour                                      c) 0.25 hour                                      d) 2 hours
32. For a first order reaction  $A \rightarrow B$ , the reaction rate at reactant concentration of 0.01 M is found to be  $2.0 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$ . The half-life of the reaction is
- a) 300 s                                      b) 30 s                                      c) 220 s                                      d) 347 s
33. In the first order reaction, the concentration of the reactants is reduced to 25% in one hour. The half life period of the reaction is
- a) 2 hr                                      b) 4 hr                                      c) 1/2 hr                                      d) 1/4 hr

34. 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
- a) 1500 s                      b) 500 s                      c) 900 s                      d) 600 s
35. In the reaction:  $2 \text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ , initial pressure is 500 atm and rate constant  $K$  is  $3.38 \times 10^{-5} \text{ sec}^{-1}$ . After 10 minutes, the final pressure of  $\text{N}_2\text{O}_5$  is
- a) 490 atm                      b) 250 atm                      c) 480 atm                      d) 420 atm
36. In the reaction:  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ , initial pressure is 500 atm and rate constant  $K$  is  $3.38 \times 10^{-5} \text{ sec}^{-1}$ . After 10 minutes, the final pressure of  $\text{N}_2\text{O}_5$  is
- a) 490 atm                      b) 250 atm                      c) 480 atm                      d) 420 atm
37. A gaseous reaction:  $\text{A}_2 (\text{g}) \rightarrow \text{B} (\text{g}) + \frac{1}{2} \text{C} (\text{g})$   
Shows increase in pressure from 100 mm to 120 mm in 5 minutes. The rate of disappearance of  $\text{A}_2$  is
- a)  $4 \text{ mm min}^{-1}$                       b)  $8 \text{ mm min}^{-1}$                       c)  $16 \text{ mm min}^{-1}$                       d)  $2 \text{ mm min}^{-1}$
38. In a zero order reaction,  $\text{A} \rightarrow \text{Products}$ , starting with  $0.5 \text{ mole L}^{-1}$ , if  $0.4 \text{ mole L}^{-1}$  are present after 10 minutes, the rate constant of the reaction will be
- a)  $0.05 \text{ mol L}^{-1} \text{ min}^{-1}$   
b)  $0.04 \text{ mol L}^{-1} \text{ min}^{-1}$   
c)  $10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$   
d) Cannot be determined with the given data
39. The reaction  $\text{A} (\text{g}) + 2\text{B} (\text{g}) \rightarrow \text{C} (\text{g}) + \text{D} (\text{g})$  is an elementary process. In an experiment, the initial partial pressure of A & B are  $P_A = 0.60$  and  $P_B = 0.80$  atm. When  $P_C = 0.2$  atm the rate of reaction relative to the initial rate is
- a)  $1/4$                       b)  $1/24$                       c)  $9/16$                       d)  $1/6$
40. For a gaseous reaction  $\text{CH}_3\text{COOCH}_3 (\text{g}) \rightarrow \text{C}_2\text{H}_4 (\text{g}) + \text{CO} (\text{g}) + \text{H}_2 (\text{g})$ . The initial pressure was found to be 0.60 atm while after 6.9 minutes, the pressure was 1.0 atm. If the reaction follows first order kinetics, rate constant of the reaction is
- a)  $0.0237 \text{ min}^{-1}$                       b)  $0.0587 \text{ min}^{-1}$                       c)  $0.489 \text{ min}^{-1}$                       d)  $0.0590 \text{ min}^{-1}$
41. For the reaction  $2 \text{N}_2\text{O}_5 (\text{g}) \rightarrow 4 \text{NO}_2 (\text{g}) + \text{O}_2 (\text{g})$ , if the concentration of  $\text{NO}_2$  increases by  $5.2 \times 10^{-3} \text{ M}$  in 100 seconds, then the rate of the reaction is
- a)  $1.3 \times 10^{-5} \text{ M s}^{-1}$                       b)  $5 \times 10^{-4} \text{ M s}^{-1}$                       c)  $7.6 \times 10^{-4} \text{ M s}^{-1}$                       d)  $2 \times 10^{-3} \text{ M s}^{-1}$
42. Which of the following statements is not correct?
- a) molecularity of a complex reaction  $\text{A} + 2\text{B} \rightarrow \text{C}$  is 3  
b) both order and molecularity have normally a maximum value of 3  
c) order of slowest elementary reaction of a complex reaction gives the order of the complex reaction  
d) Law of mass action and rate law expressions are same for single step reactions.
43. The specific reaction rate of a first order reaction is 0.02. The initial concentration of the reactant is 2 moles/litre. The rate of reaction after 60 seconds is
- a)  $0.025 \text{ mole L}^{-1} \text{ sec}^{-1}$                       b)  $0.36 \text{ mole L}^{-1} \text{ sec}^{-1}$   
c)  $0.012 \text{ mole L}^{-1} \text{ sec}^{-1}$                       d)  $3.6 \text{ mole L}^{-1} \text{ sec}^{-1}$

44. A first order reaction is 20% complete in 10 minutes. The time taken for the reaction to go to 75% completion is  
 a) 21.65 minutes      c) 59.70 sec      d) 62.18 minutes      d) 95.8 sec
45. The rate constant of a first order reaction is  $60 \text{ sec}^{-1}$ . How much time will it take to reduce the initial concentration to  $1/16^{\text{th}}$  value?  
 a)  $2.31 \times 10^{-2} \text{ sec}$       b)  $9.24 \times 10^{-2} \text{ sec}$   
 c)  $4.62 \times 10^{-2} \text{ sec}$       d)  $1.15 \times 10^{-3} \text{ sec}$
46. The ratio of the time required for  $3/4^{\text{th}}$  of the reaction of first order to complete to that required for the completion of half of the reaction  
 a) 1: 2      b) 2: 1      c) 3: 2      d) 4: 3
47. The ratio of  $t_{7/8}$  and  $t_{1/2}$  for the first order reaction is  
 a) 3      b) 5      c) 2      d) 7
48. The velocity constant of a reaction at 290 K was found to be  $3.2 \times 10^{-3} \text{ s}^{-1}$ . When the temperature is raised to 310 K, it will be about.  
 a)  $6.4 \times 10^{-3}$       b)  $3.2 \times 10^{-4}$       c)  $9.6 \times 10^{-3}$       d)  $1.28 \times 10^{-2}$
49. 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?  
 a)  $10^{-3}$       b)  $5 \times 10^{-4}$       c)  $2 \times 10^{-3}$       d)  $10^{-2}$
50. In the first order reaction, the concentration of the reactants is reduced to 25% in one hour. The half-life period of the reaction is  
 a) 2h      b) 4h      c)  $\frac{1}{2}$ h      d)  $\frac{1}{4}$ h

## KEY ANSWER & SOLUTIONS

### 1.Ans: (a)

For the reaction,  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$

$$-\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt}$$

$$-\frac{d[\text{NO}_2]}{dt} = 6 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\frac{d[\text{O}_2]}{dt} = 3 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$$

### 2.Ans: (a)

$2\text{A} \rightarrow \text{A}_2$

Rate of formation of dimer =  $k [\text{A}]^2$

$$k = \frac{\text{Rate of formation of dimer}}{[\text{A}]^2}$$

$$k = \frac{9.1 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}}{(0.01 \text{ mol L}^{-1})^2} = 9.1 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$$

### 3.Ans: (b)

The rate of reaction depends upon concentration of only A.

**4. Ans: (c)**

For a second order reaction,  $\frac{dx}{dt} = k [A]^2$

$$\frac{\text{conc.}}{\text{time}} = k [\text{conc.}]^2$$

$$\frac{\text{mol L}^{-1}}{\text{s}} = k \text{ mol L}^{-1} \times \text{mol L}^{-1}$$

$$k = \text{L mol}^{-1} \text{ s}^{-1}$$

**5. Ans: (c)**

$$a - x = \frac{80}{100} \times a = 0.8 a, t = 10 \text{ min.}$$

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{10} \log \frac{a}{0.8a}$$

$$k = 0.2303 \log \frac{10}{8} = 0.2303 (1 - 0.9030)$$

$$= 0.2303 \times 0.0970 = 0.0223 \text{ min}^{-1}.$$

**6. Ans: (b)**

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad (\text{for first order})$$

$$k = \frac{2.303}{12} \log \frac{1}{1/8} = \left( \frac{2.303}{12} \log 8 \right) \text{ min}^{-1}$$

**7. Ans: (b)**

$$k = \frac{2.303}{(t_2 - t_1)} \log \frac{[A_1]}{[A_2]}$$

$$k = \frac{2.303}{(1600 - 800)} \log \frac{1.45}{0.88} = \frac{2.303}{800} \times 0.2169$$

$$= 6.24 \times 10^{-4} \text{ s}^{-1}$$

**8. Ans: (b)**

Arrhenius equation can be given as  $k = A e^{-E_a/RT}$  where A is the Arrhenius factor of the frequency factor. It is also called pre-exponential factor. R is the gas constant and  $E_a$  is the activation energy.

**9. Ans: (d)**

Only those collision in which molecules collide with sufficient energy, called threshold energy and proper orientation are effective collisions. Rest of the molecules collide and bounce back.

**10. Ans: (b)**

If  $x$  atm be the decrease in pressure of A at time  $t$  and one mole each of B and C is being formed, the increase in pressure of B and C will also be  $x$  atm each.



At  $t = 0$   $p_i$  atm  $0$  atm  $0$  atm

At time  $t$   $(p_i - x)$  atm  $x$  atm  $x$  atm

Where,  $p_i$  is the initial pressure at time  $t = 0$

$$p_t = (p_i - x) + x + x = p_i + x$$

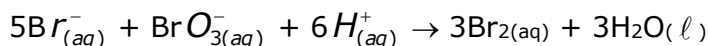
$$x = (p_t - p_i)$$

$$\text{where, } p_A = p_i - x = p_i - (p_t - p_i) = 2p_i - p_t$$

$$k = \left( \frac{2.303}{t} \right) \left( \log \frac{p_i}{2p_i - p_t} \right) = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}$$

**11.Ans: (c)**

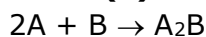
For the reaction,



$$\text{Rate} = \frac{-1\Delta[\text{Br}^-]}{5\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{-1}{6} \frac{\Delta[\text{H}^+]}{\Delta t}$$

$$\therefore \frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{5}{6} \frac{\Delta[\text{H}^+]}{\Delta t}$$

**12.Ans: (a)**



$$r_1 = k [\text{A}]^2 [\text{B}]$$

$$r_2 = k [2\text{A}]^2 [\text{B}/2]$$

$$\text{or } r_2 = 2k [\text{A}]^2 [\text{B}]$$

$$\therefore r_2 = 2r_1$$

**13.Ans: (a)**

For first order reaction:

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

For Ist case:

$$a = 100, x = 50, t = 120 \text{ min}$$

$$k = \frac{2.303}{120} \log \frac{100}{100-50}$$

$$= \frac{2.303}{120} \log 2$$

$$k = \frac{2.303 \times 0.3010}{120}$$

$$k = 0.0057 \text{ min}^{-1}$$

For the IIInd case:

$$t = \frac{2.303}{0.0057} \log \frac{100}{100-90}$$

$$= \frac{2.303}{0.0057} \log 10$$

$$t = 404 \text{ min}$$

$$\approx 400 \text{ min}$$

**14.Ans: (c)**

$$\text{From } t_{1/2} \propto C_0^{1-n}$$

Where, n = order of reaction

For second order n = 2

$$\therefore t_{1/2} \propto C_0^{1-2}$$

$$t_{1/2} \propto C_0^{-1}$$

**15.Ans: (b)**

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



$$\therefore x = \frac{3}{4} a$$

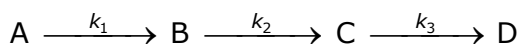
$$\therefore t = \frac{2.303}{k} \log \frac{a}{a - \frac{3}{4} a}$$

$$= \frac{2.303}{k} \log 4$$

**16. Ans: (a)**

A catalyst accelerates the rate of reaction by bringing down the energy of activation.

**17. Ans: (a)**



$$\therefore k_3 > k_2 > k_1$$

As  $k_1$  is slowest hence  $A \rightarrow B$  is the rate determining step of the reaction.

**18. Ans: (c)**

$$k = \frac{1}{t} \left[ \frac{x}{a(a-x)} \right]$$

$$k = \frac{1}{500} \left[ \frac{0.2a}{a(a-0.2a)} \right]$$

$$k = \frac{1}{2000a}$$

$$\frac{1}{2000a} = \frac{1}{t} \left[ \frac{0.6a}{a(a-0.6a)} \right]$$

$$t = 3000 \text{ s}$$

**19. Ans: (b)**

Slow step is called rate determining step

**20. Ans: (a)**

From runs I and IV, keeping [B] constant, [A] is made 4 times, rate becomes 4 times.

Hence, Rate  $\propto$  [A]. From runs II and III, keeping [A] constant, [B] is doubled, rate becomes 4 times. Hence, Rate  $\propto$  [B]<sup>2</sup>. Thus,

$$\text{Rate} \propto [A] [B]^2$$

$$\text{Or Rate} = k [A] [B]^2.$$

**21. Ans: (c)**

$$r_1 = k_1 [A], r_2 = k_2 [A]^2, r_3 = k_3 [A]^3$$

If [A] > 1 M,  $r_3 > r_2 > r_1$  or  $r_1 < r_2 < r_3$

**22. Ans: (b)**

$$T_2 = T \text{ (say)}; T = 25^\circ \text{C} = 298 \text{ K};$$

$$E_a = 104.4 \text{ kJ mol}^{-1} = 104.4 \times 10^3 \text{ J mol}^{-1};$$

$$k_1 = 3 \times 10^{-4} \text{ k}_2 = ?$$

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

$$\log \frac{k_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3 \text{ J mol}^{-1}}{2.303 \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1})}$$

$$\left[ \frac{1}{298 \text{ K}} - \frac{1}{T} \right] \text{ As } T \rightarrow \infty, 1/T \rightarrow 0$$

$$\therefore \log \frac{k_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3}{2.303 \times 8.314 \times 298}$$

$$\log \frac{k_2}{3 \times 10^{-4}} = 18.297$$

$$\frac{k_2}{3 \times 10^{-4}} = 1.98 \times 10^{18}$$

$$\text{or } k_2 = (1.98 \times 10^{18}) \times (3 \times 10^{-4}) = 6 \times 10^{14}$$

**23. Ans: (d)**

$$k = \frac{2.303}{t} \log \frac{A_0}{A} = \frac{2.303}{40} \log \frac{0.1}{0.005} = \frac{2.303}{40} \log 20 = 0.075 \text{ min}^{-1}$$

**24. Ans: (c)**

Since the reaction is of I order,  $t_{1/2}$  is independent of initial concentration of the reactant.

$\frac{3}{4}$  of the compound i.e., 75% of the compound decomposes, 25% is left behind.

100%  $\xrightarrow{t_{1/2}}$  50%  $\xrightarrow{1 \text{ hour}}$  25%  $\xrightarrow{1 \text{ hour}}$  12.5%  $\xrightarrow{1 \text{ hour}}$  6.25%  $\xrightarrow{1 \text{ hour}}$  3.125%  $\approx$  3% (Total 5 hours mean 5 half lives)

**25. Ans: (a)**

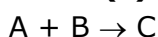
$$k_{27^\circ\text{C}} = \frac{0.693}{30} \text{ min}^{-1}, k_{47^\circ\text{C}} = \frac{0.693}{10} \text{ min}^{-1}$$

$$\therefore \frac{k_{47^\circ\text{C}}}{k_{27^\circ\text{C}}} = 3.$$

$$\text{Log } \frac{k_{47^\circ\text{C}}}{k_{27^\circ\text{C}}} = \log 3 = \frac{E_a}{2.303 \times 8.314} \left( \frac{20}{300 \times 320} \right) \text{ which gives}$$

$$E_a = \frac{0.4771 \times 2.303 \times 8.314 \times 300 \times 320}{20} = 43.84 \text{ KJ}$$

**26. Ans: (c)**



$$\text{rate} \propto [A] [B]$$

$$\text{rate}_1 \propto [2A] [B]$$

$$\text{rate}_2 \propto [A] [2B]$$

$$\frac{\text{rate}_1}{\text{rate}} = 4 = \frac{[2A]^x [B]^y}{[A]^x [B]^y} = 2^x = 4 = 2^2$$

$$\frac{\text{rate}_2}{\text{rate}} = 2 = \frac{[A]^x [2B]^y}{[A]^x [B]^y} = 2^y = 2 = 2^1$$

$$x = 2, y = 1$$

$$x + y = 3$$

**27. Ans: (d)**

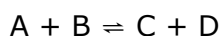
For the first order reaction

$$k = \frac{0.693}{t} = \frac{0.693}{45} \dots\dots\dots (1)$$

When  $x = 99.9\%$

$$k = \frac{2.303}{t} \log \left[ \frac{100}{100 - 99.9} \right] = \frac{2.303}{t} \log [1000] = \frac{2.303}{t} \times 3 = \frac{6.909}{t} \dots\dots\dots (2)$$

$$\text{Equating (1) + (2): } \frac{.69}{45} = \frac{6.9}{t} \therefore t = \frac{6.9 \times 45}{.69} = 450 \text{ min} = 7 \frac{1}{2} \text{ hours.}$$

**28. Ans:(d)**

$$Q = \frac{[C][D]}{[A][B]}$$

At the initial stages [C] and [D] increases and [A] and [B] decreases. As such at the initial stages Q increases.

**29. Ans: (a)**

$$k = Ae^{-E_a/RT} = \frac{A}{e^{E_a/RT}}$$

Thus, as T increases, the exponential factor in the denominator decreases or  $Ae^{-E_a/RT}$  increases. Hence, k increases exponentially as T increases.

**30. Ans: (d)**

As the half life is decreased, the rate of reaction has increased. This means that  $T_2 > T_1$ . Please note that the rate of all type of reactions (exothermic or endothermic) increase with the increase in temperature.

**31. Ans: (a)**

$$\text{In case I, fraction of A reacted} = \frac{0.6}{0.8} = \frac{3}{4}$$

$$\text{In case II, fraction of A reacted} = \frac{0.675}{0.9} = \frac{3}{4}$$

For a first order reaction, time taken for the same fraction fo reaction si independent of initial concentration.

**32. Ans:(d)**

$$\text{Rate} = k[A], \text{ i.e., } 2.0 \times 10^{-5} = k(0.01) \text{ or } k = 2.0 \times 10^{-3}$$

$$T_{1/2} = \frac{0.693}{2.0 \times 10^{-3}} = 347 \text{ s.}$$

**33. Ans: (c)**

$$k = \frac{2.303}{1} \log \frac{a}{0.25a} = 2.303 \log 2^2 = 2 \times 2.303 \log 2$$

$$t_{50\%} = \frac{2.303}{k} \log 2 = \frac{1}{2} \text{ hour.}$$

Alternatively, think from the given times. If  $t_{50\%} = 1/2$  hr, then  $t_{75\%} = 1$  hr.

**34. Ans:(b)**

$$k = \frac{0.693}{150} \text{ s}^{-1} = \frac{2.303}{t} \log \frac{1/10}{1/100} \text{ or } t = \frac{2.303 \times 150}{0.693} \log 10 = 498 \text{ s} \approx 500 \text{ s.}$$

**35. Ans:(a)**

$$\text{If } P_t \text{ is the pressure after time } t, k = \frac{2.303}{t} \log \frac{P_0}{P_t}$$

$$\therefore 3.38 \times 10^{-5} \text{ s}^{-1} = \frac{2.303}{600\text{s}} \log \frac{500\text{atm}}{P_t}$$

$$\text{or } \log \frac{500}{P_t} = 0.0088 \text{ or } \frac{500}{P_t} = 1.021 \text{ or } P_t = 490 \text{ atm}$$

**36. Ans:(a)**

$2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$  is a first order reaction

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

$$3.38 \times 10^{-5} = \frac{2.303}{600} \log \left( \frac{500}{a-x} \right)$$

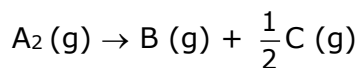
$$\log\left(\frac{500}{a-x}\right) = \frac{3.38 \times 10^{-5} \times 600}{2.303}$$

$$\log\left(\frac{500}{a-x}\right) = 8.805 \times 10^{-3}$$

$$\left(\frac{500}{a-x}\right) = \text{A.L.}(8.805 \times 10^{-3}) = \text{A.L.}(0.008805) = 1.021$$

$$\therefore (a-x) = \frac{500}{1.021} = 489.7 \text{ atm.}$$

**37. Ans: (a)**



At Equilibrium 1 - x      x      x

Total number of moles = 1 - x + x + x = 1 + x

Initial number of moles = 1,  $\Rightarrow$  100 mm Hg

Number of moles at equilibrium 1 + x = 120 mm of Hg

$$\therefore x = 0.2$$

$$\therefore \frac{\text{Change in concentration of A}_2}{\text{time}} = \frac{20 \text{ mm}}{5} = 4 \text{ mm min}^{-1}$$

**38. Ans: (c)**

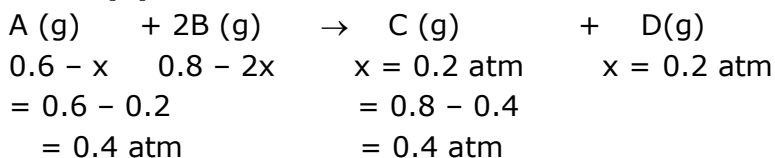
For a zero order r x z    A  $\rightarrow$  products

$$V = k[\text{A}]^0$$

Rate is a constant throughout

$$\therefore \frac{de}{dt} = \frac{0.5 - 0.4}{10} = 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$$

**39. Ans: (d)**

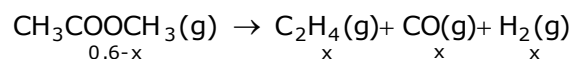


Initial rate  $v_1 = k \times p_A \times p_B^2 = k \times 0.6 \times (0.8)^2 = k (0.6) (0.8)^2$

Rate of the reaction when  $p_C = 0.2 \text{ atm}$   $v_2 = k(0.4) (0.4)^2$

$$\begin{aligned} \therefore \frac{v_2}{v_1} &= \frac{k(0.4)(0.4)^2}{k(0.6)(0.8)^2} \\ &= \frac{2}{3} \times \frac{1}{4} = \frac{2}{12} = \frac{1}{6} \end{aligned}$$

**40. Ans: (b)**



$$= 0.6 - 0.2 = 0.4$$

$\therefore$  Total number of moles after 6.9 mins is  $0.6 - x + x + x + x = 0.6 + 2x$

$$0.36 + 2x = 1.0 \Rightarrow x = 0.2$$

$$k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right) = \frac{2.303}{6.9} \log\left(\frac{0.6}{0.4}\right) = 0.0587 \text{ min}^{-1}$$

**41. Ans: (a)**



$$[\text{NO}_2] = 4x = 5.2 \times 10^{-3} \text{ M}$$

$\therefore$  Change in concentration of  $\text{N}_2\text{O}_5 = 1.3 \times 10^{-3} \text{ M}$

As only one  $\text{N}_2\text{O}_5$  takes part in r.d.s.

$$v = -\frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1.3 \times 10^{-3}}{100} = 1.3 \times 10^{-5} \text{ Ms}^{-1}$$

**42. Ans: (b)**

Order can have a large value while molecularity can be a maximum of 3

**43. Ans: (c)**

$$k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right) \Rightarrow 0.02 = \frac{2.303}{60} \log\left(\frac{2}{a-x}\right)$$

$$\frac{0.02 \times 60}{2.303} = \log 2 - \log(a-x)$$

$$\log(a-x) = 0.3010 - 0.5210 = -0.2200 = T. 7800$$

$$(a-x) = \text{A.L.}(T. 78) = 0.6026$$

$$v = k(a-x)^1 = 0.02(0.6026) = 0.012052$$

$$= 1.2052 \times 10^{-2} \text{ mole L}^{-1} \text{ s}^{-1}$$

**44. Ans: (c)**

$$k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right) = \frac{2.303}{10} \log\left(\frac{100}{80}\right) = 0.2303 [2 - 1.9031]$$

$$= 0.2303(0.0969) = 0.0223 \text{ min}^{-1}$$

$$t = \frac{2.303}{0.0223} \times \log\left(\frac{100}{25}\right) = \frac{2.303}{0.0223} \times 0.6021 = 62.181 \text{ mins}$$

**45. Ans: (c)**

$$k = 60 \text{ sec}^{-1}$$

$$\therefore t_{1/2} = \frac{0.693}{k} = \frac{0.693}{60} = 0.01155 \text{ s}$$

$$\text{No. of half lives required to get } \frac{1}{16} \text{ value} = 4t_{1/2}$$

$$= 0.01155 \times 4 = 0.04620 \text{ s} = 4.620 \times 10^{-2} \text{ s}$$

**46. Ans: (b)**

The time taken for  $\frac{3}{4}$ th of the reaction to complete =  $2t_{1/2}$ . Hence, the ratio is 2 : 1

**47. Ans: (a)**

$$t_{7/8} \Rightarrow 3t_{1/2} \text{ lives because the concentration is decreased to } \frac{1}{8}$$

**48. Ans: (d)**

When temperature is raised to 310 k from 290 k, the rate would increase by 4 times.

Hence, the velocity constant at 310 k is  $4 \times 3.2 \times 10^{-3} = 12.8 \times 10^{-3} = 1.28 \times 10^{-2} \text{ s}^{-1}$

**49. Ans: (b)**

$$\Delta n = \frac{17^0 - 27^0}{10} = -1$$

$$\frac{k_2}{k_1} = 2^{-1} \Rightarrow 2k_2 = k_1$$

$$k_2 = \frac{k_1}{2} = \frac{10^{-3}}{2} = 5 \times 10^{-4} \text{ min}^{-1}$$

**50. Ans: (c)**

When the concentration is reduced to 25%, 75% reaction is complete =  $2t_{1/2}$

$$\therefore t_{1/2} = \frac{1}{2} \text{ h}$$

## CHEMICAL KINETICS

- 1) Chemical reactions with very  $E_a$  values are generally
- 1) Very slow
  - 2) very fast
  - 3) moderately fast
  - 4) spontaneous

Sol.: (1)

A reaction with very high  $E_a$  will have small fraction of effective collision of molecules and hence very slow rate of reaction.

- 2) Half life of a reaction is found to be inversely proportional to the cube of initial concentration. The order of reaction is
- 1) 5
  - 2) 4
  - 3) 3
  - 4) 2

Sol.:(2)

$$t_{\frac{1}{2}} \propto a^{1-n} t_{\frac{1}{2}} \propto \frac{1}{a^3} \quad \text{Hence } n=4$$

- 3) The temperature coefficient of a reaction is 2. If the velocity of the reaction is 5 units at  $25^\circ\text{C}$ , then the velocity of the reaction at  $55^\circ\text{C}$  is:
- 1) 20 units
  - 2) 80 units
  - 3) 30 units
  - 4) 40 units

Sol.:(4)

$$n = \frac{55-25}{10} = 3 \quad \frac{r_2}{r_1} = \frac{k_2}{k_1} = 2^3 \Rightarrow r_2 = 5 \times 8 = 40$$

- 4) The formation of gas at the surface of tungsten due to adsorption is the reaction of order
- 1) 0
  - 2) 1
  - 3) 2
  - 4) insufficient data

Sol.: (1)

It is zero order reaction

- 5) A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will

- 1) double  
2) increase by a factor of 4  
3) triple  
4) remain unchanged

Sol.:(2)

$$r = k[\text{CO}]^2$$

$$\frac{r_{\text{new}}}{r} = \frac{k[2\text{CO}]^2}{k[\text{CO}]^2} \Rightarrow r_{\text{new}} = 4r$$

- 6) For a first order reaction, the plot of  $\log k$  against  $1/T$  is a straight line. The slope of the line is equal to

- 1)  $-\frac{E_a}{2.303R}$       2)  $-\frac{2.303}{E_a R}$       3)  $-\frac{E_a}{2.303}$       4)  $-\frac{E_a}{R}$

Sol.:(1)

$$k = A e^{-E_a/RT} \quad \log k = \log A - \frac{E_a}{2.303RT} \cdot \frac{1}{T}$$

$$\text{Equation of straight line slope} = -\frac{E_a}{2.303R}$$

- 7) The rate expression for reaction  $A(g) + B(g) \rightarrow C(g)$  is  $\text{rate} = kC_A^2 C_B^{\frac{1}{2}}$ . What changes initial concentrations of A and B will cause the rate of reaction to increase by a factor of eight?

- 1)  $C_A \times 1; C_B \times 4$       2)  $C_A \times 2; C_B \times 2$   
3)  $C_A \times 2; C_B \times 4$       4)  $C_A \times 4; C_B \times 1$

Sol.: (3)

$$\text{Rate} = kC_A^2 C_B^{\frac{1}{2}} \quad \text{Rate} = k[2C_A]^2 [4C_B]^{\frac{1}{2}} = 4 \times 2k[C_A]^2 [C_B]^{\frac{1}{2}}$$

- 8) Temperature coefficient of a reaction is 2. When temperature is increased from 30 to 100°C, the rate of reaction increases by:

- 1) 128 times      2) 500 times      3) 250 times      4) 100 times

Sol.: (1)

$$n = \frac{100-30}{10} = 7 \quad \frac{r_2}{r_1} = \frac{k_2}{k_1} = 2^7 \Rightarrow \frac{r_2}{r_1} = 128$$

- 9) The rate constant of the reaction increases by
- 1) increasing the temperature                      2) increasing the conc. Of reactants
- 3) carrying out the reaction for longer period 4) none is correct

Sol.: (1)

$$\log K = \log A - \frac{E_a}{2.303} \cdot \frac{1}{T}$$

The value of K increases with temperature.

- 10) For the reaction  $H_2 + Cl_2 \xrightarrow{\text{Sunlight}} 2HCl$ , taking place on water, the order of reaction is :

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

Sol.: (3)

All photochemical reactions, where the products do not remain with reactant, are zero order reactions

- 11) The rate of reaction between two reactants A and B decreases by a factor of 4 if the concentration of the reactant B is doubled. The order of this reaction with respect of B is:

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

Sol.: (4)

$$\frac{r}{4} = \frac{k[A]^x[2B]^y}{k[A]^x[B]^y} \Rightarrow 2^y = \frac{1}{4} = \frac{1}{2^2} = 2^{-2} \Rightarrow y = -2$$

- 12) Rate of a reaction is doubled for each 10°C rise in temp. If the temp is raised to 50°C the reaction velocity increases by about

- 1) 32 times                      2) 12 times                      3) 50 times                      4) 16 times

Sol.: (1)

There are 5 tens hence  $(2)^5=32$



13) For a given reaction  $t_{1/2} \propto \frac{1}{Kx a}$ . The order of reaction is:

- 1) 2                                      2) zero                                      3) 1                                      4) 3

Sol.:(1)

$$t_{1/2} \propto \frac{1}{a^{n-1}}, \quad \text{Given } n-1=1; \quad n=2$$

14) Which of the following is a second order reaction?

- 1)  $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$   
2)  $\text{CH}_3\text{COOCH}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$   
3)  $\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2 + 3\text{H}_2\text{O}$   
4)  $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$

Sol.:(2)

Choices (1) and (4) are photochemical reaction of zero order. Choice (3) is first order reaction. In choice (2), rate of reaction depends on 1<sup>st</sup> power of  $\text{CH}_3\text{COOCH}_3$  and  $\text{NaOH}$  both.

15) a first order reaction is 60% complete in 20 minutes. How long will be reaction take to be 84% complete?

- 1) 54 mins                                      2) 76 mins.                                      3) 68 mins                                      4) 40 mins.

Sol.: (4)

$$\frac{2.303}{t} \log \frac{100}{40} = \frac{2.303}{t} \log \frac{100}{16}$$

$$\frac{2.303}{20} \log 2.5 = \frac{2.303}{t} \log 6.25$$

$$\therefore t=40 \text{ mins}$$

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

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

Sol.: (3)

$$\frac{r_{new}}{r} = \frac{k [2A]^n \left[\frac{1}{2}B\right]^m}{k [A]^n [B]^m} = 2^n \times \frac{1}{2^m} = 2^{(n-m)}$$

17) The reaction  $N_2O_5(In\ CCl_4) \rightarrow 2N_2 + \frac{1}{2}O_2(g)$  is first order with rate constant

$6.2 \times 10^{-4} \text{ s}^{-1}$ . What is the value of rate reaction when  $[N_2O_5]=1.25 \text{ mol L}^{-1}$  ?

- 1)  $3.85 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$                       2)  $6.35 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$   
 3)  $7.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$                       4)  $5.15 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

Sol.:(3)

$$\text{Rate} = k[N_2O_5]=6.2 \times 10^{-4} \times 1.25 = 7.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

18) In a first order reaction  $A \rightarrow B$ , if k is the rate constant and initial concentration of the reactant A is 0.5 M, then the half life is

- 1)  $\frac{\ln 2}{k}$                       2)  $\frac{0.693}{0.5k}$                       3)  $\frac{\log 2}{k\sqrt{0.5}}$                       4)  $\frac{\log 2}{2}$

Sol.:(1)

Half life time of a first order reaction is always

$$\frac{\ln 2}{k}, \text{ i. e., } \frac{2.303 \log 2}{k} \text{ or } \frac{0.693}{k}$$

19) The activation energy for a simple chemical reaction  $A \rightarrow B$  is  $E_a$  in forward direction. The activation energy for reverse reaction

- 1) is always double of  $E_a$                       2) is always less than  $E_a$   
 3) can be less than or more than  $E_a$                       4) is negative

Sol.:(3)

In exothermic and endothermic reactions will be more and less than  $E_a$  respectively .

20) A radioisotope has a half life of 10 days. If today 125 mg is left over, what was the original weight 40 days earlier?

- 1) 1 g                      2) 2g                      3) 600mg                      4) 1.5g

Sol.:(2)

$$\text{No. of half lives } n = \frac{40}{10} = 4$$

$$[A] = \frac{[A]_o}{2^n} \Rightarrow [A]_o = 125\text{mg} \times 2^4\text{mg} = 2\text{g}$$

21) For a particular reversible reaction at temperature T,  $\Delta H$  and  $\Delta S$  were found to be both +ve. If  $T_e$  is the temperature at equilibrium, the reaction would be spontaneous when

- 1)  $T=T_e$                       2)  $T_e>T$                       3)  $T>T_e$                       4)  $T_e$  is 5 times T

Sol.:(3)

$\Delta G=\Delta H-T\Delta S \quad \therefore T>T_e$  as  $\Delta G$  is negative for spontaneous reaction.

22) If concentration of reactants is increased by 'x' then rate constant k becomes

- 1) k                              2)  $\ln \frac{k}{x}$                               3)  $\ln k$                               4)  $\frac{k}{x}$

Sol.:(1)

Rate constant does not change with concentration.

23) Half life period of a reaction is found to be inversely proportional to the cube of the initial concentration. The order of reaction is:

- 1) 2                              2) 3                              3) 5                              4) 4

Sol.:(4)

$$t_{1/2} \propto \frac{1}{a^{n-1}} \Rightarrow n - 1 = 3, i. e. n = 4$$

24) A first order reaction is half completed in 45 minutes. How long does it need for 99.9% of the reaction to be completed?

- 1) 5 hours                      2) 10 hours                      3) 20 hours                      4)  $7\frac{1}{2}$  hours

Sol.: (4)

$$k = \frac{0.693}{45} \text{ further } t = \frac{2.303}{0.693} \times 45 \log \frac{100}{100-99.9} = \frac{2.303 \times 45 \times 3}{0.693} = 7\frac{1}{2} \text{ hours}$$

25) The rate of first order reaction is  $1.5 \times 10^{-2} \text{ molL}^{-1}\text{min}^{-1}$  at 0.5M conc. of reaction. The half-life of the reaction is:

- 1) 0.383 min                      2) 8.73 min                      3) 7.53 min                      4) 23.1 min

Sol.: (4)

$$r = k [A], k = \frac{1.5 \times 10^{-2}}{0.5}$$

$$t_{1/2} = \frac{0.693}{k} = 0.693 \times \frac{0.5}{1.5 \times 10^{-2}} = 23.1 \text{ min}$$

26) The rate of reaction increases with rise in temperature because of :

- 1) increase in activation energy
- 2) decrease in activation energy
- 3) increase in the number of activated molecules
- 4) increase in the number of molecular collisions.

Sol.:(3)

It is Maxwell Boltzmann distribution law

27)  $3A \rightarrow 2B$ , the rate of reaction +  $\frac{d[B]}{dt}$  is equal to:

- 1)  $+2 \frac{d[A]}{dt}$
- 2)  $-\frac{3}{2} \frac{d[A]}{dt}$
- 3)  $-\frac{1}{3} \frac{d[A]}{dt}$
- 4)  $-\frac{2}{3} \frac{d[A]}{dt}$

Sol.: (4)

$$\frac{1}{2} \frac{d[B]}{dt} = -\frac{1}{3} \frac{d[A]}{dt} \Rightarrow \frac{d[B]}{dt} = -\frac{2}{3} \frac{d[A]}{dt}$$

28) A catalyst increases the rate of reaction by

- 1) decreasing enthalpy
- 2) decreasing activation energy
- 3) decreasing internal energy
- 4) increasing activation energy

Sol.: (2)

Activation energy is lowered in presence of +ve catalyst

29) The conversion 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:

- 1) 4
- 2) 2
- 3)  $\frac{1}{2}$
- 4)  $\frac{1}{4}$

Sol.:(1)

$$r = k[A]^2, r^1 = k[2A]^2 \quad \frac{r^1}{r} = 2^2 \Rightarrow r^1 = 4r$$

- 30) The rate constant of a reaction is  $10.8 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ . The order of the reaction is
- 1) 2                                      2) zero                                      3) 1                                      4) 3

Sol.:(2)

$\text{Mol dm}^{-3} \text{ s}^{-1}$  units are zero order.

- 31)  $2A \rightarrow B + C$  would be a zero order reaction when:

- 1) the rate of reaction is proportional to square of conc. A
- 2) the rate of reaction doubles if conc. Of B is increased to double
- 3) the rate remains unchanged at any concentration of B and C
- 4) The rate of reaction remains the same at any concentrations of A

Sol.(4)

For zero order reaction :  $A \rightarrow \text{Products}$ ,

$$\text{rate} - \frac{d[A]}{dt} = k[A]_0^0 \Rightarrow -\frac{d[A]}{dt} = k$$

- 32) Identify the correct statement regarding a spontaneous process:

- 1) Exothermic process is always spontaneous
- 2) Lowering of energy in the reaction process is the only criterion for spontaneity
- 3) For a spontaneous process in an isolated system the change in entropy is positive
- 4) Endothermic process is never spontaneous

Sol.:(3)

For a spontaneous process in an isolated the change in entropy is positive

- 33) The time taken for 90% of a first order reaction to complete is approximately

- 1) 1.1 times that of half-life
- 2) 2.2 times that of half-life
- 3) 3.3 times that of half-life
- 4) 4.4 times that of half-life

Sol.:(3)

$$t_{90\%} = \frac{2.303}{k} \log \frac{100}{100-90}$$

$$t_{50\%} = \frac{2.303}{k} \log \frac{100}{100-50}$$

$$\therefore \text{Dividing } \frac{t_{90\%}}{t_{50\%}} = \frac{\log 10}{\log 2}$$

34) In the first order reaction, the concentration of reactant decreases from 0.8 M to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1M to 0.025M is:

- 1) 60 min                      2) 7.5 min                      3) 30 min                      4) 15 min

Sol.: (3)

Change of conc. from 0.8M to 0.4M reveals  $t_{1/2}$  to be 15 min. Change from 0.1M to 0.025M requires two half-lives. So, the time required = 2 x 15 = 30 min.

35) Which of the following statement is incorrect?

- 1) The larger the initial reactant concentration for a second order reaction, the shorter its half-life
- 2) Activation energy for the forward reaction equals to activation energy for the reverse reaction.
- 3) For a reversible reaction, an increase an increase in temperature increases the reaction rate for both the forward and the backward reaction.
- 4) When  $\Delta t$  is infinitesimally small, the average rate equals to the instantaneous rate

Sol.: (2)

$E_{a(\text{F.R})} \neq E_{a(\text{B.R})}$ ,  $E_a$  can be calculated

36) The half life period of a first order chemical reaction is 6.93 mins. The time required for the completion of 99% of the chemical reaction will be ( $\log 2=0.301$ ):

- 1) 23.03 minutes              2) 46.06 minutes  
 3) 230.3 minutes              4) 460.6 minutes

Sol.: (2)

$$t = (2.303/\lambda) \log(100/l);$$

$$\lambda = (0.693/6.93)$$

$$\lambda = (2.303/0.1) \times 2 = 46.06 \text{ min}$$

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

1) 0.5 h                      2) 0.25 h                      3) 4 h                      4) 1 h

Sol.:(1)

$$t_{1/2} = (2-l)/K \quad \text{or } K=1 \quad \therefore t_{1/2} = (0.5-0.25)/1=0.25 \text{ Hr}$$

- 38) The activation energy of a reaction at a given temperature is found to be  $2.303 RT \text{ Jmol}^{-1}$ , The ratio of rate constant to the Arrhenius factor is \_\_\_\_\_

1) 0.001                      2) 0.1                      3) 0.01                      4) 0.02

Sol.: (2)

$$\text{Log } k = \text{log } A - \frac{E_a}{2.303RT}$$

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

$$\text{Log } k = \text{log } A - 1$$

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

- 39) 75% of a first order reaction is completed in 30 min. What is the time required for 93.75% of the reaction (in min) to be completed?

1) 90                      2) 60                      3) 45                      4) 120

Sol.:(2)

$$t_{93.75\%} = 2t_{75\%} = 2 \times 30 = 60 \text{ min}$$

- 40) In conversion of lime stone time,  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ ;

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  are  $179.1 \text{ kJ mol}^{-1}$  and  $160.2 \text{ J/k}$  receptivity at  $298\text{k}$  and

1 bar. Assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is

1) 845 K                      2) 1200 K                      3) 1118 K                      4) 1008k

Sol.: (3)

$$\Delta S = \Delta H/T$$

$T = \Delta H / \Delta S = 179.1 \times 1000 / 160.2 = 1118 \text{K}$ . At this temperature, the reaction will be at equilibrium, i.e.,  $\Delta G = 0$ . So the reaction is spontaneous above 1118 K.

- 41) The rate constants for first order and zero order reactions in terms of molarity M units respectively, are:

1)  $\text{sec}^{-1}, \text{M}$                       2)  $\text{M}, \text{sec}^{-1}$                       3)  $\text{Msec}^{-1}, \text{sec}^{-1}$                       4)  $\text{sec}^{-1}, \text{Msec}^{-1}$

Sol.:(4)

For zero order reaction:  $k=r$

Units of rate constant =  $\text{mol L}^{-1} \text{sec}^{-1} = \text{Msec}^{-1}$

For 1<sup>st</sup> order reaction:  $k = r/\text{conc.}$

Units of 1<sup>st</sup> order constant =  $\frac{\text{Msec}^{-1}}{\text{M}} = \text{sec}^{-1}$

- 42) For a given reaction at 300K and 280K, the rate constants were found to be  $k_1$  and  $k_2$  then:

1)  $k_2 = 0.5 k_1$                       2)  $k_2 = 4 k_1$                       3)  $k_2 = 0.25 k_1$                       4)  $k_2 = 2 k_1$

Sol.:(3)

$$n = \frac{300-280}{10} = 2$$

$$\frac{k_1}{k_2} = 4, \quad k_2 = 0.25 k_1 \text{ (using temperature coefficient} = 2)$$

- 43) The rate of chemical reaction doubles for every 10°C rise of temperature. If temperature raised by 50°C, the rate of the reaction increases by about

1) 10 times                      2) 24 times                      3) 32 times                      4) 64 times

Sol.: (3)

$$\text{Temperature coefficient } (\theta) = \frac{\text{rate at } (t+10)^\circ\text{C}}{\text{rate at } t^\circ\text{C}}$$

$$\theta = 2 \text{ here, So increase in rate of reaction} = (\theta)^n$$

When n is number of times by which temperature is raised by 10°C



- 44) In acidic medium the rate of reaction between  $\text{BrO}_3^-$  and  $\text{Br}^-$  ion is given by the expression

$$\frac{d(\text{BrO}_3^-)}{dt} = K[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

Which of the following is correct?

- 1) Doubling the concentration of  $\text{H}^+$  ions will increase the reaction rate by 4 times
- 2) Rate of reaction is independent of the conc. Of acid
- 3) The change in pH of the solution will not affect the rate.
- 4) Rate constant of overall reaction is  $4 \text{ sec}^{-1}$

Sol.: (1)

The rate law equation contains  $[\text{H}^+]^2$ , term. The rate will change with change in pH and new rate will be  $[2]^2=4$  times the old rate.

- 45) The rate equation for the reaction  $2\text{A} + \text{B} \rightarrow \text{C}$ , is found to be  $r=k[\text{A}][\text{B}]$ . The correct statement in relation to this reaction is that the:

- 1) unit of k must be  $\text{sec}^{-1}$
- 2) value of k is independent of the initial concentrations of A and B
- 3)  $t_{1/2}$  is a constant
- 4) rate of formation of C is twice the rate of disappearance of A

Sol.: (2)

Rate constant k has fixed value for any reaction of any order.

- 46)  $T_{50}$  of first order reactions is 10 min starting with  $10 \text{ mol L}^{-1}$ , the rate after 20 min is:

- 1)  $0.0693 \text{ mol L}^{-1} \text{ m}^{-1}$
- 2)  $0.0693 \times 5 \text{ mol L}^{-1} \text{ m}^{-1}$
- 3)  $0.0693 \times 2.5 \text{ mol L}^{-1} \text{ m}^{-1}$
- 4)  $0.0693 \times 10 \text{ mol L}^{-1} \text{ m}^{-1}$

Sol.: (4)

$$K = \frac{0.693}{t} = \frac{0.693}{10} \text{ min}^{-1} = 0.0693 \text{ min}^{-1}$$

$$\text{Rate after 20 min} = K[\text{substance}] = 0.0693 \times 10 \text{ mol L}^{-1} \text{ min}^{-1}$$

47) For the reaction  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ , the rate and rate constant are  $1.02 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$  and  $3.4 \times 10^{-5} \text{ sec}^{-1}$ . The concentration of  $\text{N}_2\text{O}_5$  at that time will be :

- 1)  $1.02 \times 10^{-4} \text{ mol L}^{-1}$     2)  $1.732 \text{ mol L}^{-1}$     3)  $3 \text{ mol L}^{-1}$     4)  $3.2 \times 10^5 \text{ mol L}^{-1}$

Sol.(3)

From the units of rate constant, it is clear that it is a first order reaction.  $r=k[\text{N}_2\text{O}_5]$

$$[\text{N}_2\text{O}_5] = \frac{1.02 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}}{3.4 \times 10^{-5} \text{ sec}^{-1}} = \frac{1.02 \times 10}{3.4} = 3 \text{ mol L}^{-1}$$

48) 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?

- 1)  $2 \times 10^{-3}$     2)  $5 \times 10^{-4}$     3)  $10^{-2}$     4)  $10^{-3}$

Sol.:(2)

Let the rate constant at  $17^\circ\text{C}$  be 'x'. So,

$$x \times 2 = 10^{-3} \text{ min}^{-1}$$

$$x = \frac{10^{-3}}{2} = 5 \times 10^{-4} \text{ min}^{-1}$$

49) Time required for 100 percent completion of a zero order reaction is \_\_\_

- 1)  $\frac{2k}{a}$     2)  $ak$     3)  $\frac{a}{2k}$     4)  $\frac{a}{k}$

Sol.:(4)

For a zero order reaction,  $\frac{dx}{dt} = k \cdot [A]^0$ ;  $dx = kdt$  or  $x = kt + c$

When  $x=0$ ,  $t=0$ , then  $x=kt$ .

When the reaction is 100% complete, then  $x=a$      $\therefore a=kt$     or  $t = \frac{a}{k}$

50) Which of these does not influence the rate of reaction?

- 1) molecularity of the reaction    2) concentration of the reactants  
3) Nature of the reactants    4) temperature of the reaction

Sol.:(1)

Molecularity of the reaction does not influence the rate of reaction. It is related to the order of the reaction.

The temperature of the reaction, concentration (or partial pressures) of the reactants and nature of the reactants influences the rate of reaction.