Chemical Kinetics

SOLUTIONS

Exercise – I (JEE-Main Pattern)

SECTION–A

1. Ans. (3)

According to stoichiometry of reaction:

$$\frac{[\text{rate of disappearance of } N_2]}{1} = \frac{(\text{rate of disappearance of } H_2)}{3}$$

$$= \frac{(\text{rate of appearance of } NH_3)}{2} = \text{rate of reaction}$$

$$\Rightarrow \text{rate of reaction} = \frac{2.5\times10^{-4}}{2}2 = 1.25\times10^{-4}\ \frac{\text{mol}}{\ell-\text{sec}}$$

$$\Rightarrow \frac{\text{rate of disappearance of } H_2}{3} = 1.25\times10^{-4}\ \frac{\text{mol}}{\ell-\text{sec}}$$

$$\Rightarrow \text{rate of disappearance} = 3.75\times10^{-4}\ \frac{\text{mole}}{\ell-\text{sec}}$$

2. Ans. (4)

Rate constant of a reaction only depends upon temperature & its value would remain same.

3. Ans. (1)

	A(g)	⟶	B(g)	+	3C(g)
t = 0	100 mm				
t = 10 sec	100 – x		x		3x

$100 - x + x + 3x = 160 \Rightarrow 3x = 160 - 100$

$$\Rightarrow x = \frac{60}{3} = 20\text{mm}$$

$$\Rightarrow \text{Avg. rate} = \frac{20}{10}\frac{\text{mm}}{\text{sec}} = \frac{2\text{mm}}{\text{sec}}$$

4. Ans. (4)

For a zero order reaction;

$A_0 - A_t = kt$; where

k = rate constant;

A_0 & A_t are initial concentration & concentration at time t of reactant

Given:

after 50 sec; A_t = ?

25 sec; A_t = 0.5 M

$k = 2\times10^{-2}$ mol/ℓsec.

⇒ substituting in zeroth order rate law;

$$\left.\begin{aligned} A_0 - 0.5 &= (2\times10^{-2})25 \\ A_0 - A_t &= [2\times10^{-2}\times50] \end{aligned}\right\}$$ solving; we get A_t

5. Ans. (4)

for a first order reaction;

$$\ell n\left(\frac{[A]_0}{[A]_t}\right) = kt;\ \text{where}$$

k = rate constant;

$|A|_0$, $[A]_t$: initial conc. & conc. at time t of reactant

$\Rightarrow$ Substituting values of given in question, we get,

$$k(20\ \text{min}) = \ell n\left(\frac{1}{0.25}\right)$$

$$k = \frac{2.303 \times 2\log 2}{20} = 0.0693\ \text{min}^{-1}$$

6. Ans. (1)

$$k = \frac{2.303}{t}\log\frac{A_0}{A_t}$$

$$2.2\times10^{-5} = \frac{2.303}{90\times60}\log\frac{100}{A_t}$$

$$\log\frac{100}{A_t} = 0.052$$

$$\frac{100}{A_t} = 1.127$$

$$A_t = \frac{100}{1.127}$$

$A_t = 88.73$

% dissociation = 11.26%

7. Ans. (1)

$t_{1/2} = k(a)^{1-n}$

or $\log t_{1/2} = (1 - n)\log a + \log k$

$y = m \quad x + c$

Slope = $1 - n = \tan 45° = 1$

$n = 0$ so zero order reaction

Intercept = $\log k = 0$

$k = 1$

8. Ans. (4)

$$R = K(A)^n(B)^m$$

$$R' = K(2A)^n\left(\frac{B}{2}\right)^m = K(A)^n 2^n (B)^m 2^{-m} = K(A)^n(B)^m 2^{n-m},$$

$$\frac{R'}{R} = \frac{K(A)^n(B)^m 2^{n-m}}{K(A)^n(B)^m} = 2^{n-m}$$

9. Ans. (3)

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

$4.2 \times 10^{-6} = K[1]^x [0.15]^y$

$8.4 \times 10^{-6} = K[2]^x [0.15]^y$

$$\frac{1}{2} = \left[\frac{1}{2}\right]^x$$

$x = 1$

$4.2 \times 10^{-6} = K[1]^x [0.15]^y$

$5.6 \times 10^{-6} = K[1]^x [0.20]^y$

$0.75 = K[0.75]^y$

$y = 1$

$r = K[A]^1 [B]^1$

10. Ans. (4)

Order is experimental value and molecularity is theoretical order & molecularity is same for elementary reaction.

11. Ans. (1)

$A \longrightarrow B$

$r = k[A]^2$

a II order reaction may be complex reaction.

12. Ans. (1)

$$k = \frac{2.303}{69.3}\log\frac{100}{50}$$

$$t_{80\%} = \frac{2.303}{k}\log\frac{100}{20}$$

$$t_{80\%} = \frac{\log\frac{100}{20}}{\log\frac{100}{50}} \times 69.3 = \frac{0.7 \times 69.3}{0.3} = 161.7$$

13. Ans. (3)

For I order :

$[A]_t = [A]_0 e^{-kt}$

$\ln[A]_t = \ln[A]_0 - kt$

$$\log[A]_t = \log[A]_0 - \frac{k}{2.303}t$$

$$\text{Slope} = -\frac{k}{2.303}$$

$$K = \frac{2.303}{t}\log\frac{[A_0]}{A_t} \Rightarrow \log A_t = \log A_0 - \frac{kt}{2.303}$$

$y = C + mx$

14. Ans. (3)

$$r = \frac{K_1 C_A}{1 + K_2 C_A}$$

If $C_A >> 1$; $K_2 C_A >> 1$

$(1 + K_2 C_A) \approx K_2 C_A$

$$r = \frac{K_1 C_A}{K_2 C_A} = \frac{K_1}{K_2}$$

$$\therefore \text{ Rate constant} = \frac{K_1}{K_2} \text{ ; Order = zero}$$

15. Ans. (2)

E_a is activation energy. The minimum amount of energy required by reactant molecule to participate in reaction is called activation energy.

16. Ans. (3)

$k_1 = k_2$

$$10^{15}e^{\frac{-3000}{T}} = 10^{14}e^{\frac{-1000}{T}}$$

$$10 = e^{\frac{2000}{T}}$$

$$\ln 10 = \frac{2000}{T}\ln e$$

$$2.303 \log 10 = \frac{2000}{T}$$

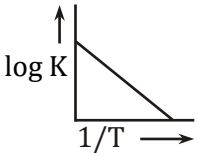
$$T = \frac{2000}{2.303} = 868.43\ K$$

17. Ans. (2)

A graph plotted between $\log k$ Vs $\frac{1}{T}$ for calculating activation energy is shown as from Arrhenius equation $K = Ae^{-E_a/RT}$

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

$y = C + mx$



18. Ans. (1)

$k_2 = 4k_1$

$$k_2 = Ae^{-E_a/RT_2}$$

$$k_1 = Ae^{-E_a/RT_1}$$

$$\frac{k_2}{k_1} = 4 = \frac{e^{-E_a/RT_2}}{e^{-E_a/RT_1}}$$

$$4 = e^{\frac{E_a}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]}$$

$$\ln 4 = \frac{E_a}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$2\times 0.693 = \frac{E_a}{8.314}\left[\frac{10}{300\times 310}\right]$$

$E_a = 107.2$ KJ / mol

19. Ans. (2)

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

$$\left(\ln\frac{k_2}{k_1}\right)_A = \left(\ln\frac{k_2}{k_1}\right)_B = \ln 2$$

$$\left[\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right]_A = \left[\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right]_B$$

$$\frac{E_a}{R}\left[\frac{1}{300}-\frac{1}{310}\right]=\frac{2E_a}{R}\left[\frac{1}{300}-\frac{1}{T_2}\right]$$

$T_2 = 304.92$ K

$(T_2 - T_1)_B = 4.92$ K

20. Ans. (2)

For zero order reaction rate = $k[R]^\circ$

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

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

$E_a \to \infty$

$e^{E_a/RT} \to \infty$

$k \to 0$

$k = A$ (if $E_a = 0$)

$\ell nk = \ell nA - \frac{E_a}{RT}$; ℓnk Vs $\frac{1}{T}$ = linear

(ii) and (v) $\Rightarrow$ correct

SECTION-B

1. Ans. (2)

$3A \to 2B$

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

$$\frac{d[B]}{dt}=2k[A]^n$$

$$\ell n\left(\frac{d[B]}{dt}\right)=n\ell n[A]+\ell n\,2k$$

comparing with $\ell n\left(\frac{d[B]}{dt}\right)=2\ell n[A]-0.04$

$n = 2$

2. Ans. (4)

Let mass of A_2 is X gram $\quad n_{A_2}=\frac{X}{20}$ moles

mass of B_2 is Y gram $\quad n_B=\frac{X}{30}$ moles

$X + Y = 10$ gram

After 6 hrs. number of half life of $A_2 = \frac{6}{2}=3$ half life

number of half life of $B_2 = \frac{6}{3}=2$ half life

Remaining concentration of $A_2 = \frac{X}{2^3}=\frac{X}{8}$ $\quad \frac{X}{20\times 8}$ moles

Remaining concentration of $B_2 = \frac{Y}{2^2} = \frac{Y}{4}$ $\frac{Y}{30\times4}$ moles

after 6 hr. $\frac{X}{8}+\frac{Y}{4}=2\text{gram}$

X = 4 gram

Y = 6 gram

3. Ans. (2)

P_0 = 365 mm $t_{1/2}$ = 420 sec.

P_0 = 170 mm $t_{1/2}$ = 880 sec.

$t_{1/2} \propto \frac{1}{(a)^{n-1}}$

$\frac{420}{880}=\left(\frac{170}{365}\right)^{n-1}$

$0.47 = (0.47)^{n-1}$

n = 2

So, reaction is second order reaction.

4. Ans. (12)

PV = nRT

$P = \left(\frac{n}{V}\right)RT$

$C = \frac{P}{RT}$

$\frac{dC}{dt}=\frac{dP}{dt}\left(\frac{1}{RT}\right)$

Rate (in mol L^{-1} min^{-1}) = $\frac{\text{Rate(in atm min}^{-1})}{RT}=\frac{6\times10^{-3}}{0.082\times300}$ = 2.4×10^{-4}

y = 2.4 $5y = 2.4 \times 5 = 12$

5. Ans. (4)

	A_2B_3	$\rightarrow$	A_2	+	$\frac{3}{2}B_2$	
t = 0	P_0		0		0	P_0 = 60 torr
eq.	$P_0 - x$		x		$\frac{3x}{2}$	$P_0 - x$ = 50 torr

$15 = \frac{3}{2}x$

x = 10

$75 = P_0 + \frac{3}{2}x$

$\text{rate} = \frac{-d[A_2B_3]}{dt} = \frac{dP}{dt} = \left|\frac{50-60}{2.5}\right|$

$= 4 \text{ torr min}^{-1}$

6. **Ans. (20)**

$$A(g) \rightarrow 2B(g)$$

t = 0 $\frac{2}{5} = 0.4$

t = 20 0.4–x 2x

According to question,

$0.4 - x = \frac{2x}{2}$

$0.4 = 2x$

$x = 0.2$

$[A]_t = 0.4 - 0.2$

$= 0.2$ mol/ltr

concentration of A becomes half in 20 min. So $t_{1/2} = 20$ min.

7. **Ans. (96)**

$$\frac{t_{99.9}}{t_{99}} = \frac{\frac{2.303}{k}\log\frac{100}{0.1}}{\frac{2.303}{k}\log\frac{100}{1}} = \frac{3}{2}$$

$t_{99.9} = \frac{3}{2} \times 64 = 96$ min

8. **Ans. (60)**

$$A_0 = \frac{6\times10^{-6}}{0.1\times10^{-3}}\left\{\text{Molarity} = \frac{\text{moles}}{\text{V(litre)}}\right\}$$

$A_0 = 6 \times 10^{-2}$

$$t_{comp} = \frac{A_0}{k} = \frac{6\times10^{-2}}{1\times10^{7}}\text{sec} = 6 \times 10^{-9} \Rightarrow 60 \times 10^{-10} \text{ sec.}$$

9. **Ans. (72)**

$$k = \frac{A_0 - A_t}{t} = \frac{A_0 - \frac{A_0}{4}}{1} = \frac{3A_0}{4}$$

Again using: $A_t = A_0 - kt \Rightarrow \frac{A_0}{10} = A_0 - \frac{3A_0}{4}(t)$

$\Rightarrow$ t = 1.2 hours $\Rightarrow 1.5 \times 60 = 72$ minute

10. **Ans. (5)**

	$2NH_3$	$\longrightarrow$	N_2	+	$3H_2$
t = 0	3atm		0		0
t = t	(3 – 2p)		p		3p

$$\text{rate} = -\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

or

$$\text{rate} = -\frac{1}{2}\frac{\Delta P_{NH_3}}{\Delta t} = k[NH_3]^0 = k = 0.1$$

$$\Rightarrow \quad \frac{-1}{2}\frac{[(3-2p)-3]}{10} = 0.1$$

$$p = 1$$

Total pressure = 3 – 2p + p + 3p = 5 atm