CHAPTER - 14
CHEMICAL KINETICS

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

2. 4 $-\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$, where [ ] is molar concentration

Given, $\frac{d[NH_3]}{dt} = 34\ ghr^{-1}$ or $2\,mol\ hr^{-1}$

Thus, $\frac{d[H_2]}{dt} = -\frac{3}{2} \times 2mol\,hr^{-1} = -3\ mol\,hr^{-1}$ or $6ghr^{-1}$

3. 3 Order of reaction can be zero and fraction

4. 4 $Rate = k[NO]^2\ [O_2]$

As volume is halved, concentration of both reactants are doubled

$\therefore$ Rate increases by $2^2 \times 2 = 8$ times

5. 3 When X is present in large excess, reaction rate becomes independent of [X]. Thus, order of reaction is 1

6. 1 $\log\frac{0.04}{0.03} = \frac{K}{2.303}(10s)$; $k = \frac{2.303}{10} \times \log\frac{4}{3} = 2.303 \times 10^{-2}\ s^{-1}$

7. 2 For first order reaction, $t_{1/2}$ is independent of $[R]_0$. In the reaction, [P] increases with time

8. 2 $\frac{r_{initial,\,1}}{r_{initial,\,0}} = \frac{k_1[R]_0}{k_0} = \frac{2 \times 0.693}{[R]_0} \times [R]_0 = 2 \times 0.693$

9. 3 $[A]_0 - [A]_t = vk_0t$

$\Rightarrow t_{½} = \frac{[A]_0}{2vk_0}$

10. 4 Temperature coefficient = $\frac{k_{T+10}}{k_T}$, where T is usually 298 K

11. 3 $\Delta H = -200 = Ea_f - Ea_b$

$-200 = 80 - Ea_b$

$Ea_b = 80 + 200 = 280\ kJ/mol$

12. 2 Catalyst does not alter enthalpy, Gibb's energy and equilibrium constant of the reaction

13. 4 According to collision theory, rate = $PZ_{AB}e^{-Ea/RT}$

14. 4

	$X_2 \longrightarrow$	Z	$+ \frac{1}{2} Y$
Initial pressure	150	0	0
Final pressure	150 – p	p	$\frac{p}{2}$

Given, (150–p) + (p) + $\left(\frac{p}{2}\right) = 170 \Rightarrow p = 40$

Rate = $\frac{(150-110)\text{mm Hg}}{10\text{ min}} = 4\text{ mm Hg min}^{-1}$

15. 0 $t_{1/2} \propto [R]_0$ for zero order reactions

16. 14 $x = \frac{Ea}{RT} = \frac{80.9\times10^3\ Jmol^{-1}}{8.314\times700} = 13.9$

17. C

$A \rightarrow Q + R + S$

P_0

$P_0 - x \quad x \quad x \quad x$

$P_0 - x + x + x + x = P$

$P_0 + 2x = P$

$x = \frac{P - P_0}{2}$

$P_A = P_0 - \left(\frac{P-P_0}{2}\right) = \frac{2P_0 - P + P_0}{2}$

$= \frac{3P_0 - P}{2}$

$\therefore k = \frac{2.303}{t} \log \frac{2P_0}{3P_0 - P}$

18. A

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$-E_a = -y$$

$$E_a = y$$

19. A

At point of intersection

$$[A] = [B]$$

But for the reaction

$$A \longrightarrow B,$$

$[A]=[B]$ possible at $t = t_{1/2}$

20. B

$V_t = 20\ mL$

$V_\infty = 40\ mL$

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

$$= \frac{2.303}{20} \log \frac{40-0}{40-20}$$

$$= \frac{2.303}{20} \log 2$$

$$= \frac{2.303}{20} \times 0.3010$$

$$= \frac{0.693}{20} = 0.03465\ min^{-1}$$

$$= 3.465 \times 10^{-2}\ min^{-1}$$

21. B

$$R_A = \frac{k_1 C_A}{1 + k_2 C_A}$$

$C_A \ll 1 \quad \therefore 1 + k_2 C_A \simeq 1$

$\therefore \quad R_A = k_1 C_A \Rightarrow$ order = 1

Rate constant = k_1

22. B,C

$$R_{av}{}_{40s} = \frac{V_3 - 0}{40} = \frac{V_3}{40}$$

$$R_{inst}{}_{40s} = \frac{V_3 - V_2}{40 - 30}$$

23. B, C

Rate : $k[A]^x [B]^y$

$x = 1$

$y = 0 \quad \therefore [B]$ does not influence the rate of reaction

$\therefore$ From I and II

$X = 0.2$

From II and III

$Y = 8 \times 10^{-2}$

From II and IV

$Z = 0.1$

24. A,C

$[R]_0 = 0.4M$

$[R]$ at $20s = 0.2[M]$

$t_{1/2} = 20s$

$[R]$ at $40s = 0.1M$

$\therefore t_{1/2} = 20s$

1st order reaction

$k = \frac{2.303}{40} \log \frac{0.4}{0.1}$

$= 3.466 \times 10^{-2}\ s^{-1}$

$Rate_{40s} = k[R]$

$= 3.466 \times 10^{-2} \times 0.1$

$= 3.466 \times 10^{-3}\ Ms^{-1}$

$[A]$ at $60s = 0.05M$

$[B]$ at $60s = 0.4 - 0.05$

$= 0.35M$

25. A,B,D

From step II

$rate = K[NOBr_2][NO]$

But $NOBr_2$ is intermediate

From step I,

$K_c = \frac{[NOBr_2]}{[NO][Br_2]}$

$[NOBr_2] = K_c[NO][Br_2]$

$\therefore rate = K K_c [NO]^2[Br_2] = k[NO]^2[Br_2]$

26. 2

$\frac{1}{[A]}$ Vs t

slope = $\tan\theta = \tan(\tan^{-1}(0.5)) = \frac{1}{2}$

y-intercept = 2

Generally

$$k = \frac{1}{(n-1)t}\left[\frac{1}{[A]_0^{n-1}} - \frac{1}{[A]^{n-1}}\right]$$

$[A]^{-1} = [A]^{-n+1}$

$\therefore n = 2$ //

27. 10

From I and II & II and III

order w.r.t $[A] = 1$

order w.r.t $[B] = 0$

$6.93 \times 10^{-3} = k(0.1)^1(0.2)^0$

$k = 6.93 \times 10^{-2}$

$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.93 \times 10^{-2}} = 10$ min

28. 3

$A + 2B \longrightarrow C$

0.40	0.60	0	$R_i = k[0.4][0.6]^2$
$0.4-x$	$0.6-2x$	$0.1-x$	
0.3	0.4	0.1	$R_f = k[0.3][0.4]^2$

$\frac{R_i}{R_f} = \frac{0.4 \times 0.6 \times 0.6}{0.3 \times 0.4 \times 0.4} = \frac{4 \times 6 \times 6}{3 \times 4 \times 4} = 3$

29. 3

$$\frac{1}{t_{eff}} = \frac{1}{(t_{1/2})_1} + \frac{1}{(t_{1/2})_2}$$

$$\frac{1}{t_{eff}} = \frac{1}{4} + \frac{1}{12} = \frac{12+4}{48} = \frac{16}{48}$$

$$t_{eff} = \frac{48}{16} = 3$$

30. B

$$t_{99.9\%\,(1st)} = \frac{2.303}{k} \log \frac{100}{0.1}$$

$$= \frac{2.303}{0.693} t_{1/2} \times 3$$

$$= 10\, t_{1/2}$$

$$t_{75\%\,(1st)} = \frac{2.303}{0.693} \times t_{1/2} \log \frac{100}{25}$$

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

$$= 2 t_{1/2}$$

$$t_{75\%\,(0)} = \frac{100 - 25}{k} = \frac{75}{k} \quad ; \quad t_{1/2} = \frac{[R]_0}{2k} = \frac{100}{2k}$$

$$\therefore t_{75\%} = \frac{75}{100} \times 2 t_{1/2} = \frac{3}{2} t_{1/2}$$

$$t_{90\%\,(1st)} = \frac{2.303}{0.693} t_{1/2} \log \frac{100}{10}$$

$$= \frac{10}{3} t_{1/2}$$