Chemical Equilibrium

SOLUTIONS

Exercise-I (Conceptual Questions)

1. Ans. (3)

For an elementary reaction :

$r = K[A]\,[B]^2$ ...(I)

$r^1 = K[4A]\,[B/2]^2$ ...(II)

Divide (I) by (II)

$$\frac{r}{r^1} = \left(\frac{1}{4}\right) \times (4)$$

$$r = r^1$$

2. Ans. (4)

Catalyst reduces the time taken to attain equilibrium by lowering activation energy.

3. Ans. (4)

At equilibrium :- rate of forward reaction = rate of backward reaction

4. Ans. (4)

5. Ans. (2)

Active mass of pure solid = 1

6. Ans. (4)

$$[CO_2] : [H_2] : [N_2] = \frac{22}{44} : \frac{3}{2} : \frac{7}{28}$$

$$= \frac{1}{2} : \frac{3}{2} : \frac{7}{4}$$

$$= 1 : 3 : 0.5$$

7. Ans. (1)

Catalyst provides an alternate path with lower activation energy.

8. Ans. (2)

Rate of forward and backward reaction is equal

9. Ans. (3)

$$K_{eq.} = \frac{k_f}{k_b}$$

$$K_f = k_{eq.} \times k_b$$

$$= 1.5 \times 7.5 \times 10^{-4}$$

$$= 11.25 \times 10^{-4}$$

$$= 1.12 \times 10^{-3}$$

10. Ans. (3)

$$K_{eq.} = \frac{k_f}{k_b} = \frac{[B]}{[A]}$$

$$[B] = \frac{k_f}{k_b} . [A]$$

$$= k_f . k_b^{-1} [A]$$

11. Ans. (1)

$$K_C = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$$

$$= \frac{\left(10^{-1}\right)}{\left(10^{-1}\right)\left(10^3\right)^2} = 10^{-6}$$

12. Ans. (4)

$K_p = K_C\,(RT)^{\Delta ng}$

$\Delta n_g = (3 + 1) - (1 + 2) = 1$

$K_p = K_C\,(RT)^1$

$$K_C = \frac{k_p}{(RT)} = \frac{.05}{(R \times 1000)}$$

$= 5 \times 10^{-5}\ R^{-1}$

13. Ans. (4)

$$K_p = \frac{(P_{CO})^2}{(P_{CO_2})} = \frac{(2)^2}{(4)} = 1$$

14. Ans. (3)

For $\Delta n_g = 0 \Rightarrow K_P = K_C$

15. Ans. (4)

$K_P = P^2_{H_2O}$

$K_C = [H_2O]^2$

$K_P = K_C(RT)^2$

16. Ans. (2)

$$\log \frac{k_p}{k_c} + \log(RT) = 0$$

$$\log \frac{k_p}{k_c} = -\log(RT)$$

$$\frac{k_p}{k_c} = (RT)^{-1}$$

$k_P = k_C(RT)^{-1}$

$\Delta n_g = -1$

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$\Delta n_g = -1$

17. Ans. (2)

$k_P = k_C(RT)^{\Delta ng}$

$\frac{k_p}{k_c} = (RT)^{\Delta ng}$

for $\frac{k_p}{k_c} = \text{minimum} \Rightarrow \Delta ng \rightarrow \text{minimum}$

for $\frac{k_p}{k_c} = \text{maximum} \Rightarrow \Delta ng \rightarrow \text{maximum}$

18. Ans. (1)

Reverse (1) & multiply by 4.

$K_2 = \frac{1}{(k_1)^4}$

19. Ans. (4)

Add all given reactions to get K of target equation:

Hence K of $A \rightleftharpoons D$ is $2 \times 4 \times 6 = 48$

20. Ans. (1)

Stability $\propto$ Conc.

For reactant to be stable ; conc. of reactant should be more.

Hence K should be less.

So minimum K is of first reaction.

21. Ans. (3)

Equilibrium constant depends only on temperature.

22. Ans. (1)

Equilibrium constant of a reaction changes with temperature.

23. Ans. (3)

Equilibrium constant of a reaction changes with temperature.

24. Ans. (2)

Equilibrium constant of a reaction changes with temperature.

25. Ans. (1)

$\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \Rightarrow \left[\frac{T_1 - T_2}{T_1 T_2}\right] < 0.$

26. Ans. (1)

On $\uparrow$sing Temperature, value of K is increasing. Hence reaction is endothermic.

27. Ans. (2)

Equilibrium constant depends only on temperature.

28. Ans. (4)

$K = [B]^2 [C]^3$

$K = [B^1]^2 [C^1]^3$

Given : $[C^1] = [2C]$

$[B]^2 [\not{C}]^3 = [B^1]^2 [2\not{C}]^3$

$[B^1]^2 = \frac{[B]^2}{8} \Rightarrow [B^1] = \frac{[B]}{2\sqrt{2}}$

29. Ans. (1)

Equilibrium constant depends only on temperature.

30. Ans. (3)

Equilibrium constant depends only on temperature.

31. Ans. (3)

Equilibrium constant depends only on temperature.

32. Ans. (3)

Equilibrium constant depends only on temperature.

33. Ans. (3)

(a) Active mass $\rightarrow$ Concentration.

(b) Dynamic nature $\rightarrow$ Chemical equilibrium.

(c) A + heat $\rightleftharpoons$ B $\rightarrow$ forward reaction increases on $\uparrow$sing temperature.

(d) $\log\left(\frac{k_2}{k_1}\right) = \frac{\Delta H}{2.303}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\Rightarrow$ Vant Hoff's equation.

(e) $2A_{(g)} + B_{(g)} \rightleftharpoons 3C_{(g)} \rightarrow \Delta n_g = 0$

34. Ans. (3)

	P	$\rightleftharpoons$	Q	+	R
t = 0	2		0		0
t = eq.	2 – x		x		x
Given			x	=	0.5

$\alpha = \frac{x}{2} = \frac{0.5}{2} = 0.25$

35. Ans. (1)

	$2CO_2$	$\rightleftharpoons$	2CO	+	O_2
t = 0	2mol		0		0
t = eq.	2 – 0.8		0.8		0.4
	= 1.2		0.8		0.4

40% of 2 = 0.8

Moles total at equilibrium

= 1.2 + 0.8 + 0.4 = 2.4 moles.

36. Ans. (4)

	$A_3(g)$	$\rightleftharpoons$	$3A(g)$
t = 0	a		0
t = eq.	a – y		3y

$x = \frac{y}{a}$

$y = ax$

total moles at equilibrium

= a – y + 3y

= a + 2y

= a + 2 ax

37. Ans. (1)

	$2P_{(g)}$	+	$Q_{(g)}$	$\rightleftharpoons$	$3R_{(g)}$	+	$S_{(g)}$
t = 0	2mol		2mol		0		0
t = eq.	2 – 2x		2 – x		3x		x

At eq. [Q] > [P]

38. Ans. (1)

	A	+	B	$\rightleftharpoons$	C	+	D
t = 0	3n		n		0		0
t = eq.	3n–x		n – x		x		x

Given $[C]_{eq.} = [B]_{eq.}$

$x = n - x$

$x = n/2$

$[D] = x = n/2$

39. Ans. (1)

	X_2	+	Y_2	$\rightleftharpoons$	2xy
t = 0	1mol		2mole		0
t = eq.	1 – x		2 – x		2x

Given [xy] = 0.6

$\frac{2x}{3} = 0.6$

$x = 0.9$

$[X_2] = \frac{1-x}{3} = \frac{1-0.9}{3} = \frac{0.1}{3}$

$[Y_2] = \frac{2-x}{3} = \frac{2-0.9}{3} = \frac{1.1}{3}$

40. Ans. (2)

	CO	+	H_2O	$\rightleftharpoons$	CO_2	+	H_2
t = 0	1		1		1		0
t = eq.	1 – x		1 – x		1 + x		x

$x < 1$ always

Hence n_{CO} & n_{H_2O} & n_{H_2} always less than 1 mole.

41. Ans. (2)

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
t = 0	4mol		0		0
t = eq.	4 – x		x		x

Given $\alpha = 0.5 = \frac{x}{4}$

$x = 2$

total moles = 4 – x + x + x

= 4 + x

= 4 + 2 = 6 moles

42. Ans. (1)

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2

At = equilibrium $n_{PCl_3} = n_{Cl_2}$

Hence $X_{PCl_3} = X_{Cl_2}$

So, $X_{PCl_3} = 0.3$

43. Ans. (2)

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
t = 0	8		0		0
t = eq.	8 – 25% of 8		2		2

8 – 2 = 6

$K_P = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$

$= \frac{\frac{2}{10} \times P \times \frac{2}{10} \times P}{\frac{6}{10} \times P}$

$= \frac{P}{15}$

44. Ans. (3)

$K_P = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$

$K_P = \frac{0.3 \times 0.2}{0.6} = 0.1$

$K_P = \frac{P^1_{PCl_3} \times P^1_{Cl_2}}{P^1_{PCl_5}}$

$0.1 = \frac{0.6 \times 0.4}{P^1_{PCl_5}}$

$P^1_{PCl_5} = 2.4$

45. Ans. (3)

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

At equilibrium $n_{PCl_3} = n_{Cl_2}$

Hence $X_{PCl_3} = X_{Cl_2}$

Also; $P_{PCl_3} = P_{Cl_2}$

$P_{PCl_3} = X_{PCl_3} . P_T$

$= 0.25 \times 2$

Hence $P_{Cl_2} = 0.5$

46. Ans. (1)

	$2NO$	$\rightleftharpoons$	N_2	+	O_2
t = 0	4mole		0		0
t = eq.	4 – 2x		x		x

Gives $\alpha = 0.1 = \frac{2x}{4}$

$\Rightarrow x = 0.2$

$K_P = \frac{P_{N_2} \times P_{O_2}}{(P_{NO})^2} = \frac{0.2 \times 0.2}{(3.6)^2}$

$= \left(\frac{1}{18}\right)^2$

47. Ans. (4)

	A	+	B	$\rightleftharpoons$	C	+	D
t = 0	1mole		1mole		0		0
t = eq.	1 – x		1 – x		x		x

Gives x = 0.4

$K_C = \frac{[C]\,[D]}{[A]\,[B]} = \frac{\frac{1.4}{V} \times \frac{0.4}{V}}{\frac{0.6}{V} \times \frac{0.6}{V}}$

$K_C = \frac{4}{9}$

48. Ans. (2)

$CH_3COOH_{(\ell)} + C_2H_5OH_{(\ell)} \rightleftharpoons CH_3COOC_2H_{5(\ell)} + H_2O_{(\ell)}$

t = 0	4	4	0	0
t = eq.	4 – x	4 – x	x	x

$K_C = \frac{\frac{x}{v} \times \frac{x}{v}}{\left(\frac{4-x}{v}\right)\left(\frac{4-x}{v}\right)}$

$4 = \frac{x^2}{(4-x)^2}$

$2 = \frac{x}{4-x}$

$8 - 2x = x$

$3x = 8$

$X = \frac{8}{3}$

[Acid] $= 4 - x$

$= 4 - \frac{8}{3}$

$= \frac{4}{3}$

49. Ans. (2)

	H_2	+	I_2	$\rightleftharpoons$	2HI
t = 0	2		2		0
t = eq.	2 – x		2 – x		2x

Gives $n_{HI} = 2$

$2x = 2$

$x = 1$

$K = \frac{(2)^2}{(1)\,(1)} = 4$

50. Ans. (2)

	A	+	B	$\rightleftharpoons$	C	+	D
t = 0	4		4		0		0
t = eq.	4 – x		4 – x		x		x

Gives x = 2

$K = \frac{\left(\frac{2}{v}\right)\left(\frac{2}{v}\right)}{\left(\frac{2}{v}\right)\left(\frac{2}{v}\right)} = 1$

51. Ans. (2)

	$2NH_3(g)$	$\rightleftharpoons$	$N_2(g)$	+	$3H_2(g)$
t = 0	2mole		0		0
t = eq.	2 – 2x		x		3x

Gives $n_{NH_3} = 1$mole

$2 - 2x = 1$

$x = \frac{1}{2} = 0.5$

$K = \frac{\left(\frac{0.5}{1/2}\right)\left(\frac{3 \times 0.5}{1/2}\right)^3}{\left(\frac{2 - 2 \times 0.5}{1/2}\right)^2} = 6.75$

52. Ans. (1)

	H_2 +	I_2 ⇌	2HI
t = 0	4.5	4.5	0
t = eq.	4.5 – x	4.5 – x	2x

Gives $n_{HI} = 3$mole

$2x = 3$

$x = 1.5$

$$K = \frac{\left(\frac{2\times1.5}{V}\right)^2}{\left(\frac{3}{V}\right)\left(\frac{3}{V}\right)} = 1$$

53. Ans. (2)

	2AB(g) ⇌	2A(g) +	B_2(g)
t = 0	500	0	0
t = eq.	500 – 2P	2P	P

Gives $P_T = 500 - 2P + 2P + P = 625$

$P = 125$

$$K_p = \frac{(P_A)^2 . (P_{B_2})}{(P_{AB})^2}$$

$$= \frac{(2\times125)^2 (125)}{(250)^2} = 125$$

54. Ans. (2)

On ↑Sing concentrations of product at equilibrium, reaction shifts backward & more reactant will be formed.

55. Ans. (3)

$$NaNO_3(s) \rightleftharpoons NaNO_2(s) + \frac{1}{2}O_2(g)$$

On ↑Sing pressure; reaction shifts forward less gaseous moles.

i.e. above reaction will shift backward.

56. Ans. (3)

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

Above reaction is endothermic. Increasing temperature will favours forward reaction.

57. Ans. (3)

On ↑Sing pressure; reaction will shift toward less gaseous moles.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

58. Ans. (2)

$$SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} + \text{Heat}$$

On ↓Sing temperature & ↑Sing pressure Reaction shifts forward.

59. Ans. (2)

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 21.9 \text{ KCal}$$

On ↓Sing temperature & ↑sing pressure reaction shifts forward.

60. Ans. (3)

$2A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + 326$Kcal

On ↓Sing temperature & ↑sing pressure reaction shifts forward.

61. Ans. (1)

On compressing V↓ ⇒ P↑ Hence on ↑sing pressure equation shifts towards less gas moles.

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Hence balkward reaction is favoured.

62. Ans. (2)

For $\Delta ng = 0$ equation is unaffected by pressure.

63. Ans. (3)

On adding inert gas at constant volume. Equation is unaffected.

64. Ans. (2)

On ↑sing pressure ; equilibrium shifts towards less volume.

$V_{H_2O(\ell)} < V_{H_2O(g)}$

Hence B.P. ↑ses.

65. Ans. (3)

Heat + $CO_2(s) \rightleftharpoons CO_2(g)$

On cooling temperature ↓ses. Reaction shifts backward.

66. Ans. (2)

$$\alpha = \frac{D_T - D_0}{(n-1)D_0}$$

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$D_T = \frac{208.5}{2} = 104.25$$

$d = 104.25$

$n = 2$

$$\alpha = \frac{104.25 - 104.25}{(2-1)\times104.25} = 0$$

67. Ans. (1)

$$\alpha = \frac{D_T - D_0}{(n-1)D_0}$$

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$n = 2$

$$\alpha_{200^\circ C} = \frac{104.25-70.2}{(2-1)\times 70.2} = 48.50\%$$

$$\alpha_{250^\circ C} = \frac{104.25-57.9}{(2-1)\times 57.9} = 80\%$$

68. Ans. (2)

Choose that options for which sum of stoichiometric coefficient of gas product = n

$$A \rightleftharpoons \frac{nB}{3} + \left(\frac{2n}{3}\right)C$$

$$\Rightarrow \quad \frac{n}{3} + \frac{2n}{3} = n$$

Exercise-II (Previous Year Questions)

1. Ans. (4)

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + Heat$

By decreasing temperature & increasing pressure forward reaction Proceeds.

2. Ans. (1)

For a exothermic reaction on increasing temperature K_p decreases

3. Ans. (2)

When $K_{eq.} > 10^3$ product dominates over reactant.

4. Ans. (3)

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

Multiply above reaction by $\frac{1}{2}$ to get target reaction hence $K' = (K)^{\frac{1}{2}}$

5. Ans. (1)

Reverse (I)

ADD in (II)

Multiply (III) × 3

$$\frac{1}{K_1} \times K_2 \times (K_3)^3$$

6. Ans. (4)

$P_1 \quad V_1 \quad = \quad P_2 \quad V_2$

$0.4 \times 20 \quad = \quad 1.6 \times V_2$

$V_2 = 5$ litre

7. Ans. (1)

$A_2(g) + B_2(g) \rightleftharpoons X_2(g)$

On decreasing temperature & increasing pressure forward reaction proceeds.

8. Ans. (1)

	H_2	+	I_2	$\rightleftharpoons$	$2HI$
t = 0	a		a		0
t = eq.	a – 0.8a		a – 0.8a		2 × 0.8a
	0.2a		0.2a		1.6a

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{1.6\cancel{a}\times 1.6\cancel{a}}{0.2\cancel{a}\times 0.2\cancel{a}} = 64$$

9. Ans. (3)

$PV = nRT$

$n_T = n_{O_2} + n_{H_2}$

$$= \frac{4}{32} + \frac{2}{2} = \frac{1}{8} + 1 = \frac{9}{8}$$

$$P = \frac{nRT}{V} = \frac{\frac{9}{8}\times .0821\times 273}{1} = 25.18 \text{ atm}$$

10. Ans. (3)

According to dalton's law :

$P_A = X_A . P_T$

11. Ans. (4)

$$K_c = \frac{[O_3]^2}{[O_2]^3}$$

$$3 \times 10^{-59} = \frac{[O_3]^2}{[0.040]^3}$$

$[O_3] = 4.38 \times 10^{-32}$

12. Ans. (2)

$K_p = K_c (RT)^{\Delta ng}$

$\Delta ng = 2 - 1 = 1$

$$K_c = \frac{Kp}{(RT)} = \frac{3}{(.083)(1000)} = 3.6 \times 10^{-2}$$

13. Ans. (2)

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

If [A] is tripled and [B] is kept constant.

$r^1 = k [3A]^2 [B]$

$r^1 = 9k [A]^2 [B]$

$r^1 = 9r$

Increased by a factor of nine

14. Ans. (1)

$K_p = K_c(RT)^{\Delta n_g}$

when $\Delta n_g = 0$ then $K_p = K_c$

$\Delta n_g \neq 0$ $K_p \neq K_c$

(1) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

$\Delta n_g \neq 0$

$K_p \neq K_c$

15. Ans. (3)

$2A \rightleftharpoons B + C$; $K_c = 4 \times 10^{-3}$

At a given time $\Rightarrow$ [A] = [B] = [C] = 2×10^{-3} M

$$Q_c = \frac{[B][C]}{[A]^2}$$

$Q_c = 1$

as $Q_c > K_c$

Reaction has a tendency to go in backward direction.

16. Ans. (4)

$$\underset{t=t_{eq}}{2NO(g)} \rightleftharpoons \underset{(3\times10^{-3})M}{N_2(g)} + \underset{(4.2\times10^{-3})M}{O_2(g)}$$
$(2.8\times10^{-3})M$

$$K_C = \frac{3\times10^{-3}\times4.2\times10^{-3}}{(2.8\times10^{-3})^2} = \frac{3\times4.2}{2.8\times2.8} = 1.60$$

$$\underset{t=t_{eq}}{2NO(g)} \rightleftharpoons \underset{\frac{C\alpha}{2}}{N_2(g)} + \underset{\frac{C\alpha}{2}}{O_2(g)}$$
$(C-C\alpha)$

$$K_C = \frac{(C\alpha)^2}{4C^2(1-\alpha)^2}$$

$$\left(\frac{\alpha}{1-\alpha}\right)^2 = 4\times1.6$$

$$\frac{\alpha}{1-\alpha} = 2\times1.26$$

$$\frac{\alpha}{1-\alpha} = 2.52$$

$\Rightarrow \alpha = 2.52 - 2.52\,\alpha$

$$\Rightarrow \alpha = \frac{2.52}{3.52} = 0.717$$

17. Ans. (4)

For a reaction

$3A_2 + B_2 \rightleftharpoons 2A_3B$, K_1 ....(I)

$A_3B \rightleftharpoons \frac{3}{2}A_2 + \frac{1}{2}B_2$, K_2 ....(II)

On multiplying by (2) in equation (II)

$2A_3B \rightleftharpoons 3A_2 + B_2$, K_2^2 .....(III)

from (I) & (III)

$$K_2^2 = \frac{1}{K_1}$$

$$K_2 = \frac{1}{\sqrt{K_1}}$$

18. Ans. (4)

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -Q$

for forward direction high pressure, low temperature, and higher concentration of H_2.

Exercise-III (Analytical Questions)

1. Ans. (2)

Equilibrium constant only on depends on temperature.

2. Ans. (1)

According to Le-chatelier principle on addition of helium gas at constant pressure and temperature dissociation of PCl_5 is increases.

3. Ans. (4)

Dissolution of gas in liquid in exothermic phenomena.

According to Le-chatelier principle

T ↑ gas dissolution ↓

vise-versa

4. Ans. (2)

$$\log\frac{K_2}{K_1} = \frac{\Delta H^0}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

5. Ans. (1)

Statement-I $\rightarrow$ incorrect

$K_p = K_c$ when $RT = 1$ or $\Delta n_g = 0$

$K_{eq.} \rightarrow$ only depends on temperature

6. Ans. (4)

Equilibrium constant only depends on temperature.

7. Ans. (2)

At equilibrium

$r_f = r_b$

$\Delta G = 0$

$r_{net} = 0$

$\Delta G = -nFE_{cell}$

$E_{cell} = 0$

8. Ans. (1)

At equilibrium

$\Delta G = 0$

$K_p = Q_p$

9. Ans. (3)

$K_c > 10^3$ product dominates

$K_c < 10^{-3}$ reactant dominates

$10^{-3} < K_c < 10^3$ both reactant & product are in appreciable concentration.

$Q_c > K_c$ reaction shifts backward.

10. Ans. (2)

On increasing temperature if value of K increases reaction is endothermic.

11. Ans. (4)

$\Delta G^0 < 0$