Answers and Solutions

Reversible and Irreversible reaction

1. (b) Reversible reaction always attains equilibrium which proceeds both sides and never go for completion.

2. (c) In a reversible reaction some amount of the reactants remains unconverted into products.

3. (d) In lime klin CO_2 escaping regularly so reaction proceeds in forward direction.

7. (b) The reaction is not reversible.

Equilibrium state

1. (c) When rate of forward reaction is equal to the rate of backward reaction then equilibrium is supposed to be established.

2. (b) Equilibrium can be achieved only in closed vessel.

4. (c) When rate of forward reaction is equal to rate of backward reaction the reaction is said to be in equilibrium.

6. (d) At equilibrium rate of forward reaction is equal to the rate of backward reaction.

7. (c) According to Le-chatelier principle when concentration of reactant increases, the equilibrium shift in favour of forward reaction.

8. (b) At equilibrium, the rate of forward & backward reaction become equal.

Law of mass action

1. (b) According to law of mass-action, "at a given temperature, the rate of a reaction at a particular instant is proportional to the product of the active masses of the reactants at that instant raised to powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the reaction".

3. (d) $[HI]=\dfrac{64gm}{128\times 2\,litre}=0.25$

Active mass is the concentration in *moles/litre.*

8. (a) As we increase the concentration of substance, then speed of the reaction increases.

9. (c) Chemical reaction quantitatively depend on the reactant and product molecule.

Law of equilibrium and Equilibrium constant

1. (d) Equilibrium constant for the reaction , $3A+2B \rightleftharpoons C$ is

$$K=\frac{[C]}{[A]^3[B]^2}.$$

2. (d) Suppose 1 mole of A and B each taken then 0.8 *mole/litre* of C and D each formed remaining concentration of A and B will be (1 – 0.8) = 0.2 *mole/litre* each.

$$Kc=\frac{[C]\,[D]}{[A]\,[B]}=\frac{0.8\times 0.8}{0.2\times 0.2}=16.0$$

3. (c) $A+B \rightleftharpoons C+D$

Initial conc. 4, 4 0 0

After T time conc. (4-2) (4-2) 2 2

Equilibrium constant = $\dfrac{[C]\,[D]}{[A]\,[B]}=\dfrac{2\times 2}{2\times 2}=1$

4. (a) $H_2+I_2 \rightleftharpoons 2HI$; $[HI]=0.80$, $[H_2]=0.10$, $[I_2]=0.10$

$$K_c=\frac{[HI]^2}{[H_2]\,[I_2]}=\frac{0.80\times 0.80}{0.10\times 0.10}=64$$

5. (a) Those reaction which have more value of K proceeds towards completion.

6. (d) K_c is a characteristic constant for the given reaction.

7. (c) Equilibrium constant is independent of original concentration of reactant.

8. (a) K_p is constant and does not change with pressure.

9. (a) For reaction $A+2B \rightleftharpoons C$

$$K=\frac{[C]}{[A]\,[B]^2}=\frac{0.216}{0.06\times 0.12\times 0.12}=250.$$

11. (b) $A+2B \rightleftharpoons C+3D$

$$K=\frac{[pC]\,[pD]^3}{[pA]\,[pB]^2}=\frac{0.30\times 0.50\times 0.50\times 0.50}{0.20\times 0.10\times 0.10}=18.75$$

13. (a) $\underset{2}{PCl_5} \rightleftharpoons \underset{0}{PCl_3}+\underset{0}{Cl_2}$

$$\frac{2\times 60}{100}\quad \frac{2\times 40}{100}\quad \frac{2\times 40}{100}$$

Volume of container = 2 *litre*.

$$K_c=\frac{\dfrac{2\times 40}{100\times 2}\times\dfrac{2\times 40}{100\times 2}}{\dfrac{2\times 60}{100\times 2}}=0.266.$$

14. (d) $\Delta n=1$ for this change

So the equilibrium constant depends on the unit of concentration.

15. (d) Unit of $K_p=(atm)^{\Delta n}$

Unit of $K_c=(mole/litre)^{\Delta n}$

$=[mole/litre]^0=0$

16. (c) $$K=\frac{[NO_2]^2}{[N_2O_4]}=\frac{\left[2\times\dfrac{10^{-3}}{2}\right]^2}{\left[\dfrac{.2}{2}\right]}=\frac{10^{-6}}{10^{-1}}=10^{-5}.$$

19. (b) For $A+B \rightleftharpoons C+D$

$$K=\frac{[C]\,[D]}{[A]\,[B]}=\frac{0.4\times 1}{0.5\times 0.8}=1.$$

20. (c) $A+B \rightleftharpoons C+D$

Initial 1 1 0 0

remaining at equilibrium 0.4 0.4 0.6 0.6

$$K=\frac{[C]\,[D]}{[A]\,[B]}=\frac{0.6\times 0.6}{0.4\times 0.4}=\frac{36}{16}=2.25.$$

21. (a) $$K=\frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

23. (d) $A+B \rightleftharpoons C+D$

$x \quad x \quad 0 \quad 0$

$2x \quad 2x$

$$K_c = \frac{[C][D]}{[A][B]} = \frac{2x\,.\,2x}{x\,.\,x} = 4$$

24. (d) $\underset{\substack{1\\(1-\alpha)}}{N_2O_4} \rightleftharpoons \underset{\substack{0\\2\alpha}}{2NO_2}$

total mole at equilibrium $= (1-\alpha) + 2\alpha = 1 + \alpha$

25. (b) $K = \frac{[C_2H_6]}{[C_2H_4]\,[H_2]} = \frac{[mole/litre]}{[mole/litre]\,[mole/litre]}$

= *litre/mole*. or litre mole^{-1}.

27. (c) $K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]} = \frac{\frac{0.2}{10} \times \frac{0.2}{10}}{[0.1/10]} = 0.04$.

28. (b) $K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$; $64 = \frac{x^2}{0.03 \times 0.03}$

$x^2 = 64 \times 9 \times 10^{-4}$

$x = 8 \times 3 \times 10^{-2} = 0.24$

x is the amount of *HI* at equilibrium amount of I_2 at equilibrium will be

$0.30 - 0.24 = 0.06$

29. (c) $K_c = \frac{K_f}{K_b}$

$K_f = K_c \times K_b = 1.5 \times 7.5 \times 10^{-4} = 1.125 \times 10^{-3}$

30. (a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Initial conc. 1 3 0

at equilibrium 1-0.81 3-2.43 1.62

0.19 0.57

No. of moles of $N_2 = \frac{28}{28} = 1$ *mole*

No. of moles of $H_2 = \frac{6}{2} = 3$ *mole*

No. of moles of $NH_3 = \frac{27.54}{17} = 1.62$ *mole*

$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = \frac{[1.62]^2}{[0.19]\,[0.57]^3}$ =75

31. (b) $K_c = \frac{[YX_2]}{[X]^2[Y]} = \frac{2}{4 \times 4 \times 2} = \frac{1}{16} = 0.0625$.

32. (d) $NH_4HS \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$

a 0.5atm

a − x 0.5+x x

Total pressure $= 0.5 + 2x = 0.84$

i.e., $x = 0.17$

$K_p = P_{NH_3}.P_{H_2S} = (0.67).(0.17)$=0.1139

33. (c) $A + 2B \rightleftharpoons 2C$

Initial conc. 2 3 2

at eqm. 2.5 4 1

Molar $\frac{2.5}{2} = 1.25 \quad \frac{4}{2} = 2 \quad \frac{1}{2} = 0.5$

$$K = \frac{[0.5]^2}{[1.25] \times [2]^2} = 0.05$$

34. (b) $CO + Cl_2 \rightleftharpoons COCl_2$

$[CO] = \frac{0.1}{0.5}$, $[Cl_2] = \frac{0.1}{0.5}$, $[COCl_2] = \frac{0.2}{0.5}$

$$= \frac{[COCl_2]}{[CO]\,[Cl_2]} = 0\frac{\frac{0.2}{0.5}}{\frac{0.1}{0.5} \times \frac{0.1}{0.5}} = \frac{2}{5} \times 25 = 10$$

35. (a) $A + B \rightleftharpoons C + D$

at equilibrium $a \quad a \quad 2a \quad 2a$

$$K = \frac{2a \times 2a}{a \times a} = 4$$

36. (a) $H_2 + I_2 \rightleftharpoons 2HI$

Initial conc. 4.5 4.5 0

$x \quad x \quad 2x$

from question $2x = 3$

$$x = \frac{3}{2} = 1.5$$

So conc. at eqm. $4.5 - 1.5$ of H_2

$= 4.5 - 1.5$ of I_2 and 3 of *HI*

$$K = \frac{[HI]^2}{[I_2]\,[H_2]} = \frac{3 \times 3}{3 \times 3} = 1.$$

37. (c) $K = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{[0.10]^2[0.4]}{[0.5]^2} = 0.016$

38. (a) $K_p = \frac{[P_{CO}]^2[P_{O_2}]}{[P_{CO_2}]^2} = \frac{[0.4]^2 \times [0.2]}{[0.6]^2} = 0.0888$.

39. (d) $K_f = 1.1 \times 10^{-2}$; $K_b = 1.5 \times 10^{-3}$

$$K_c = \frac{K_f}{K_b} = \frac{1.1 \times 10^{-2}}{1.5 \times 10^{-3}} = 7.33.$$

40. (a) $\underset{\substack{100\\50}}{2HI} \rightleftharpoons \underset{\substack{0\\25}}{H_2} + \underset{\substack{0\\25}}{I_2}$

$$\frac{[H_2]\,[I_2]}{[HI]^2} = \frac{25 \times 25}{50 \times 50} = 0.25.$$

41. (d) $\underset{(3-0.75)}{A} + \underset{(1-0.75)}{B} \rightarrow \underset{1.5}{2C}$

$$K = \frac{[C]^2}{[A]\,[B]} = \frac{(1.5)^2}{2.25 \times 0.25} = \frac{2.25}{2.25 \times 0.25} = 4.0.$$

42. (d) $6HCHO \overset{K_1}{\rightleftharpoons} C_6H_{12}O_6$ forward reaction

$C_6H_{12}O_6 \overset{K_2}{\rightleftharpoons} 6HCHO$ backward reaction

$K_2 = \left[\frac{1}{K_1}\right]^{1/6}$; $K_2 = \left[\frac{1}{6 \times 10^{22}}\right]^{1/6}$

$K_2 = 1.6 \times 10^{-4}$ *M*

43. (b) $K_c = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{[0.7]^2}{[0.1]\,[0.1]} = 49$

44. (c) $K_c = \dfrac{[NH_3]^2}{[N_2]\,[H_2]^3}$

$$2.37 \times 10^{-3} = \frac{x^2}{[2]\,[3]^3} = x^2 = 0.12798$$

$x = 0.358\ M.$

45. (d) $A + B \rightleftharpoons 2C$

$$K_c = \frac{[C]^2}{[A]\,[B]} = \frac{[0.6]^2}{[0.2]\,[0.2]} = 9$$

46. (a)
$$\begin{array}{ccccc} H_2 & + & I_2 & \rightleftharpoons & 2HI \\ 15 & & 5.2 & & 0 \\ (15-5) & & (5.2-5) & & 10 \end{array}$$

$$K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{10 \times 10}{10 \times 0.2} = 50$$

47. (c) Rate of backward reaction = Rate of forward reaction

48. (b) $K_c = \dfrac{[HI]^2}{[H_2]\,[I_2]} = \dfrac{(28)^2}{8 \times 3} = 32.66$

49. (a) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$; $\Delta n = 2 - 2 = 0$

50. (b) The rate of forward reaction is two times that of reverse reaction at a given temperature and identical concentration $K_{\text{equilibrium}}$ is 2 because the reaction is reversible. So $K = \dfrac{K_1}{K_2} = \dfrac{2}{1} = 2$.

52. (b) $K_c = \dfrac{K_f}{K_b}\ \therefore K_b = \dfrac{K_f}{K_c} = \dfrac{10^5}{100} = 10^3$

53. (c) $K_c = \dfrac{[NO_2]^2}{[N_2O_4]} = \dfrac{4 \times (0.05)^2}{0.05} = 4 \times 0.05 = 0.2$

54. (d)
$$\begin{array}{lcccccc} & 2NH_3 & \rightleftharpoons & N_2 & + & 3H_2 \\ \text{initial} & 2 & & 0 & & 0 \\ \text{at.equil.} & 1 & & 1 & & 3 \end{array} ;\ K\frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1 \times 3^3}{1} = 27$$

56. (c) $K_c = \dfrac{[PCl_3]\,[Cl_2]}{[PCl_5]} = \dfrac{0.2 \times x}{0.4} = 0.5$, $x = 1$

57. (c)
$$\begin{array}{ccccc} N_2 & + & 3H_2 & \rightleftharpoons & 2NH_3 \\ 30 & & 30 & & 0 \\ 30\text{-}x & & 30\text{-}3x & & 2x \end{array}$$

$2x = 10$; $x = \dfrac{10}{2} = 5$

$N_2 = 30 - 5 = 25$ *litre*

$H_2 = 30 - 3 \times 5 = 15$ *litre*

$NH_3 = 2 \times 5 = 10$ *litre*

58. (c) $K = \dfrac{[NO_2]^2}{[N_2O_4]} = \dfrac{[1.2 \times 10^{-2}]^2}{[4.8 \times 10^{-2}]} = 0.3 \times 10^{-2} = 3 \times 10^{-3}$

59. (a) $\dfrac{22}{100} \times 3.2 = 0.704$

$\therefore$ at equil. moles of HI $= 3.2 - 0.704 = 2.496$

60. (c)
$$\begin{array}{lccc} & N_2 & + 3H_2 \rightleftharpoons & 2NH_3 \quad \text{..... (i)} \\ \text{at } t = 0 & 56\,gm & 8\,gm & 0\,gm \\ & = 2\,mole & 4\,mole & 0\,mole \\ \text{at equilibrium} & 2 - 1 & 4 - 3 & 34\,gm \\ & = 1\,mole & = 1\,mole & = 2\,mole \end{array}$$

According to eq. (i) 2 mole of ammonia are present & to produce 2 mole of NH_3, we need 1 mole of N_2 and 3 mole of H_2 hence $2 - 1 = 1$ mole of N_2 and $4 - 3 = 1$ mole of H_2 are present at equilibrium in vessel.

61. (d) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

For $1dm^3$ $R = k[SO_2]^2[O_2]$

$$R = K\left[\frac{1}{T}\right]^2\left[\frac{1}{1}\right] = 1$$

For $2dm^3$ $R = K\left[\dfrac{1}{2}\right]^2\left[\dfrac{1}{2}\right] = \dfrac{1}{8}$

So, the ratio is 8 : 1

62. (d) $K = \dfrac{[C][D]}{[A][B]} = \dfrac{\frac{1}{3} \times \frac{1}{3}}{\frac{2}{3} \times \frac{2}{3}} = \dfrac{1}{4} = 0.25$

So, $K = 0.25$

63. (b) Given, $CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)\uparrow$

$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$

$$Kp_2 = \frac{[pCO]^2}{[pCO_2]}\ ;\ pCO = \sqrt{[Kp_1 \times Kp_2]}$$

$$pCO = \sqrt{[8 \times 10^{-2} \times 2]} = \sqrt{16 \times 10^{-2}} = 4 \times 10^{-1} = 0.4$$

64. (b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$$Kc = \frac{[NO]^2}{[N_2][O_2]} = 4 \times 10^{-4}$$

$$NO_2 \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$$

$$K'_c = \frac{[N_2]^{1/2}[O_2]^{1/2}}{[NO]} = \frac{1}{\sqrt{Kc}} = \frac{1}{\sqrt{4 \times 10^{-4}}}$$

$$= \frac{1}{2 \times 10^{-2}} = \frac{100}{2} = 50$$

65. (d) $P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$

$$K_c = \frac{[P_4O_{10}(s)]}{[P_4(s)][O_2(g)]^5}$$

We know that concentration of a solid component is always taken as unity $K_c = \dfrac{1}{[O_2]^5}$

66. (d)
$$\begin{array}{ccccc} H_2 & + & I_2 & \rightleftharpoons & 2HI \\ 0.4 & & 0.4 & & 0.50 \\ 0.4 - 0.25 = 0.15 & & 0.4 - 0.25 = 0.15/2 & & 0.50/2 \end{array}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left[\frac{0.5}{2}\right]^2}{\left[\frac{0.15}{2}\right]\left[\frac{0.15}{2}\right]} = \frac{0.5 \times 0.5}{0.15 \times 0.15} = 11.11$$

67. (d) $NH_2COONH_4 \rightleftharpoons 2NH_3 + CO_2$

$\alpha = \dfrac{D - d}{(n-1)d}$ where D is the density (initial)

$$D=\frac{mol.wt}{2}=\frac{78}{2}=39$$

$n=$ no. of product = 3 $d=$ final density

$$\alpha=\frac{39-13}{(3-1)13}=1\text{ , so }\alpha=1$$

68. (a) $\underset{(a-x)}{\overset{a}{N_2}}+\underset{(b-3x)}{\overset{b}{3H_2}} \rightleftharpoons \underset{(2x)}{\overset{0}{2NH_3}}$

50% Dissociation of N_2 take place so,

At equilibrium $\frac{2\times 50}{100}=1$; value of $x=1$

$$K_c=\frac{[2]^2}{[1][3]^3}=\frac{4}{27}\text{ so, }K_c=\frac{4}{27}$$

69. (c) The equilibrium constant does not change when concentration of reactant is changed as the concentration of product also get changed accordingly.

70. (d) We know that $PV=nRT$

P become $\frac{1}{2}P$ & V bcome $2V$ so,

$$\frac{1}{2}P\times 2V=PV=nRT$$

So there is no effect in equation.

71. (abcd)All options are true for that equilibrium.

72. (a) $H_{2(g)}+CO_{2(g)} \rightleftharpoons CO_{(g)}+H_2O_{(l)}$

Initial conc.	1	1	0	0
At equili	(1– x)	(1 – x)	x	x

$$K_p=\frac{p_{CO}\cdot p_{H_2O}}{p_{H_2}\cdot p_{CO_2}}=\frac{x.x}{(1-x)(1-x)}=\frac{x^2}{(1-x)^2}$$

K_p & K_c Relationship and Characteristics of K

1. (a) $n_p=n_r$ then $K_p=K_c$

where n_p = no. of moles of product

n_r = no. of moles of reactant.

2. (d) $K_1=\frac{[NO_2]}{[NO][O_2]^{1/2}}$; $K_2=\frac{[NO]^2[O_2]}{[NO_2]^2}$

$$\Rightarrow \frac{[NO_2]^2}{[NO]^2[O_2]}=\frac{1}{K_2}\Rightarrow \frac{[NO_2]}{[NO][O_2]^{1/2}}=\frac{1}{\sqrt{K_2}}$$

$$\Rightarrow K_1=\frac{1}{\sqrt{K_2}}\text{ ; }K_2=\frac{1}{K_1^2}.$$

3. (a) $K_p=K_c(RT)^{\Delta n}=26(0.0821\times 523)^{-1}=0.61$.

$\Delta n_g=1-2=-1$

5. (d) In presence of little H_2SO_4 (as catalyst) about 2/3 mole of each of CH_3COOH and C_2H_5OH react to form 2/3 mole of the product at equilibrium.

6. (d) K_1 for reaction $2HI \rightleftharpoons H_2+I_2$ is 0.25 K_2 for reaction $H_2+I_2 \rightleftharpoons 2HI$ will be $K_2=\frac{1}{K_1}=\frac{1}{0.25}=4$

Because IInd reaction is reverse of Ist.

9. (a) For the reaction,

$$CaCO_{3(g)} \rightleftharpoons CaO_{(s)}+CO_{2(g)}$$

$K_p=P_{CO_2}$ and $K_c=[CO_2]$

($\because$ $[CaCO_3]=1$ and $[CaO]=1$ for solids]

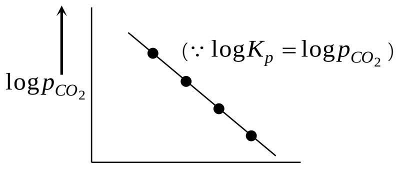
According to Arrhenius equation we have

$$K=Ae^{-\Delta H^\circ{}_r/RT}$$

Taking logarithm, we have

$$\log K_p=\log A-\frac{\Delta H_r^o}{RT(2.303)}$$

This is an equation of straight line. When log K_p is plotted against 1 / T. we get a straight line.



The intercept of this line = log A, slope = $-\Delta H^\circ_r$ / 2.303 R

Knowing the value of slope from the plot and universal gas constant R, ΔH°_r can be calculated.

(Equation of straight line : $Y=mx+C$. Here,

$$\underset{Y}{\log K_p}=\underset{m}{-\frac{\Delta H_r^o}{2.303R}}\underset{x}{\left(\frac{1}{T}\right)}+\underset{C}{\log A}$$

10. (b) $K_p=K_c(RT)^{\Delta n}$; When $\Delta n=2-(2+1)=-1$, *i.e.* negative, $K_p<K_c$.

11. (c) $K_1=\frac{[SO_3]}{[SO_2]\,[O_2]^{1/2}}$ and $K_2=\frac{[SO_2]^2[O_2]}{[SO_3]^2}$; $K_2=\frac{1}{K_1^2}$.

13. (c) Reaction is reversed. Hence

$$K=\frac{1}{(2.4\times 10^{-3})}=4.2\times 10^2$$

14. (c) $K_p=\frac{[P_{co}]^2}{[P_{CO_2}]}=\frac{4\times 4}{2}=8$.

15. (d) K_{c_1} for $H_2+I_2 \rightleftharpoons 2HI$ is 50

K_{c_2} for $2HI \rightleftharpoons H_2+I_2$

$$K_{c_2}=\frac{1}{K_{c_1}}=\frac{1}{50}=0.02$$

16. (c) $K_p=K_c(RT)^{\Delta n}$

$\Delta n=-1$ for reaction $2SO_2+O_2 \rightleftharpoons 2SO_3$

So for this reaction K_p is less than K_c.

17. (c) $K_p=K_c(RT)^{\Delta n}$; $\Delta n=2-2=0$

18. (c) For the reaction $H_2+I_2 \rightleftharpoons 2HI$

$\Delta n=0$

So $K_p=K_c$ $\therefore$ 50.0

19. (d) For reaction $2SO_3 \rightleftharpoons O_2+2SO_2$

Δn is + *ve* so K_p is more than K_c.

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

20. (c) $\Delta n = 2-1=1$

$K_p = K_c(RT)$

21. (c) For this reaction there is no change in equilibrium constant by change of volume.

22. (c) If $\Delta n = 0$ then $K_p = K_c$

23. (a) $k_p = k_c(RT)^{\Delta n}$

$\Delta n = 3-2=1$; $k_p > k_c$.

24. (d) Equilibrium constant depends upon temperature.

25. (d) $2NOCl_{(g)} = 2NO_{(g)} + Cl_{2(g)}$

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

$K_p = 3 \times 10^{-6}\ (0.0821 \times 700) = 172.41 \times 10^{-6}$

$= 1.72 \times 10^{-4}$

27. (b) $K' = K^n$; Hence $n = \frac{1}{2}$

$\therefore K' = K^{1/2} = \sqrt{K}$

29. (c) $2NO_2 \rightleftharpoons 2NO + O_2$ ......(i)

$K = 1.6 \times 10^{-12}$

$NO + \frac{1}{2}O_2 \rightleftharpoons NO_2$ ......(ii)

Reaction (ii) is half of reaction (i)

$K = \frac{[NO]^2[O_2]}{[NO_2]^2}$ ......(i)

$K' = \frac{[NO_2]}{[NO]\,[O_2]^{1/2}}$ ......(ii)

On multiplying (i) and (ii)

$$K \times K' = \frac{[NO]^2[O_2]}{[NO_2]^2} \times \frac{[NO_2]}{[NO]\,[O_2]^{1/2}} = \frac{[NO]\,[O_2]^{1/2}}{[NO_2]} = \frac{1}{K'}$$

$$K \times K' = \frac{1}{K'};\quad K = \frac{1}{K'^2};\quad K' = \frac{1}{\sqrt{K}}.$$

30. (b) $K_p = K_c(RT)^{\Delta n}$; $\Delta n = 1$

So K_c will be less than K_p.

32. (d) K_1 for $N_2 + 3H_2 \rightleftharpoons 2NH_3$

K_2 for $NH_3 \rightleftharpoons \frac{1}{2}N_2 + \frac{3}{2}H_2$

$$K_1 \times K_2 = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} \times \frac{[N_2]^{1/2}[H_2]^{3/2}}{[NH_3]}$$

$$K_1 \times K_2 = \frac{1}{K_2};\quad K_2 = \frac{1}{\sqrt{K_1}}$$

34. (a) $K_p = K_c(RT)^{\Delta n}$; $\Delta n = 2-4=-2$

$K_p = 6 \times 10^{-2} \times (0.0812 \times 773)^{-2}$

$$K_p = \frac{6 \times 10^{-2}}{(0.0812 \times 773)^2} = 1.5 \times 10^{-5}.$$

35. (b) $2.303 \log \frac{K_2}{K_1} = \frac{\Delta H}{R} \frac{[T_2 - T_1]}{T_1 \times T_2}$

$\Delta H = +$ve for the reaction

36. (d) $\underset{4}{N_2 + 3H_2} \rightleftharpoons \underset{2}{2NH_3}$

$\Delta n = 2 - 4 = -2$

$K_p = K_c[RT]^{\Delta n}$; $K_p = K_c[RT]^{-2}$

$$K_c = \frac{K_p}{[RT]^{-2}} = \frac{1.44 \times 10^{-5}}{[0.082 \times 773]^{-2}}$$

37. (d) Catalyst does not affect equilibrium constant.

38. (d) K for dissociation of HI =?

$H_2 + I_2 \rightleftharpoons 2HI$

$K_a = 50$, $K_b = \frac{1}{50} = 0.02$

39. (b) $\underset{3}{2SO_2 + O_2} \rightleftharpoons \underset{2}{2SO_3}$ for this reaction

$\Delta n = -1$; $\therefore K_c > K_p$

40. (b) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

$K_p = P_{CO_2}$

Solid molecule does not have partial pressure so in calculation of K_p only P_{CO_2} is applicable.

41. (d) $NH_3 \rightleftharpoons \frac{1}{2}N_2 + \frac{3}{2}H_2$

$K_c = \frac{[N_2]^{1/2}[H_2]^{3/2}}{NH_3}$ and $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$

$K_c = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$

So for dissociation $= \frac{1}{K_c}$

42. (b) Given $x = \frac{22}{100}$ and $a = 3.2$

$\therefore [HI]$at equilibrium $= 3.2\left[1 - \frac{22}{100}\right] = 2.496$

43. (b) K_c does not depend upon initial concentration of reactants or product.

44. (d) K_p and K_c are characteristic for a given reaction if $\Delta n = 0$ then there is no change.

45. (c) $K_{c_1} = \frac{[NO]^2[O_2]}{[NO_2]^2} = 1.8 \times 10^{-6} \Rightarrow K_{c_2} = \frac{[NO_2]}{[NO]\,[O_2]^{1/2}}$

$K_{c_1} = \frac{1}{K_{c_2}^2}$; $1.8 \times 10^{-6} = \frac{1}{K_{c_2}{}^2} \Rightarrow K_{c_2} = 7.5 \times 10^2$

46. (c) $K_1 = \frac{[H_2S]}{[H_2]\,[S_2]^{1/2}}$; $K_2 = \frac{[HBr]^2}{[H_2]\,[Br_2]}$

$K_3 = \frac{[HBr]^2 \times [S_2]^{1/2}}{[Br_2] \times [H_2S]}$; $\frac{K_2}{K_1} = K_3$

47. (b) $K_p=\frac{p^2}{4};\ 0.11=\frac{p^2}{4}\Rightarrow p^2=0.44$

or $p=\sqrt{0.44}=0.66444\approx 0.665\,atm$

50. (a) $C_{12}H_{22}O_{11(s)}+12O_{2(g)}\rightarrow 12CO_{2(g)}+11H_2O$

$\Delta n=12-12=0$

51. (a) In this reaction gaseous molecule count

$MgCO_3\rightarrow MgO_{(s)}+CO_{2(g)}$

$K_p=P_{CO_2}$

53. (a) $K_p=K_c[RT]^{\Delta n};\ \Delta n=-1,\ K_c=26$

$R=0.0812, T=250+273=523K$

$K_p=26[0.0812\times 523]^{-1}=0.605\approx 0.61$

55. (a) $2AB\rightleftharpoons A_2+B_2$

$$K_c=\frac{[A_2][B_2]}{[AB]^2}$$

For reaction $AB\rightleftharpoons \frac{1}{2}A_2+\frac{1}{2}B_2$

$$K_c{}'=\frac{[A_2]^{1/2}[B_2]^{1/2}}{[AB]};\ K_c{}'=\sqrt{K_c}=\sqrt{49}=7.$$

56. (a) For this reaction Δn is negative & ΔH is positive so it take forward by decrease in temperature.

57. (b) Chemical equilibrium of reversible reaction is not influenced by catalyst. It is affected by pressure, temperature & concentration of reactant.

58. (c) ΔH is positive so it will shift toward the product by increase in temperature.

59. (c) $CO(g)+Cl_2(g)\rightleftharpoons COCl_2(g)$

$\Delta n=1-2=-1$

$$K_p=K_c[RT]^{\Delta n};\ \therefore\ \frac{K_p}{K_c}=[RT]^{-1}=\frac{1}{RT}$$

60. (c) ΔH is positive so reaction move forward by increase in temperature & value of $\Delta n=3-2=+1$ is positive so it forward with decrease in pressure.

61. (b) $2A(g)\rightleftharpoons 3C(g)+D(s)$

For this reaction, $\Delta n_g=3-2=1$

$$\therefore K_p=K_c[RT]^1 \text{ or } \frac{K_p}{K_c}=RT \text{ or } K_c=\frac{K_p}{RT}$$

62. (a) According to Le-Chatelier principle exothermic reaction is forwarded by low temperature, in forward direction number of moles is less, hence pressure is high.

63. (d) In this reaction ΔH is negative so reaction move forward by decrease in temperature while value of $\Delta n=2-3=-1$ *i.e.*, negative so the reaction move forward by increase in pressure.

64. (a) $PCl_5(g)\rightleftharpoons PCl_3(g)+Cl_2(g)$

For this reaction $\Delta n=2-1=1$

Value of Δn is positive so the dissociation of PCl_5 take forward by decrease in pressure & by increase in pressure the dissociation of PCl_5 decrease.

65. (b) $N_2+O_2\rightleftharpoons 2NO$ .....(i)

$\frac{1}{2}N_2+\frac{1}{2}O_2\rightleftharpoons NO$ ......(ii)

For equation number (i)

$$K_1=\frac{[NO]^2}{[N_2][O_2]} \qquad \text{..... (iii)}$$

For equation number (ii)

$$K_2=\frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}} \qquad \text{...... (iv)}$$

From equation (iii) & (iv) it is clear that

$K_2=(K_1)^{1/2}=\sqrt{K_1}$; Hence, $K_2=\sqrt{K_1}$

66. (b) $K_p=K_c[RT]^{\Delta n_g}$

$\Delta n_g=1-1.5=-0.5$

$$K_p=K_c[RT]^{-1/2}\quad \therefore\ \frac{K_p}{K_c}=[RT]^{-1/2}$$

67. (b) $N_{2(g)}+O_{2(g)}\rightleftharpoons 2NO_{(g)}$

$K_c=0.1, K_p=K_c(RT)^{\Delta n}$

$\Delta n=0, K_p=K_c=0.1$

68. (c)

$$\begin{array}{ccccc} A & + & 3B & \rightleftharpoons & 4C \\ a & & b & & 0 \\ (a-x) & & (b-3x) & & 4x \end{array}$$

$$K_C=\frac{[C]^4}{[A][B]^3}=\frac{4x.4x.4x.4x}{(a-x)(b-3x)}$$

Given $a=b, a-x=4x\Rightarrow a=5x=b$

$$K_C=\frac{4x.4x.4x.4x}{(5x-x)(5x-3x)}=\frac{4x.4x.4x.4x}{4x.2x.2x.2x}=8.$$

69. (b) Equilibrium pressure = 3atm

$NH_4COONH_{2(s)}\rightleftharpoons 2NH_{3(g)}+CO_{2(g)}$

$K_p=p^2_{NH_3}\cdot p_{CO_2}=3^2.3=27$

Activation energy, Standard free energy and Degree of dissociation and Vapour density

1. (b) $\frac{\text{Normal molecular weight}}{\text{experimental molecular wt.}}=1+\alpha$

$NH_4Cl\rightleftharpoons NH_3+HCl$

$\because \alpha=1\ \therefore$ Experimental Molecular wt $=\frac{\text{nor.mol.wt.}}{2}$

2. (b) If $\Delta G^o=0$

$\Delta G^o=-2.303\ RT\ \log K_p$

$\log K_p=0 \qquad (\because \log 1=0)$

$K_p=1.$

5. (d) $\Delta G^o=-2.303\times 8.314\times 10^{-3}\times 298\ \log K_p$

$$1.7 = -2.303 \times 8.314 \times 10^{-3} \times 298 \times \log K_p$$

$$K_p = 0.5$$

6. (a) Equilibrium shifts backward by Le-chatelier's principle.

7. (c) Decreases the activation energy of both forward and backward reaction.

8. (d) Equilibrium constant changes with temperature, pressure and the concentration of either reactant or product.

9. (a) As we know that, $\Delta G^o = -2.303 RT \log K_p$

Therefore, $\Delta G^o = -2.303 \times (8.314) \times (298)$

$$(\log 2.47 \times 10^{-29})$$

$$\Delta G^o = 16{,}3000\, J\, mol^{-1} = 163\, KJ\, mol^{-1}$$

Le-Chaterlier principle and It's application

2. (a) $N_2 + O_2 \rightleftharpoons 2NO;\ Q\ cal$

The above reaction is endothermic so for higher production of *NO*, and the temperature should be high.

4. (c) At low pressure, reaction proceeds where volume is increasing. This is the favourable condition for the reaction. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$.

6. (c) Reaction is exothermic and volume is decreasing from left to right so for higher production of SO_3 there should be low temperature and high pressure.

7. (a) $\underset{\text{more volume}}{\text{Ice}} \rightleftharpoons \underset{\text{less volume}}{\text{Water}}$

On increasing pressure, equilibrium shifts forward.

8. (c) Exothermic reaction is favoured by low temperature to proceed in forward direction.

9. (a) Effect of catalyst is that it attains equilibrium quickly by providing a new reaction path of low activation energy. It does not alter the state of equilibrium.

11. (a) On increasing temperature equilibrium will shift in forward direction due to decrease in intermolecular forces of solid.

12. (c) Both Δn and ΔH are negative. Hence, high pressure and low temperature will forward reaction.

13. (b) Exothermic reaction, favoured by low temperature.

14. (c) $\Delta n = 0$, No effect of pressure.

15. (b) The reaction is endothermic in reverse direction and hence increase in temperature will favour reverse reaction.

16. (c) A reaction is in equilibrium it will shift in reverse or backward direction when we increase the concentration of one or more product (from Le chatelier's principle).

17. (a) According to Le chatelier's principle.

18. (c) The reaction takes place with a reduction in number of moles (volume) and is exothermic. So high pressure and low temperature with favour the reaction in forward direction

19. (b) At equilibrium, the addition of $(CN)^-$ would decrease the (H^+) ion concentration to produce more and more *HCN* to nullified the increase of CN^-_{aq}.

20. (b) $H_2X_2 + \text{heat} \rightleftharpoons 2HX.$

Reaction is endothermic and volume increasing in forward direction so according to Le chatelier's principle for formation of *HX*, Temperature of the reaction should be high and pressure should be low.

21. (b) According to Le chatelier's principle.

22. (d) In reaction $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$

Volume is decreasing in forward direction so on increasing pressure the yield of product will increase.

25. (a) In endothermic reaction rate of forward reaction can be increased by raising temperature.

26. (a) Being endothermic, the forward reaction is favoured by high temperature.

27. (c) According to Le chatelier's principle.

28. (b) On adding more PCl_5, equilibrium shifts forward.

29. (a) According to Le chatelier's principle.

30. (b) Increase in pressure causes the equilibrium to shift in that direction in which no. of moles (volume) is less.

32. (b,c) According to Le-chatelier's principle.

37. (d) By increasing the amount of F_2 in the reaction the amount of ClF_3 increases.

39. (b) According to Le chatelier's principle when we increase pressure reaction proceeds in that direction where volume is decreasing.

40. (a) Factors affecting equilibrium are pressure, temperature and concentration of product or reactant.

42. (b) According to Le chatelier's principle.

43. (d) Increase in volume, *i.e.*, decrease in pressure shifts the equilibrium in the direction in which number of moles increases (Δn positive)

46. (d) At constant volume. Three is no change in concentration (closed container).

47. (c) $H_2O(g) \rightleftharpoons H_{2(g)} + \frac{1}{2} O_{2(g)}$

In this reaction volume is increasing in the forward reaction. So on increasing temperature reaction will proceed in forward direction.

48. (b) When temperature increases precipitation of sodium sulphate takes place. Because reaction is exothermic so reverse reaction will take place.

49. (a) For high yield of ammonia low temperature, high pressure and high concentration of the reactant molecule.

53. (c) Since $\Delta n = 0$.

54. (a) The rate of backward reaction favoured by increase of pressure in the reaction as Δn is positive

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

55. (a) $H_{2(g)} \underset{2}{+} I_{2(g)} \rightleftharpoons 2\underset{2}{H}I$

$\Delta n = 0$; $\because$ $K_c = K_p$

56. (c) Solid + liquid $\rightleftharpoons$ Solution ΔH =+ve

Increase in temperature favours forward reaction.

57. (a) Addition of an inert gas of constant volume condition to an equilibrium has no effect.

58. (b) Le chatelier principle is not applicable to solid-solid equilibrium.

59. (a) $\underset{2}{A+B}+Q \rightleftharpoons \underset{2}{C+D}$

The reaction is endothermic so on increase temperature concentration of product will increase.

60. (a) In that type of reaction the state of equilibrium is not effected by change in volume (hence pressure) of the reaction mixture.

61. (c) $N_2+O_2 \rightleftharpoons 2NO\,;\ \Delta n=0$

65. (c) High temperature and low pressure.

66. (d) High temperature and excess concentration of the reactant concentration.

68. (c) Low temperature and high pressure.

69. (a) $H_2+I_2 \rightleftharpoons 2HI \Rightarrow \Delta n=2-2=0$.

70. (d) Low temperature and low pressure.

73. (c) It is an exothermic reaction hence low temperature and increasing pressure will favour forward reaction

Critical Thinking Questions

1. (b) $K_c=\dfrac{[PCl_3][Cl_2]}{[PCl_5]}=\dfrac{\left[\dfrac{20}{100}\right]\times\left[\dfrac{20}{100}\right]}{\left[\dfrac{80}{100}\right]}$

$$=\frac{0.2\times0.2}{0.8}=\frac{0.04}{0.8}=0.05$$

2. (b) $2NH_3 \rightleftharpoons N_2+\ 3H_2$

Initial mole a 0 0

Mole at equilibrium $(a-2x)$ x $3x$

Initial pressure of NH_3 of a mole = 15 atm at 27^oC

The pressure of 'a' mole of $NH_3=p$ atm at 347^oC

$\therefore\ \dfrac{15}{300}=\dfrac{p}{620}$

$\therefore\ p=31$ atm

At constant volume and at 347^oC, mole $\propto$ pressure

$a\propto 31$ (before equilibrium)

$\therefore\ a+2x\propto 50$ (after equilibrium)

$\therefore\ \dfrac{a+2x}{a}=\dfrac{50}{31}$

$\therefore\ x=\dfrac{19}{62}a$

$\therefore$ % of NH_3 decomposed $=\dfrac{2x}{a}\times100$

$$=\frac{2\times19a}{62\times a}\times100=61.33\%$$

3. (d) $K_p=K_c(RT)^{\Delta n}$ R = Gas constant

$$K_c=\frac{K_p}{(RT)^{\Delta n}}=\frac{1.3\times10^{-3}}{(0.0821\times700)^{-1}}=7.4\times10^{-2}$$

4. (b) Reaction is reversed and halved.

$$K=\sqrt{1/1.8\times10^{-6}}=7.5\times10^2$$

5. (d) Conc. is not known so we can't calculate.

6. (a) $\underset{2}{2SO_3} \rightleftharpoons \underset{3}{2SO_2+O_2}$

$\Delta n=3-2=+1;\ \ K_p=1.80\times10^{-3}$

$[RT]^{\Delta n}=(8.314\times700)^1$

$$K_c=\frac{K_p}{(RT)^{\Delta n}}=\frac{1.8\times10^{-3}}{(8.314\times700)^1}$$

$=3.09\times10^{-7}$ *mole-litre.*

7. (c) $\underset{0.1}{N_2O_4} \rightleftharpoons \underset{0}{2NO_2}$

$(.1-\alpha)$ 2α

$\because$ P $\propto$ 0.1

If V and T are constant (P$\propto$0.1+ α)

$\mathrm{P}=(0.1+\alpha)/0.1$

$$K_p=\frac{[2\alpha]^2}{[0.1-\alpha]}\times\left[\frac{P}{0.1+\alpha}\right]\ \text{or}\ K_p=\frac{40\alpha^2}{[0.1-\alpha]}=0.14$$

$\alpha=0.017$

$NO_2=0.017\times2=0.034$ *mole*

8. (d) $CH_3OH\rightarrow CO+2H_2$

$$\frac{[H_2]^2[CO]}{[CH_3OH]}=\frac{0.1\times0.1\times1}{2}=\frac{0.01}{2}=\frac{10\times10^{-3}}{2}$$

$=5\times10^{-3}$.

9. (d)

$$\begin{array}{lcccccc} & AB & + & CD & \rightleftharpoons & AD & + & CD \\ \text{mole at } t=0 & 1 & & 1 & & 0 & & 0 \\ \text{Mole at equilibrium} & \left(1-\frac{3}{4}\right) & & \left(1-\frac{3}{4}\right) & \rightleftharpoons & \left(\frac{3}{4}\right) & & \left(\frac{3}{4}\right) \\ & 0.25 & & 0.25 & \rightleftharpoons & 0.75 & & 0.75 \end{array}$$

$$K_c=\frac{0.75\times0.75}{0.25\times0.25}=\frac{0.5625}{0.0625}=9$$

10. (d) According to Le-chatelier's principle.

11. (d) K_p (equilibrium constant) is independent of pressure and concentration.

Assertion & Reason

2. (e) Assertion is false but reason is true.

$K_p\neq K_c$ for all reaction.

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

$\Delta n=$ number of moles of products – number of moles of reactants in the balanced chemical equation.

So, if for a reaction $\Delta n=0$. Then $K_p=K_c$

3. (e) Assertion is false but reason is true.

$K_c = [H_2O]^2$, because concentration of solids is taken to be unity.

4. (a) Both assertion and reason are true and reason is the correct explanation of assertion.

$CO(H_2O)_6^{2+}$ (Pink) while $CoCl_4^{2-}$ (blue). So, on

Cooling because of Le-chatelier's principle the reaction tries to over come the effect of temperature.

5. (e) Assertion is false but reason is true.

$$aA+bB \rightleftharpoons cC+dD,\ Qc = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

If $Q_c > K_c$, reaction will proceed in the direction of reactants.

If $Q_c < K_c$, reaction will move in direction of products.

If $Q_c = K_c$, the reaction mixture is already at equilibrium.

6. (c) Assertion is true but reason is false. This is based on common ion effect.

$$NaCl \rightleftharpoons Na^+ + Cl^-;\quad HCl \rightleftharpoons H^+ + Cl^-$$

Concentration of Cl^- ions increases due to ionisation of HCl which increases the ionic product $[Na^+][Cl^-]$. This result in the precipitation of pure $NaCl$.

7. (b) Both assertion and reason are true and reason is not the correct explanation of assertion, solid+heat $\rightleftharpoons$ liquid, so on heating forward reactions is favoured and amount of solid will decrease.

8. (a) $aA+bB \rightleftharpoons cC+dD$

$$K_C = \frac{[C]^C[D]^d}{[A]^a[B]^b}$$

For $2aA+2bB \rightleftharpoons 2cC+2dD$

$$K_C = \frac{[C]^{2c}[D]^{2d}}{[A]^{2a}[B]^{2b}}.$$

9. (a) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

$$K_C = \frac{[HI]^2}{[H_2][I_2]}$$

For reverse reaction $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$

$$K_C = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{K_C}.$$

10. (c) The value of *K* depends on the stoichiometry of reactants and products at the point of equilibrium. For *e.g.,* if the reaction is multiplied by 2, the equilibrium constant is squared.

11. (d) Catalyst does not affect the final state of the equilibrium. It enables the system to attain equilibrium state earlier by providing an alternative path which involve lower energy of activation.

12. (e) $K_p = \frac{p_{H_2}^3 \times p_{N_2}}{p_{NH_3}} = \frac{(atm)^3(atm)}{(atm)^2} = (atm)^2$

or $\Delta n = 4-2 = 2$.

Unit of K_p for given reaction $= (atm)^2$.

13. (c) According to Le-Chatelier's principle endothermic reaction favours increase in temperature. However exothermic reaction favours decrease in temperature.

14. (d) $K_p = K_c(RT)^{\Delta n}$; where $\Delta n = (l+m)-(x+y)$

Concentration of solids and liquids is taken to be unity.

15. (e) Increase in pressure favours melting of ice into water because at higher pressure melting point of ice is lowered.

16. (e) As assertion is exothermic, low temperature favours forward reaction. High pressure favours forward reaction as it is accompanied by decrease in the number of moles.

17. (e) There is no change in number of gas molecules. Therefore the expression for *K* is independent of volume. Hence *K* will remain same.