Chapter 4

Chemical Kinetics

Solutions

SECTION - A

Objective Type Questions

(Rate of Reaction, Factors Affecting the Reaction Rate)

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 between K_1, K_2 and K_3 is

(1) $2K_1 = K_2 = 4K_3$ (2) $K_1 = K_2 = K_3$

(3) $2K_1 = 4K_2 = K_3$ (4) $K_1 = 2K_2 = 3K_3$

Sol. Answer (1)

$$r = \frac{-d(N_2O_5)}{dt} = +\frac{1}{2}\frac{d(NO_2)}{dt} = \frac{2d(O_2)}{dt}$$

$$r \Rightarrow K_1[N_2O_5] = \frac{K_2[N_2O_5]}{2} = 2 \times K_3[N_2O_5]$$

$\therefore$ $2K_1 = K_2 = 4K_3$

2. For the reaction, $N_2O_4\,(g) \underset{K_2}{\overset{K_1}{\rightleftharpoons}} 2NO_2(g)$, the rate of disappearance of NO_2 will be

(1) $K_1[N_2O_4] - K_2[NO_2]^2$

(2) $2K_1[N_2O_4] - 2K_2[NO_2]^2$

(3) $K_2[NO_2]^2 - K_1[N_2O_4]$

(4) $2K_2[NO_2]^2 - 2K_1[N_2O_4]$

Sol. Answer (4)

$N_2O_4 \underset{K_2}{\overset{K_0}{\rightleftharpoons}} 2NO_2$

for reversible reaction $\boxed{r = r_f - r_b}$

(forward) (backward)

for disappearance of $NO_2 \rightarrow 2NO_2 \underset{K_1}{\overset{K_2}{\rightleftharpoons}} N_2O_4$

$r_f \Rightarrow K_2[NO_2]^2$

$r_b = K_1[N_2O_4]$

$r = K_2[NO_2]^2 - K_1[N_2O_4]$

For disappearance of NO_2

$\left[\frac{-d(NO_2)}{dt}\right]$

$r = (-)\frac{1}{2}\frac{d(NO_2)}{dt}$

$2r = \frac{-d(NO_2)}{dt}$

$\frac{-d(NO_2)}{dt} = 2[K_2[NO_2]^2 - K_1[N_2O_4]]$

$= \boxed{2K_2[NO_2]^2 - 2K_1[N_2O_4]}$

3. For the reaction A + B $\rightarrow$ products, it is found that order of A is 2 and the order of B is 3 in the rate expression. When the concentrations of both A and B are doubled the rate will increase by a factor

(1) 10 (2) 16 (3) 32 (4) 28

Sol. Answer (3)

$r_1 = K[A]^2[B]^3$

$r_2 = K[2A]^2[2B]^3$

$= 32K[A]^2[B]^3$

$= 32r_1$

4. Nitric oxide (NO) reacts with oxygen to produce nitrogen dioxide

$2NO_{(g)} + O_2(g) \rightarrow 2NO_{2(g)}$,

If the mechanism of reaction is

$NO + O_2 \underset{}{\overset{K}{\rightleftharpoons}} NO_3$ (fast)

$NO_3 + NO \xrightarrow{K_1} NO_2 + NO_2$ (slow)

then rate law is

(1) Rate = K′ [NO][O_2] (2) Rate = K′ [NO][O_2]^2 (3) Rate = K′ [NO]^2[O_2] (4) Rate = K′ [NO]^3[O_2]

Sol. Answer (3)

(i) $K = \frac{[NO_3]}{[NO][O_2]} \rightarrow \boxed{(NO_3) = K[NO][O_2]}$

(ii) $r = K[NO_3][NO]$

$= K[K[NO][O_2][NO]$

$\therefore$ K × K $\Rightarrow$ K′ (new constant)

$\boxed{r = K'[NO]^2[O_2]}$

5. If the volume of closed vessel in which the following simple reaction is carried out is reduced to one-third of original volume, the rate of reaction becomes

$2NO\ (g) + O_2\ (g) \longrightarrow 2NO_2\ (g)$

(1) One-third (2) Three times (3) Nine times (4) Twenty seven times

Sol. Answer (4)

$$V_2 = \frac{V_1}{3} \rightarrow C_2 = 3C_1 \qquad \left(\text{conc.} \propto \frac{1}{\text{volume}}\right)$$

$r_1 = K[NO]^2[O_2]$

$r_2 \Rightarrow K[3NO]^2(3O_2)$

$\Rightarrow 27K[NO]^2[O_2] = 27r_1$

6. For a gaseous phase reaction $2A + B_2 \rightarrow 2AB$, the following rate data was obtained at 300K

Rate of disappearance of B_2 (mole/litre min)	**Concentration [A]**	**[B_2]**
(i) 1.8×10^{-3}	0.015	0.15
(ii) 1.08×10^{-2}	0.09	0.15
(iii) 5.4×10^{-3}	0.015	0.45

The rate constant for the reaction is

(1) 0.5 mol^{-1} min^{-1} litre (2) 0.8 mol^{-1} min^{-1} litre (3) 1.5 $mole^{-1}$ min^{-1} litre (4) 2 mol^{-1} min^{-1} litre

Sol. Answer (2)

$$r = -\frac{1}{2}\frac{d(A)}{dt} = \underbrace{\boxed{-\frac{d(B_2)}{dt}}}_{\text{Rate of disappearance of } B_2} = +\frac{1}{2}\frac{d(AB)}{dt}$$

$$r = \frac{-d(B)_2}{dt} = 1.8\times10^{-3} = K[A]^x[B_2]^y$$

$1.8 \times 10^{-3} = K[0.015]^x[0.15]^y$ ...(i)

$1.08 \times 10^{-2} = K[0.09]^x[0.15]^y$ ...(ii)

$5.4 \times 10^{-3} = K[0.015]^x[0.45]^y$ ...(iii)

(i)/(ii) divide

$$\frac{1.8\times10^{-3} = K[0.015]^x[0.15]^y}{1.08\times10^{-2} = K[0.09]^x[0.15]^y}$$

$(0.16) = [0.16]^x$

i.e., [x = 1]

(i)/(iii) divide

$$\frac{1.8\times10^{-3} = K[0.015]^x[0.15]^y}{5.4\times10^{-3} = K[0.015]^x[0.45]^y}$$

$0.33 = (0.33)y$

$\therefore$ i.e., $\boxed{y = 1}$

$1.8 \times 10^{-3} = K[0.015]^1[0.15]^1$

$$K \Rightarrow \frac{1.8\times10^{-3}}{0.00225} \Rightarrow 0.8\ mol^{-1}\ min^{-1}\ litre$$

(Integrated Rate Equations, Pseudo First Order Reaction)

7. For a first order reaction, the time taken to reduce the initial concentration to a factor of $\frac{1}{4}$ is 10 minute If the reduction in concentration is carried out to a factor of $\frac{1}{16}$, then time required will be

(1) 10 minutes (2) 20 minutes (3) 40 minutes (4) 60 minutes

Sol. Answer (2)

$$K = \frac{2.303}{10}\log\frac{a}{\frac{1}{4}a} \quad ...(i)$$

$$K = \frac{2.303}{t}\log\frac{a}{\frac{1}{16}a} \quad ...(ii)$$

$$\frac{1}{t}\log 16 = \frac{1}{10}\log 4$$

$$\frac{1}{t}\log(4)^2 = \frac{1}{10}\log 4$$

$$\frac{1}{t}\times 2\log 4 = \frac{1}{10}\times\log 4$$

t = 20 minute

8. Consider the data below for a reaction $A \rightarrow B$

Time (sec)	0	10	20	30
Rate	1.60×10^{-2}	1.60×10^{-2}	1.60×10^{-2}	1.59×10^{-2}

From the above data the order of reaction is

(1) Zero (2) 1 (3) 2 (4) 3

Sol. Answer (1)

According to given table rate does not change with time which shows zero order reaction.

$r = K[A]^0$

9. For a homogeneous gaseous reaction $A \rightarrow B + C + D$, the initial pressure was P_0 while pressure after time 't' was P if $(P > P_0)$. The expression for the rate constant K is

(1) $K = \frac{2.303}{t}\log\left(\frac{2P_0}{3P_0 - P}\right)$ (2) $K = \frac{2.303}{t}\log\left(\frac{3P_0}{2P_0 - P}\right)$

(3) $K = \frac{2.303}{t}\log\left(\frac{P_0}{P_0 - P}\right)$ (4) $K = \frac{2.303}{t}\log\left(\frac{2P_0}{4P_0 - P}\right)$

Sol. Answer (1)

	A	$\rightarrow$	B	+ C	+	D
t = 0	P_0		0	0		0
t = t	$P_0 - X$		X	X		X

Total pressure $P_0 - X + X + X = P$

$$\boxed{P = P_0 + 2X} \rightarrow \boxed{P - P_0 = 2X} \rightarrow \boxed{X = \frac{P - P_0}{2}}$$

$$\boxed{K = \frac{2.303}{t}\log\frac{p_0}{P_0 - X}} \Rightarrow \frac{2.303}{t}\log\frac{p_0}{p_0 - \left(\frac{P - P_0}{2}\right)} = \frac{2.303}{t}\log\left(\frac{p_0}{3P_0 - P}\right)$$

10. Inversion of a sugar follows first order rate equation which can be followed by noting the change in rotation of the plane of polarization of light in the polarimeter. If r_∞, r_t and r_0 are the rotations at $t = \infty$, $t = t$ and $t = 0$ then, first order reaction can be written as

(1) $K = \frac{1}{t}\log_e\frac{r_1 - r_\infty}{r_0 - r_\infty}$

(2) $K = \frac{1}{t}\ln\frac{r_0 - r_\infty}{r_t - r_\infty}$

(3) $K = \frac{1}{t}\ln\frac{r_\infty - r_0}{r_t - r_\infty}$

(4) $K = \frac{1}{t}\ln\frac{r_\infty - r_t}{r_\infty - r_0}$

Sol. Answer (2)

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\left[K = \frac{2.303}{t}\log\frac{r_0 - r_8}{r_t - r_8}\right]$$

11. The rate constant of the production of 2B(g) by the reaction, $A(g) \xrightarrow{\Delta} 2B(g)$ is 2.48×10^{-4} s^{-1}

A 1 : 1 molar ratio of A to B in the reaction mixture is attained after

(1) 26.25 minute

(2) 27.25 minute

(3) 28.25 minute

(4) 0 minute

Sol. Answer (2)

	$A(g) \xrightarrow{\Delta} 2B(g)$	
$t = 0$	1	0
$t = t$	$1 - x$	$2x$

Given $\frac{1-x}{2x} = \frac{1}{1}$

$1 - x = 2x$

$x = \frac{1}{3}$

$K = 2.48 \times 10^{-4}$ S^{-1} → First order

$$K = \frac{2.303}{t}\log\frac{1}{1-x} = \frac{2.303}{t}\log\frac{1}{1-\frac{1}{3}} = 2.48\times10^{-4}$$

$$2.48\times10^{-4} = \frac{2.303}{t}\log\frac{3}{2}$$

$$t = \frac{2.303}{2.48\times10^{-4}}(\log3 - \log2) = \frac{2.303}{2.48\times10^{-4}} \times \frac{[0.4770 - 0.30]}{60}$$

$$\boxed{t = 27.25 \text{ minutes}}$$

12. Two substances A and B are present such that $[A]_0 = 4[B]_0$ and half life of A is 5 minute and that of B is 15 minute. If they start decaying at the same time following first order kinetics how much time will the concentration of both of them would be the same?

(1) 15 minute (2) 10 minute (3) 5 minute (4) 12 minute

Sol. Answer (1)

$[A]_0 = 4[B]_0 \rightarrow$ $[A]_{t_{½}}$ = 5 min. $\rightarrow$ fast

$[B]_{t_{½}}$ = 15 min. $\rightarrow$ slow

Half life for first order reaction doesn't depend on initial concentration, so, rate of reaction calculated by slow reaction concentration of [A] = [B]) at same initial time = 15 min.

or

$$[A]_t = [A]_0 e^{-K_1 t} \quad \Big| \quad \therefore (A)_0 = 4[B]_0$$
$$[B]_t = [B]_0 e^{-K_2 t} \quad \Big| \quad \boxed{[A]_t = [B]_t}$$

$$[A]_0 e^{-K_1 t} = [B]_0 e^{-K_2 t}$$

$$4[B]_0 e^{-K_1 t} = [B]_0 e^{-K_2 t}$$

$$\frac{e^{-K_1 t}}{e^{-K_2 t}} = \frac{1}{4} \longrightarrow e^{K_2 t - K_1 t} = \frac{1}{4}$$

or $e^{K_1 t - K_2 t} = 4$

$K_1 t = K_2 t = \log_e 4 = 2.303 \log_{10} 4$

$$\frac{0.693}{(t_{1/2})_1} t - \frac{0.693}{(t_{1/2})_2} t = 2.303 \times 0.3010 \times 2$$

$$\frac{0.693}{5} t - \frac{0.693}{15} t = 2.303 \times 0.3010 \times 2$$

$$\frac{0.693}{5} t \left[1 - \frac{1}{3}\right] = 2.303 \times 0.3010 \times 2$$

$$\frac{t}{5} \times \frac{2}{3} = 2 \qquad \boxed{t = 15 \text{ minute}}$$

13. The reaction A $\longrightarrow$ B follows first order kinetics. The time taken for 0.80 mole of A to produce 0.60 mole of B is 1 hour. What is the time taken for conversion of 0.90 mole of A to produce 0.675 mole of B?

(1) 1 hour (2) 30 min (3) 15 min (4) 5 min

Sol. Answer (1)

	A	B		A	B
t = 0	0.80	0	t = 0	0.90	0
t = 1 hr	0.80 – x	0.60	t = ?	0.90 – x	0.675

0.80 – x = 0.60	0.90 – x = 0.675
x = 0.80 – 0.60	x = 0.90 – 0.675
$\Rightarrow$ 0.20	x = 0.225

$$k = \frac{2.303}{1}\log\frac{0.80}{0.20} \;\Big|\; k = \frac{2.303}{t}\log\frac{0.90}{0.225}$$

divide

$$\frac{k = \frac{2.303}{1}\log\frac{0.80}{0.20}}{k = \frac{2.303}{t}\log\frac{0.90}{0.225}} \Rightarrow \frac{1}{t}\log 4 = \log 4$$

$t \Rightarrow 1$ hr

14. If, A $\xrightarrow{K_1 = 2 \times 10^3\ s^{-1}}$ B
A $\xrightarrow{K_2 = 6 \times 10^3\ s^{-1}}$ C

find B%

(1) 25% (2) 50% (3) 75% (4) 80%

Sol. Answer (1)

$$\text{Percentage B} = \frac{k_1}{k_1 + k_2} = \frac{2\times10^3}{2\times10^3 + 6\times10^3} = \frac{2\times10^3}{8\times10^3} = 25\%$$

(Effect of Temperature on the reaction rate, Effect of Catalyst)

15. The graph between the log K versus $\frac{1}{T}$ is a straight line. The slope of the line is

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

(3) $\frac{2.303R}{E_a}$ (4) $\frac{E_a}{2.303R}$

Sol. Answer (2)

$$\log K = \log A - \left(\frac{E_a}{2.303R}\right)\frac{1}{T}$$

$y = c - mx$

$\therefore \quad x = \frac{1}{T}$

$$m = -\frac{E_a}{2.303R} = \text{slope}$$

16. The temperature coefficient for most of the reaction lies between

(1) 1 & 3 (2) 2 & 3

(3) 1 & 4 (4) 2 & 4

Sol. Answer (2)

When temperature rises by 10°C then rate of reaction becomes double / triple (2/3) known as temperature coefficient.

17. Which of the following is correct?

(1) $\log\frac{K_2}{K_1}=\frac{E_a}{2.303}\left[\frac{\Delta T}{T_1T_2}\right]$

(2) For zero order $t_{1/2}$ is inversely proportional to initial concentration

(3) Catalyst decreases the activation energy

(4) All of these

Sol. Answer (3)

1. $\log\frac{K_2}{K_1}=\frac{E_a}{2.303R}\left[\frac{\Delta T}{T_1T_2}\right]$
2. for zero order $t_{1/2}\propto a$
3. catalyst $\rightarrow \boxed{E_a\downarrow = r\uparrow}$

18. The rate constant of a reaction is 1.5×10^7 s^{-1} at 50°C and 4.5×10^7 s^{-1} at 100°C. What is the value of activation energy?

(1) 2.2×10^3 J mol^{-1} (2) 2300 J mol^{-1} (3) 2.2×10^4 J mol^{-1} (4) 220 J mol^{-1}

Sol. Answer (3)

$$\log\frac{4.5\times10^7}{1.5\times10^7}=\frac{E_a}{2.303\times8.314}\left[\frac{373-323}{373\times323}\right]$$

$$\begin{cases}T_1=50+273=323\\T_2=100+273=373\end{cases}$$

$$\log3=\frac{E_a}{2.303\times8.314}\left[\frac{50}{373\times323}\right]$$

$$\frac{0.4770\times2.303\times8.314\times373\times323}{50}=E_a$$

$E_a = 22007$ J $mol^{-1}\approx 2.2\times10^4$

19. In Arrhenius equation, $k=Ae^{\frac{-E_a}{RT}}$, A may not be termed as rate constant

(1) When 100% reactant will convert into the product

(2) When the temperature becomes infinite

(3) When the fraction of molecule crossing over the energy barrier becomes unity

(4) At very low temperature

Sol. Answer(4)

$K=Ae^{\frac{-E_a}{RT}}$

1. 100% reactant will convert into the product i.e., $[E_a = 0]$

   So, $K = Ae^\circ \rightarrow [K = A]$

2. T = 8 $\quad K=Ae^{\frac{-E_a}{R\times8}}$

   $K = Ae^0 \rightarrow (K = A)$

3. Fraction of molecule crossing over the energy barrier becomes unity (100%) $\rightarrow (E_a = 0)$.

   So, again (K = A)

4. At very low temperature $K=Ae^{-E_a/RT}$

   $\boxed{K\neq A}$

20. If the rate of reaction increases by 27 times, when temperature is increased by 30 K, then temperature coefficient of the reaction is

(1) 3 (2) 2 (3) 1 (4) 2.5

Sol. Answer (1)

$= 2^{\frac{T_2-T_1}{10}} = 2^{\frac{30-0}{10}} \Rightarrow 2^3 \Rightarrow 8$

$= 3^{\frac{T_2-T_1}{10}} = 3^{\frac{30-0}{10}} \Rightarrow 3^3 \Rightarrow 27 \rightarrow$ i.e., temperature coefficient is 3.

SECTION - B

Previous Years Questions

1. When initial concentration of the reactant is doubled, the half-life period of a zero order reaction **[NEET-2018]**

(1) Is halved (2) Is doubled

(3) Remains unchanged (4) Is tripled

Sol. Answer (2)

Half life of zero order

$t_{1/2} = \frac{[A_0]}{2K}$

$t_{1/2}$ will be doubled on doubling the initial concentration.

2. The correct difference between first and second order reactions is that

(1) The rate of a first-order reaction does not depend on reactant concentrations; the rate of a second-order reaction does depend on reactant concentrations

(2) The half-life of a first-order reaction does not depend on $[A]_0$; the half-life of a second-order reaction does depend on $[A]_0$

(3) The rate of a first-order reaction does depend on reactant concentrations; the rate of a second-order reaction does not depend on reactant concentrations

(4) A first-order reaction can catalyzed; a second-order reaction cannot be catalyzed **[NEET-2018]**

Sol. Answer (2)

- For first order reaction, $t_{1/2} = \frac{0.693}{k}$, which is independent of initial concentration of reactant.
- For second order reaction, $t_{1/2} = \frac{1}{k[A_0]}$, which depends on initial concentration of reactant.

3. A first order reaction has a specific reaction rate of 10^{-2} s^{-1}. How much time will it take for 20 g of the reactant to reduce to 5 g? **[NEET-2017]**

(1) 238.6 second (2) 138.6 second

(3) 346.5 second (4) 693.0 second

Sol. Answer (2)

$t_{1/2} = \frac{0.693}{10^{-2}}$ second

For the reduction of 20 g of reactant to 5 g, two $t_{1/2}$ is required.

$\therefore \quad t = 2 \times \frac{0.693}{10^{-2}}$ second = 138.6 second

4. Mechanism of a hypothetical reaction $X_2 + Y_2 \rightarrow 2XY$ is given below :

(i) $X_2 \rightarrow X + X$ (fast)

(ii) $X + Y_2 \rightleftharpoons XY + Y$ (slow)

(iii) $X + Y \rightarrow XY$ (fast)

The overall order of the reaction will be **[NEET-2017]**

(1) 1 (2) 2

(3) 0 (4) 1.5

Sol. Answer (4)

The solution of this question is given by assuming step (i) to be reversible which is not given in question

Overall rate = Rate of slowest step (ii)

$= k[X]\ [Y_2]$ ...(1)

k = rate constant of step (ii)

Assuming step (i) to be reversible, its equilibrium constant,

$$k_{eq} = \frac{[X]^2}{[X_2]} \Rightarrow [X] = k_{eq}^{\frac{1}{2}}[X_2]^{\frac{1}{2}} \quad ...(2)$$

Put (2) in (1)

Rate = $kk_{eq}^{\frac{1}{2}}[X_2]^{\frac{1}{2}}[Y_2]$

Overall order = $\frac{1}{2} + 1 = \frac{3}{2}$

5. The decomposition of phosphine (PH_3) on tungsten at low pressure is a first-order reaction. It is because the **[NEET-Phase-2-2016]**

(1) Rate is proportional to the surface coverage

(2) Rate is inversely proportional to the surface coverage

(3) Rate is independent of the surface coverage

(4) Rate of decomposition is very slow

Sol. Answer (1)

Rate is proportion to the surface coverage

6. The addition of a catalyst during a chemical reaction alters which of the following quantities? **[NEET-2016]**

(1) Activation energy

(2) Entropy

(3) Internal energy

(4) Enthalpy

Sol. Answer (1)

Catalyst decreases the activation energy and thus increases the rate of reaction.

7. The rate of a first-order reaction is 0.04 mol l^{-1} s^{-1} at 10 seconds and 0.03 mol l^{-1} s^{-1} at 20 seconds after initiation of the reaction. The half-life period of the reaction is **[NEET-2016]**

(1) 54.1 s (2) 24.1 s (3) 34.1 s (4) 44.1 s

Sol. Answer (2)

$$K = \frac{2.303}{10} \times \log \frac{0.04}{0.03} = \frac{2.303 \times 0.124}{10}$$

$$\therefore \quad t_{1/2} = \frac{2.303 \times 0.301 \times 10}{2.303 \times 0.124}$$

$$= 24.27 \text{ s}$$

$$\therefore \quad t_{1/2} \approx 24.1 \text{ s}$$

8. The rate constant of the reaction A $\longrightarrow$ B is 0.6×10^{-3} mole per second. If the concentration of A is 5 M, then concentration of B after 20 minutes is **[Re-AIPMT-2015]**

(1) 0.36 M (2) 0.72 M (3) 1.08 M (4) 3.60 M

Sol. Answer (2)

Order of reaction is zero as unit of rate constant is mole per second.

$$\therefore \quad K = \frac{[A]_0 - [A]}{t}$$

$$\Rightarrow \quad 0.6 \times 10^{-3} = \frac{5 - [A]}{20 \times 60}$$

$$\therefore \quad [A] = 5 - 0.72$$

$\therefore$ Concentration of B after 20 minutes is 0.72 M.

9. The activation energy of a reaction can be determined from the slope of which of the following graphs? **[AIPMT-2015]**

(1) $\frac{T}{\ln K}$ vs $\frac{1}{T}$ (2) ln K vs T (3) $\frac{\ln K}{T}$ vs T (4) ln K vs $\frac{1}{T}$

Sol. Answer (4)

$$\because \quad K = Ae^{-E_a/RT}$$

$$\text{i.e. } \ln K = \ln A - \frac{E_a}{R} \times \frac{1}{T}$$

10. When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is **[AIPMT-2015]**

(1) More than zero but less than first (2) Zero

(3) First (4) Second

Sol. Answer (3)

$t_{1/2} \propto \frac{1}{(a_0)^{n-1}}$; where n is order of reaction.

11. A reaction having equal energies of activation for forward and reverse reactions has **[NEET-2013]**

(1) $\Delta G = 0$ (2) $\Delta H = 0$ (3) $\Delta H = \Delta G = \Delta S = 0$ (4) $\Delta S = 0$

Sol. Answer (2)

$\Delta H = (E_a)_f - (E_a)_b$

$\therefore \quad (E_a)_f = (E_a)_b \rightarrow [\Delta H = 0]$

12. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 20°C to 35°C? ($R = 8.314\ J\ mol^{-1}K^{-1}$) **[NEET-2013]**

(1) 269 kJ mol^{-1} (2) 34.7 kJ mol^{-1} (3) 15.1 kJ mol^{-1} (4) 342 kJ mol^{-1}

Sol. Answer (2)

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$\because \quad K_2 = 2K_1$

$$\Rightarrow \quad \log\frac{2K_1}{K_1} = \frac{E_a}{2.303\times 8.314}\left[\frac{1}{293} - \frac{1}{308}\right] \Rightarrow \qquad \log 2 = \frac{E_a}{2.303\times 8.314}\left[\frac{308-293}{293\times 308}\right]$$

$$\therefore \quad E_a = \frac{0.3010\times 2.303\times 8.314\times 293\times 308}{15} = 34.7 \text{ kJ/mol}$$

13. In a zero order reaction for every 10° rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C, the rate of the reaction will become **[AIPMT (Prelims)-2012]**

(1) 64 times (2) 128 times (3) 256 times (4) 512 times

Sol. Answer (4)

$$K = 2^{\frac{T_2-T_1}{10}} = 2^{\frac{100-10}{10}} = 2^{\frac{90}{10}} = 2^9 = 512 \text{ times}$$

14. In a reaction, A + B $\rightarrow$ Product, rate is doubled when the concentration of B is doubled, and rate increases by a factor of 8 when the concentrations of both the reactants (A and B) are doubled, rate law for the reaction can be written as **[AIPMT (Prelims)-2012]**

(1) Rate = k[A] [B] (2) Rate = $k[A]^2[B]$ (3) Rate = k[A] $[B]^2$ (4) Rate = $k[A]^2[B]^2$

Sol. Answer (2)

$r_1 = k[A]^x[B]^y$

$2r_1 = k[A]^x[2B]^y$ ...(i) w.r.t. (B) order y = 1

$8r_1 = k[2A]^x[2B]^y$ ...(ii) w.r.t. (A) order x = 2

$r = k[2A]^2[2]^1$

$\Rightarrow \quad 8k[A]^2B = 8r_1$

15. Which one of the following statements for the order of a reaction is incorrect? **[AIPMT (Prelims)-2011]**

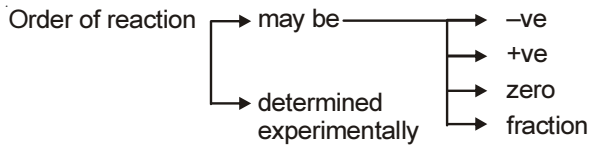
(1) Order of reaction is always whole number

(2) Order can be determined only experimentally

(3) Order is not influenced by stoichiometric coefficient of the reactants

(4) Order of reaction is sum of power to the concentration terms of reactants to express the rate of reaction

Sol. Answer (1)



16. The unit of rate constant for a zero order reaction is **[AIPMT (Mains)-2011]**

(1) $L^2\ mol^{-2}\ s^{-1}$ (2) s^{-1}

(3) $mol\ L^{-1}\ s^{-1}$ (4) $L\ mol^{-1}\ s^{-1}$

Sol. Answer (3)

$K = (conc.)^{1 - order}$ $\because$ order = 0

$K = (conc.)^{1 - 0}$

$mol\ L^{-1}\ s^{-1}$

17. The half life of a substance in a certain enzyme- catalysed reaction is 138 s. The time required for the concentration of the substance to fall from 1.28 mg L^{-1} to 0.04 mg L^{-1} is **[AIPMT (Mains)-2011]**

(1) 690 s (2) 276 s

(3) 414 s (4) 552 s

Sol. Answer (1)

Enzyme catalysed reaction is first order.

$$K = \frac{2.303}{t}\log\frac{[R]_0}{[R]_t}$$

$$\Rightarrow \frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log\frac{1.28}{0.04}$$

$$\Rightarrow \frac{0.693}{138} = \frac{2.303}{t}\log 32$$

$$\therefore t = \frac{2.303\times 138}{0.693}\times\log(2)^5 = 690.2\,s$$

18. For the reaction, $N_2O_5(g) \rightarrow 2NO_2(g) + 1/2\ O_2(g)$, the value of rate of disappearance of N_2O_5 is given as 6.25×10^{-3} mol $L^{-1}s^{-1}$. The rate of formation of NO_2 and O_2 is given respectively as **[AIPMT (Prelims)-2010]**

(1) 6.25×10^{-3} mol $L^{-1}s^{-1}$ & 6.25×10^{-3} mol $L^{-1}s^{-1}$

(2) 1.25×10^{-2} mol $L^{-1}s^{-1}$ & 3.125×10^{-3} mol $L^{-1}s^{-1}$

(3) 6.25×10^{-3} mol $L^{-1}s^{-1}$ & 3.125×10^{-3} mol $L^{-1}s^{-1}$

(4) 1.25×10^{-2} mol $L^{-1}s^{-1}$ & 6.25×10^{-3} mol $L^{-1}s^{-1}$

Sol. Answer (2)

$$r = \frac{(-)d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = \frac{2d[O_2]}{dt}$$

$$\Rightarrow 6.25\times10^{-3} = \frac{1}{2}\frac{d[NO_2]}{dt}$$

rate of formation of (NO_2), $\frac{d(NO_2)}{dt} = 2\times6.25\times10^{-3} = 1.25 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}$

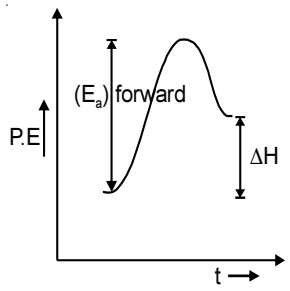
rate of formation of (O_2), $\frac{d[O_2]}{dt} = \frac{6.25\times10^{-3}}{2} = 3.125\times10^{-3}\,mol L^{-1}\,s^{-1}$

19. For an endothermic reaction, energy of activation is E_a and enthalpy of reaction is ΔH (both of these in kJ/mol). Minimum value of E_a will be **[AIPMT (Prelims)-2010]**

(1) Less than ΔH (2) Equal to ΔH (3) More than ΔH (4) Equal to zero

Sol. Answer (3)

For endothermic reaction,



i.e., $\boxed{(E_a) > \Delta H}$

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

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

Based on the above data which one of the following is correct ? **[AIPMT (Prelims)-2010]**

(1) Rate = $K[A]^2[B]$ (2) Rate = $K[A][B]$

(3) Rate = $K[A]^2[B]^2$ (4) Rate = $K[A][B]^2$

Sol. Answer (4)

According to table When concentration of (A) = constant (II, III)

then (B) = doubles, r = four times.

i.e., order w.r.t. (B) = 2

When concentration of (B) = constant (I & IV)

(A) = four times, r = four times.

i.e., order w.r.t. (A) = 1

$\boxed{r = k[A]^1[B]^2}$

21. The rate of the reaction, $2NO + Cl_2 \longrightarrow 2NOCl$ is given by the rate equation rate = $k[NO]^2[Cl_2]$

The value of the rate constant can be increased by **[AIPMT (Mains)-2010]**

(1) Increasing the temperature (2) Increasing the concentration of NO

(3) Increasing the concentration of the Cl_2 (4) Doing all of these

Sol. Answer (1)

$r = K[NO]^2[Cl_2]$

On increasing temperature → (K) increases

22. For the reaction, $N_2 + 3H_2 \rightarrow 2NH_3$,

if $\frac{d[NH_3]}{dt} = 2\times10^{-4}$ mol L^{-1} s^{-1}, the value of $\frac{-d[H_2]}{dt}$ would be **[AIPMT (Prelims)-2009]**

(1) 4×10^{-4} mol L^{-1} s^{-1} (2) 6×10^{-4} mol L^{-1} s^{-1}

(3) 1×10^{-4} mol L^{-1} s^{-1} (4) 3×10^{-4} mol L^{-1} s^{-1}

Sol. Answer (4)

$$r = -\frac{d[N_2]}{dt} = \frac{(-)d[H_2]}{3\ dt} = \frac{+1d[NH_3]}{2\ dt}$$

$$\frac{-1}{3}\frac{d[H_2]}{dt} = \frac{2\times10^{-4}}{2}$$

$$\frac{-d[H_2]}{dt} = 3\times10^{-4}\,mol\,L^{-1}\ s^{-1}$$

23. In the reaction,

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+ \rightarrow 3Br_2(l) + 3H_2O(l)$$

The rate of appearance of bromine (Br_2) is related to rate of disappearance of bromide ions as following

[AIPMT (Prelims)-2009]

(1) $\frac{d(Br_2)}{dt} = -\frac{5}{3}\frac{d(Br^-)}{dt}$ (2) $\frac{d(Br_2)}{dt} = \frac{5}{3}\frac{d(Br^-)}{dt}$

(3) $\frac{d(Br_2)}{dt} = \frac{3}{5}\frac{d(Br^-)}{dt}$ (4) $\frac{d(Br_2)}{dt} = -\frac{3}{5}\frac{d(Br^-)}{dt}$

Sol. Answer (4)

$$r = \frac{-d[BrO_3]^-}{dt} = \frac{-1}{5}\frac{d[Br^-]}{dt} = \frac{-1}{6}\frac{d[H^+]}{dt} = +\frac{1}{3}\frac{d[Br_2]}{dt}$$

$$\therefore \quad \frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$$

24. Half life period of a first-order reaction is 1386 seconds. The specific rate constant of the reaction is

[AIPMT (Prelims)-2009]

(1) $0.5 \times 10^{-2}\ s^{-1}$ (2) $0.5 \times 10^{-3}\ s^{-1}$

(3) $5.0 \times 10^{-2}\ s^{-1}$ (4) $5.0 \times 10^{-3}\ s^{-1}$

Sol. Answer (2)

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{1386} = 0.5\times10^{-3}\ s^{-1}$$

25. For the reaction A + B $\longrightarrow$ Products, it is observed that

(a) On doubling the initial concentration of A only, the rate of reaction is also doubled and

(b) On doubling the initial concentrations of both A and B, there is a change by a factor of 8 in the rate of the reaction.

The rate of this reaction is given by **[AIPMT (Prelims)-2009]**

(1) Rate = k [A] $[B]^2$ (2) Rate = k $[A]^2[B]^2$

(3) Rate = k [A] [B] (4) Rate = k$[A]^2$[B]

Sol. Answer (1)

$r_1 = k[A]^x[B]^y$

$2r_1 = k[2A]^x[B]^y \rightarrow$ *i.e.*, order w.r.t. (A) $\rightarrow 1$; (x = 1)

$8r_1 = k[2A]^1[2B]^y \rightarrow$ *i.e.*, order w.r.t. (B) $\rightarrow 2$; (y = 2)

$= k[2A]^1[2B]^2 = 8r_1$

$\boxed{r = k[A][B]^2}$

26. The rate constants k_1 and k_2 for two different reactions are $10^{16}\ e^{-2000/T}$ and $10^{15}\ e^{-1000/T}$ respectively. The temperature at which $k_1 = k_2$ is **[AIPMT (Prelims)-2008]**

(1) $\frac{1000}{2.303}K$ (2) 1000 K

(3) $\frac{2000}{2.303}K$ (4) 2000 K

Sol. Answer (1)

$\because \quad k = Ae^{-E_a/RT}$;

$\therefore \quad k_1 = 10^{16}.e^{\frac{-2000}{T}} \ \& \ k_2 = 10^{15}.e^{\frac{-1000}{T}}$

$\therefore \quad k_1 = k_2$

$\therefore \quad 10^{16}.e^{\frac{-2000}{T}} = 10^{15}.e^{\frac{-1000}{T}}$

$\Rightarrow \quad 10 = \frac{e^{\frac{-1000}{T}}}{e^{\frac{-2000}{T}}}$

$\Rightarrow \quad 10 = e^{\frac{-1000}{T}+\frac{2000}{T}}$

$\Rightarrow \quad 10 = e^{\frac{1000}{T}}$

$\Rightarrow \quad \log_e 10 = \log_e e^{\frac{1000}{T}}$

$\Rightarrow \quad \log_e 10 = \frac{1000}{T}\log_e e$

$\Rightarrow \quad 2.303\log_{10} 10 = \frac{1000}{T}$

$\boxed{T = \frac{1000}{2.303}\ \text{kelvin}}$

27. The bromination of acetone that occurs in acid solution is represented by this equation

$CH_3COCH_3(aq) + Br_2(aq) \rightarrow CH_3COCH_2Br(aq) + H^+(aq) + Br^-(aq)$

These kinetic data were obtained for given reaction concentrations

Initial concentrations, M			Initial rate, disappearance of Br_2, M s^{-1}
$[CH_3COCH_3]$	$[Br_2]$	$[H^+]$	
0.30	0.05	0.05	5.7×10^{-5}
0.30	0.10	0.05	5.7×10^{-5}
0.30	0.10	0.10	1.2×10^{-4}
0.40	0.05	0.20	3.1×10^{-4}

Based on these data, the rate equation is **[AIPMT (Prelims)-2008]**

(1) Rate = $k[CH_3COCH_3][Br_2][H^+]$

(2) Rate = $k[CH_3COCH_3][H^+]$

(3) Rate = $k[CH_3-\overset{\overset{O}{\|}}{C}-CH_3][Br_2]$

(4) Rate = $k[CH_3COCH_3][Br_2][H^+]^2$

Sol. Answer (2)

Given data shows that when concentration of CH_3COCH_3 & H^+ are constant and $[Br_2]$ doubles but rate of reaction does not changed it means rate of reaction independent on concentration of (Br_2).

So, $r = K[CH_3COCH_3][H^+]$

28. In a first-order reaction $A \longrightarrow B$, if K is rate constant and initial concentration of the reactant A is 0.5M then the half-life is **[AIPMT (Prelims)-2007]**

(1) $\frac{\ln 2}{K}$ (2) $\frac{0.693}{0.5K}$ (3) $\frac{\log 2}{K}$ (4) $\frac{\log 2}{K\sqrt{0.5}}$

Sol. Answer (1)

For first order reaction $t_{1/2}$ is independent of initial concentration.

$$t_{1/2} = \frac{0.693}{K} = \frac{2.303 \log 2}{K} = \frac{\ln 2}{K}$$

29. The reaction of hydrogen and iodine monochloride is given as

$$H_{2(g)} + 2ICl_{(g)} \rightarrow 2HCl_{(g)} + I_{2(g)}$$

This reaction is of first order with respect to $H_{2(g)}$ and $ICl_{(g)}$, following mechanisms were proposed

Mechanism A:

$H_{2(g)} + 2ICl_{(g)} \rightarrow 2HCl_{(g)} + I_{2(g)}$

Mechanism B:

$H_{2(g)} + ICl_{(g)} \rightarrow HCl_{(g)} + HI_{(g)}$; slow

$HI_{(g)} + ICl_{(g)} \rightarrow HCl_{(g)} + I_{2(g)}$; fast

Which of the above mechanism(s) can be consistent with the given information about the reaction?

[AIPMT (Prelims)-2007]

(1) A only (2) B only (3) Both (1) & (2) (4) Neither (1) nor (2)

Sol. Answer (2)

Mechanism (B) can be consistent because it involves slow step which is rate determining step, showing order one with respect to both H_2 & ICl.

30. If 60% of a first order reaction was completed in 60 minutes, 50% of the same reaction would be completed in approximately (log 4 = 0.60, log 5 = 0.69) **[AIPMT (Prelims)-2007]**

(1) 40 minutes (2) 50 minute

(3) 45 minutes (4) 60 minutes

Sol. Answer (3)

$$K = \frac{2.303}{60}\log\frac{100}{100-60} \quad ...(i)$$

$$K = \frac{2.303}{t}\log\frac{100}{100-50} \quad ...(ii)$$

Dividing equation (i) by equation (ii)

$$\frac{K}{K} = \frac{\frac{2.303}{60}\times\log\frac{100}{40}}{\frac{2.303}{t}\times\log\frac{100}{50}}$$

$$\Rightarrow \quad \frac{1}{t}\log 2 = \frac{1}{60}\log\frac{10}{4}$$

$$\Rightarrow \quad \frac{1}{t}\times 0.3010 = \frac{1}{60}[\log 10 - \log 4]$$

$$\Rightarrow \quad \frac{1}{t}\times 0.3010 = \frac{1}{60}[1-0.60]$$

$$\therefore \quad t = \frac{0.3010\times 60}{0.40} = 45.15 \simeq 45 \text{ min.}$$

31. For the reaction, 2A + B $\rightarrow$ 3C + D. Which of the following does not express the reaction rate?

[AIPMT (Prelims)-2006]

(1) $-\frac{d[C]}{3dt}$ (2) $-\frac{d[B]}{dt}$ (3) $\frac{d[D]}{dt}$ (4) $-\frac{d[A]}{2dt}$

Sol. Answer (1)

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

32. Consider the reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. The equality relationship between $\frac{d[NH_3]}{dt}$ and $-\frac{d[H_2]}{dt}$ is

[AIPMT (Prelims)-2006]

(1) $\frac{d[NH_3]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt}$ (2) $+\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$

(3) $+\frac{d[NH_3]}{dt} = -\frac{3}{2}\frac{d[H_2]}{dt}$ (4) $\frac{d[NH_3]}{dt} = -\frac{d[H_2]}{dt}$

Sol. Answer (2)

$$r = \frac{-d[N_2]}{dt} = \frac{-d[H_2]}{3dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

$$\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$$

33. For a first order reaction A $\longrightarrow$ B, the reaction rate at reactant concentration of 0.01 M is found to be 2.0×10^{-5} mol L^{-1} s^{-1}. The half life period of the reaction is **[AIPMT (Prelims)-2005]**

(1) 220 s (2) 30 s (3) 300 s (4) 347 s

Sol. Answer (4)

$r = K[A]^1$

$2 \times 10^{-5} = K[0.01]$

$K = \frac{2\times10^{-5}}{0.01} = 2\times10^{-3}\,s^{-1}$

$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{2\times10^{-3}}$

$\Rightarrow \quad 346.5 \simeq 347$ sec.

34. A nuclide of an alkaline earth metal undergoes radioactive decay by emission of three α-particles in succession. The group of the periodic table to which the resulting daughter element would belong is **[AIPMT (Prelims)-2005]**

(1) Group 14 (2) Group 16 (3) Group 4 (4) Group 6

Sol. Answer (1)

Release of one α-particle decreases the atomic number by two of the resulting elements.

35. The rate of reaction between two reactants A and B decreases by a factor of 4, if the concentration of reactant B is doubled. The order of this reaction with respect to reactant B is **[AIPMT (Prelims)-2005]**

(1) –1 (2) –2 (3) 1 (4) 2

Sol. Answer (2)

$r_2 = K[A]^x[B]^y$

$\frac{1}{4}r_1 = K[A]^x[2B]^y$

So, order w.r.t. (B) $\rightarrow$ (–2)

$\frac{1}{4}r_1 = K[2B]^{-2}$

36. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. The order of reaction is

(1) 0 (2) 1 (3) 2 (4) 3

Sol. Answer (2)

For zero order reaction, $K = \frac{[A]_0 - [A]}{t}$

$\therefore \quad 50 = K \times 2 \quad \& \quad 75 = K \times 4$

$K = 25$ ...(i) $\qquad K = \frac{75}{4} = 18.75$ ...(ii)

K is not constant

$K = \frac{2.303}{2}\log\frac{100}{100-50} = 1.15\log 2 = 0.34$

$K = \frac{2.303}{4}\log\frac{100}{100-75} = 0.57\log 4 = 0.34$

} constant

K = constant so, $\boxed{\text{order} = \text{first}}$

37. Activation energy (E_a) and rate constants (k_1 and k_2) of a chemical reaction at two different temperatures (T_1 and T_2) are related by

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

(2) $\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

(3) $\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} + \frac{1}{T_1}\right)$

(4) $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

Sol. Answer (2, 4)

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

or $$\log_e\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

38. The half life time of 2g sample of radioactive nuclide 'X' is 15 min. The half life time of 1g sample of X is

(1) 7.5 min (2) 15 min (3) 22.5 min (4) 30 min

Sol. Answer (2)

Radioactive nuclide follows first order kinetics and for Ist order reaction $t_{1/2}$ is independent of initial mole/ concentration that is why $t_{1/2}$ remains constant *i.e.*, 15 min.

39. The rate of the reaction : $2N_2O_5 \longrightarrow 4NO_2 + O_2$ can be written in three ways :

$$\frac{-d[N_2O_5]}{dt} = k[N_2O_5]$$

$$\frac{d[NO_2]}{dt} = k'[N_2O_5]$$

$$\frac{d[O_2]}{dt} = k''[N_2O_5]$$

The relationship between k and k′ and between k and k″ are

(1) k′ = 2k; k″ = 2k (2) k′ = k; k″ = k (3) k′ = 2k; k″ = k (4) k′ = 2k; k″ = $\frac{k}{2}$

Sol. Answer (4)

$$r = -\frac{1}{2}\frac{d(N_2O_5)}{dt} = +\frac{1}{4}\frac{d(NO_2)}{dt} = \frac{+d(O_2)}{dt}$$

$$\Rightarrow \frac{k[N_2O_5]}{2} = \frac{+1}{4}k'[N_2O_5] = k''[N_2O_5]$$

i.e., k′ = 2K

$$k'' = \frac{K}{2}$$

40. For the following reaction $C_6H_{12}O_6(aq) + H_2(g) \rightleftharpoons C_6H_{14}O_6(aq)$. Which one of the following is *not* affected by the addition of catalyst?

(1) Rate of forward reaction (2) Rate of backward reaction

(3) Time required to reach the equilibrium (4) Spontaneity

Sol. Answer (4)

$$\text{Catalyst}\begin{cases}\text{decreases } E_a\\ \text{rate of reaction increases}\end{cases}$$

But does not affect spontaneity.

41. A chemical reaction proceeds into the following steps

Step I, $2A \rightleftharpoons X$ fast

Step II, $X + B \rightleftharpoons Y$ slow

Step III, $Y + B \rightleftharpoons$ Product fast

The rate law for the overall reaction is

(1) Rate = $k[A]^2$

(2) Rate = $k[B]^2$

(3) Rate = $k[A][B]$

(4) Rate = $k[A]^2[B]$

Sol. Answer (4)

(i) $k_C = \frac{[X]}{[A]^2} \Rightarrow [X] = k_C[A]^2$

(ii) slow rate law $r = k[X][B] = k \times k_c[A]^2 \times [B]$

i.e., $\boxed{r = k[A]^2[B]}$

42. The data for the reaction A + B $\rightarrow$ C, is

Exp.	$[A]_0$	$[B]_0$	Initial rate
(i)	0.012	0.035	0.10
(ii)	0.024	0.070	0.80
(iii)	0.024	0.035	0.10
(iv)	0.012	0.070	0.80

The rate law corresponds to the above data is

(1) Rate = $k[A][B]^3$

(2) Rate = $k[A]^2[B]^2$

(3) Rate = $k[B]^3$

(4) Rate = $k[B]^4$

Sol. Answer (3)

$[A]_0$	$[B]_0$	Rate
0.012	0.035	0.10
0.024	0.070	0.80
0.024	0.035	0.10
0.012	0.070	0.80

From exp-I & exp-III, when $[B]_0$ is constant and $[A]_0$ doubles then rate remains constant.

So, w.r.t. $[A]_0 \rightarrow$ order = 0

From exp-I & exp-IV, when $[A]_0$ is constant and $[B]_0$ doubles then rate becomes four times

So, w.r.t. $[B]_0$ order = 3

So, rate = $K[B]^3$

43. Half-life for radioactive ^{14}C is 5760 years. In how many years 200 mg of ^{14}C will be reduced to 25 mg?

(1) 17280 years (2) 23040 years

(3) 5760 years (4) 11520 years

Sol. Answer (1)

Radioactive decay follows 1st order kinetics; $t_{1/2} = \frac{0.693}{K}$

$$K = \frac{2.303}{t}\log\frac{200}{25}$$

$$\Rightarrow \quad \frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log 8$$

$$\Rightarrow \quad t = \frac{2.303\times 5760}{0.693}\log(2)^3 = \frac{2.303\times 5760\times 3\times 0.3010}{0.693} = 17280 \text{ years}$$

44. A chemical reaction is catalyzed by a catalyst X. Hence X

(1) Reduces enthalpy of the reaction (2) Does not affect equilibrium constant of reaction

(3) Decreases rate constant of the reaction (4) Increases activation energy of the reaction

Sol. Answer (2)

A catalyst does not affect the equilibrium constant of the reaction

45. The given reaction $2\,FeCl_3 + SnCl_2 \rightarrow 2\,FeCl_2 + SnCl_4$ is an example of

(1) Third order reaction (2) First order reaction

(3) Second order reaction (4) None of these

Sol. Answer (1)

$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$

For elementary chemical reaction, the order of the reaction is the sum of the coefficients of the reactants.

46. Carbon-14 dating method is based on the fact that

(1) Ratio of carbon-14 and carbon-12 is constant (2) Carbon-14 is the same in all objects

(3) Carbon-14 is highly insoluble (4) All of these

Sol. Answer (1)

Fact.

47. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the rate of reaction is expressed as

(1) $\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[I_2]}{\Delta t} = -\frac{\Delta[HI]}{\Delta t}$ (2) $-\frac{\Delta[I_2]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} - \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$

(3) $-\frac{\Delta[I_2]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} - \frac{\Delta[HI]}{2\Delta t}$ (4) None of these

Sol. Answer (4)

$$-\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = +\frac{1}{2}\frac{d[HI]}{dt}$$

48. The experimental data for the reaction

$2A + B_2 \rightarrow 2AB$ is

Exp.	[A]	$[B_2]$	Rate(mole s^{-1})
1	0.50	0.50	1.6×10^{-4}
2	0.50	1.00	3.2×10^{-4}
3	1.00	1.00	3.2×10^{-4}

The rate equation for the above data is

(1) rate = $k [A]^2 [B]^2$ (2) rate = $k [A]^2 [B]$

(3) rate = $k [B_2]$ (4) rate = $k [B_2]^2$

Sol. Answer (3)

From exp-I & exp-II, when [A] is constant and [B] doubles, rate becomes twice.

$\therefore$ Order w.r.t. [B] is I

Similarly, From exp-I & exp-II order w.r.t. [A] is zero.

49. Activation energy of a chemical reaction can be determined by

(1) Evaluating rate constants at two different temperatures

(2) Evaluating velocities of reaction at two different temperatures

(3) Evaluating rate constant at standard temperature

(4) Changing concentration of reactants

Sol. Answer (1)

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

50. For a first-order reaction, the half-life period is independent of

(1) First power of final concentration

(2) Cube root of initial concentration

(3) Initial concentration

(4) Square root of final concentration

Sol. Answer (3)

$t_{1/2} \propto a^0 \rightarrow$ for 1st order

51. The half-life of ${}_6C^{14}$, if its λ is 2.31×10^{-4} $year^{-1}$, is

(1) 3.5×10^4 years (2) 3×10^3 years

(3) 2×10^2 years (4) 4×10^3 years

Sol. Answer (2)

$\lambda = 2.31 \times 10^{-4}$ $year^{-1} \rightarrow$ first order.

$$t_{1/2} = \frac{0.693}{2.31\times10^{-4}} = 3\times10^3 \text{ years}$$

52. A 300 gram radioactive sample has a half life 3 hours. After 18 hours remaining quantity

(1) 4.68 gram (2) 2.34 gram (3) 3.34 gram (4) 9.37 gram

Sol. Answer (1)

$$[R]_t = \frac{[R]_0}{2^n} \qquad n = \frac{18}{3} = 6$$

$$\Rightarrow \quad \frac{300}{2^6} = 4.68 \text{ gram}$$

53. How enzymes increases the rate of reactions?

(1) By lowering activation energy (2) By increasing activation energy

(3) By changing equilibrium constant (4) By forming enzyme substrate complex

Sol. Answer (1)

Enzymes $\rightarrow$ used as a catalyst which decreases E_a and increases rate of reaction.

54. For the reaction; $2N_2O_5 \rightarrow 4NO_2 + O_2$ rate and rate constant are 1.02×10^{-4} Ms^{-1} and 3.4×10^{-5} s^{-1} respectively, then concentration of N_2O_5 at that time will be (in molarity)

(1) 1.732 (2) 3 (3) 1.02×10^{-4} (4) 3.4×10^5

Sol. Answer (2)

$2N_2O_5 \rightarrow 4NO_2 + O_2$

Experimentally it is a 1st order reaction.

$r = K[N_2O_5]^1$

$1.02 \times 10^{-4} = 3.4 \times 10^{-5} [N_2O_5]$

$$N_2O_5 = \frac{1.02 \times 10^{-4}}{3.4 \times 10^{-5}} = 3$$

55. A human body required 0.01 m activity of radioactive substance after 24 hours. Half life of radioactive substance is 6 hours. Then injection of maximum activity of radioactive substance that can be injected

(1) 0.08 (2) 0.04 (3) 0.16 (4) 0.32

Sol. Answer (3)

$$[R]_t = \frac{[R]_0}{2^n} \qquad n = \frac{24}{6} = 4$$

$$0.01 = \frac{[R]_0}{2^4} \qquad [R]_0 = 0.01 \times 16 = 0.16$$

56. When a biochemical reaction is carried out in laboratory, outside the human body in absence of enzyme, then rate of reaction obtained is 10^{-6} times, the activation energy of reaction in the presence of enzyme is

(1) $\frac{6}{RT}$ (2) P is required

(3) Different from E_a obtained in laboratory (4) Can't say anything

Sol. Answer (3)

In the presence of enzyme $\rightarrow$ rate of reaction increases by decreasing activation energy because it acts as a catalyst.

i.e., different E_a

57. $3A \rightarrow 2B$, rate of reaction $\frac{+d(B)}{dt}$ is equal to

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

Sol. Answer (2)

$3A \rightarrow 2B$

$$r = -\frac{1}{3}\frac{d(A)}{dt} = \frac{+1}{2}\frac{d(B)}{dt}$$

$$\frac{d(B)}{dt} \Rightarrow -\frac{2d(A)}{3\,dt}$$

58. $2A \rightarrow B + C$

It would be a zero order reaction when

(1) The rate of reaction is proportional to square of conc. of A

(2) The rate of reaction remains same at any conc. of A

(3) The rate remains unchanged at any conc. of B and C

(4) The rate of reaction doubles if conc. of B is increased to double

Sol. Answer (2)

$2A \rightarrow B + C$ $\quad r = -\frac{1}{2}\frac{d(A)}{dt} = \frac{+d(B)}{dt} = \frac{+d(C)}{dt}$

for zero order reaction $\quad r = K[A]^0$

i.e., rate of reaction independent on concentration of (A).

59. 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 negative of E_a (2) Is always less than E_a

(3) Can be less than or more than E_a (4) Is always double of E_a

Sol. Answer (3)

$\Delta H = (E_a)_{forward} - (E_a)_{backward}$

for Endothermic $\quad (E_a)_{forward} > (E_a)_{backward}$

for Exothermic $\quad (E_a)_{forward} < (E_a)_{backward}$

60. 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?

(1) 1 hour (2) 0.5 hour (3) 0.25 hour (4) 2 hours

Sol. Answer (1)

$$K = \frac{2.303}{t}\log\frac{(R)_0}{(R)_t}$$

$$K = \frac{2.303}{1}\log\frac{0.8}{0.6} \quad ...(i)$$

$$K = \frac{2.303}{t}\log\frac{0.9}{0.675} \quad ...(ii)$$

$$\frac{K = \frac{2.303}{1}\log\frac{0.8}{0.6}}{K = \frac{2.303}{t}\log\frac{0.9}{0.675}}$$

$$\frac{1}{t}\log\frac{0.9}{0.675} = \log\frac{0.8}{0.6}$$

$$\frac{1}{t}\log 1.33 = \log 1.33$$

$t = 1$ hr

61. If the rate of the reaction is equal to the rate constant, the order of the reaction is

(1) 0 (2) 1

(3) 2 (4) 4

Sol. Answer (1)

$r = K[A]^0 \leftarrow$ for zero order.

$$\boxed{r = K}$$

62. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation, $k = A.e^{-E^*/RT}$. Activation energy (E^*) of the reaction can be calculated by plotting

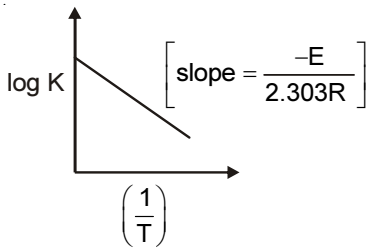
(1) k Vs T (2) k Vs $\frac{1}{\log T}$

(3) log k Vs $\frac{1}{T}$ (4) log k Vs T

Sol. Answer (3)

$$K = Ae^{-E^*/RT}$$

$$\log K = \log A - \frac{E}{2.303RT}$$



63. The radioisotope, tritium (^3_1H) has a half-life of 12.3 years. If the initial amount of tritium is 32 mg, how many milligrams of it would remain after 49.2 years?

(1) 1 mg (2) 2 mg

(3) 4 mg (4) 8 mg

Sol. Answer (2)

$$(R)_t = \frac{(R)_0}{2^n}$$

$$(R)_t = \frac{32}{2^n} = \frac{32}{2^4}$$

$$= \frac{32}{16}$$

$= 2$ mg

$$n = \frac{49.2}{12.3} = 4$$

64. The rate of a first order reaction is 1.5×10^{-2} mol L^{-1} min^{-1} at 0.5 M concentration of the reactant. The half-life of the reaction is

(1) 0.383 min

(2) 23.1 min

(3) 8.73 min

(4) 7.53 min

Sol. Answer (2)

$r = K[A]^1$

$1.5 \times 10^{-2} = K[0.5]$

$$K = \frac{1.5\times10^{-2}}{0.5} = 3\times10^{-2}$$

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{3\times10^{-2}}$$

$t_{1/2} = 23.1$ min.

SECTION - C

Assertion - Reason Type Questions

1. A : Rate of reaction depends upon the concentration of the reactants.

R : The order of reaction can be negative with respect to a substance present in the reaction.

Sol. Answer (2)

$$\text{Rate} = -\frac{dC}{dt} \propto C$$

and for zero order reaction,

$\Rightarrow$ order can be positive negative or zero.

2. A : $NO_2 + CO \xrightarrow{\text{slow}} CO_2 + NO$

$\text{Rate} = K[NO_2]^2$

R : Rate does not depend upon [CO] because it is involved in the first step.

Sol. Answer (4)

$R = K[NO_2][CO]$

All reactant concentration term (in slow state) must be included in Rate law.

3. A : If temperature does not affect the rate of reaction, $E_a = 0$.

R : Less the activation energy, slower will be the reaction.

Sol. Answer (3)

Lesser the activation energy, faster will be the rate.

4. A : The rate constant of first order reaction is used to calculate population if growth rate is given.

R : The rate constant is independent of concentration for first order reaction.

Sol. Answer (2)

$$R = -\frac{dC}{dt} = KC$$

$$\text{or } K = \frac{2.303}{t}\log\left[\frac{A_0}{A_t}\right]$$

$$\text{and } \left(K = \frac{0.693}{t_{½}}\right)$$

5. A : A positive catalyst increases the rate of reaction.

   R : A positive catalyst alters reaction mechanism and decreases activation energy.

Sol. Answer (1)

Positive catalyst favours rate of reaction by decreasing activation energy.

6. A : The molecularity of reaction can never be fractional.

   R : Molecularity is the number of molecules needed to form activated complex, which will never be fractional.

Sol. Answer (1)

Molecularity means number of molecules participate [in an elementary reaction] in a reaction to form activated complex.

7. A : The decomposition of gaseous N_2O_5 follows first order kinetics.

   R : The plot of log of its partial pressure versus time is linear with slope, $-\frac{k}{2.303}$ and having intercept equal to P.

Sol. Answer (1)

$$K = \frac{2.303}{t}\log\frac{P_0}{P_t}$$

$$t\left(\frac{K}{2.303}\right) = \log P_0 - \log P_t$$

$$\underbrace{\log P_t}_{y} = -\underbrace{\left(\frac{K}{2.303}\right)}_{m}\underbrace{t}_{x} + \underbrace{\log P_0}_{\text{interecept}}$$

8. A : Order and molecularity of a reaction are always equal.

   R : Complex reactions takes place in steps and fastest step determine the molecularity of reaction.

Sol. Answer (4)

Order can be fractional but molecularity can never be fractional.

Slowest rate determines the molecularity of reaction.

9. A : Rate constant increases with temperature.

   R : Rate of exothermic reaction increases with temperature.

Sol. Answer (2)

Rate constant $\propto$ temperature

Rate always increases with increase in temperature.

10. A : Hydrolysis of ester in acidic medium follows first order kinetics.

R : Hydrolysis of ester is independent of the concentration of acid used.

Sol. Answer (1)

Hydrolysis of ester is an example of pseudo first order reaction.

$\because$ Concentration of acid is large.

11. A : The rate constant for zero order reaction is equal to rate of reaction.

R : $t_{1/2}$ for zero order reaction is directly proportional to initial concentration.

Sol. Answer (2)

Rate = KC°

Rate = K

$$\left[t_{½} = \frac{C_0}{2K}\right]$$

12. A : For exothermic reaction,

$\Delta H = E_a$ (forward) – E_a (backward).

R : The value of activation energy for forward direction is less than activation energy for backward reaction.

Sol. Answer (1)

$\Delta H = E_a(\text{forward}) - E_a(\text{backward}) < 0$

$[E_a < E_b]$

[ΔH = –ve $\Rightarrow$ exothermic reaction]

13. A : Arrhenius parameter

(A) = P(steric factor) × z (collision frequency)

R : On increasing temperature, the value of A increases.

Sol. Answer (3)

A = P(steric factor) × Z(collision frequency)

A is constant.

14. A : In presence of +ve catalyst, activation energy & threshold energy decreases.

R : Minimum energy required to permit a reaction is known as threshold energy.

Sol. Answer (2)

Positive catalyst favours rate of reaction by decreasing activation energy and threshold energy.

2nd statement is a definition of threshold energy.

15. A : When temperature becomes ∞ infinite then the value of rate constant is maximum.

R : A is also known as maximum rate constant.

Sol. Answer (2)

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

$T \rightarrow \infty$

$E_a/RT \rightarrow 0$

$e^0 = 1$

$K = A$

[$\because$ K increases as temperature increases.]

[K_{max} = A = maximum rate constant]

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