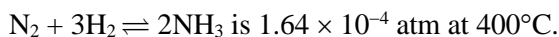


<H1>Additional Objective Questions

<H2>Single Correct Choice Type

1.(C) Physical equilibrium do not include any chemical change.

2.(D) The equilibrium constant K for the reaction



3.(D) Since, the product in reaction given in option (D) is not much stable, therefore, the reaction is reversible.

4.(A) For reaction $2\text{NO}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$; $\Delta n_g > 0$

So, if volume increases, pressure decreases and n decreases, therefore, the reaction will move in the direction where n increases, that is in the forward direction which in turn will favor the formation of products.

5.(B) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

Applying law of mass action,

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

Given that $[\text{H}_2] = 8.0 \text{ mol L}^{-1}$, $[\text{I}_2] = 3.0 \text{ mol L}^{-1}$ $[\text{HI}] = 28.0 \text{ mol L}^{-1}$

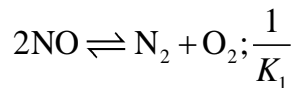
$$K_c = \frac{(28.0)^2}{(8.0) \times (3.0)} = 32.66$$

6.(C) According to Le Chatelier's principle, for an exothermic reaction, on lowering the temperature will shift the reaction in forward direction. Also, as the number of gaseous moles is decreasing, so on increasing the pressure, the reaction will shift in forward direction.

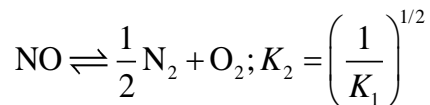
7.(A) For first reaction,



On reversing reaction,



For second reaction



Therefore,

$$K_2 = \left(\frac{1}{K_1} \right)^{1/2}$$

\Rightarrow

$$K_2^2 = \left(\frac{1}{K_1} \right)$$

Or

$$K_1 = \left(\frac{1}{K_2^2} \right)$$

8.(D) We know

$$\Delta G^{\circ} = \Delta G_{\text{NO}_2}^{\circ} - \Delta G_{\text{NG}}^{\circ} = (52 - 87) \text{ kJ mol}^{-1} = -35 \text{ kJ mol}^{-1}$$

Since, $\Delta G^{\circ} = -2.303 RT \log K$

$$\log K = \frac{-35 \text{ kJ mol}^{-1}}{-8.301 \text{ kJ mol}^{-1} \times 298 \text{ K}}$$

On solving, we get

$$K = 1.365 \times 10^6$$

9.(A) For $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SO}_3$ $K'_C = (1/K_C)$;

For $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ $K'_C = (1/K_C)^2$

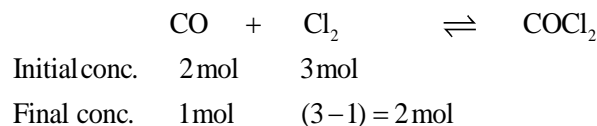
Therefore,

$$K'_C = \left(\frac{1}{4.9 \times 10^{-2}} \right)^2 = \frac{10^4}{4.9 \times 4.9} = \frac{10000}{24.01} = 4.1649 \times 100 = 416.49$$

10.(D) K_C is a characteristic constant for the given reaction.

11.(C) This is because according to Le Chatelier's principle, increase in H^+ ions will shift the equilibrium in the forward direction.

12.(B) We have



Equilibrium constant can be calculated as $K_C = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]}$

Therefore, $K_C = \frac{(1 \text{ mol}/5 \text{ L})}{(1 \text{ mol}/5 \text{ L}) \times (2 \text{ mol}/5 \text{ L})} = 2.5$

13.(B) From the given reaction, we have

$$K_p = p_{\text{H}_2\text{O}}^4 = 6.89 \times 10^{-12} \text{ therefore } p_{\text{H}_2\text{O}} = 1.62 \times 10^{-3} \text{ atm}$$

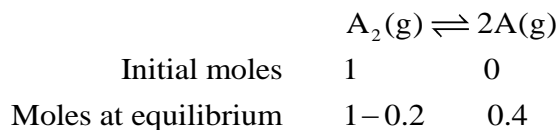
14.(B) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$

$$K_p = \frac{[p_{\text{SO}_3}]^2}{[p_{\text{SO}_2}]^2 [p_{\text{O}_2}]} = \frac{(0.331)^2}{(0.559)^2 (0.101)} = 3.47$$

SO₂ and SO₃ have same number of moles; their partial pressure will be equal

$$p_{\text{SO}_3} = p_{\text{SO}_2}, \text{ therefore } p_{\text{SO}_2} \frac{1}{3.47} = 0.288 \text{ atm}$$

15.(A) The answer should be



$$\text{So, } x_{\text{A}(\text{g})} = \frac{0.4}{1.2} = 0.33 \text{ and } x_{\text{A}_2(\text{g})} = 1 - 0.33 = 0.67$$

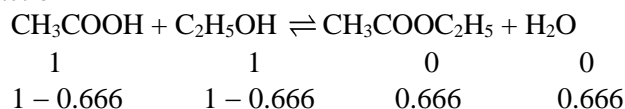
$$\text{Now, } K_p = \frac{(p_{\text{A}(\text{g})})^2}{p_{\text{A}_2(\text{g})}} = \frac{(x_{\text{A}(\text{g})})^2 \times (1)^2}{(x_{\text{A}_2(\text{g})}) \times (1)} \quad (\text{as } p_{\text{total}} = 1)$$

Thus, we get $K_p = 1/6$

$$\text{Now, } \Delta G = RT \ln K_p = -8.314 \times 320 \times \ln(6) = -4766 \text{ J mol}^{-1}$$

16.(D) Since, equilibrium constant depends on temperature only, therefore, K remains unchanged but degree of dissociation changes.

17.(D) For the given reaction



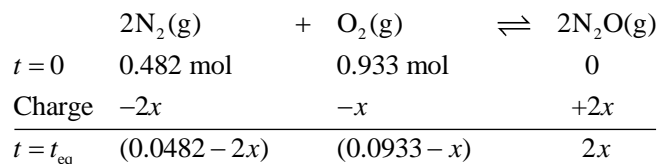
The equilibrium constant is

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{[0.666][0.666]}{[0.333][0.333]}$$

Let x mol of ester is formed from 1 mol of acid and 0.5 mol of alcohol, then

$$K_c = \frac{x^2}{(1-x)(0.5-x)} = 4 \Rightarrow x = 0.43$$

18.(C) The reaction involved is



The equilibrium constant is

$$K_c = 2 \times 10^{-37} = \frac{(2x)^2}{(0.0482 - 2x)^2 \times (0.0933 - x)}$$

As K_c has small value, x should be low

$$0.0482 - 2x \approx 0.0482$$

$$0.0933 - x - x = 0.0933$$

$$2 \times 10^{-37} = \frac{4x^2}{0.0482 \times 0.0933}$$

On solving, we get

$$x = 3.3 \times 10^{-21}$$

As,

$$[\text{N}_2\text{O}] = 2x = 6.6 \times 10^{-21}$$

Therefore,

$$[\text{N}_2] \approx 0.0482 \text{ M}; [\text{O}_2] = 0.0993 \text{ M}$$

19.(B) When the denominator is increased by 2, $p_{\text{HCl}}^2 = 2$

$$\text{Therefore } p_{\text{HCl}} = \sqrt{2} = 1.414$$

20.(C) By writing the equation for the reverse reaction



as $\frac{1}{K_p}$ and relating it to the desired reaction, the result can be obtained.

21.(A) Since, equilibrium is affected by temperature and pressure, therefore, at equilibrium, the amount of X_3Y is also affected by temperature and pressure.

22.(D) Concept based.

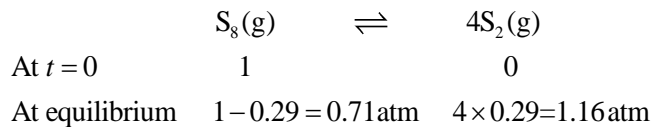
23.(A) (i) $K_p = K_c(RT)^{\Delta n}$

(ii) Therefore, $\Delta n = 1$ and

$$K_c = \frac{K_p}{RT} = \frac{167}{0.0821 \times 1073} = 1.90$$

$$\text{Since } \Delta n = 1, \text{ therefore } K_c = \frac{K_p}{RT} = \frac{1.8 \times 10^{-2}}{0.082 \times 500} = 4.4 \times 10^{-4}$$

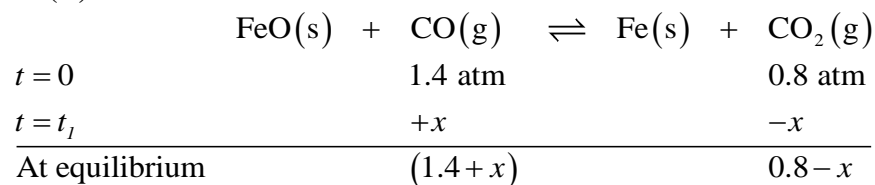
24.(C) The reaction is



The equilibrium constant is

$$K_p = \frac{[p_{\text{S}_2}]^4}{[p_{\text{S}_8}]} = \frac{(1.16)^4}{(0.71)} = 2.55 \text{ atm}^3$$

25.(A)



The reaction quotient is

$$Q = \frac{0.8}{1.4} = \frac{4}{7} = 0.55$$

Since, $Q > K$, system is not at equilibrium, and to attain equilibrium, it will shift in backward direction

$$K_p = 0.265 = \frac{0.8 - x}{1.4 + x}$$

On solving, we get $x = 0.339$

Therefore $[p_{\text{CO}}] = 1.739 \text{ atm}$ and $p_{\text{CO}_2} = 0.461 \text{ atm}$

26.(C) As K_C is neither too high nor very low, reactants and products will be present in comparable amounts.

$$27.\text{(C) Moles of I}_2 \text{ taken} = \frac{46}{254} = 0.181$$

$$\text{Moles of H}_2 \text{ taken} = \frac{1}{2} = 0.5$$

$$\text{Moles of I}_2 \text{ remaining} = \frac{1.9}{254} = 0.0075$$

$$\text{Moles of I}_2 \text{ used} = 0.181 - 0.0075 = 0.1735$$

$$\text{Moles of H}_2 \text{ used} = 0.1735$$

$$\text{Moles of H}_2 \text{ remaining} = 0.5 - 0.1735 = 0.3265$$

$$\text{Moles of HI formed} = 0.1735 \times 2 = 0.347$$

28.(B) The equilibrium constant for the given reaction is,

$$K_p = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}} \times P_{\text{H}_2}^2} = \frac{2.0}{1.0 \times (0.1)^2} = 200 \text{ atm}^{-1}$$

29.(A) Given that $K_p = 1.64 \times 10^{-4} \text{ atm}$, $K_{p2} = ?$; $T_1 = 400 + 273 = 673 \text{ K}$, $T_2 = 500 + 273 = 773 \text{ K}$; $\Delta H = -105185.8 \text{ J}$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Applying the equation

$$\log K_{p_2} - \log K_{p_1} = \frac{\Delta H}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log K_{p_2} = \log 1.64 \times 10^{-4} - \frac{105185.8}{2.303 \times 8.314} \left(\frac{773 - 673}{773 \times 673} \right)$$

or

$$K_{p2} = 0.144 \times 10^{-4} \text{ atm.}$$

30.(D) Increasing the amount of CO(g) in reactant part, the amount of CO₂(g) in product can be increases.

31.(B) The reaction quotient for the given reaction is

$$Q_p = \frac{(p_{\text{NH}_3})^2}{p_{\text{N}_2} \times (p_{\text{H}_2})^3} = \frac{(3)^2}{(1)(2)^3} = \frac{9}{8} \text{ atm}^{-1} = 1.125 \text{ atm}^{-2}$$

32.(A) For the given reaction $p_{\text{CO}} \gg p_{\text{CO}_2}$, hence $K_p = \frac{1}{p_{\text{CO}}} = \frac{1}{400 \times 10^6} = 2500$

$$\Delta G^\circ = -RT \ln K_p; \ln K_p = \frac{\Delta G^\circ}{RT} = \frac{20700 + 11.97T}{RT}$$

The equation when solved for T using $R = 8.314 \text{ K}^{-1} \text{ mol}^{-1}$ gives $T = 399 \text{ K}$.

33.(C) From the given equation,

$$\log K_p = 30.0 - \frac{6.36 \times 10^3}{T} - 5.7 \log T$$

We know

$$\Delta G^\circ = -RT \ln K_p = -2.303RT \log K_p$$

Therefore,

$$\begin{aligned} \Delta G^\circ &= -2.303 \times 1.987 \times 600 \left[30.1 - \frac{6.36 \times 10^3}{600} - 5.7 \log 600 \right] \\ &= -2.303 \times 1.987 \times 600 [30.1 - 10.6 - 5.7 \times 2.778] \\ &= -[2.303 \times 1.987 \times 600 \times 3.6654] \text{ cal mol}^{-1} \\ &= -10063.9 \text{ cal mol}^{-1} = -10.064 \text{ kcal mol}^{-1} \end{aligned}$$

34.(B) We know

$$\text{Vapor density} = \frac{\text{Molecular weight of } \text{PCl}_5}{2} = \frac{208.5}{2} = 104.25$$

Applying the formula,

$$0.8 = \frac{104.25 - d}{(2-1)d}$$

⇒

$$0.8d = 104.25 - d$$

⇒

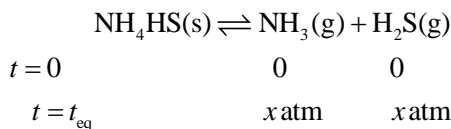
$$1.8d = 104.25$$

⇒

$$d = \frac{104.25}{1.8} = 57.9$$

35.(B) According to Le Chatelier's principle, if CO₂ escapes from the system, then carbonic acid will not be form and as a result the hydrogen ion concentration will diminish.

36.(A) The reaction is



Now, $p_T = 2x = 1.12 \Rightarrow x = 0.56$; $K_p = x^2 = 0.3136 \text{ atm}^2$

37.(D) $\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}$, molecular mass of $\text{N}_2\text{O}_4 = (28 + 64) = 92$

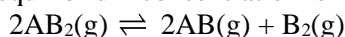
Vapor density, $D = \frac{92}{6} = 46$

Let the degree of dissociation be x . Applying the relationship,

$$x = \frac{D - d}{d} = \frac{(46 - 30)}{30} = \frac{16}{30} = 0.533$$

Degree of dissociation = 53.3%.

38.(A) For the given equilibrium, the equilibrium concentration is



Equilibrium concentration $c(1 - \alpha)$, $c\alpha$, $\frac{c\alpha}{2}$

Therefore,
$$K_p = \frac{(p_{\text{B}_2})(p_{\text{AB}})^2}{(p_{\text{AB}_2})^2} = \frac{(c\alpha/2) \times (c\alpha)^2}{[c(1-\alpha)]^2} \times \frac{p_T}{[c(1+\alpha/2)]} = \frac{\alpha^3 \times p_T}{2(1-\alpha)^2 \left(1 + \frac{\alpha}{2}\right)}$$

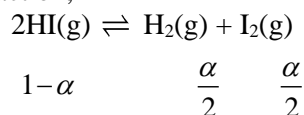
As α is small compared with unity, so $1 - \alpha \approx 1$ and $1 + \frac{\alpha}{2} \approx 1$ therefore $K_p = \frac{\alpha^3 \times p_T}{2}$

39.(A) Melting of ice is the endothermic process, and on melting, volume decreases. Hence, high temperature and high pressure is favorable.

40.(B) $K_p = K_C (RT)^{\Delta n}$ where $K_p = 1.44 \times 10^{-5}$, $\Delta n = 2 - 4 = -2$. Hence,

$$K_C = \frac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$$

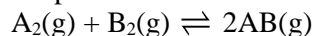
41.(D) For the given reaction,



The equilibrium constant is

$$K_p = \frac{\left(\frac{\alpha}{2} p_T\right)^2}{(1 - \alpha)^2 p_T^2} \text{ or } \frac{\alpha}{1 - \alpha} = 2\sqrt{K_p} \text{ or } \alpha = \frac{2\sqrt{K_p}}{1 + 2\sqrt{K_p}}$$

42.(A) The equilibrium is represented as:



Initial concentration 1 2 0

Moles at equilibrium $1-x$ $2-x$ $2x$

Total volume = $1 + 2 = 3$ L

$$[A_2] = \frac{1-x}{3}, [B_2] = \frac{2-x}{3}, [AB] = \frac{2x}{3}$$

$$K = \frac{[AB]^2}{[A_2][B_2]} = \frac{2x/3}{(1-x)/3(2-x)/3} = 50$$

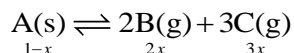
On solving, we get $23x^2 - 75x + 50 = 0 \Rightarrow x = 2.31$ or 0.943 .

As x cannot be more than 1, so $x = 0.943$

Number of moles of AB formed = $2 \times 0.943 = 1.886$ mol.

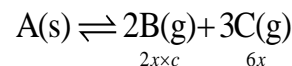
43.(A) The degree of dissociation cannot be calculated from the vapor density data because here, the number of moles remains unchanged before and after reaching equilibrium.

44.(D) For the given reaction,



The equilibrium constant is

$$K_C = 4x^2 \times 27x^3 = 108x^5$$



$$108x^5 = 4x^2 \times c^2 \times 27x^3 \Rightarrow 108 = c^2 \times 216 \times 4$$

$$c^2 = \frac{108}{4 \times 216} \Rightarrow c = \frac{1}{2\sqrt{2}}$$

45.(B) The ratio of number of moles will be the same as the ratio of volume.

According to Dalton's law, the partial pressure of a gas in a mixture is given by the product of its volume fraction and the total pressure.

Therefore, the equilibrium pressure of each gas is,

$$p_{NH_3} = \frac{9.6}{100} \times 50 \text{ atm} = 4.8 \text{ atm}$$

$$p_{N_2} = \frac{22.6}{100} \times 50 \text{ atm} = 11.3 \text{ atm}$$

$$p_{H_2} = 67.6 / 100 \times 50 \text{ atm} = 33.9 \text{ atm}$$

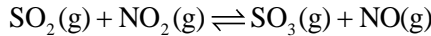
Total pressure = 50 atm

$$K_p = \frac{[p_{NH_3}]^2}{[p_{N_2}][p_{H_2}]^3}$$

Substituting the values of partial pressures,

$$K_p = \frac{(4.80 \text{ atm})^2}{(11.3 \text{ atm})(33.9 \text{ atm})^3} = 5.23 \times 10^{-5} \text{ atm}^{-2}$$

46.(C) The reaction is



Initial concentration 1 1 1 1

At equilibrium $1-x$ $1-x$ $1+x$ $1+x$

The equilibrium constant is

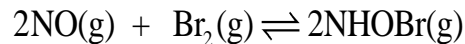
$$K = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]} = \frac{(1+x)(1+x)}{(1-x)(1-x)}$$

$$16 = \frac{(1+x)^2}{(1-x)^2} \Rightarrow \frac{(1+x)}{(1-x)} = 4 \quad \text{or } x = 0.6$$

$$[\text{NO}_2] = 1 - x = 1 - 0.6 = 0.4 \text{ mol L}^{-1}$$

47.(D) Since, equilibrium constant (K) depends on temperature only, therefore, it remains constant with change in p and x .

48.(B) The given reaction is,



Initial 98.4 41.3 0

At equilibrium $98.4 - x$ $41.3 - \frac{x}{2}$ x

Total pressure at equilibrium = 110.5 torr.

$$(98.4 - x) + \left(41.3 - \frac{x}{2}\right) + x = 110.5$$

Solving, we get $x = 58.4$ torr (760 torr = 1 atm)

$$p_{\text{NOBr}} = 58.4 \text{ torr} = 7.68 \times 10^{-2} \text{ atm.}$$

$$p_{\text{NO}} = 98.4 - 58.4 = 40 \text{ torr} = 5.26 \times 10^{-2} \text{ atm.}$$

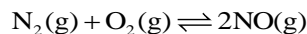
$$K_p = \frac{p_{\text{NOBr}}^2}{p_{\text{NO}}^2 \times p_{\text{Br}_2}} = \frac{(7.68 \times 10^{-2})^2}{(5.26 \times 10^{-2})^2 (1.59 \times 10^{-2})} = 134$$

49.(C) At 40% SO_2 and 40% CO_2 by volume $p_{\text{CO}_2} = \left(\frac{40}{100}\right)p$ and $p_{\text{SO}_2} = \left(\frac{40}{100}\right)p$

So, $p_{\text{SO}_2\text{Cl}_2} = \left(\frac{20}{100}\right)p$ and given that $p = 10$ atm. Therefore,

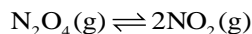
$$\text{Therefore, } K_p = \frac{(p_{\text{CO}_2})(p_{\text{SO}_2})}{(p_{\text{SO}_2\text{Cl}_2})} = \frac{(40/100)p \times (40/100)p}{(20/100)p} = \frac{16 \times 10}{2 \times 10} = 8 \text{ atm}$$

50.(B) For first equation



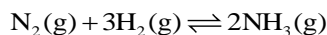
$$\frac{K_p}{K_c} = (RT)^{\Delta n_g} = (RT)^0 = 1$$

For second equation



$$\frac{K_p}{K_c} = (RT)^1 = 24.62 \text{ dm}^3 \text{ atm mol}^{-1}$$

For third equation



$$\frac{K_p}{K_c} = (RT)^{-2} = \frac{1}{(RT)^2} = 1.65 \times 10^{-3} \text{ dm}^{-6} \text{ atm}^{-2} \text{ mol}^2$$

<H2> Multiple Correct Choice Type

1.(B, C, D) The reaction is endothermic as ΔH has a positive sign. Therefore, on increasing temperature, more amount of heat is supplied to the system. So, by Le Chatelier's principle, the system will try to release heat and thus reaction will try to move in the reverse direction.

The no. of moles of gaseous substances reduces as we go from reactant to product side, so on increasing the pressure, the system will try to reduce the pressure by moving in the forward direction. Addition of catalyst will help in adsorption of the gaseous reactants on its surface and help lower the $E_{\text{activation}}$ for conversion of reactants to products. On removing C, again by Le Chatelier's principle, the system will try to produce more and more C, by moving in the forward direction.

2.(A, C)

3.(A, B, C) The relation is expressed as

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

If $T_2 > T_1$ and $\Delta H = 0$, we have

$$\log(K_2/K_1) = 0$$

\Rightarrow

$$K_2/K_1 = 1$$

\Rightarrow

$$K_2 = K_1$$

If $T_2 > T_1$ and $\Delta H > 0$, we have

$$\log(K_2/K_1) > 0$$

\Rightarrow

$$K_2/K_1 > 1$$

\Rightarrow

$$K_2 > K_1$$

If $T_2 > T_1$ and $\Delta H < 0$, we have

$$\log(K_2/K_1) < 0$$

$$\Rightarrow K_2/K_1 < 1$$

$$\Rightarrow K_2 < K_1$$

4.(A, B, C) Catalyst only speeds up the reaction.

5.(A, B, C) As the concentration of reaction (gaseous) is increased at equilibrium, reaction will go in the forward direction. Also, the above reaction is endothermic. Therefore, an increase in temperature will favor it.

6.(B, C) As Q varies as reaction proceeds, therefore, Q may be less, more or equal to K_C .

7.(B, C, D) In accordance with Le Chatelier's principle.

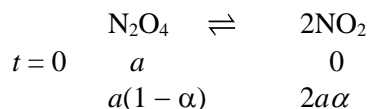
8.(A, C, D)

(A) As the reaction is endothermic, therefore it will go in the forward direction. Hence, moles of CaO will increase.

(C) With the increase or decrease of volume, partial pressure of the gases will remain same.

(D) Due to the addition of inert gas at constant pressure, reaction will proceed in the direction in which more number of gaseous moles are formed.

9.(B, C, D) The reaction is



$$\text{Vapor density} = \frac{46}{1 - \alpha} = 30.67 \Rightarrow \alpha = 0.5 = 50\%$$

$$\text{Total pressure} = \frac{1.5 \times 1.5 \times 0.082 \times 300}{8.2} = 6.67 \text{ atm}$$

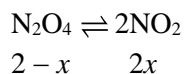
$$\text{So, } K_p = \frac{4\alpha^2}{1 - \alpha^2} p = 9 \text{ atm}$$

$$\text{and density of mixture} = \frac{138}{8.2} \text{ g L}^{-1} = 16.83 \text{ g L}^{-1}$$

10.(B, C) Since, in reactions given in option (B) and (C), the number of moles of products are more than reactants, therefore, the application of high pressure does not increase the yield of product.

11.(A, C) With the increase in pressure, forward reaction is favored, because for forward reaction, lesser number of molecules are involved. This is in accordance with Le Chatelier's principle.

12.(B, C) For the given reaction



The equilibrium constant is

$$K_p = \frac{4x^2}{2} = 2 \times 10^{-4} \Rightarrow x = 0.01$$

$[\text{NO}] = 2x = 0.02 \text{ M}$, $[\text{N}_2\text{O}_4] = 2/1 = 2 \text{ M}$

13.(A, B, D) On adding Cl^- ion, the equilibrium will shift in the backward direction. So, $[\text{CoCl}_4]^{2-}$ will increase on dilution and hence the volume will increase.

Now,

$$K_c = \frac{n_{[\text{Co}(\text{H}_2\text{O})_6]^{2+}} \cdot n_{\text{Cl}^-}^4}{n_{\text{CoCl}_4^{2-}}} \cdot \frac{1}{V^4}$$

So, Q will get decreased and equilibrium will shift in the forward direction. Although the amount of $[\text{Co}(\text{H}_2\text{O})]^{2+}$ will get increased, but its concentration cannot get doubled as volume has increased. As the reaction is exothermic in nature, so increasing temperature will shift the equilibrium in backward direction.

14.(B, C) The pressure of NH_3 will decrease due to addition of CO_2 , (backward, shifting Le Chatelier's principle). The pressure of CO_2 will be more than 0.1 atm.

15.(A, B) At constant volume, the addition of inert gas does not affect equilibria. Since, the number of moles of reactant is more in (I) and that of product is more in (III), while they are same in (II), therefore, addition of an inert gas at constant pressure favors the forward reaction in (III), backward reaction in (I), and has no effect on (II).

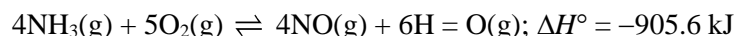
16.(A, B, C, D) At constant volume, the addition of inert gas does not affect equilibria.

<H2> Assertion–Reasoning Type

1.(A)

2.(C) The concentration of pure liquids and solids remain constant, and these terms are amalgamated (or merged) in the equilibrium constant. That is why pure liquids and solids are ignored while writing the equilibrium constant expressions.

In the first step of Ostwald's process for synthesis of nitric acid, ammonium is oxidized to NO by the reaction



3.(D) Reaction is exothermic, and low temperature favors forward reaction. High pressure favors forward reaction; it is accompanied by a decrease in the number of moles.

4.(B) Using the equation,

$$\log_{10} \left(\frac{K_2}{K_1} \right) = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

5.(C) $K_p = \frac{n_{\text{PCl}_3} \times n_{\text{Cl}_2}}{n_{\text{PCl}_5}} \times \left(\frac{P}{n_T}\right)^1$ with addition of more and more inert gas n_T will increase that leads to decrease in the value of p/n_T , and hence to keep K_p constant, moles of the product would increase, that is, α increases.

6.(B) $Q < K_c$ forward reaction; $Q = K_c$ equilibrium; $Q > K_c$ backward direction.

7.(A) Since, the given reaction is a heterogeneous reaction, therefore, it will not be affected by addition of solid or liquid.

8.(C) In the exothermic reaction, equilibrium constant increases by decreasing the temperature.

<H2>Comprehension Type

1.(B) As $\Delta n = 0$, so $K_C = K_p = K_x$

$$K_x = \frac{x_{\text{H}_2}^4}{x_{\text{H}_2\text{O}}^4} = \frac{(2/2)^4}{(1/18)^4} = 18^4 = 1.05 \times 10^5$$

2.(C) For the given reaction, the equilibrium constant is

$$K_p = (p_{\text{NH}_3})^2 \times p_{\text{CO}_2} = (2p)^2 \times p = 4p^3$$

$$p = \left(\frac{K_p}{4}\right)^{1/3} = 0.0667 \text{ atm}$$

3.(C) $\frac{1}{2}\text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{NO}(\text{g})$ $K_C = \left(\frac{1}{2.4 \times 10^{30}}\right)^{1/2}$

$\text{NO}(\text{g}) + \frac{1}{2}\text{Br}_2(\text{g}) \rightleftharpoons \text{NOBr}(\text{g})$ $K_2 = 1.4$

$\frac{1}{2}\text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) + \frac{1}{2}\text{Br}_2(\text{g}) \rightleftharpoons \text{NOBr}(\text{g})$ $K = K_C \times K_2 = 9.03 \times 10^{-16}$

4.(A) For the given reaction, the equilibrium constant is

$$K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \cdot P_{\text{O}_2}}$$

Therefore $p_{\text{O}_2} = \frac{1}{K_p} = \frac{1}{3.5} \text{ atm} = 0.29 \text{ atm}$

5.(B) More is the degree of dissociation, less is the vapor density of PCl_5

6.(B) Clearly, concentration of Y is not changing with the time. Hence, it will be pure solid or liquid. Concentration of X is decreasing. Hence, it will be in reactant and Z will be in product.

7.(C) The equilibrium constant for the reaction is

$$K_c = \frac{[Z(g)]_{\text{eq}}}{[X(g)]_{\text{eq}}} = \frac{4}{6} = \frac{2}{3}$$

8.(D) From the graph, we can see that 4 mol L⁻¹ of Z is formed. Therefore, 4 × 2 mol of solid will be required.

9.(C) For reversible process, the Gibbs free energy and equilibrium relation is,

$$\Delta G^\circ = -2.303RT \log K$$

10.(D) We know $\Delta G^\circ = -2.303RT \log K$

$$\log K = \bar{1}.665 \Rightarrow K = \text{Antilog of } \bar{1}.665 = 0.4625$$

	A	+	B	\rightleftharpoons	C	+	D
Initial concentration	2		2		0		0
At equilibrium	2 - x		2 - x		x		x

$$K_e = \frac{x^2}{(2-x)^2} = 0.4625 \Rightarrow \frac{[C]}{[A]} = \frac{x}{2-x} = 0.68$$

11.(D) We know

$$\Delta G^\circ = -2.303RT \log K_p \quad (1)$$

Substituting the values in Eq. (1), we get

$$\Delta G^\circ = -2.303 \times 1.98 \times 763 \times \log 45.9$$

$$\Delta G^\circ = -5.79 \text{ kcal}$$

<H2> Integer Answer Type

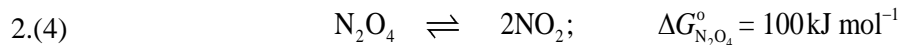
1.(1) Density of ammonium carbamate before dissociation

$$D = \frac{\text{Molecular weight}}{2} = \frac{78}{2} = 39$$

Density after dissociation (D) = 13.0 (given). Hence,

$$\alpha = \frac{D-d}{(n-1)d} = \frac{39-13}{(3-1) \times 13} = \frac{26}{26} = 1$$

So, ammonium carbamate will be 100% dissociated.

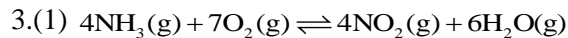


Concentration at $t = 0$ 5 5 $\Delta G_{\text{NO}_2}^\circ = 50 \text{ kJ mol}^{-1}$

$$\Delta G^\circ \text{ for reaction} = 2 \times \Delta G_{\text{NO}_2}^\circ - \Delta G_{\text{N}_2\text{O}_4}^\circ = 2 \times 50 - 100 = 0$$

$$\Delta G = \Delta G^\circ + 2.303RT \log Q$$

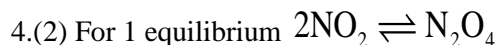
Now, $\Delta G = 0 + 2.303 \times 8.314 \times 10^{-3} \times 298 \log \frac{5^5}{5} = +3.99 \text{ kJ} \approx 4 \text{ kJ}$



Water and oxygen will not contribute to partial pressure.

$$K_p = \frac{(p_{\text{NO}_2})^4}{(p_{\text{NH}_3})^4} = 1$$

Answer should be -1.

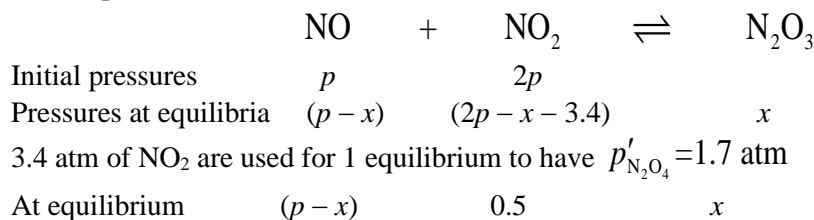


$$K_p = \frac{p'_{\text{N}_2\text{O}_4}}{(p_{\text{NO}_2})^2} = 6.8 \quad (1)$$

$p'_{\text{N}_2\text{O}_4} = 1.7 \text{ atm}$ therefore by Eq. (1) $p'_{\text{NO}_2} = 0.5 \text{ atm}$.

The equilibria are maintained using NO and NO₂ in the ratio of 1:2

For 2 equilibria

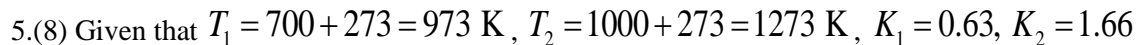


(Since p'_{NO_2} is same for both the equilibria, as both reactions are at equilibrium at a time)

$$\text{Total pressure at equilibrium} = p'_{\text{NO}} + p'_{\text{NO}_2} + p'_{\text{N}_2\text{O}_3} + p'_{\text{N}_2\text{O}_4} = p - x + 0.5 + x + 1.7$$

$$5.05 = p + 2.20 \Rightarrow p = 2.85 \text{ atm}$$

$$2p - x - 3.4 = 0.5 \Rightarrow 2 \times 2.85 - x - 3.4 = 0.5 \Rightarrow x = 1.80 \text{ atm} \approx 2 \text{ atm}$$



Using the van't Hoff equation

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log \left(\frac{1.66}{0.63} \right) = \frac{\Delta H^\circ}{2.303 \times 1.99} \left(\frac{1273 - 973}{1273 \times 973} \right) \Rightarrow \Delta H^\circ = 8.0 \times 10^3 \text{ cal} = 8.0 \text{ kcal}$$

Note: The units of R and ΔH must be same.

6.(8) For the reaction

$$K_c = \frac{[\text{SO}_3]_{\text{initial}}^2}{[\text{SO}_2]^2 [\text{O}_2]} \quad (1)$$

When concentrations of SO₂ and O₂ are quadrupled, the expression becomes

$$K_c = \frac{[\text{SO}_3]_{\text{final}}^2}{[4\text{SO}_2]^2 [4\text{O}_2]} \quad (2)$$

Dividing Eq. (2) by Eq. (1), we get

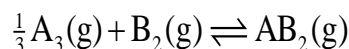
$$\frac{[\text{SO}_3]_{\text{final}}^2}{[4\text{SO}_2]^2[4\text{O}_2]} = \frac{[\text{SO}_3]_{\text{initial}}^2}{[\text{SO}_2]^2[\text{O}_2]} \Rightarrow \frac{[\text{SO}_3]_{\text{final}}^2}{[\text{SO}_3]_{\text{initial}}^2} = \frac{[4\text{SO}_2]^2[4\text{O}_2]}{[\text{SO}_2]^2[\text{O}_2]} = 16 \times 4 = 64$$

Hence,
$$\frac{[\text{SO}_3]_{\text{final}}}{[\text{SO}_3]_{\text{initial}}} = 8$$

7.(4) The equilibrium constant is

$$K_C = \frac{[\text{AB}_2]^3}{[\text{A}_3][\text{B}_2]^3} = 64$$

For the reaction



The new equilibrium is

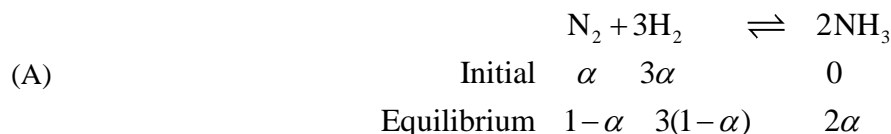
$$K'_C = \frac{[\text{AB}_2]}{[\text{A}_3]^{1/3}[\text{B}_2]} = K_C^{1/3}$$

Therefore,
$$K'_C = (64)^{1/3} = 4$$

<H2>Matrix–Match Type

1.(A) → (r); (B) → (p); (C) → (q); (D) → (s, t)

The expression for relation between dissociation constant and equilibrium pressure is as follows:



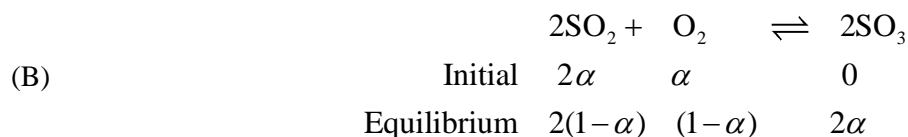
Total number of moles at equilibrium = $1 - \alpha + 3 - 3\alpha + 2\alpha = 4 - 2\alpha = 2(2 - \alpha)$

Partial pressures of N_2 , H_2 and NH_3 are as follows:

$$p_{\text{N}_2} = \frac{1-\alpha}{2(2-\alpha)} p_T \quad p_{\text{H}_2} = \frac{3(1-\alpha)}{2(2-\alpha)} p_T \quad p_{\text{NH}_3} = \frac{2\alpha}{2(2-\alpha)} p_T$$

$$K_p = \frac{(p_{\text{NH}_3})^2}{p_{\text{N}_2} \times (p_{\text{H}_2})^3} = \frac{\left[\frac{2\alpha}{2(2-\alpha)} p_T \right]^2}{\frac{1-\alpha}{2(2-\alpha)} p_T \times \left(\frac{3(1-\alpha)}{2(2-\alpha)} p_T \right)^3} = \frac{16\alpha^2(2-\alpha)^2}{27(1-\alpha)^4(p_T)^2}$$

Now, $1 - \alpha \approx 1$, $2 - \alpha \approx 1$ so $K_p = \frac{64\alpha^2}{27(p_T)^2} \Rightarrow \alpha = \frac{3}{8} p_T \sqrt{3K_p} \Rightarrow \alpha \propto p_T$



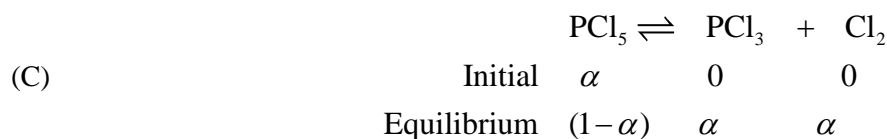
Total number of moles at equilibrium = $2 - 2\alpha + 1 - \alpha + 2\alpha = 3 - \alpha$

Partial pressures of SO₂, O₂ and SO₃ are as follows:

$$p_{\text{SO}_2} = \frac{2(1-\alpha)}{3-\alpha} p_T \quad p_{\text{O}_2} = \frac{(1-\alpha)}{(3-\alpha)} p_T \quad p_{\text{SO}_3} = \frac{2\alpha}{(3-\alpha)} p_T$$

$$K_p = \frac{(p_{\text{SO}_3})^2}{p_{\text{O}_2} \times (p_{\text{SO}_2})^2} = \frac{\left[\frac{2\alpha}{(3-\alpha)} p_T \right]^2}{\frac{1-\alpha}{(3-\alpha)} p_T \times \left(\frac{2(1-\alpha)}{(3-\alpha)} p_T \right)^2} = \frac{\alpha^2 (3-\alpha)}{(1-\alpha)^3} \frac{1}{p_T}$$

Now, $1-\alpha \approx 1$, $2-\alpha \approx 1$, $3-\alpha \approx 1$ as so $K_p = \frac{3\alpha^2}{p_T} \Rightarrow \alpha = \sqrt{\frac{p_T K_p}{3}} \Rightarrow \alpha \propto \sqrt{p_T}$



Total number of moles at equilibrium = $1-\alpha + \alpha + \alpha = 1+\alpha$

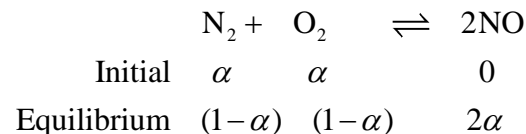
Partial pressures of PCl₅, Cl₂ and PCl₃ are as follows:

$$p_{\text{PCl}_5} = \frac{(1-\alpha)}{(1+\alpha)} p_T \quad p_{\text{Cl}_2} = \frac{\alpha}{(1+\alpha)} p_T \quad p_{\text{PCl}_3} = \frac{\alpha}{(1+\alpha)} p_T$$

$$K_p = \frac{p_{\text{Cl}_2} \times p_{\text{PCl}_3}}{p_{\text{PCl}_5}} = \frac{\left(\frac{\alpha}{(1+\alpha)} p_T \right) \times \left(\frac{\alpha}{(1+\alpha)} p_T \right)}{\left(\frac{1-\alpha}{(1+\alpha)} p_T \right)} = \frac{\alpha^2 p_T}{(1-\alpha^2)}$$

Now, $1-\alpha \approx 1$, so $K_p = \alpha^2 p_T \Rightarrow \alpha = \sqrt{\frac{K_p}{p_T}} \Rightarrow \alpha \propto \sqrt{\frac{1}{p_T}}$

(D)



Total number of moles at equilibrium = $1-\alpha + 1-\alpha + 2\alpha = 2$

Partial pressures of N₂, O₂ and NO are as follows:

$$p_{\text{N}_2} = \frac{(1-\alpha)}{2} p_T \quad p_{\text{O}_2} = \frac{(1-\alpha)}{2} p_T \quad p_{\text{NO}} = \frac{2\alpha}{2} p_T$$

$$K_p = \frac{(p_{\text{NO}})^2}{p_{\text{N}_2} \times p_{\text{O}_2}} = \frac{\left(\frac{2\alpha}{2} p_T \right)^2}{\left(\frac{1-\alpha}{2} p_T \right) \times \left(\frac{1-\alpha}{2} p_T \right)} = \frac{4\alpha^2}{(1-\alpha)^2} \text{ which is equal to } K_c$$

Now, $1 - \alpha \approx 1$, so $K_p = 4\alpha^2 p_T \Rightarrow \alpha = \frac{1}{2} \sqrt{K_p} \Rightarrow \alpha \propto (p_T)^0$

2.(A) \rightarrow (r); (B) \rightarrow (p, q); (C) \rightarrow (p); (D) \rightarrow (p, q)

(A) Backward reaction is favored.

(B) α is affected by both temperature and pressure.

(C) K_C is affected by temperature only.

(D) On increasing temperature and pressure, ice melts.

3.(A) \rightarrow (s, t); (B) \rightarrow (q, r); (C) \rightarrow (q); (D) \rightarrow (p)

4.(A) \rightarrow (s); (B) \rightarrow (r); (C) \rightarrow (p); (D) \rightarrow (q)

Using the relation $K_p = K_C(RT)^{\Delta n}$

5.(A) \rightarrow (r),(s); (B) \rightarrow (r); (C) \rightarrow (q); (D) \rightarrow (p),(s)

(A) As $\Delta n > 0$ therefore if $p \uparrow$, reaction will go in the backward direction.

(B) As $\Delta n < 0$ therefore if $V \uparrow$, $p \downarrow$ reaction will go in the direction in which more number of gaseous moles are formed that is backward direction.

(C) As $\Delta n = 0$, hence no effect.

(D) If concentration of the product is decreased, reaction will go in the forward direction.