

CHEMICAL EQUILIBRIUM

LAW OF MASS ACTION

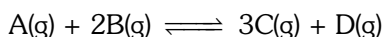
1. In a chemical equilibrium, the rate constant for the backward reaction is 7.5×10^{-4} and the equilibrium constant is 1.5. The rate constant for the forward reaction is:-

- (1) 2×10^{-3} (2) 5×10^{-4}
(3) 1.12×10^{-3} (4) 9.0×10^{-4}

2. In this reaction $\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+$ at 298K molar concentration of Ag^+ , $\text{Ag}(\text{NH}_3)_2^+$ and NH_3 is 10^{-1} , 10^{-1} , and 10^3 . The value of K_c at 298K for this equilibrium :-

- (1) 10^{-6} (2) 10^6
(3) 2×10^{-3} (4) 2×10^6

3. At 1000 K, the value of K_p for the reaction :



is 0.05 atm. The value of K_c in terms of R would be :-

- (1) 20000 R (2) 0.02 R
(3) 5×10^{-5} R (4) $5 \times 10^{-5} \times R^{-1}$

4. For the reaction



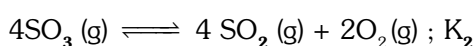
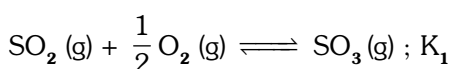
Which one is correct representation :-

- (1) $K_p = p_{\text{H}_2\text{O}}^2$ (2) $K_c = [\text{H}_2\text{O}]^2$
(3) $K_p = K_c(RT)^2$ (4) All

5. $\log \frac{K_p}{K_c} + \log RT = 0$ is true relationship for the following reaction:-

- (1) $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$
(2) $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$
(3) $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$
(4) (2) and (3) both

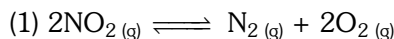
6. Consider the two gaseous equilibrium involving SO_2 and the corresponding equilibrium constants at 299 K



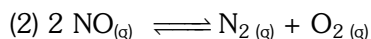
The value of the equilibrium constant are related by :-

- (1) $K_2 = \frac{1}{(K_1)^4}$ (2) $K_2 = K_1^4$
(3) $K_2 = \left(\frac{1}{K_1}\right)^{\frac{1}{4}}$ (4) $K_2 = \frac{1}{K_1}$

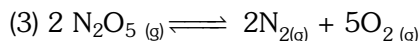
7. Which Oxide of Nitrogen is most stable :-



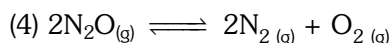
$$K = 6.7 \times 10^{16} \text{ mol L}^{-1}$$



$$K = 2.2 \times 10^{30}$$



$$K = 1.2 \times 10^{34} \text{ mol}^5 \text{ L}^{-5}$$



$$K = 3.5 \times 10^{33} \text{ mol L}^{-1}$$

8. For a reaction $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$, the value of K_c does not depends upon :-

- (a) Initial concentration of the reactants
(b) Pressure
(c) Temperature
(d) Catalyst

- (1) Only c (2) a, b, c
(3) a, b, d (4) a, b, c, d

9. Effect of increasing temperature on equilibrium

constant is given by $\log K_2 - \log K_1 = \frac{-\Delta H}{2.303R}$

$\left[\frac{1}{T_2} - \frac{1}{T_1} \right]$. Then for an endothermic reaction the false statement is:-

- (1) $\left[\frac{1}{T_2} - \frac{1}{T_1} \right] = \text{positive}$ (2) $\log K_2 > \log K_1$
(3) $\Delta H = \text{positive}$ (4) $K_2 > K_1$

10. In system $\text{A(s)} \rightleftharpoons 2\text{B(g)} + 3\text{C(g)}$ at equilibrium if concentration of 'C' is doubled then concentration of B at equilibrium.

- (1) Double its original concentration
(2) Half its original concentration
(3) $2\sqrt{2}$ its original concentration
(4) $\frac{1}{2\sqrt{2}}$ its original concentration

11. The equilibrium constant (K_p) for the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ is 16. If the volume of the container is reduced to one-half its original volume, the value of K_p for the reaction at the same temperature will be :-

- (1) 32 (2) 64 (3) 16 (4) 4

12. The equilibrium constant for the reaction :

$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ at 2000 K is 4×10^4 . In presence of catalyst the equilibrium is established ten times faster at the same temperature. What is the value of equilibrium constant in presence of catalyst :-

- (1) 40×10^{-4} (2) 4×10^{-4}
(3) 4×10^4 (4) None

DEGREE OF DISSOCIATION AND APPLICATION OF LAW OF MASS ACTION

13. For the reaction : $\text{P} \rightleftharpoons \text{Q} + \text{R}$. Initially 2 mol of P was taken. Up to equilibrium 0.5 mol of P was dissociated. What would be the degree of dissociation :-

- (1) 0.5 (2) 1 (3) 0.25 (4) 4.2

14. The dissociation of CO_2 can be expressed as $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$. If the 2 mol of CO_2 is taken initially and 40% of the CO_2 is dissociated completely. What is the total number of moles at equilibrium:-

- (1) 2.4 (2) 2.0 (3) 1.2 (4) 5

15. In a 13 L vessel initially following reaction occur $\text{C}(\text{s}) + \text{S}_2(\text{g}) \rightleftharpoons \text{CS}_2(\text{g})$ by 12 g C, 64 g S_2 , 76 g CS_2 at 1027°C temperature then total pressure is.

- (1) 200R (2) 158R (3) 100R (4) 79R

16. The reaction $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$ is studied in a one litre Vessel at 250°C. The initial concentration of A was 3n and of B was n. After equilibrium was attained then equilibrium concentration of C was found to be equal to equilibrium concentration of B. What is the concentration of D at equilibrium :-

- (1) $\frac{n}{2}$ (2) $\left(3n - \frac{n}{2}\right)$
(3) $\left(n + \frac{n}{2}\right)$ (4) n

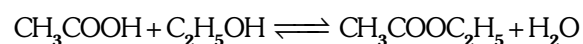
17. In the reaction $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ the partial pressure of PCl_3 , Cl_2 and PCl_5 are 0.3, 0.2 and 0.6 atm respectively at equilibrium. If partial pressure of PCl_3 and Cl_2 was increased twice, what will be the partial pressure of PCl_5 is in atm at new equilibrium condition :-

- (1) 0.3 (2) 1.2 (3) 2.4 (4) 0.15

18. In a 0.25 L tube dissociation of 4 mol of NO is take place. If its degree of dissociation is 10%. The value of K_p for reaction $2\text{NO} \rightleftharpoons \text{N}_2 + \text{O}_2$ is :-

- (1) $\frac{1}{(18)^2}$ (2) $\frac{1}{(8)^2}$
(3) $\frac{1}{16}$ (4) $\frac{1}{32}$

19. K_c for the esterification reaction :



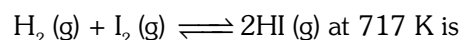
is 4. If 4 mol each of acid and alcohol are taken initially, what is the equilibrium concentration of the acid in 1 litre container :-

- (1) $\frac{2}{3}$ (2) $\frac{4}{3}$ (3) $\frac{3}{4}$ (4) $\frac{3}{2}$

20. 4 moles of A are mixed with 4 moles of B, when 2 mol of C are formed at equilibrium, according to the reaction, $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$. The equilibrium constant is :-

- (1) 4 (2) 1 (3) $\sqrt{2}$ (4) $\sqrt{4}$

21. 1.50 mol each of hydrogen and iodine were placed in a sealed 10 L container maintained at 717 K. At equilibrium 1.25 mol each of hydrogen and iodine were left behind. The equilibrium constant, K_c for the reaction



- (1) 0.4 (2) 0.16 (3) 25 (4) 50

LE-CHATLIER'S PRINCIPLE

22. When NaNO_3 is heated in a closed vessel, O_2 is liberated and NaNO_2 is left behind. At equilibrium -

- (1) Addition of NaNO_3 favours forward reaction
(2) Addition of NaNO_2 favours reverse reaction
(3) Increasing pressure favours reverse reaction.
(4) Decreasing temperature favours forward reaction.

23. In which of the following equilibrium reactions, the equilibrium would shift to right side, if total pressure is decreased :-

- (1) $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$
(2) $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$
(3) $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$
(4) $\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2\text{HCl}$

- 24.** For the manufacture of ammonia by the reaction

$$\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 + 21.9 \text{ k Cal},$$
the favourable conditions are :-

- (1) Low temperature, low pressure & catalyst
- (2) Low temperature, high pressure & catalyst
- (3) High temperature, low pressure & catalyst
- (4) High temperature, high pressure & catalyst

- 25.** In the reaction $2\text{A}_{(\text{g})} + \text{B}_{(\text{g})} \rightleftharpoons \text{C}_{(\text{g})} + 362 \text{ kCal}$. Which combination of pressure and temperature gives the highest yield of C at equilibrium:-

- (1) 1000 atm and 500°C
- (2) 500 atm and 500°C
- (3) 1000 atm and 50°C
- (4) 500 atm and 100°C

- 26.** The reaction in which yield of production cannot be increased by the application of high pressure is :-

- (1) $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$
- (2) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
- (3) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
- (4) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$

- 27.** In a vessel containing SO_3 , SO_2 and O_2 at equilibrium, some helium gas is introduced so that the total pressure increases while temperature and volume remain constant. According to Le-Chatelier principle, the dissociation of SO_3 ,

- (1) Increases
- (2) Decreases
- (3) Remains unaltered
- (4) None of these

PHYSICAL EQUILIBRIUM

- 28.** For the equilibrium reaction, $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$, What happens, if pressure is applied:-

- (1) More water evaporates
- (2) The boiling point of water is increased
- (3) No effect on boiling point
- (4) None of the above

- 29.** On cooling of following system at equilibrium

$$\text{CO}_{2(\text{s})} \rightleftharpoons \text{CO}_{2(\text{g})} :-$$

- (1) There is no effect on the equilibrium state
- (2) More gas is formed
- (3) More gas is solidifies
- (4) None of above

CALCULATION OF DEGREE OF DISSOCIATION BY V.D. METHOD

- 30.** Vapour density of PCl_5 is 104.25 at $t^\circ\text{C}$. Then degree of dissociation of PCl_5 is. (Mw = 208.5)

- (1) 20%
- (2) 0%
- (3) 30%
- (4) 15%

- 31.** When heating PCl_5 then it decompose PCl_3 and Cl_2 in form of gas, The vapour density of gas mixture is 70.2 and 57.9 at 200°C and 250°C . The degree of dissociation of PCl_5 at 200°C and 250°C is

- (1) 48.50% & 80%
- (2) 60% & 70%
- (3) 70% & 80%
- (4) 80% & 90%

- 32.** The equation $\alpha = \frac{D-d}{(n-1)d}$ is correctly matched for

Where D = Theoretical vapour density

d = Observed vapour density

(1) $\text{A} \rightleftharpoons \frac{n\text{B}}{2} + \frac{n\text{C}}{3}$

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

(3) $\text{A} \rightleftharpoons \left(\frac{n}{2}\right)\text{B} + \left(\frac{n}{4}\right)\text{C}$

(4) $\text{A} \rightleftharpoons \left(\frac{n}{2}\right)\text{B} + \text{C}$

SOLUTION

CHEMICAL EQUILIBRIUM

1. $K_c = \frac{k_f}{k_b} \Rightarrow k_f = k_c \cdot k_b$
 $= 1.5 \times 7.5 \times 10^{-4}$
 $= 1.12 \times 10^{-3}$
2. $\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+$
 At eq^m 10^{-1}M 10^3M 10^{-1}M
 $K_c = \frac{10^{-1}}{(10^{-1})(10^3)^2} = 10^{-6}$
3. $K_p = K_c (RT)^{\Delta ng}$
 $\Delta ng = (3 + 1) - (1 + 2) = 1$
 So $K_c = \frac{K_p}{RT}$
 $K_c = \frac{.05}{R \times 1000} = 5 \times 10^{-5} \text{R}^{-1}$
4. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O(s)} \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O(s)} + 2\text{H}_2\text{O(g)}$
 $k_p = P_{\text{H}_2\text{O}}^2$
 $k_c = [\text{H}_2\text{O}]^2$
 $k_p = k_c (RT)^2 \quad (\Delta ng = 2)$
5. $\log\left(\frac{k_p}{k_c}\right) + \log(RT) = 0$
 $= \log 1$
 $\log\left(\frac{k_p}{k_c} \times RT\right) = \log 1$
 $\frac{k_p}{k_c} \cdot (RT) = 1$
 $k_p = k_c (RT)^{-1}$
 $\Delta ng = -1$
 $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3 ; \Delta ng = -1$
6. equation (1) = $\frac{-eq^n(ii)}{4}$
 $k_1 = \frac{1}{k_2^{1/4}} \Rightarrow k_1^4 = \frac{1}{k_2}$
or
 $k_2 = \frac{1}{k_1^4}$
7. Low value of k_c means extent of reactant is low
 means reactant is stable.
 So NO_2 is stable among others
8. $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$
 k_c depends upon temp.
 It does not depend upon pressure, initial concentration, catalyst.

$$9. \log k_2 - \log k_1 = \frac{-\Delta H}{2.303R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

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

on increasing temperature means

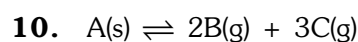
$$T_2 > T_1$$

$$\text{So } \left(\frac{1}{T_2} - \frac{1}{T_1} \right) < 0$$

Endothermic Reaction $\Delta H > 0$

$$k_2 > k_1$$

$$\log k_2 > \log k_1$$



$$k_c = [\text{B}]^2[\text{C}]^3 = [\text{B}_{\text{New}}]^2[2\text{C}]^3$$

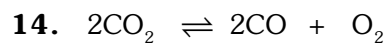
$$[\text{B}_{\text{new}}] = \frac{[\text{B}]}{2\sqrt{2}}$$

11. k_p does not depend upon change in volume of container

12. k_p or k_c does not depend upon catalyst

$$13. \alpha = \frac{n_{\text{dissociated}}}{n_{\text{initial}}} = \frac{0.5}{2} = .75$$

$$= 75\%$$

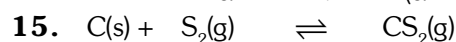


2mole

$2(1 - \alpha)$ 2α α

$$n_T = 2(1 - \alpha) + 2\alpha + \alpha$$

$$= 2 + \alpha = 2.4 \quad (\alpha = 40\%)$$



12gm

64gm

76gm

1mole

1mole

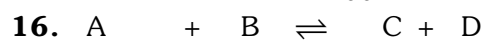
1mole

(solid)

$$PV = nRT$$

$$P \times 13 \text{ Lit} = 2 \times R \times 1300$$

$$P = 200 \text{ R}$$



3n

n

-

-

3n-x

n-x

x

x

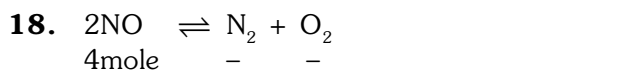
$$\text{given } [\text{C}] = [\text{B}] \Rightarrow x = n - x \Rightarrow x = \frac{n}{2}$$

$$[\text{D}]_{\text{eq}} = \frac{n}{2}$$

$$17. k_p = \frac{P_{\text{PCl}_3} \cdot P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{P'_{\text{PCl}_3} \cdot P'_{\text{Cl}_2}}{P'_{\text{PCl}_5}}$$

$$\Rightarrow \frac{0.3 \times 0.2}{0.6} = \frac{0.6 \times 0.4}{P'_{\text{PCl}_5}}$$

$$P'_{\text{PCl}_5} = 2.4$$

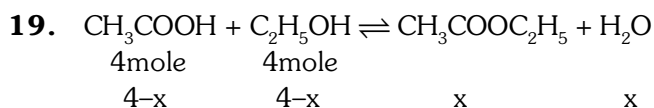


$$4(1-\alpha) \quad \frac{4\alpha}{2} \quad \frac{4\alpha}{2} \quad (\alpha = 10\% = 0.1)$$

$$3.6 \quad .2 \quad .2 \quad \text{moles}$$

$$k_p = k_c (\Delta n_g = 0)$$

$$= \frac{\left(\frac{.2}{V}\right)\left(\frac{.2}{V}\right)}{\left(\frac{3.6}{V}\right)^2} = \frac{1}{(18)^2}$$



$$k_c = 4 = \frac{x \cdot x}{(4-x)(4-x)}$$

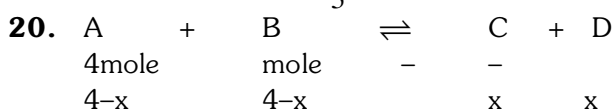
$$2 = \frac{x}{4-x}$$

$$8-2x = x$$

$$x = 8/3$$

$$[\text{CH}_3\text{COOH}] = 4 - \frac{8}{3}$$

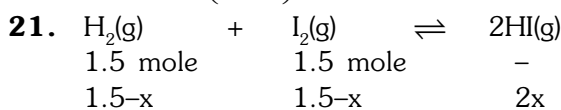
$$[\text{CH}_3\text{COOH}] = \frac{4}{3} \text{ M in 1 lit container}$$



$$\text{given } n(\text{C}) = 2 \Rightarrow x = 2$$

$$k_c = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\left(\frac{4-x}{v}\right)\left(\frac{4-x}{v}\right)} = \left(\frac{x}{4-x}\right)^2$$

$$= \left(\frac{2}{4-2}\right)^2 = 1$$



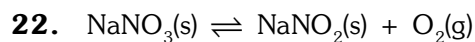
$$\text{given } 1.5 - x = 1.25$$

$$x = 0.25$$

$$k_c = \frac{(2x/v)^2}{\left(\frac{1.5-x}{v}\right)\left(\frac{1.5-x}{v}\right)}$$

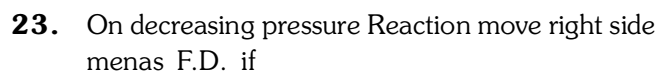
$$= \left(\frac{2x}{1.5-x}\right)^2$$

$$= \left(\frac{0.25 \times 2}{1.25}\right)^2 = \frac{4}{25} = 0.16$$

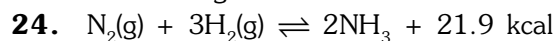


Addition of solid does not effect on equilibrium state

P ↑ reaction move BD



$$\Delta n_g > 0$$

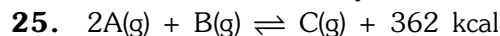


manufacturing of NH_3 favoure

High pressure ($\Delta n_g < 0$)

low temperature ($\Delta H < 0$)

and suitable catalyst

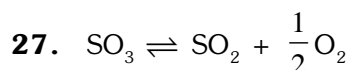
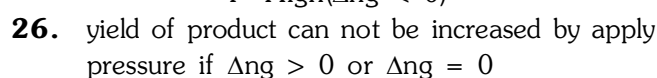


High yeild of C(g) means reaction

favoured in F.D if

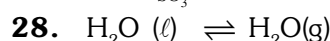
$$T \text{ low } (\Delta H < 0)$$

$$P \text{ High } (\Delta n_g < 0)$$



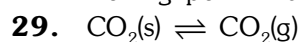
Addition of He inert gas of constant volume Re^n
 neither goes to F.D. nor B.D.

So α_{SO_3} remain same



P ↑ ; $\Delta n_g > 0$; Re^n goes B.D.

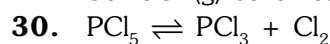
Boiling point increases.



On cooling reaction goes B.D

$$(\Delta H > 0)$$

So $\text{CO}_2(\text{g})$ solidifies.

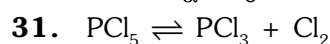


$$\frac{D}{d} = 1 + (n-1)\alpha$$

$$\frac{M_0/2}{d} = 1 + (2-1)\alpha$$

$$\frac{208.5/2}{104.25} = 1 + \alpha$$

$$\alpha = 0$$



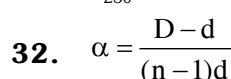
$$\frac{D}{d} = 1 + (n-1)\alpha$$

$$\frac{208.5/2}{70.2} = 1 + \alpha \quad (\text{At } 200^\circ\text{C})$$

$$\alpha_{200} = 0.485 = 48.5\%$$

$$\frac{208.5/2}{57.9} = 1 + \alpha_{250}$$

$$\alpha_{250} = 0.80 = 80\%$$



n : sum of stoichiometric coefficient of product