

## CHEMICAL KINETICS-2

- Which of the following statements is correct regarding order of reaction?
  - First order reaction is always bimolecular
  - Order of reaction is always a finite number.
  - Order is determined theoretically from stoichiometric equation.
  - Order is determined by experimental results
- If the rate of reaction is independent of concentration of reactants, the order of reaction is
  - 0
  - 1
  - 2
  - 3
- For the reaction, the rate expression is,  $\text{rate} = K [\text{H}_2] [\text{Br}_2]^{1/2}$  which statement is true about this reaction
  - The reaction is of second order
  - Order of the reaction is  $3/2$
  - The unit of  $K$  is  $\text{sec}^{-1}$
  - Order of the reaction is  $1/2$
- In  $\text{SN}^1$  reaction of  $t$ -butyl iodide the molecularity for the elementary step  $(\text{CH}_3)_3\text{C-I}_{(\text{aq})} \rightarrow (\text{CH}_3)_3\text{C}^+_{(\text{aq})} + \text{I}^-_{(\text{aq})}$  is

- Zero
- 1
- 2
- fractional

- The units of rate constant for the reaction obeying rate expression,  $r = k[\text{A}][\text{B}]^{2/3}$  is
  - $\text{mole}^{-2/3} \text{ lit}^{2/3} \text{ time}^{-1}$
  - $\text{mole}^{2/3} \text{ lit}^{-2/3} \text{ time}^{-1}$
  - $\text{mole}^{-5/3} \text{ lit}^{5/3} \text{ time}^{-1}$
  - $\text{mole}^{2/3} \text{ lit}^{2/3} \text{ time}^{-1}$

**Hint:**  $\text{order} = 1 + 2/3 = 5/3$  units of rate constant =  $\text{mole}^{1-5/3} \text{ lit}^{5/3-1} \text{ time}^{-1}$

- In the following sequence of reactions  $\text{A} \xrightarrow{K_1} \text{B} \xrightarrow{k_2} \text{C} \xrightarrow{k_3} \text{D}$  if  $K_1 < K_2 < K_3$ , then the rate determining step is
  - $\text{A} \rightarrow \text{B}$
  - $\text{B} \rightarrow \text{C}$
  - $\text{C} \rightarrow \text{D}$
  - $\text{A} \rightarrow \text{C}$

**Hint:** slowest step of reaction is the rate determining step.

- Taking the reaction  $x + 2y \rightarrow \text{products}$  to be of second order, which of the following is / are the rate law expression/s for the reaction

$$\text{I) } \frac{dx}{dt} = K[x][y] \quad \text{II) } \frac{dx}{dt} = K[x]^2 \quad \text{III) } \frac{dx}{dt} = K[x][y]^2 \quad \text{IV) } \frac{dx}{dt} = K \frac{[x]}{[y]^2}$$

Then the correct answers can be

- I only
  - I and III only
  - I and II only
  - I and IV only
- For a reaction  $p\text{A} + q\text{B} \rightarrow \text{products}$ , the rate law expression is  $r = k [\text{A}]^l [\text{B}]^m$  then
    - $(p+q) = (l+m)$
    - $(p+q) > (l+m)$
    - $(p+q)$  may or may not be equal to  $(l+m)$
    - $(p+q) (l+m)$

- 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
- 2<sup>nd</sup>
- 3<sup>rd</sup>

**Hint:** for zero order  $t_{1/2} \propto \text{initial concentration}$

- The hydrolysis of Ethyl acetate in alkaline solution is

- 1st order
- 2nd order
- 3rd order
- zero order

11. The half-life of a first order reaction is
- 1) independent of the initial concentration of the reactant
  - 2) directly proportional to the initial concentration of the reactant
  - 3) inversely proportional to the initial concentration of the reactant
  - 4) directly proportional to the square of the initial concentration of the reactant.
12. Acid hydrolysis of ester is a
- 1) Second order reaction with molecularity 2
  - 2) First order reaction with molecularity 2
  - 3) Second order reaction with molecularity 1
  - 4) First order reaction with molecularity 2
13. The following data were obtained for the reaction  $2NO_{(g)} + Br_{2(g)} \rightarrow 2NOBr_{(g)}$

Expt	Initial conc. [NO]	Initial rate [Br <sub>2</sub> ]	Initial rate mol/lit/sec
I	0.10	0.10	1.3X10 <sup>-6</sup>
II	0.20	0.10	5.2X10 <sup>-6</sup>
III	0.20	0.30	1.56X10 <sup>-5</sup>

The order of reaction is

- 1) 1    2) 2    3) 3    4) 0

**Solution:**

$$r = k[NO]^n [Br_2]^m \quad - (1)$$

$$4r = k[2NO]^n [Br_2]^m \quad - (2)$$

$$12r = k[2NO]^n [3Br_2]^m \quad - (3)$$

$$\frac{2}{1} \Rightarrow n = 2, \quad \frac{3}{1} \Rightarrow 12 = 2^n \cdot 3^m \quad \therefore \text{order} = 1 + 2 = 3$$

$$12 = 2^2 \cdot 3^m$$

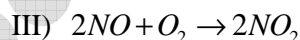
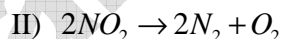
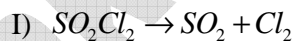
$$3 = 3^m$$

$$m = 1$$

14. The rate constant of a first order reaction is 0.0693. What is the time (in minutes) required for reducing an initial concentration of 20M to 2.5M?
- 1) 40    2) 30    3) 20    4) 10

**Solution:**  $k = \frac{2.303}{t} \log \frac{a}{a-x}$ ,  $0.0693 = \frac{2.303}{t} \log \frac{20}{2.5} \Rightarrow t = \frac{2.303 \times \log 8}{0.0693} = 30$

15. **Type - I**



**Type - II**

a) pseudo unimolecular reaction

b) first order reaction

c) second order reaction

d) third order

The correct matching is

- 1) I - a, II - b, III - c, IV - d      2) I - b, II - a, III - d, IV - c  
3) I - d, II - c, III - b, IV - a      4) I - b, II - c, III - d, IV - a

16. Type - I

- I) first order reaction  
 II) Zero order reaction  
 III) Trimolecular reaction  
 IV) Half life period of 'n' th order

- 1) I - a, II - b, III - c, IV - d  
 2) I - b, II - c, III - d, IV - a  
 3) I - c, II - d, III - b, IV - a  
 4) I - d, II - c, III - b, IV - a

Type - II

- a)  $\alpha \frac{1}{a^{n-1}}$   
 b) Radio active decay  
 c) Photochemical reactions  
 d)  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$

17. The rate of a reaction between A and B increases by a factor of 1000 times when the concentration of A is changed from  $0.1 \text{ mole litre}^{-1}$  to  $1 \text{ mole litre}^{-1}$ . The order of the reaction with respect of A is

- 1) 2      2) 1      3) 3      4) 4

**Solution:**

$$r = k[A]^n[B]^m \quad (1)$$

$$1000r = k[10A]^n[B]^m \quad (2)$$

$$\frac{2}{1} \Rightarrow n = 3$$

18. After how many seconds will the concentration of the reactant in a first order reaction be halved, if the rate constant is  $1.155 \times 10^{-3} \text{ sec}^{-1}$

- 1) 600      2) 100      3) 60      4) 10

**Hint;**  $t_{1/2} = \frac{0.693}{k}$

19. The rate of a certain reaction at different times is as follows

Time	0	10	20	30
Rate	$3.2 \times 10^{-2}$	$3.18 \times 10^{-2}$	$3.22 \times 10^{-2}$	$3.19 \times 10^{-2}$

The order of the reaction is

- 1) 1      2) zero      3) 2      4) Can not be predicted.

**Hint:** For zero order rate remains constant with time.

20. The half life of a reaction is 46 minutes when the initial concentration of the reactant is 0.4 moles/lit and 92 minutes when the initial concentration is 0.2 moles/lit. The order of the reaction is

- 1) Zero      2) 0.5      3) 2      4) 1

**Hint;** from given data  $t_{1/2} \propto \frac{1}{a}$  .so the reaction is the second order

21. In a first order reaction, 50 minutes time is taken for the completion of 93.75% of a reaction. Half life of the reaction is

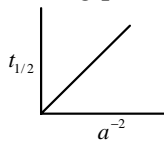
- 1) 25 min      2) 12.5 min      3) 20 min      4) 10 min

**Hint;**  $t_{93.75\%} = 4 t_{1/2}$ ,  $t_{1/2} = 50/4 = 12.5 \text{ min}$

22. Which order reaction obeys the expression  $t_{1/2} = \frac{1}{k.a}$  in chemical kinetics?

- 1) 0      2) 1      3) 2      4)

23. The following plot of,  $t_{1/2}$  Vs concentration



Corresponds to

- 1) Second order      2) Third order      3) First order      4) Zero order

**Hint;** For Third order  $t_{1/2} \propto \frac{1}{a^2}$  (or)  $t_{1/2} \propto a^{-2}$

24. If initial concentration is reduced to 1/4th in a zero order reaction, the time taken for half the reaction to complete

- 1) Remains same      2) becomes 4 times      3) becomes one-fourth      4) doubles

25. For a first order reaction  $t_{75\%}$  is 1386 seconds therefore, the specific rate constant in  $\text{Sec}^{-1}$  is.

- 1)  $10^{-3}$       2)  $10^{-2}$       3)  $10^{-9}$       4)  $10^{-5}$

**Hint:**  $t_{75\%} = 2t_{50\%}$  and  $t_{50\%} = \frac{0.693}{k}$

26. A first order reaction was commenced with 0.2 M solution of the reactants. If the molarity of the solution falls to 0.02M after 100 minutes the rate constant of the reaction is

- 1)  $2 \times 10^{-2} \text{ min}^{-1}$       2)  $2.3 \times 10^{-2} \text{ min}^{-1}$       3)  $4.6 \times 10^{-2} \text{ min}^{-1}$       4)  $2.3 \times 10^{-1} \text{ min}^{-1}$

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

27. For a reaction  $2A+3B \rightarrow \text{Products}$ , the rate law expression is given by  $\text{rate} = K (A)^1 (B)^2$ . The order of the reaction with respect to A,B and over all order of reaction are

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

28. In a first order reaction when  $\log \left[ \frac{a}{(a-x)} \right]$  is plotted against time the graph obtained is

- 1) a straight line whose slope is  $\frac{2.303}{k}$   
 2) a straight line whose slope is  $\frac{k}{2.303}$   
 3) a straight line whose slope is  $-\frac{k}{2.303}$   
 4) a straight line whose slope is  $-\frac{2.303}{k}$

**Hint:**  $k = \frac{2.303}{t} \log \frac{a}{a-x}$ ,  $\log \frac{a}{a-x} = \frac{kt}{2.303}$ ,  $y = mx$  where  $m = k/2.303$

Assertion - Reason type

- 1) Both (A) and (R) are true and (R) is the correct explanation of (A)  
 2) Both (A) and (R) are true and (R) is not the correct explanation of A  
 3) (A) is true but (R) is false  
 4) Both (A) and (R) are false
29. Assertion (A): For zero order reaction the rate of reaction does not decrease with time  
 Reason (R): For zero order reaction amount of substance reacted is proportional to time
30. Assertion (A): The order of reaction is equal to molecularity of simple reactions.  
 Reason (R): Molecularity of the reaction can not be fractional.
31. Assertion (A): Hydrolysis of cane sugar is a first order reaction  
 Reason (R): Water is present in large excess during hydrolysis
32. **Assertion (A):** The molecularity of a reaction is a whole number other than zero, but generally less than 3  
**Reason (R):** The order of a reaction is always whole number
33. **Assertion (A):** Molecularity of a reaction cannot be more than three  
**Reason (R):** Probability of simultaneous collision between more than three particles is very less
34. Assertion (A): Half life period is always inversely proportional to rate constant  
 Reason (R): Half life period is always independent of initial concentration.
35. Assertion (A): For a first order reaction  $t_{1/2}$  is independent of the initial concentration of reactants.  
 Reason (R): For a first order reaction  $t_{87.5\%}$  is thrice the  $t_{50\%}$
36. In a first order reaction, 20% reaction is completed in 24 minutes. The percentage of reactant remaining after 48 minutes is  
 1) 60 2) 64 3) 81 4) 80  
**Solution;** In First order reaction time required for completion of given % is same.  
 In 24min 20% completes. So 80 left. In another 24min 20% of 80 =  $20 \times 80 / 100 = 16$  react.  
 $\therefore 80 - 16 = 64\%$  left after 48 min.
37. 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) 20 hours 2) 10 hours 3) 7 1/2 hours 4) 5 hours  
**Solution;** For 1<sup>st</sup> order  $t_{99.9\%} = 10 t_{1/2} = 10 \times 45 = 450 \text{ min} = 7.5 \text{ hours}$ .
38. The concentration of the reactant A in the reaction AB 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  
 1)  $0.001 \text{ M}^{-2} \text{ s}^{-1}$  2)  $0.001 \text{ M}^{-2} \text{ s}^{-1}$  3)  $0.001 \text{ s}^{-1}$  4)  $0.001 \text{ Ms}^{-1}$   
**Hint;** As the change in concentration at regular time intervals is same, it is zero order.  
 Unit of k for zero order is  $\text{M S}^{-1}$
39. 99% of a first order reaction was completed in 32 min. When will 99.9% of the reaction complete?  
 1) 50 min 2) 46 min 3) 49 min 4) 48 min  
**Hint;**  $t_{99.9\%} : t_{99\%} = 3:2$

40. 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  
1) 1500 s    2) 500 s    3) 900 s    4) 600 s

**Hint;**  $k = \frac{2.303}{t} \log \frac{a}{a-x}$ ,  $k=0.693/t_{1/2}$

41. A reaction which is of first order w.r.t reactant A, has a rate constant is  $6 \text{ min}^{-1}$ . If we start with  $[A] = 0.5 \text{ mol.L}^{-1}$ , when would  $[A]$  reach the value of  $0.05 \text{ mol.L}^{-1}$ .  
1) 0.384 min    2) 15 min    3) 20 min    4) 3.84 min

**Hint;**  $k = \frac{2.303}{t} \log \frac{a}{a-x}$ ,

42. For a first order reaction  $A \rightarrow B$ , the reaction rate at reactant concentration of  $0.01 \text{ M}$  is found to be  $2.0 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$ . The half life period of the reaction is  
1) 220s    2) 30 s    3) 374 s    4) 347 s

**Hint;**  $\text{rate}=k[A]$ ,  $t_{1/2}=0.693/k$

43. In the case of a first order reaction, the ratio of the time required for 99.9% completion of the reaction to its half life is nearly  
1) 1    2) 10    3) 20    4) 8

44. Out of 300g substance [decomposes as per  $1^{\text{st}}$  order], how much will remain after 18 hr?  
( $t_{0.5} = 3 \text{ hr}$ )  
1) 4.6 gm    2) 5.6 gm    3) 9.2 gm    4) 6.4 gm

**Solution;** no, half lives  $n=18/3=6$ , amount left=initial amount  $(1/2)^n$   
Amount left= $300(1/2)^6=300/64=4.6\text{gm}$

45. 75% of a first order process is completed in 30 min. The time required for 93.75% completion of same process (in hr)?  
1) 1    2) 120    3) 2    4) 0.25

**Hint;**  $t_{75\%} : t_{93.75\%} = 1:2$

### KEY

- 1) 4    2) 1    3) 2    4) 2    5) 1    6) 1    7) 3    8) 3    9) 1    10) 2  
11) 1    12) 2    13) 3    14) 2    15) 4    16) 2    17) 3    18) 1    19) 2    20) 3  
21) 2    22) 3    23) 2    24) 3    25) 1    26) 2    27) 2    28) 2    29) 1    30) 2  
31) 1    32) 3    33) 1    34) 3    35) 2    36) 2    37) 3    38) 4    39) 4    40) 2  
41) 1    42) 4    43) 2    44) 1    45) 1