#### Class\_04

# **Chemical Kinetics**

## **Practice Questions**

- **1.** Rate of which of the following reactions can be determined easily?
  - (a) Rusting of iron in the presence of air and moisture
  - (b) Hydrolysis of starch
  - (c) Reaction of silver nitrate with sodium chloride
  - (d) All of the above
- **2.** For the reaction,

$$2X + Y \longrightarrow X$$

What will be the expression for instantaneous rate of the reaction?

(a) 
$$\frac{-d[X]}{2dt}$$
 (b)  $+\frac{1}{2}\frac{d[Y]}{dt}$   
(c)  $-\frac{1}{2}\frac{d[X_2Y]}{dt}$  (d) None of these

**3.** Choose the correct value of  $\frac{d[NH_3]}{dt}$  for the reaction,

$$N_{2} + 3H_{2} \longrightarrow 2NH_{3}$$

$$(a) -\frac{2}{3} \frac{d[H_{2}]}{dt} \qquad (b) \frac{2}{3} \frac{d[H_{2}]}{dt}$$

$$(c) \frac{3}{2} \frac{d[N_{2}]}{dt} \qquad (d) -\frac{3}{2} \frac{d[N_{2}]}{dt}$$

**4.** In a reaction,  $2x \rightarrow y$ , the concentration of x decreases from 3.0 M to 1.5 M in 4 min.

The rate of the reaction is

(a) 
$$0.187 \text{ M min}^{-1}$$
 (b)  $1.87 \text{ M min}^{-1}$   
(c)  $3.75 \times 10^{-1} \text{ M min}^{-1}$  (d)  $0.75 \text{ M min}^{-1}$ 

- - (c) It is a sequence of elementary reacting (1) D at (1) D at (2)
  - (*d*) Both (*a*) and (c)
- **6.** On mixing 1 dm<sup>3</sup> of 3M ethanol with 1 dm<sup>3</sup> of 2 M ethanoic acid, an ester is formed.

$$C_2H_5OH + CH_3COOH \longrightarrow CH_3COOC_2H_5 + H_2O$$

If each solution is diluted with an equal volume of water, the decrease in the initial rate would be (a) 0.5 times (b) 3 times (c) 0.25 times (d) 2 times

**7.** Which of the following rate expression is correct against its reaction?

(a) 
$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$
; Rate =  $k[NO]^2 [O_2]$   
(b)  $CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$ ;  
Rate =  $k[CHCl_3] [Cl_2]^{1/2}$ 

(c) 
$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH;$$
  
Rate =  $k[CH_3COOC_2H_5]^1 [H_2O]^0$ .

(d) All of the above

8. Consider the following reactions,

$$\begin{array}{ccc} \mathrm{O}_3 \mathchoice{\longleftarrow}{\leftarrow}{\leftarrow} \mathrm{O}_2 + \mathrm{O} \ (\mathrm{fast}) & \dots (\mathrm{i}) \\ \mathrm{O} + \mathrm{O}_3 \mathchoice{\longrightarrow}{\leftarrow}{\rightarrow}{\rightarrow} 2\mathrm{O}_2 \ (\mathrm{slow}) & \dots (\mathrm{ii}) \end{array}$$

The rate law expression should be

(a) 
$$r = k [O_3]^2 [O_2]^{-1}$$
 (b)  $r = k [O_3][O_2]$   
(c)  $r = k [O_3]^2$  (d)  $r = k [O_2]^{-1}$ 

**9.** Reaction of chloroform with chlorine is an example of fraction order reaction.

Its rate law expression is rate =  $k[CHCl_3][Cl_2]^{1/2}$ . If both are assumed in gaseous state and pressure is measured in bar, then units of rate and rate constant respectively are

(a) bar 
$$\min^{-1}$$
,  $\tan^2 \min^{-1}$ 

- (b) bar  $\min^{-1}$ , bar<sup>-1/2</sup>,  $\min^{-1}$
- (c)  $bar^{-1/2}$ ,  $min^{-1}$ ,  $bar^2 min^{-1}$
- (d) bar min<sup>-1</sup>, bar<sup>-1/2</sup> min<sup>-1</sup>
- **10.** The rate constant is numerically equal for three reactions of first, second and third order respectively. Which of the following is true?

(a) If 
$$[A] > 1; r_3 > r_2 > r_1$$
 (b) If  $[A] = 1; r_1 = r_2 = r_3$   
(c) If  $[A] < 1; r_1 > r_2 > r_3$  (d) All of the above

**11.** For the reaction,  $I^- + OCI^- \longrightarrow IO^- + CI^$ in aqueous medium, the rate of a reaction is given by  $\frac{d[IO^-]}{dt} = k \frac{[I^-][OCI^-]}{[OH^-]}$  the overall order of the reaction is

$$(a) -1 \qquad (b) \ 1 \qquad (c) \ 0 \qquad (d)$$

- **12.** The reaction,  $2N_2O_5 \implies 2N_2O_4 + O_2$  is
  - (a) bimolecular and first order
  - (b) unimolecular and second order
  - *(c)* bimolecular and second order
  - (d) unimolecular and first order
- **13.** Four reactions are given below. Which one of them is of zero order?
  - (a)  $PCl_5 \longrightarrow PCl_3 + Cl_2$
  - (b)  $2\text{FeCl}_3 + \text{SnCl}_2 \longrightarrow 2\text{FeCl}_2 + \text{SnCl}_4$
  - (c)  $H_2 + Cl_2 \xrightarrow{hv} 2HCl$

(d) 
$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

**14.** Which of the following graph is correct for a zero order reaction?





- 15. For a zero order reaction, a graph of concentration (along *y*-axis) and time (along *x*-axis) is linear with (*a*) a zero intercept and a +ve slope
  - (*b*) a zero intercept and a -ve slope
  - (c) a non-zero intercept and a -ve slope
  - (d) a non-zero intercept and a +ve slope
- **16.** The rate constant of the reaction,  $A \rightarrow B$  is  $0.6 \times 10^{-3}$ mole per litre per second. If the concentration of A is 5 M then, concentration of B after 20 min is (a) 1.08 M (b) 3.60 M (c) 0.36 M (d) 0.72 M
- **17.** A first order reaction has a rate constant of  $2.303 \times 10^{-3} \text{ s}^{-1}$ . The time required for 40 g of this reactant to reduce to 10 g will be [Given that  $\log_{10} 2 = 0.3010$ ] (a) 230.3 s (b) 301 s (c) 2000 s (d) 602 s
- **18.** For a first order reaction,

(a) 
$$t_{1/2} = \frac{k}{a}$$
 (b)  $t_{3/4} = 2t_{1/2}$   
(c)  $t_{1/2} = \frac{0.693}{2k}$  (d)  $t_{1/2} = k \times 0.693$ 

- **19.** If half-life of a substance is 36 minutes. The amount left after 2 hrs will be [Given  $(A_0) = 10$ g] (a) 1 g (b) 2 g (c) 3 g (d) 4 g
- **20.** 99% completion of a first order reaction takes place in 32 min. The time taken in 99.9% completion of the reaction will be

(a)	48 min	<i>(b)</i>	52 min
(c)	56 min	<i>(d)</i>	44 min

- **21.** The temperature coefficient of a reaction is *(a)* the ratio of rate constant at two temperatures
  - (b) the ratio of rate constant differing by 10° preferably 25°C and 35°C
  - (c) the rate constant at a fixed temperature
  - (d) None of the above
- **22.** A chemical reaction was carried out at 300 K and 280 K. The rate constant were found to be  $k_1$  and  $k_2$  respectively, then

(a) 
$$k_2 = 4k_1$$
 (b)  $k_2 = 0.25k_1$   
(c)  $k_2 = 2k_1$  (d)  $k_1 = 0.5k_1$ 

**23.** What is the activation energy (kJ/mol) for a reaction if its rate constant doubles when the temperature is raised from 300 K to 400 K ?

$(R = 8.314 \text{ Jmol}^{-1} \text{ K}^{-1}).$	
<i>(a)</i> 69.1	<i>(b)</i> 6.91
<i>(c)</i> 34.4	<i>(d)</i> 3.44

- **24.** In order to produce the effective collisions, the colliding molecules must have
  - (a) a certain minimum amount of energy
  - (b) proper orientation
  - (c) Both threshold energy and proper orientation
  - (d) energy equal to or greater than threshold energy
- **25** Higher order (>3) reactions are rare due to
  - *(a)* low probability of simultaneous collision of all the reacting species
  - *(b)* increase in entropy and activation energy as more molecules are involved
  - *(c)* shifting of equilibrium towards reactants due to elastic collisions
  - (d) loss of active species on collision

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

## **Hints & Solutions**

**1.** (*b*) Rate of only those chemical reactions can be determined easily which occurs at moderate speed, e.g. hydrolysis of starch, inversion of cane sugar etc.

**2.** (*a*) For the reaction,

 $2X + Y \longrightarrow X_2Y$ 

The instantaneous rate of the reaction is given as,

$$-\frac{d[X]}{2dt} = \frac{-d[Y]}{dt} = +\frac{d[X_2Y]}{dt}$$

**3.** (*a*) For the reaction,

$$N_{2} + 3H_{2} \longrightarrow 2NH_{3}$$
The instantaneous rate of reaction is given as
$$-\frac{d [N_{2}]}{dt} = -\frac{d [H_{2}]}{3dt} = +\frac{d [NH_{3}]}{2dt}$$

$$\therefore \qquad \frac{d [NH_{3}]}{dt} = -\frac{2}{3} \frac{d [H_{2}]}{dt}$$
**4.** (a) Rate of reaction  $= -\frac{1}{2} \frac{d [x]}{dt} = -\frac{1}{2} \frac{[1.5 - 3.0]}{4}$ 

$$= \frac{1.5}{8} = 0.187 \text{ M min}^{-1}$$

**6.** (*c*) For the given reaction,

$$C_{2}H_{5}OH + CH_{3}COOH \longrightarrow CH_{3}COOC_{2}H_{5} + H_{2}C$$
$$r = k[CH_{3}COOH][C_{2}H_{5}OH] \text{ or } r = k\left[\frac{n}{V}\right]\left[\frac{n}{V}\right]$$

Increasing volume (V) by twice (due to dilution) will reduce the rate by 4 times.

 $r = k' [O_3]^2 [O_2]^{-1} [k' = k \times K_{eq}]$ 

i.e.  $r = 0.25 k [CH_3COOH][C_2H_5OH]$ 

**8.** (a) Given, 
$$O_3 \rightleftharpoons O_2 + O$$
 (fast) ...(i)  
 $O + O_3 \longrightarrow 2O_2$  (Slow) ...(ii)

From Eq. (i) 
$$K_{eq} = \frac{[O_2][O]}{[O_3]}$$

or

or

$$[O] = \frac{K_{eq}[O_3]}{[O_2]}$$
m Eq. (ii)

From Eq.

rate law = 
$$k[O_3][O]$$
  
 $r = \frac{k[O_3][O_3]}{[O_2]}K_{eq}$ 

**9.** (*d*) Given, rate =  $k[CHCl_3] [Cl_2]^{1/2}$ 

$$\therefore \quad \text{Order} = 1 + \frac{1}{2} = \frac{3}{2}$$
  
$$\therefore \text{Units of rate constant} = \frac{\text{Units of rate}}{[\text{CHCl}_3] [\text{Cl}_2]^{1/2}}$$
$$= \frac{\text{bar min}^{-1}}{\text{bar}^{3/2}} = \text{bar}^{-1/2} \text{min}^{-1}$$

and units of rate is bar  $\min^{-1}$ .

(d) Consider a reaction A → Products
 Let r<sub>1</sub>, r<sub>2</sub> and r<sub>3</sub> are the rate for first, second and third order respectively.

- $\therefore$   $r_1 = k[A]^1$  for 1st order ...(i)
  - $r_2 = k[A]^2$  for 2nd order ...(ii)
  - $r_3 = k[A]^3$  for 3rd order ...(iii)

 $\therefore$  k is same in all the three cases.

Therefore, 
$$If[A]=1$$
,  $r_1 = r_2 = r_3$   
 $If[A]<1$ ,  $r_1 > r_2 > r_3$   
 $If[A]>1$ ,  $r_3 > r_2 > r_1$ 

**11.** (b): The rate of reaction is given by,

$$\frac{d[\mathrm{IO}^-]}{dt} = \frac{k[\mathrm{I}^-][\mathrm{OCI}^-]}{[\mathrm{OH}^-]}.$$

Therefore, overall order of reaction = 1 + 1 - 1 = 1

- 12. (a) The given reaction,
   i.e. 2N<sub>2</sub>O<sub>5</sub> → 2N<sub>2</sub>O<sub>4</sub> + O<sub>2</sub>
   occurs in two steps and, hence biomolecular reaction and the rate determining step is the slowest step which is of first order.
- **13.** (*c*) Among the given reactions, reaction between hydrogen and chlorine under influence of UV-light is an example of zero order reaction,

i.e. 
$$H_2 + Cl_2 \xrightarrow{hv} 2HCl$$

**14.** (*d*) For a zero order reaction,

 $[R] = (-k) t + [R]_0$ 

On comparing with equation of straight line; v = mx + c

$$y = mx + c$$
  
 $y = [R]$  concentration  
 $x = t$  (time)  
Slope  $(m) = -k$  (rate constant)

Intercept (c) =  $[R]_0$  (initial concentration)

Thus, the graph between conc. of reactant and time is given as,

...(i)



Time —

Moreover, on rearranging Eq. (i)  

$$\frac{[R] - [R]_0}{t} = -$$

$$\frac{[R] - [R]_0}{t} = -k$$

$$\frac{[R] - [R]_0}{t} = -kt^0$$
Rate  $\propto t^0$ 

Therefore, the graph between reaction rate and time is given as,



- **15.** (*c*) For a zero order reaction, a graph of concentration and time is linear with a non-zero intercept,  $[R]_0$  and a (–)ve slope, -k.
- **16.** (d) For a zero order reaction, unit of rate constant is  $(\text{mol } L^{-1} s^{-1})$ .

Hence, we can easily calculate the concentration of B after 20 min by the following formula,

...(i)

$$X = kt = 0.6 \times 10^{-3} \times 20 \times 60 = 0.72$$
 M

**17.** (*d*) For first order reaction,

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

Given:  $k = 2.303 \times 10^{-3} \text{ s}^{-1}$ ,

a = 40 g, a - x = 10 g

On substituting the given values in Eq. (i), we get

$$t = \frac{2.303}{2.303 \times 10^{-3}} \log \frac{40}{10}$$
$$= 10^3 \log 2^2 = 2 \times 10^3 \times \log 2$$
$$= 2 \times 10^3 \times 0.3010 = 602 \text{ s}$$

#### Alternative method

For first order reaction,

$$t_{1/2} = \frac{0.693}{k} \implies t_{1/2}(t_{50\%}) = \frac{0.693}{2.303 \times 10^{-3}} = 301s$$

Also,  $t_{75\%} = 2t_{50\%}$ 

- :.  $t_{75\%} = 2 \times 301 = 602 \text{ s}$
- **18.** (*b*) Decomposition of benzene diazonium chloride occur the following manner.

$$C_6H_5 \stackrel{+}{N} \equiv NC\overline{l} \longrightarrow C_6H_5Cl + N_2$$

The volume of nitrogen obtained shows the extent of decomposition of benzene diazonium chloride, so

$$a \propto V_{\infty} = 162 \text{ mL}$$
  
 $(a-x) \propto (V_{\infty} - V_t) \text{ mL}$ 

For first order reaction,

$$k = \frac{2.303}{t} \log_{10} \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$
  
$$k = \frac{2.303}{t} \log_{10} \frac{V_{\infty}}{V_t} \qquad (\because V_0 = 0)$$

At 20 min,

or

$$k = \frac{2.303}{20} \log_{10} \frac{162}{162 - 10} = \frac{2.303}{20} \log_{10} \frac{162}{152}$$
$$= 3.18 \times 10^{-3} \text{ min}^{-1} \approx 3.2 \times 10^{-3} \text{ min}^{-1}$$

19. (a) Given,

 $t_{1/2} = 36 \text{ min}, t = 2 \text{ hrs} = 120 \text{ min}, [A]_0 = 10 \text{ g}$ For first order reaction,

$$k = \frac{0.093}{t_{1/2}}$$

$$k = \frac{0.693}{36} = 0.01925$$
As, we know that,  $t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$ 
where,  $[A]_0 = \text{initial amount}$ 

$$[A] = \text{final amount}$$

$$120 = \frac{2.303}{0.019} \log \frac{[A]_0}{[A]}$$

$$\log 10 - \log[A] = 1 \Rightarrow 1 - \log[A] = 1$$

$$\log[A] = 0$$
Thus,  $[A] = 1$ g

**20.** (a) For first order reaction, 2202

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

$$\therefore k = \frac{2.303}{32 \min} \log \frac{a}{a - 0.99a} = 0.1439 \min^{-1}$$
  

$$\Rightarrow t = \frac{2.303}{0.1439} \log \frac{a}{a - 0.999a} = 48 \min$$

- **21.** (*b*) The temperature coefficient of a reaction is the ratio of rate constant differing by 10° preferably 25°C and 35°C.
- (b) For every 10°C rise, rate constant gets doubled. Hence, for every 20° C rise, rate constant will be 4 times. Therefore, according to the given statement, Temperature 280K 300K

Rate constant
$$k_2$$
 $k_1(4k_2)$ Thus, $k_1 = 4k_2$  $\Rightarrow$  $k_2 = 0.25k_1$ 

**23.** (b) Given, 
$$T_1 = 300 \text{ K}$$
,  $T_2 = 400 \text{ K}$ 

$$\Rightarrow \frac{k_2}{k_1} = \frac{2}{1} \Rightarrow \log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$
  
Thus,  $\log \frac{2}{1} = \frac{E_a}{2.303 \times 8.314} \left[ \frac{1}{300} - \frac{1}{400} \right]$   
 $E_a = 0.3010 \times 2.303 \times 8.314 \times 3 \times 400$   
 $E_a = 6.91 \text{ kJ mol}^{-1}$ 

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- **24.** (*d*) Energy  $\geq$  threshold energy and proper orientation both results in effective collisions.
- 25. (a) The main conditions for the occurrence of a reaction are proper orientation and effective collision of the reactants. Since, the chances of simultaneous collision with proper orientation between two species in high order reactions are very rare, so reaction with order greater than 3 are rare.