8 Chapter

EQUILIBRIUM-1 (Chemical Equilibrium)

A SINGLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

1. Consider the following equilibrium in a closed vessel $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$. At a fixed temperature if the volume of the reaction vessel is halved, which of the following statements holds true regarding the equilibrium constant (K_p) and the degree of dissociation (α) of N_2O_4 ?
(a) Neither K_p nor α changes
(b) Both K_p and α change
(c) K_p does not change but α increases
(d) K_p does not change but α decreases

2. In a closed system : $A_{(s)} \rightleftharpoons 2B_{(g)} + 3\ C_{(g)}$, if the partial pressure of *C* is doubled, then partial pressure of *B* will be:
(a) two times the original value
(b) one-half of its original value
(c) $\frac{1}{2\sqrt{2}}$ times the original value
(d) $2\sqrt{2}$ times its original value

3. NO_2 is involved in the formation of smog and acid rain. It is formed importantly as:
$NO_{(g)} + O_{3(g)} \rightleftharpoons NO_{2(g)} + O_{2(g)}$; $K_c = 6.0 \times 10^{34}$
The air over a metopolitan city contained 1.0×10^{-5} *M* NO, 1.0×10^{-6} *M* O_3, 2.5×10^{-4} *M* NO_2 and 8.2×10^{-3} *M* O_2. These data suggest that
(a) more of NO and O_3 tend to be formed
(b) more of NO_2 and O_2 tend to be formed
(c) more of NO_2 and O_3 tend to be formed
(d) no tendency to change because the reaction is at equilibrium

4. For a gaseous reversible reaction, which of the following expressions is correct?
(a) $K_c = K_p\ (RT)^{\Delta n}$ (b) $K_p = K_c + \Delta n\ RT$
(c) $K_p = K_x\ (P)^{\Delta n}$ (d) $K_p = K_c\ (RT/\Delta n)$

5. A hypothetical reaction : $A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$ occurs in a single step, the specific rate constant of forward reaction at *TK* is 2.0×10^{-3} mol^{-1} L s^{-1}. When start is made with equimolar amounts of *A* and *B*, it is found that the concentration of *A* is twice that of *C* at equilibrium. The specific rate constant of the backward reaction is
(a) 5.0×10^{-4} mol^{-1} Ls^{-1} (b) 8.0×10^{-3} $mol^{-1}Ls^{-1}$
(c) 1.5×10^{2} $mol^{-1}Ls^{-1}$ (d) none of these

6. Sulphide ion reacts with solid sulphur to form $S_{2\ (aq)}^{2-}$ and $S_{3\ (aq)}^{2-}$ with equilibrium constants 12 and 132 respectively. The equilibrium constant for the formation of $S_{3\ (aq)}^{2-}$ from $S_{2\ (aq)}^{2-}$ and sulphur is
(a) 132×12 (b) 1/11
(c) 11 (d) none of these

7. In the following hypothetical reaction $A + 3\ B \rightleftharpoons 2\ C + D$, initial moles of *A* is twice that of *B*. If at equilibrium moles of *B* and *C* are equal, % of *B* reacted is
(a) 10% (b) 20%
(c) 40% (d) 60%

8. Consider the following equilibria at 25° C, $2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$; $K_1 = 4 \times 10^{30}$ and
$NO_{(g)} + \frac{1}{2}Br_{2(g)} \rightleftharpoons NOBr_{(g)}$; $K_2 = 1.4$ $mol^{-1/2}$ $L^{1/2}$. The value of K_c for the reaction (at the same temperature)
$\frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)} + \frac{1}{2}Br_{2(g)} \rightleftharpoons NOBr_{(g)}$ is:
(a) 3.5×10^{-31} (b) 2.8×10^{15}
(c) 7.0×10^{-16} (d) 5.6×10^{30}

MARK YOUR RESPONSE					
	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ		

9. Ammonium hydrogen sulphide dissociates as :

$NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$. Solid NH_4HS is heated to a temperature TK in a closed vessel containing NH_3 at 0.1 atm. If the equilibrium pressure is 0.5 atm, the equilibrium constant K_p for the dissociation reaction is :

(a) $0.25 atm^2$ (b) $0.0625\ atm^2$

(c) $0.04\ atm^2$ (d) $0.06\ atm^2$

10. Ammonium carbamate dissociates on heating as :

$NH_2COO\ NH_{4(g)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$

The equilibrium constant K_p for the reaction, at some temperature is $3.2 \times 10^{-5}\ atm^3$. Calculate the partial pressure of NH_3 in the equilibrium system at the same temperature.

(a) 2.0×10^{-2} atm (b) 4.0×10^{-2} atm

(c) 3.2×10^{-2} atm (d) 6.4×10^{-2} atm

11. On heating $CaCO_3$ in open container, the formation of lime commences at temperature when K_p of the reaction $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ is :

(a) 1 atm

(b) < partial pressure of CO_2 in the air

(c) = partial pressure of CO_2 in the air

(d) none of these

12. Based upon the following hypothetical equilibrium at 273 K

$X Cl_2 . 6H_2O_{(s)} \rightleftharpoons X Cl_2 . 2H_2O_{(s)} + 4\ H_2O_{(g)}$;

$K_p = 8.1 \times 10^{-11}\ atm^4$

$Y_2HPO_4 . 12H_2O_{(s)} \rightleftharpoons Y_2HPO_4 . 7H_2O_{(s)} + 5H_2O_{(g)}$;

$K_p = 3.2 \times 10^{-9}\ atm^5$

$Z_2SO_4 . 10H_2O_{(s)} \rightleftharpoons Z_2SO_{4(s)} + 10H_2O_{(g)}$;

$K_p = 1.0 \times 10^{-30}\ atm^{10}$

Which is the most effective dehydrating agent at 273 K (Aqueous tension at 273 K = 6.0×10^{-3} atm)

(a) $X Cl_2 . 6H_2O_{(s)}$ (b) $Y_2 HPO_4 . 7H_2O_{(s)}$

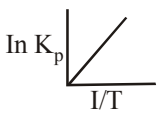
(c) $Z_2SO_{4(s)}$ (d) $Z_2SO_4 . 10H_2O_{(s)}$

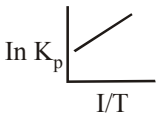
13. Consider the data given in the above problem. At what relative humidity $X Cl_2 . 2H_2O_{(s)}$ be deliquescent when exposed to air at 0° C ?

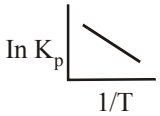
(a) below 40% (b) below 50%

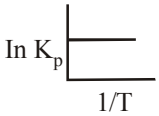
(c) above 50% (d) none of these

14. An exothermic reaction is represented by the graph :

(a) 

(b) 

(c) 

(d) 

15. Rate of disappearance of the reactant A in the reversible and one step reaction $A \rightleftharpoons B$ at two temperatures is given by

$$\frac{-d[A]}{dt} = 2.0 \times 10^{-3} s^{-1}[A] - 5.0 \times 10^{-4} s^{-1}[B] \quad (\text{at } 27°C)$$

$$\frac{-d[A]}{dt} = 8.0 \times 10^{-2} s^{-1}[A] - 4.0 \times 10^{-3} s^{-1}[B] \quad (\text{at } 127°C)$$

The enthapy of the reaction in the given temperture range is

(a) $-\frac{2.303 \times 8.314 \times 300 \times 400}{100} \log 5\ J$

(b) $\frac{2.303 \times 8.314 \times 300 \times 400}{100} \log 50\ J$

(c) $\frac{2.303 \times 8.314 \times 300 \times 400}{100} \log 5\ J$

(d) $\frac{100}{2.303 \times 8.314 \times 300 \times 400} \log 5\ J$

16. For the reversible reaction $N_2 + O_2 \rightleftharpoons 2\ NO$, activation energy of the forward reaction is greater than that of backward reaction. The slope of ln K *vs* $1/T$ (abscissa) graph will be :

(a) Zero (b) $-\frac{\Delta H}{2.303\ R}$

(c) $\frac{\Delta H}{2.303\ R}$ (d) $-\frac{\Delta H}{R}$

17. In a reaction : $A_{(g)} + 2B_{(g)} \rightleftharpoons 2C_{(g)}$ 2.0 mole of A, 3.0 mole of B and 2.0 mole of C are placed in a 2.0 L closed flask. If equilibrium concentration of C is 0.5 mol L^{-1}, the equilibrium constant for the dissociation of C is :

(a) 0.05 (b) 20.0

(c) 0.073 (d) 0.147

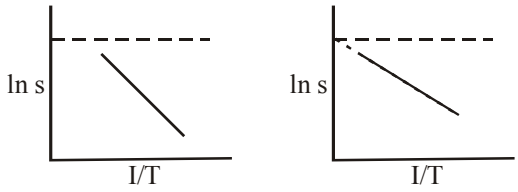
18. The ratio of equilibrium constant in terms of partial pressures and that in terms of molar concentrations for the reaction : $NH_2COO\ NH_{4(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$ at 27° C is:

(a) $(8.314 \times 27)^3$ (b) $(8.314 \times 300)^3$

(c) $(0.082 \times 300)^2$ (d) $(0.082 \times 300)^3$

MARK YOUR RESPONSE					
	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ
	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ

19. The solubility of a solute in water varies with temperature as given by : $S = A\ e^{-\Delta H/RT}$, ΔH being the enthalpy of solution. For a given solute, variation of ln S with temperature is as shown in the figure. The solute is expected to be



(a) CaO (b) $CuSO_4$
(c) $MgSO_4$ (d) $CuSO_4.5H_2O$

20. 1.0 mole of $AB_{5(g)}$ is placed in a closed container under one atmosphere and at 300K. It is heated to 600K when 20% by mass of it dissociates as : $AB_{5(g)} \rightarrow AB_{(g)} + 2\ B_{2(g)}$.
The resultant pressure is
(a) 1.2 atm (b) 2.4 atm
(c) 2.8 atm (d) 1.4 atm

21. a moles of PCl_5 is heated in a closed container to equilibriate $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ at a pressure of P atm. If x moles of PCl_5 dissociate at equilibrium, then

(a) $\frac{x}{a} = \frac{K_p}{K_p + P}$ (b) $\frac{x}{a} = \left(\frac{K_p + P}{K_p}\right)^{1/2}$

(c) $\frac{x}{a} = \left(\frac{K_p}{P}\right)^{1/2}$ (d) $\frac{x}{a} = \left(\frac{K_p}{K_p + p}\right)^{1/2}$

22. The equilibrium constant for the dissociation of water at elevated temperature takes place as :

$$H_2O_{(g)} \rightleftharpoons H_{2(g)} + \tfrac{1}{2}\ O_{2(g)}.$$

If α is the degree of dissociation at equilibrium pressure P atm, then K_p is given by :

(a) $K_p = \alpha^3\left(\frac{P}{2}\right)^{1/2}$ (b) $K_p = \frac{\alpha^3 P^{3/2}}{(1-\alpha)(2+\alpha)}$

(c) $K_p = \frac{\alpha^{3/2} P^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

(d) $K_p = \frac{\alpha^3 P^{1/2}}{(1+\alpha)(2-\alpha)^{1/2}}$

23. Consider the reaction : $AB_{2(g)} \rightleftharpoons AB_{(g)} + B_{(g)}$. If the initial pressure of AB_2 is 500 torr and equilibrium pressure is 600 torr, the equilibrium constant K_p in terms of torr is :
(a) 20 (b) 50
(c) 25 (d) 100

24. Equilibrium constant K_p for the reaction $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ is 0.82 atm at 727° C.
If 1 mole of $CaCO_3$ is placed in a closed container of 20L and heated to this temperature, what amount of $CaCO_3$ would dissociate at equilibrium ?
(a) 0.2 g (b) 80 g
(c) 20 g (d) 50 g

25. N_2 and H_2 in 1 : 3 molar ratio are heated in a closed container having a catalyst. When the following equilibrium $N_{2(g)} + 3\ H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is attained, the total pressure is 10 atm and mole fraction of NH_3 is 0.60. The equilibrium constant K_p for the dissociation of NH_3 is :
(a) $1.333\ atm^{-2}$ (b) $0.75\ atm^2$
(c) $0.75\ atm^{-2}$ (d) $1.333\ atm^2$

26. Starting with 100 mm (Hg) pressure of SO_2Cl_2 in a closed container, the following equilibrium is set up at some temperature: $SO_2Cl_{2(g)} \rightleftharpoons SO_{2(g)} + Cl_{2(g)}$. If mole fraction of SO_2Cl_2 at equilibrium is 1/3, K_p for the reaction is :
(a) 25 mm (b) 50 mm
(c) 100 mm (d) 150 mm

27. 28 g of N_2 and 6.0 g of H_2 are heated over a catalyst in a closed 1L flask at 450° C. The entire equilibrium mixture required 500 ml of 1.0 M H_2SO_4 for naturalization. The value of K_c for the reaction :
$N_{2(g)} + 3\ H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is
(a) $1.69\ mol^2\ L^{-2}$ (b) $0.03\ mol^2\ L^{-2}$
(c) $0.59\ mol^{-2}\ L^2$ (d) $0.06\ mol^{-2}\ L^2$

28. At temperature TK, PCl_5 is 50% dissociated at an equilibrium pressure of 4 atm. At what pressure it would dissociate to the extent of 80% at the same temperature ?
(a) 0.50 atm (b) 0.60 atm
(c) 0.75 atm (d) 2.50 atm

MARK YOUR RESPONSE					
	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ
	24. ⓐⓑⓒⓓ	25. ⓐⓑⓒⓓ	26. ⓐⓑⓒⓓ	27. ⓐⓑⓒⓓ	28. ⓐⓑⓒⓓ

29. For the complexation reaction

$Ag^{+}_{(aq)} + 2NH_{3(aq)} \rightleftharpoons [Ag(NH_3)^{+}_2]_{(aq)}$,

the rates of forward and reverse reactions are given by :
$(rate)_f = 1.0 \times 10^6\ L^2\ mol^{-2}\ s^{-1}[Ag^+][NH_3]^2$
$(rate)_r = 2.0 \times 10^{-2}\ s^{-1}\ [Ag(NH_3)_2]^+$
The instability constant of the complex is :

(a) 5.0×10^9 (b) 2.0×10^{-4}
(c) 2.0×10^{-4} (d) 2.0×10^{-8}

30. Vapour density of the equilibrium mixture of the reaction $SO_2Cl_{2(g)} \rightleftharpoons SO_{2(g)} + Cl_{2(g)}$ is 50.0. Percent dissociation of SO_2Cl_2 is :

(a) 33.33 (b) 35.0
(c) 30.0 (d) 66.67

31. A gaseous compound of molecular mass 82.1 dissociates on heating to 400K as : $X_2Y_{4(g)} \rightarrow X_{2(g)} + 2Y_{2(g)}$. The density of the equilibrium mixture at a pressure of 1 atm and temperature of 400 K is 2.0g L^{-1}. The compound dissociates to the extent of :

(a) 95.1% (b) 47.6%
(c) 12.5% (d) none of these

32. The activation energies for the forward and reverse elementary reactions in the system $A \rightleftharpoons B$ are 10.303 and 8.000 k cal respectively at 500K. Assuming the pre-exponential factor to be the same for both the forward and reverse steps and R =2 cal K^{-1} mol^{-1}, calculate equilibrium constant of the reaction :

(a) 1.00 (b) 10.0
(c) 100 (d) 0.1

33. If the enthalpy of a reversible reaction is 8.314 kJ mol^{-1} over the temperature range 400 – 500 K, the value of $\ln K_{500}/K_{400}$ for the reaction is

(a) 1.0 (b) 2.0
(c) 2.5 (d) 0.5

34. 1 mol N_2 and 3 mol H_2 are placed in a closed container at a pressure of 4 atm. The pressure falls to 3 atm at the same temperature when the following equilibrium is attained.
$N_{2(g)} + 3\ H_{2(g)} \rightleftharpoons 2NH_{3(g)}$. The equilibrium constant K_p for dissociation of NH_3 is :

(a) $\frac{1}{0.5} \times (1.5)^3\ atm^{-2}$ (b) $0.5 \times (1.5)^3\ atm^2$

(c) $\frac{0.5 \times (1.5)^3}{3 \times 3} atm^2$ (d) $\frac{3 \times 3}{0.5 \times (1.5)^3} atm^{-2}$

35. 2 mol of SO_2 and 1 mol of O_2 are heated in a closed vessel to reach the equilibrium :
$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2\ SO_{3(g)}$. The equilibrium mixture exerted a pressure of 5 atm and required 1/3 mol of $K_2Cr_2O_7$ in acidic medium. K_p for the reaction is

(a) 2.0 (b) 0.5
(c) 1.0 (d) none of these

36. I^- ion reacts with I_2 in aqueous solution to form I^-_3 ion as

$I^-_{(aq)} + I_{2(aq)} \rightleftharpoons I^-_{3(aq)}$.

When L of solution containing 1 mol of KI and 0.25 mol of I_2 was reacted with excess of $AgNO_3$, 0.80 mol of yellow precipitate was obtained. The stability constant of I_3^- ion is

(a) 5.0 (b) 0.20
(c) 20.0 (d) 0.05

37. Equilibrium constant for the reaction
$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$
is 4.0. The mole fraction of the ester present at equilibrium on mixing 120.0 g of CH_3COOH and 92.0 g of C_2H_5OH will be

(a) 0.100 (b) 0.250
(c) 0.333 (d) 0.667

38. K_c for a gaseous state reversible reaction is 300 $mol^{-2}\ L^2$ at 127° C. Hence, K_p of the reaction will be

(a) $300 \times (0.082 \times 400)$ atm
(b) $300 \times (8.314 \times 400)^2\ atm^2$
(c) $300 \times (0.082 \times 400)^{-2}\ atm^{-2}$
(d) $300 \times (0.082 \times 127)^2\ atm^2$

39. The molecular mass of PCl_5 is 208.32 but when heated to 230° C, it is recduced to 124. The extent of dissociation of PCl_5 at this temperature will be

(a) 6.8% (b) 46%
(c) 64% (d) 68%

40. K_p of the reaction : $N_{2(aq)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is affected by :

(a) increasing the volume of reaction vessel
(b) introducing helium gas keeping total pressure constant
(c) introducting a catalyst
(d) changing the temperature.

MARK YOUR RESPONSE					
	29. ⓐⓑⓒⓓ	30. ⓐⓑⓒⓓ	31. ⓐⓑⓒⓓ	32. ⓐⓑⓒⓓ	33. ⓐⓑⓒⓓ
	34. ⓐⓑⓒⓓ	35. ⓐⓑⓒⓓ	36. ⓐⓑⓒⓓ	37. ⓐⓑⓒⓓ	38. ⓐⓑⓒⓓ
	39. ⓐⓑⓒⓓ	40. ⓐⓑⓒⓓ			

41. The standard free energy changes for the reactions : $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$ and $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$ are – 457.0 kJ and – 28.5 kJ respectively. Standard free energy for the reaction : $2CO_2 \rightleftharpoons 2CO_{(g)} + O_{2(g)}$ will be :

(a) 485.5 kJ (b) 514.0 kJ
(c) –514.0 kJ (d) – 485.5 kJ

42. Using the data of the preceding problem, calculate log K_p for the reaction : $2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$ at 298 K

(a) 98.08 (b) – 98.08
(c) – 85.00 (d) 85.00

43. In a flask colourless N_2O_4 is in equilibrium with brown coloured NO_2. On heating the equilibrium system to 100ºC the brown colour deepens while on cooling the intensity of the colour demunishes. The enthalpy of the reaction $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$ is :

(a) positive (b) zero
(c) negative (d) incomplete information

44. For the reaction $NH_4HS_{(g)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$ in a closed flask, the equilibrium pressure is P atm. The standard free energy of the reaction would be:

(a) $-RT \ln p$ (b) $-RT(\ln p - \ln 2)$
(c) $-2RT \ln p$ (d) $-2RT(\ln p - \ln 2)$

45. Which of the following expressions relates equilibrium constant to temperature ?

(a) $\ln K_2 - \ln K_1 = -\frac{\Delta H^\circ}{R}\int_{T_1}^{T_2} d(1/T^2)$

(b) $\ln K_2 - \ln K_1 = \frac{\Delta H^\circ}{R}\int_{T_1}^{T_2} d(1/T)$

(c) $\ln K_2 - \ln K_1 = -\frac{\Delta H^\circ}{R}\int_{T_1}^{T_2} d(1/T)$

(d) $\ln K_2 - \ln K_1 = -\frac{\Delta H^\circ}{R}\int_{T_1}^{T_2} dT/T$

46. A plot of Gibbs energy of a reaction system *versus* the extent of reaction has :

(a) positive slope before equilibrium
(b) negative slope after equilibrium
(c) a maximum at equilibrium
(d) a minimum at equilibrium

47. Which of the following reactions has the equilibrium constant to be unity ?

(a) $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$
(b) $NH_2COONH_{4(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$
(c) $Fe_2O_{3(s)} + 2Al_{(s)} \rightleftharpoons Al_2O_{3(s)} + 2Fe_{(s)}$
(d) $Fe_{(s)} + H_2S_{(s)} \rightleftharpoons FeS_{(s)} + H_{2(g)}$

48. In the manufacture of NH_3 in Haber's continuous flow process involving the reaction

$$N_{2(g)} + 3H_{2(g)} \underset{}{\overset{[Fe_2O_3]}{\rightleftharpoons}} 2NH_{3(g)}, \Delta H = -22.08 \text{ kcal.}$$

The favourable conditions are :

(a) High pressure and low temperature due to low activation energy (E_a).
(b) Low pressure and low temperature due to low E_a
(c) High pressure and elevated optimum temperature due to high E_a.
(d) None of these

49. At constant pressure, addition of helium to the reaction system : $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

(a) favours the formation of ammonia
(b) reduces the formation of ammonia
(c) reduces the dissociation of ammonia
(d) does not affect the position of equilibrium

50. Equilibrium constant for the reaction $NH_4OH_{(aq)} + H^+_{(aq)} \rightleftharpoons NH_{4(aq)}^+ + H_2O_{(l)}$ is 1.80×10^9. Hence equilibrium constant for the ionization $NH_3 + H_2O(l) \rightleftharpoons NH_{4(aq)}^+ + OH^-_{(aq)}$ is

(a) 5.55×10^{-10} (b) 1.80×10^{-9}
(c) 1.80×10^5 (d) 1.80×10^{-5}

51. Ice and water are placed in a closed container at a pressure of 1 atm and temperature 273.15 K. If pressure of the system is increased to 2 atm while keeping temperature constant, which of the following would be the correct observation?

(a) The liquid phase disappears completely
(b) The amount of ice decreases
(c) The solid phase (ice) disappears completely
(d) Volume of the system increases

MARK YOUR RESPONSE					
	41. ⓐⓑⓒⓓ	42. ⓐⓑⓒⓓ	43. ⓐⓑⓒⓓ	44. ⓐⓑⓒⓓ	45. ⓐⓑⓒⓓ
	46. ⓐⓑⓒⓓ	47. ⓐⓑⓒⓓ	48. ⓐⓑⓒⓓ	49. ⓐⓑⓒⓓ	50. ⓐⓑⓒⓓ
	51. ⓐⓑⓒⓓ				

52. The equilibrium pressure in the reaction system :

$2NF_{3(g)} \rightleftharpoons N_{2(g)} + 3F_{2(g)}$

is increased ten times, the equilibrium constant in terms of mole fractions (K_x) would :

(a) increase ten times
(b) decrease ten times
(c) increase hundred times
(d) decrease hundred times

53. A cylinder fitted with a movable and air tight piston contains a few drops of water and nitrogen gas at a pressure of 760 torr. If the piston is moved forward and volume is reduced to half of its initial volume while keeping temperature constant, the resulting pressure of the system would be : (neglect the volume occupied by water; aqueous tension at the given temperature is 20 torr)

(a) 1520 torr (b) 1480 torr
(c) 1500 torr (d) none of these

54. Which of the following statement is correct for a reversible process in a state of equilibrium?

(a) $\Delta G = -RT \ln K$ (b) $\Delta G = RT \ln K$
(c) $\Delta G^\circ = -2.303RT \log K$ (d) $\Delta G^\circ = RT \ln K$

55. Consider the reversible reactions :

I. $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$ K_1

II. $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$ K_2

III. $CO_{2(g)} + 4H_2 \rightleftharpoons CH_{4(g)} + 2H_2O_{(g)}$ K_3

Which of the following is true?

(a) $\log K_3 = \log K_1 + \log K_2$
(b) $\log K_1 + \log K_2 + \log K_3 = 0$
(c) $\log K_3 = \log K_1 - \log K_2$
(d) $\log K_3 = \frac{1}{2}(\log K_1 + \log K_2)$

56. K_p for the process $CuSO_4 . 5H_2O_{(s)} \rightleftharpoons CuSO_4.3H_2O_{(s)} + 2H_2O_{(g)}$ is 1.21×10^{-4} atm^2 at certain temperature. If aqueous tension at that temperature is 30 torr, then at what relative humidity of air will $CuSO_4.5H_2O$ efforsce?

(a) 50% (b) 40%
(c) 30% (d) Below 28%

57. K_p for the reaction

$CuSO_4.3H_2O_{(s)} + 2H_2O_{(g)} \longrightarrow CuSO_4.5H_2O_{(s)}$ is

1.0×10^4 atm^{-2} at certain temperature. What lowest relative humidity of air can be achieved using $CuSO_4.3H_2O$ as drying agent at that temperature? Aqueous tension at the given temperature = 16 torr

(a) 20% (b) 30%
(c) 47.5 % (d) 50%

58. $2NOBr_{(g)} \rightleftharpoons 2NO_{(g)} + Br_{2(g)}$. If NOBr is dissociated to the extent of 20% at T K and a total pressure of 1.1 atm, then K_p for the formation of NOBr is

(a) 80 (b) 160
(c) $\frac{1}{80}$ (d) $\frac{1}{160}$

59. At temperature T K, K_p for the reaction of CO_2 with excess of hot graphite to form CO is 9 atm. Calculate the mole% of CO in the equilibrium mixture of gases at a pressure of 4 atm ?

(a) 20% (b) 25%
(c) 60% (d) 75%

60. For the reaction of $XO_{(g)}$ and $O_{2(g)}$ to form $XO_{2(g)}$, the equilibrium constant is 2×10^{-4} Lmol^{-1}. If 1 mol of XO and 2 mol of O_2 are heated in a closed vessel of 1L, then mol of XO_2 at equilibrium will be

(a) 0.01 (b) 0.02
(c) 0.05 (d) 0.2

61. In a reaction $AB_{(g)} \rightleftharpoons A_{(g)} + B_{(g)}$, the value of K_p is numerically equal to one third of the total equilibrium pressure P. The percent dissociation of AB is

(a) 25 (b) 30.5
(c) 40 (d) 50

MARK YOUR RESPONSE					
	52. ⓐⓑⓒⓓ	53. ⓐⓑⓒⓓ	54. ⓐⓑⓒⓓ	55. ⓐⓑⓒⓓ	56. ⓐⓑⓒⓓ
	57. ⓐⓑⓒⓓ	58. ⓐⓑⓒⓓ	59. ⓐⓑⓒⓓ	60. ⓐⓑⓒⓓ	61. ⓐⓑⓒⓓ

62. For a reaction the free energy change, $\Delta G = -RT\ln K_p + RT\ln Q_p$ where K_p = equilibrium constant, Q_p = reaction quotient. For the reaction to be in equilibrium state

(a) $\frac{Q_p}{K_p} > 1$ (b) $\frac{Q_p}{K_p} < 1$

(c) $\frac{Q_p}{K_p} = 1$ (d) $Q_p K_p = 1$

63. Which of the following statements is true for a reversible reaction ?

(a) Free energy decreases to a minimum value with the progress of the reaction from either side

(b) Free energy decreases with the progress of the forward reaction and increases for the reverse reaction.

(c) Free energy increases to a maximum value with the progress of the reaction from either side

(d) $\Delta G° = 0$ for the reaction to be in equilibrium state

64. 60 g of water gas and 18 g of steam are heated in a closed vessel to a temperature of 450°C so that the equilibrium: $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$ is reached. If K for the reaction is 3, the mass of CO_2 present will be

(a) 11 g (b) 22 g
(c) 44 g (d) 66 g

65. At certain temperature, a compound AB_2 dissociates as: $2AB_{2(g)} \longrightarrow 2AB_{(g)} + B_{2(g)}$ with a degree of dissociation α, which is very small compared to unity. The expression of K_p in terms of α and total pressure P is

(a) $\frac{\alpha^2 P}{2}$ (b) $\frac{\alpha^2 P}{3}$

(c) $\frac{\alpha^3 P}{3}$ (d) $\frac{\alpha^3 P}{2}$

66. When sulphur in the form of $S_{8(g)}$ at 1 atm is heated to a temperature of 800K in a closed vessel, pressure rises to 1.6 atm at equilibrium. This is because of conversion of some $S_{8(g)}$ into $S_{2(g)}$. K_p for this reaction is

(a) 0.512 atm^3 (b) 0.39 atm^3
(c) 0.64 atm^3 (d) none of these

67. In an aqueous solution of $1L$, when the reaction $2Ag^+_{(aq)} + Cu_{(s)} \rightleftharpoons Cu^{2+}_{(aq)} + 2Ag_{(s)}$ reaches equilibrium, $[Cu^{2+}] = x\,M$ and $[Ag^+] = y$ M. If volume of solution is doubled by adding water, then at equilibrium

(a) $[Cu^{2+}] = \frac{x}{2}M,\ [Ag^+] = \frac{y}{2}M$

(b) $[Cu^{2+}] > \frac{x}{2}M,\ [Ag^+] > \frac{y}{2}M$

(c) $[Cu^{2+}] < \frac{x}{2}M,\ [Ag^+] > \frac{y}{2}M$

(d) $[Cu^{2+}] < \frac{x}{2}M,\ [Ag^+] < \frac{y}{2}M$

68. $\Delta G°$ For the ration $X + Y \rightleftharpoons C$ is -4.606 k cal at 1000K. The equilibrium constant for the reverse mode of the reaction is

(a) 100 (b) 10
(c) 0.01 (d) 0.1

69. A plot of $\ln K$ against $\frac{1}{T}$ (abscissa) is expected to be a straight line with intercept on ordinate axis equal to

(a) $\frac{\Delta S°}{2.303R}$ (b) $\frac{\Delta S°}{R}$

(c) $-\frac{\Delta S°}{R}$ (d) $R \times \Delta S°$

MARK YOUR RESPONSE					
	62. ⓐⓑⓒⓓ	63. ⓐⓑⓒⓓ	64. ⓐⓑⓒⓓ	65. ⓐⓑⓒⓓ	66. ⓐⓑⓒⓓ
	67. ⓐⓑⓒⓓ	68. ⓐⓑⓒⓓ	69. ⓐⓑⓒⓓ		

70. At the equilibrium of the reaction :

$A_{(g)} + 2B_{(s)} \rightleftharpoons C_{(s)} + 2D_{(s)} + E_{(g)}$, A reacts to the extent of 20% at 400K and to the extent of 25% at 300K. The equilibrium shifts in forward direction

(a) On increasing both pressure and temperature

(b) On decreasing both pressure and temperature

(c) On decreasing temperature only

(d) On using the catalyst

71. A reversible reaction is endothermic in forward direction. Then which of the following is correct?

(a) $ln\ K$ versus $1/T$ will be a straight line with negative slope

(b) $\frac{d}{dT} ln\ K > 0$

(c) A plot of $d\ ln\ K$ against $1/T^2$ will have positive slope

(d) all

72. For the reaction $A + 2B \rightleftharpoons C + D$, the equilibrium constant is 1.0×10^8. Calculate the equilibrium concentration of A if 1.0 mole of A and 3.0 mole of B are placed in 1L flask and allowed to attain the equilibrium.

(a) $1.0 \times 10^{-2}\ mol\ L^{-1}$ (b) $2.1 \times 10^{-4}\ mol\ L^{-1}$

(c) $5 \times 10^{-5}\ mol\ L^{-1}$ (d) $1.0 \times 10^{-8}\ mol\ L^{-1}$

73. In a 10 L closed vessel, the equilibrium $2SO_2 + O_2 \rightleftharpoons 2SO_3$ is maintained at certain temperature. If K_c for this reaction is $100 L\ mol^{-1}$ and number of moles of SO_2 and SO_3 at equilibrium are in the ratio of 1 : 2, molar concentration of O_2 will be

(a) $0.4\ mol\ L^{-}$ (b) $0.04\ mol\ L^{-}$

(c) $0.004\ mol\ L^{-}$ (d) $0.002\ mol\ L^{-}$

74. If we add CrO_4^{2-} ions to a saturated solution of solid Ag_2CrO_4, it will result in a/an

(a) increase in Ag^+ concentration

(b) decrease in Ag^+ concentration

(c) increase in solubility product

(d) shift of Ag^+ ions from solid Ag_2CrO_4 into the solution

75. Three sparingly soluble salts A_2B, AB and AB_3 have the same values of solubility products (K_{sp}). In a saturated solution the correct order of their solubilities is

(a) $AB_2 > AB > A_2B$

(b) $AB_3 > A_2B > AB$

(c) $AB > AB_3 > A_2B$

(d) $AB > A_2B > AB_3$

76. The K_P/K_C ratio will be highest in case of

(a) $CO(g) + \frac{1}{2} O_2(g) \rightleftharpoons CO_2(g)$

(b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

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

(d) $7H_2(g) + 2NO_2(g) \rightleftharpoons 2NH_3(g) + 4H_2O(g)$

77. At a pressure of 2 atmosphere, N_2O_4 is 35% dissociated into NO_2. The value of K_p is

(a) 1.117 (b) 0.170

(c) 1.414 (d) 0.558

MARK YOUR RESPONSE					
	70. ⓐⓑⓒⓓ	71. ⓐⓑⓒⓓ	72. ⓐⓑⓒⓓ	73. ⓐⓑⓒⓓ	74. ⓐⓑⓒⓓ
	75. ⓐⓑⓒⓓ	76. ⓐⓑⓒⓓ	77. ⓐⓑⓒⓓ		

B COMPREHENSION TYPE

This section contains groups of questions. Each group is followed by some multiple choice questions based on a paragraph. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

PASSAGE-1

The essential stages in the manufacture of H_2SO_4 involve the burning of sulfur or roasting of sulfide ores in air to produce SO_2. This is then mixed with air, purified and passed over a vanadium catalyst (either VO_3^{2-} or V_2O_5) at 450°C. Thus the following reaction occurs.

Reaction - I :

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) \qquad \Delta H = -197\,kJ\,mol^{-1}$$

If SO_2 is very carefully dissolved in water, sulfurous acid (H_2SO_3) is obtained. The first proton of this acid ionizes as if from a strong acid while the second ionizes as if from a weak acid.

Reaction - II :

$$H_2SO_3 + H_2O \longrightarrow H_3O^+ + HSO_3^-$$

Reaction - III :

$$HSO_3^- + H_2O \longrightarrow H_3O^+ + SO_3^{2-} \qquad K_a = 5.0 \times 10^{-6}$$

The concentration of H_2SO_3 in cleaning fluid was determined by titration with 0.10 M NaOH (strong base) as shown in Fig-1. Two equivalence points were determined using 30 ml and 60 ml of NaOH respectively :

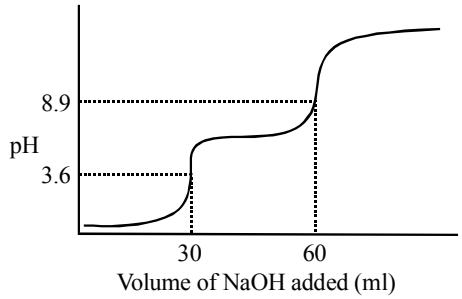


Figure-1

1. What is the oxidation number of sulfur in sulfurous acid?
(a) +3 (b) +4
(c) +5 (d) +6

2. Which of the following acid-base indicators is most suitable for the determination of the first end point of the titration shown in Figure-1?
(a) Cresol red (color change between pH = 0.2 and pH = 1.8)
(b) p-Xylenol blue (color change between pH = 1.2 and pH = 2.8)
(c) Bromophenol blue (color change between pH = 3.0 and pH = 4.6)
(d) Bromocresol green (color change between pH = 3.8 and pH = 5.4)

3. H_2SO_3 acts as a Lewis acid probably because sulfurous acid :
(a) is a proton donor
(b) accepts a pair of electrons from another species
(c) reacts with NaOH which is a strong base
(d) possesses oxygen atoms

4. If no catalyst was used in Reaction - I, which of the following would experience a change in its partial pressure when the same system reaches equilibrium?
(a) There will be no change in the partial pressure of any of the reactants
(b) $SO_3(g)$
(c) $SO_2(g)$ (d) $O_2(g)$

5. If the temperature was decreased in Reaction - I, which of the following would experience an increase in its partial pressure when the same system reaches equilibrium?
(a) There will be no change in the partial pressure of any of the reactants
(b) $SO_3(g)$
(c) $SO_2(g)$ (d) $O_2(g)$ and $SO_2(g)$

6. Reaction - I is usually carried out at atmospheric pressure. During the reaction, before equilibrium was reached, the mole fractions of $SO_2(g)$ and $SO_3(g)$ were $\frac{1}{2}$ and $\frac{1}{6}$ respectively. What was the partial pressure of $O_2(g)$?
(a) 0.66 atm (b) 0.16 atm
(c) 0.50 atm (d) 0.33 atm

7. What is the pH of 0.01 M H_2SO_3 ?
(a) 1.0 (b) 2.0
(c) 3.0 (d) 4.0

MARK YOUR RESPONSE					
	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ			

PASSAGE-2

Physical and chemical equilibria respond stress, e.g. change in pressure, temperature and concentration of reactants and products. According to Le Chatelier's principle a system at equilibrium, when subjected to a disturbance (stress), responds in a way that tends to minimize the effect of the disturbance.

Effect of pressure **:** The principle implies that if a system at equilibrium is compressed, the reaction will adjust so as to minimize the increase in pressure. Thus, if volume of gas phase reaction system is reduced, the equilibrium shifts in the direction in which number of moles decreases. Although equilibrium constant is independent of pressure (at a fixed temperature), the various concentrations are changed on reducing the volume of the system, i.e. on increasing the pressure.

However, if increase in pressure is effected by introducing an inert gas to the reaction vessel of constant volume, partial pressures or concentrations of various species remain unchanged as they continue to occupy the same volume. But at constant pressure condition, introduction of inert gas into the reaction system will lead to increase in volume and in consequence to the change in concentrations of various species. Under this condition, the equilibrium shifts in the direction in which number of moles of gaseous species increases.

Effect of temperature **:** Le-Chatelier's principle predicts that a system at equilibrium will tend to shift in the endothermic direction when temperature is raised, for then energy is absorbed as heat and the rise in temperature is opposed. Conversely, an equilibrium will shift in the exothermic direction if the temperature is lowered, for then heat energy is released and the reduction in temperature is opposed.

Van't Hoff equation shows the dependence of equilibrium constant K on temperature as :

$$\frac{d}{dT}\log K = \frac{\Delta H^\circ}{RT^2} \quad or \quad \log K = \text{constant} - \frac{\Delta H^\circ}{2.303\,R}\cdot\frac{1}{T}$$

Effect of addition of reactants or products **:** On addition of one or more reactants, the equilibrium will shift to the products side so that the added reactants are consumed and increase in their concentrations is opposed. Addition of one or more products causes the equilibrium to shift in backward direction.

8. Consider the equilibrium, $2CO + O_2 \rightleftharpoons 2CO_2$ + heat.
If O_2 is added and volume of the reaction vessel is reduced, the equilibrium will
(a) shift in forward direction
(b) shift in reverse direction
(c) remain unchanged
(d) be unpredictable

9. A system at equilibrium is described by the equation

$$\text{Heat} + SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$$

If some Cl_2 is added to the equilibrium mixture at constant volume, the temperature of the system will
(a) decrease (b) increase
(c) fluctuate (d) not change

10. The volume of the systems describing the equilibria

(I) $\text{Heat} + MgCO_{3(s)} \rightleftharpoons MgO_{(s)} + CO_{2(s)}$

(II) $2C_{(s)} + O_{2(g)} \rightleftharpoons 2CO_{(s)} + \text{heat}$

is decreased. The equilibria will shift
(a) to the right in both (I) and (II)
(b) to the left in both (I) and (II)
(c) to the left in (I) and to the right in (II)
(d) to the right in (I) and to the left in (II)

11. Manufacture of lime from lime stone as :

$CaCO_{3(s)} + \text{Heat} \longrightarrow CaO_{(s)} + CO_{2(g)}$ is most favoured by
(a) heating lime stone in a closed chamber
(b) heating lime stone is an open chamber
(c) adding more lime stone to the reaction chamber
(d) removing lime from the reaction chamber

12. Consider the reaction

$$A + B \rightleftharpoons C + D + \text{Heat}$$

What will happen when temperature is raised?
(a) The rate constant of forward reaction would decrease and that of reverse reaction would increase
(b) The rate constant of forward reaction would increase and that of reverse reaction would decrease
(c) The rate constants of both forward and reverse reactions would increase, former increasing less rapidly
(d) The equilibrium constant of the reaction increases

13. The plot of $\log K$ against $\frac{1}{T}$ is a straight line with positive slope (K being the equilibrium constant of a reaction), which of the following is then correct?
(a) The reaction causes cooling effect
(b) The reaction causes heating effect
(c) The reaction goes to farther extent on raising the temperature
(d) None of these

MARK YOUR RESPONSE	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ
	13. ⓐⓑⓒⓓ				

PASSAGE-3

There are three different ways of expressing the equilibrium constant for a system of ideal gases.

(i) in terms of partial pressure (K_p)

(ii) in terms of concentration (K_c)

(iii) in terms of mole fracion (K_x)

For the general equilibrium reaction

$$n_1A + n_2B \rightleftharpoons m_1C + m_2D$$

$$K_p = \frac{P_C^{m_1} \times P_D^{m_2}}{P_A^{n_1} \times P_B^{n_2}} \qquad K_c = \frac{[C]^{m_1} \times [D]^{m_2}}{[A]^{n_1} \times [B]^{n_2}}$$

$$K_x = \frac{X_c^{m_1} \times X_D^{m_2}}{X_A^{n_1} \times X_B^{n_2}}$$

Relationship between K_p, K_c and K_x

$K_p = K_c (RT)^{\Delta n}$ $\qquad K_x = K_p . P^{-\Delta n}$

or $K_p = K_x (P)^{\Delta n}$

[Δn = difference in number of moles of gasesous products and gaseous reactants]

14. *A* and *B* were mixed in a vessel at 25°C. The following equilibrium was established

$$A + B \rightleftharpoons C + D$$

The initial concentration of *A* was twice the initial concentration of *B*. At equilibrium, the concentration of *C* was three times the concentration of *B*. The value of *K* for this reaction is

(a) 1.5 (b) 1.8

(c) 2.1 (d) 2.4

15. 0.02 g of hydrogen and 2.54 g of iodine are allowed to react to equilibrium at 460°C. On analysis the equilibrium mixture is found to contain 0.0021 moles of iodine. The value of K_c for the reaction is

(a) 46 (b) 128

(c) 56.6 (d) 21

16. A mixture containing 25 mole of hydrogen and 18 mole of iodine was heated at 448°C till equilibrium was reached and 30.8 mole of hydrogen iodide was obtained. The degree of dissociation (α) of HI at 448°C is

(a) 0.308 (b) 0.448

(c) 0.245 (d) 0.25

PASSAGE-4

The Van't Hoff equation or van't Hoff Isochore is

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$$

If we integrate this equation between limits T_1 and T_2, we get

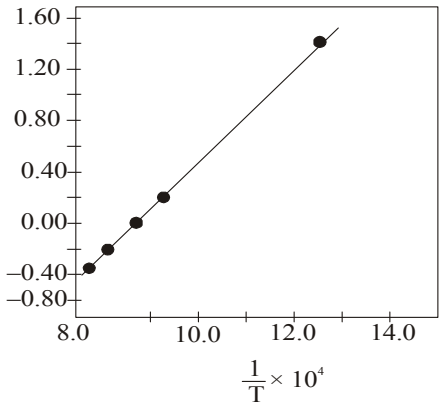
$$\text{In } K_p = -\frac{\Delta H^\circ}{RT} + C \quad (C = \text{Integration constant})$$

According to this equation a plot of $\log_{10} K_P$ vs $\frac{1}{T}$ should be a straight line with slope equal to $\frac{-\Delta H^\circ}{2.303R}$

or $\Delta H^\circ = -2.303\, R \times$ slope.

17. The plot of $\log_{10} K_p$ and $\frac{1}{T}$ for the homogeneous reaction

$SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g)$ is shown below



The slope of graph is equal to 4930

ΔH° for the reaction is

(a) +49.30 kJ (b) –49.30 kJ

(c) +94.39 kJ (d) –94.39 kJ

MARK YOUR RESPONSE	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	

18. For an exothermic reaction

(a) K_p will increase as $\frac{1}{T}$ increases

(b) K_p will decrease as $\frac{1}{T}$ increases

(c) K_p will remain constant as $\frac{1}{T}$ increases

(d) none of the above is correct.

19. The equilibrium constant K_p for the reaction

$NH_3(g) \rightleftharpoons \frac{1}{2} N_2(g) + \frac{3}{2} H_2(g)$ is 1.22×10^{-3} at 298K.

The value of K_p at the temperature 498K will be

[Given $\Delta H^\circ = 46190$J]

(a) 2.44×10^{-2} (b) 2.16

(c) 6.12 (d) 1.26

MARK YOUR RESPONSE	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ			

C REASONING TYPE

In the following questions two Statement-1 (Assertion) and Statement-2 (Reason) are provided. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct. Mark your responses from the following options:

(a) Both Statement-1 and Statement-2 are true and Statement-2 is the correct explanation of Statement-1.
(b) Both Statement-1 and Statement-2 are true and Statement-2 is not the correct explanation of Statement-1.
(c) Statement-1 is true but Statement-2 is false.
(d) Statement-1 is false but Statement-2 is true.

1. **Statement-1** : Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.
Statement-2 : Equilibrium constant depends upon the way in which the reaction is written.

2. **Statement-1** : On cooling in a freezing mixture, colour of the following mixture turns to pink from deep blue for a reaction.
$Co(H_2O)_6^{2+}{}_{(aq)} + 4Cl^-_{(aq)} \rightleftharpoons CoCl_4^{2-}{}_{(aq)} + 6H_2O_{(l)}$
Statement-2 : Reaction is endothermic. So on cooling, the reaction moves to backward direction.

3. **Statement-1** : If Q_c (reaction quotient) $< K_C$ (equilibrium constant) reaction moves in direction of reactants.
Statement-2 : Reaction quotient is defined in the same way as equilbrium constant at any stage of the reaction.

4. **Statement-1** : NaCl solution can be purified by passage of hydrogen chloride through brine.
Statement-2 : This type of purification is based on Le Chatelier's principle.

5. **Statement-1** : Water acts as levelling solvent for various acids.
Statement-2 : Levelling effect of water is due to its high dielectric constant and strong proton accepting tendency.

6. **Statement-1** : HNO_3 is a stronger acid than HNO_2.
Statement-2 : In HNO_3 there are two nitrogen-to-oxygen bonds whereas in HNO_2 there is only one.

7. **Statement-1** : The solubility of HgI_2 in aqueous solution of KI is expected to be less as compared to the solubility of HgI_2 in water (common ion effect). However we get a clear solution when Hg I_2 is added to an aqueous solution of KI.
Statement-2 : Iodide ion (I^-) is highly polarisable.

8. **Statement-1** : State of equilibrium of a system can not be changed by some external factors such as pressure, volume, concentration.
Statement-2 : Any change in the state of equilibrium caused by external factors is nullifed by the system.

9. **Statement-1** : On increasing pressure there occurs a decrease in melting point of ice.
Statement-2 : On melting ice contracts.

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	

D MULTIPLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONE OR MORE is/are correct.

1. Which of the following relation(s) hold good for gaseous and reversible reactions :

(a) $\frac{K_p}{K_c} = (RT)^{\Delta n}$ (b) $\frac{K_p}{K_x} = P^{\Delta n}$

(c) $\frac{K_c}{K_x} = \left(\frac{P}{RT}\right)^{\Delta n}$ (d) $\frac{K_c}{K_x} = \left(\frac{RT}{P}\right)^{\Delta n}$

2. For a reaction to be spontaneous in neither direction which of the following is/are true regarding the closed system?

(a) $(\Delta G)_{P,T} = 0$ (b) $(\Delta G)_{P,T} < 0$

(c) $(\Delta U)_{S,V} = 0$ (d) $(\Delta S)_{U,V} = 0$

3. Which of the following statements is/are correct for a reversible reaction ?

(a) Reaction quotient (Q) is the ratio of the product of arbitrary molar concentrations of the products to those of the reactants.

(b) Q may be $< > = K$

(c) At a given temperature both Q and K vary with the progress of the reaction.

(d) When $Q > K$, the reaction proceeds in backward direction before coming to stand still.

4. The position of equilibrium will shift, by the addition of inert gas at constant pressure condition, in the following case(s) :

(a) $N_{2(g)} + 3F_{2(g)} \rightleftharpoons 2NF_{3(g)}$; forward direction

(b) $COCl_{2(g)} \rightleftharpoons CO_{2(g)} + Cl_{(g)}$; forward direction

(c) $CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$; backward direction

(d) $2C_{(s)} + O_{2(g)} \rightleftharpoons 2CO_{(g)}$; backward direction

5. Yield of NH_3 in Haber's process : $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, $\Delta H = -22$ kcal ; can be increased by

(a) compressing the reaction system

(b) raising the temperature to an optimum value of 450°C

(c) decreasing the temperature

(d) using the catalyst to lower down the activation energy

6. Which of the following statements is/are correct regarding the solubility of a non-reacting gas into a fixed amount of water :

(a) The dissolution of gas results in the decrease of temperature.

(b) The solubility is favoured by high pressure and low temperature.

(c) The volume of gas dissolved at a fixed temperature and measured at the equilibrium pressure remains constant.

(d) The amount dissolved increases exponentially with the pressure of the gas.

7. Lime is manufactured on heating lime stone in kilns as :

$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)},\ \Delta H = x$ kJ

Which of the following statement(s) is/ are correct regarding the process :

(a) Dissociation of $CaCO_3$ starts at a temperature when $K_p = P_{CO_2}$ in the atmosphere

(b) Dissociation stops when equilibrium is established.

(c) Although the reaction is reversible but equilibrium is never set up due to removal of CO_2 by the atmosphere.

(d) Dissociation of $CaCO_3$ goes to completion.

8. The volume of the reaction flask is reduced to half of its initial value, temperature being constant. In which of the following cases the position of the equilibrium would shift?

(a) $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(s)}$

(b) $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$

(c) $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

(d) $I_{2(g)} \rightleftharpoons 2I_{(g)}$

9. The variation of equilibrium constant K with temperature is represented by :

(a) $\left(\frac{d \ln K}{dT}\right)_p = -\frac{\Delta H}{RT}$

(b) $\ln K = \text{constant} - \frac{\Delta H}{RT}$

(c) $\ln K_2 - \ln K_1 = -\frac{\Delta H}{R}\int_{T_1}^{T_2} d\left(\frac{1}{T}\right)$

(d) $\log K = \text{constant} - \frac{\Delta H}{RT}$

MARK YOUR RESPONSE					
	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	

10. In which of the following cases does the equilibrium constant represent the solubility product ?

(a) $Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)} \rightleftharpoons BaSO_{4(s)}$

(b) $HgI_{2(s)} + 2I^{-}_{(aq)} \rightleftharpoons HgI^{2-}_{4(aq)}$

(c) $Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^{-}_{(aq)}$

(d) $CaF_{2(s)} + 2H^{+} \rightleftharpoons Ca^{2+}_{(aq)} + H_2F_{2(aq)}$

11. $KNO_{3(s)}$ dissociates on heating as :

$$KNO_{3(s)} \rightleftharpoons KNO_{2(s)} + \frac{1}{2}O_{2(g)}$$

At equilibrium in a closed container

(a) addition of $KNO_{3(s)}$ favours forward reaction

(b) addition of $KNO_{2(s)}$ favours reverse reaction

(c) increasing temperature favours forward reaction

(d) decreasing pressure favours forward reaction

12. Which of the following expression(s), is/are correct ?

(a) $\Delta G = \Delta G^{\circ} + RT \ln K$ (b) $\Delta G = \Delta G^{\circ} + RT \ln Q$

(c) $E^{\circ}_{cell} = \frac{0.0591}{n} \log K$ (d) $\Delta G^{\circ} = RT \ln K$

13. Which of the following equilibria will not be disturbed by the addition of inert gas at constant volume?

(a) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

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

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

(d) $CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$

14. Water gas, an industrial fuel, consisting CO and H_2 in equimolar amounts is obtained by passing steam over red-hot carbon in accordance with the reaction :

$$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}; \quad \Delta H = 130.5 \text{ kJ}$$

The yield of water gas can be increased by

(a) introducing hot carbon

(b) increasing pressure of steam

(c) raising the temperature

(d) reducing the total pressure of the system

15. The equilibrium constant of the following reaction in equilibrium at 27ºC

$A + B \rightleftharpoons C + D$ is 10 .

Which of the following statements are correct?

(a) Free energy change of the reaction is zero

(b) Standard free energy of the reaction is zero

(c) Standard free energy of the reaction is –5.74 kJ

(d) Free energy change when all the reactants and products are 1 *m* each will be –5.74 kJ

16. Select the correct statements of the following :

The larger is ΔG°

(a) the reaction is more likely to be spontaneous

(b) the reaction is less likely to be spontaneous

(c) the smaller is the value of equilibrium constant

(d) the greater is the value of equilibrium constant

17. The equilibrium constant for the reaction

$I_{2(aq)} + I^{-}_{(aq)} \rightleftharpoons I^{-}_{3(aq)}$ is 7×10^2

What will happen of the following when KI is added to saturated solution of iodine in water?

(a) Iodine will be precipitated out

(b) More iodine can be dissolved in the solution

(c) Concentration of free iodine in solution will decrease

(d) Concentration of free iodine in solution will remain unchanged

18. For the following equilibrium :

$$NH_2COONH_{4(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$$

partial pressure of NH_3 will increase if

(a) $NH_2COONH_{4(s)}$ is added to the system at equilibrium

(b) $NH_{3(g)}$ is added to the system

(c) $CO_{2(g)}$ is added to the system

(d) temperature of the system is raised

19. The equilibrium constant for the reaction :

$$H_{2(g)} + I_{2(g)} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 2HI_{(g)} \text{ at 700 K is 49.}$$

Select the correct statements of the following :

(a) Equilibrium constant for the reaction $HI \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}I_2$ will be 7.

(b) Equilibrium constant for the reaction $HI \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}I_2$ will be $\frac{1}{7}$

(c) Rate constant for formation of HI will be smaller than the rate constant for dissociation of HI

(d) Rate constant for formation of HI will be greater than that for dissociation of HI

MARK YOUR RESPONSE					
	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ
	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ

20. If α is neglible as compared to 1 for the following reaction

$XY_2(g) \rightleftharpoons XY(g) + Y(g)$

The degree of dissociation (α) for the above reaction is

(a) directly proportional to square root of V.

(b) inversely proportional to V.

(c) inversely proportional to P.

(d) inversely proportional to square root of P.

21. For the reaction

$2\,CO(g) + O_2(g) \rightleftharpoons 2\,CO_2(g) + \text{Heat}$

Select the conditions under whcih the shift can't be determined.

(a) addition of O_2 (g) and decrease in volume

(b) addition of CO (g) and removal of CO_2 (g) at constant volume

(c) Increase in temperature and decrease in volume

(d) addition of CO (g) and increase in temperature at constant volume.

22. Which of the following relationships are correct for calculating the degree of dissociation (α) from density measurements. The following reaction be considered to answer the above questions :

$A(g) \rightleftharpoons n\,B(g)$

(a) $\dfrac{d}{D} = \dfrac{1}{1+\alpha(n-1)}$ (b) $\dfrac{D}{d} = 1+\alpha(n-1)$

(c) $\alpha = \dfrac{D-d}{d(n-1)}$ (d) none of these

23. Select the correct statements.

(a) K_P is independent of pressure for ideal gases.

(b) K_C is independent of pressure for ideal gases

(c) K_x is independent of pressure

(d) For ideal gases the position of equilibrium does not depend on total pressure.

24. Select the correct statement (s)

(a) When total number of moles in a reaction remains constant K_p is same as K_C or K_X.

(b) When $\Delta n < 0$, K_x increases with increasing pressure.

(c) When $\Delta n > 0$, K_x decreases with increasing pressure

(d) Only (b) and (c) are correct.

MARK YOUR RESPONSE	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ	24. ⓐⓑⓒⓓ

E MATRIX-MATCH TYPE

Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labeled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column -I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:
If the correct matches are A–p, s and t; B–q and r; C–p and q; and D–s then the correct darkening of bubbles will look like the given.

	p	q	r	s	t
A	ⓟ	ⓠ	ⓡ	ⓢ	ⓣ
B	ⓟ	ⓠ	ⓡ	ⓢ	ⓣ
C	ⓟ	ⓠ	ⓡ	ⓢ	ⓣ
D	ⓟ	ⓠ	ⓡ	ⓢ	ⓣ

1. **K_p, K_c and K_x are the equilibrium constants for a gaseous reaction in terms of partial pressures, molar concentrations and mole fractions. If P and T are the equilibrium pressure and temperature, match the following :**

Column I	Column II
(A) K_p/K_c for synthesis of ammonia	p. P^2
(B) K_p/K_x for dissociation of ammonia	q. R^2T^2
(C) K_p/K_c for $NH_4HS_{(s)} \rightleftharpoons NH_{3\,(g)} + H_2S_{(g)}$	r. $R^{-2}T^{-2}$
(D) K_p/K_x for $CS_{2(g)} + 4H_{2(g)} \longrightarrow CH_{4(g)} + 2H_2S_{(g)}$	s. P^{-2}

MARK YOUR RESPONSE

1.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

2. For the dissociation reaction in gaseous state D = Density for no dissociation; d = density after equilibrium, pressure and temperature being the same. Then match the following :

Column I		Column II	
(A)	D/d is always	p.	1
(B)	D/d for the reaction $A_{(g)} \rightleftharpoons 3\ B_{(g)}$ at 50% dissociation	q.	3
(C)	Maximum value of D/d for the above reaction	r.	>1
(D)	$\frac{(D-d)}{d}$ for 50% dissociation of $A_{(g)}$	s.	2

3. $PCl_{5\,(g)}$ at an initial pressure of 1 atm is placed in a closed vessel containing chlorine at a pressure of 0.2 atm. If PCl_5 dissociates to the extent of 20%, then match the following :

Column I		Column II	
(A)	Partial pressure of PCl_5	p.	0.4 atm
(B)	Partial pressure of PCl_3	q.	0.8 atm
(C)	Partial pressure of Cl_2	r.	0.10 atm
(D)	Equilibrium constant (in terms of partial pressures) for dissociation of PCl_5	s.	0.2 atm.

4. Match the processes mentioned in Column I with the characteristics listed in Column II.

Column I		Column II	
(A)	$2N_2O_{(g)} \longrightarrow 2N_{2(g)} + O_{2(g)} + 2$ kJ	p.	Spontaneous at low temperatures but non-spontaneous at high temperature
(B)	$H_2O_{(g)} \longrightarrow H_2O_{(\ell)}$	q.	Spontaneous at high temperatures and non-spontaneous at low temperatures
(C)	$2NH_{3\,(g)} + 2kJ \longrightarrow N_{2(g)} + 3H_{2(g)}$	r.	Non-spontaneous at all temperatures
(D)	$3O_2 + 2$ kJ $\longrightarrow 2O_3$	s.	Spontaneous at all temperatures

5. Match the favourable conditions listed in Column II with the reactions listed in Column I.

Column I		Column II	
(A)	$CO_{2(g)} + H_2O_{(\ell)} \longrightarrow H_2CO_{3\,(aq)}$	p.	Low temperature
(B)	$CO_{(g)} + 2H_{2(g)} \longrightarrow CH_3OH_{(g)}$, ΔH=-91kJ	q.	High temperature
(C)	$N_2O_{4\,(g)}$ ($H° = 9.2$ kJ mol^{-1}) $\longrightarrow$ $2NO_{2(g)}$ ($H°$=33.2 kJ mol^{-1})	r.	Low pressures
(D)	$N_{2\,(g)} + O_{2\,(g)} \longrightarrow 2NO_{(g)}$ ($H°$=90 kJ mol^{-1})	s.	High Pressure

MARK YOUR RESPONSE

	p	q	r	s
2. A	Ⓟ	Ⓠ	Ⓡ	Ⓢ
B	Ⓟ	Ⓠ	Ⓡ	Ⓢ
C	Ⓟ	Ⓠ	Ⓡ	Ⓢ
D	Ⓟ	Ⓠ	Ⓡ	Ⓢ

	p	q	r	s
3. A	Ⓟ	Ⓠ	Ⓡ	Ⓢ
B	Ⓟ	Ⓠ	Ⓡ	Ⓢ
C	Ⓟ	Ⓠ	Ⓡ	Ⓢ
D	Ⓟ	Ⓠ	Ⓡ	Ⓢ

	p	q	r	s
4. A	Ⓟ	Ⓠ	Ⓡ	Ⓢ
B	Ⓟ	Ⓠ	Ⓡ	Ⓢ
C	Ⓟ	Ⓠ	Ⓡ	Ⓢ
D	Ⓟ	Ⓠ	Ⓡ	Ⓢ

	p	q	r	s
5. A	Ⓟ	Ⓠ	Ⓡ	Ⓢ
B	Ⓟ	Ⓠ	Ⓡ	Ⓢ
C	Ⓟ	Ⓠ	Ⓡ	Ⓢ
D	Ⓟ	Ⓠ	Ⓡ	Ⓢ

6.

Column I - (Reaction)	Column II - (Favourable condition)
(A) Formation of ammonia by Haber's process.	p. Increase in temperature
(B) Formation of SO_3 in contact process for manufacture of H_2SO_4	q. Decrease in temperature
(C) Formation of NO in Birk-land Eyde process for manufacture of HNO_3.	r. Decrease in pressure
(D) Formation of NO_2 (g) by following reaction	s. Increase in pressure

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g) + 200\ KJ$$

MARK YOUR RESPONSE

6.

	p	q	r	s
A	●	●	●	●
B	●	●	●	●
C	●	●	●	●
D	●	●	●	●

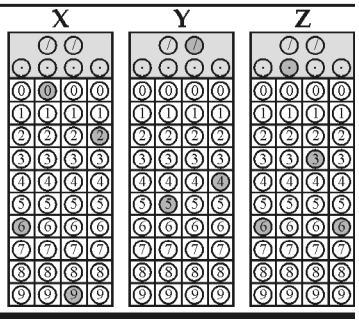
F NUMERIC/INTEGER ANSWER TYPE

The answer to each of the questions is either numeric (eg. 304, 40, 3010, 3 etc.) or a fraction (2/3, 23/7) or a decimal (2.35, 0.546).

The appropriate bubbles below the respective question numbers in the response grid have to be darkened.

For example, if the correct answers to question X, Y & Z are 6092, 5/4 & 6.36 respectively then the correct darkening of bubbles will look like the following.

For single digit integer answer darken the extreme right bubble only.



1. 0.20 mole of CO was taken in a 2.50 L flask maintained at 750 K along with a catalyst so that the following reaction could take place :

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$$

Hydrogen was introduced until the total pressure in the flask at equilibrium was 12.30 atm and 0.10 mole of CH_3OH was formed. Calculate the equilibrium constant (in terms of 10^{-2} atm^{-2}) of the reaction in terms of partial pressures.

2. 31.2 g of ammonium carbamate (NH_2COONH_4) was heated in a flask of 5.0 L to a temperature of 77°C. The flask initially contained 1.70 g of NH_3. NH_2COONH_4 dissociated to the extent of 50% when equilibrium reaches. Calculate K_p (in terms of 10^{-2} atm^3) for dissociation of NH_2COONH_4.

3. For the following equilibrium,

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

Vapour density is found to be 100 when 1 mole of PCl_5 is taken in 10 L flask at 27°C. Calculate equilibrium pressure (in atm) of the system.

4. Equilibrium constant for the reaction :

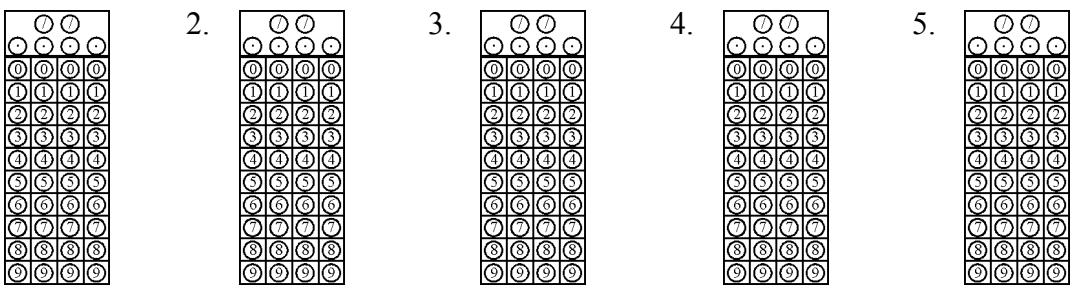
$$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$$

at 25°C is 2.5×10^{18}. Calculate silver ion concentration (in terms of 10^{-18} M) in a solution which was originally 0.10 M in KCN and 0.03 M in $AgNO_3$.

5. 1.0 mole of nitrogen and 3.0 mole of PCl_5 are placed in 100 L flask heated to 227°C. The equilibrium pressure is 2.05 atm. Calculate K_P for the dissociation (in atm) of PCl_5.

MARK YOUR RESPONSE

1. 2. 3. 4. 5.



Answerkey

A Single Correct Choice Type

1.	d	**2.**	c	**3.**	b	**4.**	c	**5.**	b	**6.**	c	**7.**	d	**8.**	c	**9.**	d	**10.**	b
11.	c	**12.**	c	**13.**	c	**14.**	b	**15.**	c	**16.**	d	**17.**	b	**18.**	d	**19.**	d	**20.**	c
21.	d	**22.**	b	**23**	c	**24.**	c	**25.**	b	**26.**	b	**27.**	c	**28.**	c	**29.**	d	**30.**	b
31.	c	**32.**	d	**33.**	d	**34.**	b	**35.**	c	**36.**	a	**37.**	c	**38.**	c	**39.**	d	**40.**	d
41.	b	**42.**	a	**43.**	c	**44.**	d	**45.**	c	**46.**	d	**47.**	c	**48.**	c	**49.**	b	**50.**	d
51.	c	**52.**	d	**53.**	c	**54**	c	**55**	b	**56**	d	**57**	c	**58**	b	**59**	d	**60**	b
61	d	**62**	c	**63**	a	**64**	b	**65**	d	**66**	a	**67**	c	**68**	d	**69**	b	**70**	c
71	d	**72**	d	**73**	b	**74**	b	**75**	b	**76**	c	**77**	d						

B Comprehension Type

1	(b)	**4**	(a)	**7**	(b)	**10**	(b)	**13**	(b)	**16**	(c)	**19**	(b)
2	(c)	**5**	(b)	**8**	(a)	**11**	(b)	**14**	(b)	**17**	(d)		
3	(b)	**6**	(d)	**9**	(b)	**12**	(c)	**15**	(c)	**18**	(a)		

C Reasoning Type

1	(a)	**3**	(d)	**5**	(a)	**7**	(b)	**9**	(a)
2	(a)	**4**	(c)	**6**	(c)	**8**	(d)		

D Multiple Correct Choice Type

1.	a,b,c	**2.**	a,c,d	**3.**	a,b,d	**4.**	b,c	**5.**	a,b,d	**6.**	b,c	**7.**	a,c,d	**8.**	a,b,d	**9.**	b,c	**10.**	c
11.	c,d	**12.**	b,c,d	**13.**	a,b,c,d	**14.**	b,c,d	**15.**	a,c,d	**16.**	b,c	**17.**	b,c	**18.**	b,d	**19.**	b,d	**20.**	a,d
21.	a,d	**22.**	a,b,c	**23.**	a,b,d	**24.**	a,b,c												

E Matrix-Match Type

1. **A-r; B-p; C-q; D-s**
2. **A-r; B-s; C-q; D-p**
3. **A-q; B-s; C-p; D-r**
4. **A-s; B-p; C-q; D-r**
5. **A-p,s; B - p,s; C-q, r; D-q;**
6. **A - q, s; B - q, s; C -p; D - q**

F Numeric/Integer Answer Type

1	1.83	**2**	1.15	**3**	2.56 atm	**4**	7.5	**5**	0.205 atm

Solutions

A Single Correct Choice Type

1. **(d)** K_p does not change as T is constant. Since pressure increases on halving the volume, equilibrium shifts in backward direction as $\Delta n < 0$ in this direction. Hence α decreases.

2. **(c)** $K_p = p_{B(1)}^2 p_{C(1)}^3 = p_{B(2)}^2 p_{C(2)}^3 = p_{B(2)}^2 (2p_{C(1)})^3$;

hence $\frac{p_{B(2)}^2}{p_{B(1)}^2} = \frac{1}{8}$, $Br \frac{p_{B(2)}}{p_{B(1)}} = \frac{1}{2\sqrt{2}}$

3. **(b)** Concentration quotient

$$Q = \frac{[NO_2][O_2]}{[NO][O_3]} = \frac{2.5\times10^{-4}\times8.2\times10^{-3}}{1.0\times10^{-5}\times1.0\times10^{-6}} = 2.05\times10^5$$

$Q < K_c (= 6.0\times10^{34})$; reaction goes in forward direction.

5. **(b)**

	A	+	B	$\rightleftharpoons$	C	+	D
	a		a		0		0
	$a-x$		$a-x$		x		x

Given: $a - x = 2x, x = a/3$; $K_c = \frac{x\times x}{(a-x)(a-x)} = 0.25$

$$K_c = \frac{K_f}{K_b} \qquad K_b = \frac{K_f}{K_c} = \frac{2\times10^{-3}}{0.25} = 8\times10^{-3}$$

6. **(c)** $S_{(aq)}^{2-} + S_{(s)} \rightleftharpoons S_{2(aq)}^{2-}$ $\quad K_1 = 12$

$S_{(aq)}^{2-} + 2S_{(s)} \rightleftharpoons S_{3(aq)}^{2-}$ $\quad K_2 = 132$

$S_{2(aq)}^{2-} + S_{(s)} \rightleftharpoons S_{3(aq)}^{2-}$ $\quad K_3 = ?$

$$K_3 = \frac{K_2}{K_1} = \frac{132}{12} = 11$$

7. **(d)**

	A	+	$3B$	$\rightleftharpoons$	$2C$	+	D
	$2a$		a		0		0
	$2a-x$		$a-3x$	=	$2x$		x

Given: $a - 3x = 2x$, $x = a/5$

Hence, % of B reacted $= \frac{3x}{a}\times100 = 60\%$

8. **(c)** $2NO \rightleftharpoons N_2 + O_2, K_1 = 4.0\times10^{30}$

$NO + \frac{1}{2}Br_2 \rightleftharpoons NOBr$, $\quad K_2 = 1.4$

$\frac{1}{2}N_2 + \frac{1}{2}O_2 + \frac{1}{2}Br_2 \rightleftharpoons NOBr, K_3 = ?$

$$K_3 = \frac{K_2}{\sqrt{K_1}} \frac{1.4}{= (4.0\times10^{30})^{1/2}} = 7.0\times10^{-16}$$

9. **(d)**

	$NH_4HS_{(s)}$ $\rightleftharpoons$	$NH_{3(g)}$	+	$H_2S_{(g)}$
		0.1 atm		0 atm
		0.1+x atm		x atm

Given: $0.1 + x + x = 0.5, x = 0.2$ atm;

$K_p = p_{NH_3} \times p_{H_2S} = (0.1+x)\times x = 0.3\times0.2$ atm

10. **(b)**

	$NH_2COONH_{4(s)}$ $\rightleftharpoons$	$2NH_{3(g)}$	+	$CO_{2(g)}$
		$2p$		p

$$K_p = p_{NH_3}^2 \times p_{CO_2} = (2p)^2 \times p = 3.2\times10^{-5}\,\text{atm}^3$$

$$\Rightarrow p = 2\times10^{-2}\,\text{atm}; \qquad p_{NH_3} = 2p\times2\times10^{-2}\,\text{atm}$$

12. **(c)** (i) $p_{H_2O} = K_p^{1/4} = (8.1\times10^{-11})^{1/4} = 3.0\times10^{-3}$ atm

(ii) $p_{H_2O} = (K_P)^{1/5} = (3.2\times10^{-9})^{1/5} = 2.0\times10^{-2}$ atm

(iii) $p_{H_2O} = (K_p)^{1/10} = (1.0\times10^{-30})^{1/10} = 1.0\times10^{-3}$ atm

Smaller is the equilibrium p_{H_2O}, more effective will be the lower hydrate or anhydrous salt as dehydrating agent. Hence, Z_2SO_4.

13. **(c)** Lower hydrate or anhydrous salt will absorb water vapour from air when the dissociation pressure of higher hydrate is greater than the partial pressure of water vapour in the air.

$$\therefore \text{Relative humidity} > \frac{3.0\times10^{-3}\times100}{6.0\times10^{-3}} = 50\%$$

14. **(b)** $ln\, K_p = \text{Constant} - \frac{\Delta H}{RT}$

Since ΔH is negative for exothermic reaction, the plot (straight line) not passing through the origin will have a positive slope. Hence the graph (b).

15. **(c)** K_1 at $27°C = \frac{2.0\times10^{-3}}{5\times10^{-4}} = 4.0$

K_2 at $127°C = \frac{8\times10^{-2}}{4.0\times10^{-3}} = 20$

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

$T_1 = 300$K, $T_2 = 400$K

16. **(d)** $\ln K = \text{Constant} - \frac{\Delta H}{R}\frac{1}{T}$

Since, E_a (forward) > E_a (backward), the reaction is endothermic, $\Delta H > 0$. Hence slope $= -\frac{\Delta H}{R}$

17. **(b)**

	A	+	$2B$	$\rightleftharpoons$	$2C$
Initial	$2/2 = 1M$		$3/2 = 1.5\,M$		$2/2 = 1M$
Equib	$(1 + .025)M$		$(1.5 + 0.5)M$		$0.5M$

K_c for reverse reaction $= \frac{[A][B]^2}{[C]^2} = \frac{1.25 \times 2^2}{0.5^2} = 20$

18. **(d)** $\frac{K_p}{K_c} = (RT)^{\Delta n} = (0.082 \times 300)^3; \Delta n = 2 + 1 - 0 = 3$

19. **(d)** $\ln S = \ln A - \frac{\Delta H}{R} \times \frac{1}{T}$

The slope of the graph is negative, so $\Delta H > 0$. Hence, dissolution is endothermic. Hydrated salt dissolves endothermically.

20. **(c)**

	$AB_{5(g)}$	$\rightleftharpoons$	$AB_{(g)}$	+	$2B_{2(g)}$
	$1-\alpha$		α		2α

Moles at equilibrium

$= 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha = 1 + \frac{20}{100} \times 2 = 1.4$

$\frac{p_1}{p_2} = \frac{n_1 T_1}{n_2 T_2}; \frac{1}{p_2} = \frac{1 \times 300}{1.4 \times 600}, P_2 = 2.8$ atm

21. **(d)**

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

$\alpha = \frac{x}{a}$ (degree of dissociation)

Total moles $= 1 - \alpha + \alpha + \alpha = 1 + \alpha$

$K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{\left[\frac{\alpha}{1+\alpha} \cdot p\right]\left[\frac{\alpha}{1+\alpha} \cdot p\right]}{\frac{1-\alpha}{1+\alpha} \cdot p}$

$= \frac{\alpha^2 p}{1-\alpha^2} \Rightarrow \alpha = \left(\frac{K_p}{K_p + P}\right)^{1/2}$

23. **(c)**

	$AB_{2(g)}$	$\rightleftharpoons$	$AB_{(g)}$	+	$B_{(g)}$
	500 torr		0		0
	$500 - x$		x		x

Given $500 - x + x + x = 500 + x = 600 \Rightarrow x = 100$ torr

$K_p = \frac{p_{AB} \times p_B}{p_{AB_2}} = \frac{x \times x}{500 - x} = \frac{100 \times 100}{500 - 100} = 25$ torr

24. **(c)**

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

$K_p = P_{CO_2} = 0.82$ atm;

$n_{CO_2} = \frac{PV}{RT} = \frac{0.82 \times 20}{0.082 \times 1000} = 0.2$ mol

Mol of $CaCO_3$ dissociated $= n_{CO_2} = 0.2$;

Amount dissociated $= 0.2 \times 100 = 20$ g

25. **(b)** $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$X_{NH_3} = 0.6; X_{N_2} + X_{H_2} = 1 - 0.6 = 0.4$,

$X_{N_2} = \frac{0.4}{4} = 0.1; X_{H_2} = \frac{3}{4} \times 0.4 = 0.3$

$P_{N_2} = 0.1 \times 10 = 1$ atm; $P_{H_2} = 0.3 \times 10 = 3$ atm

$P_{NH_3} = 0.6 \times 10 = 6$ atm

K_p for dissociation of NH_3

$= \frac{P_{N_2} \times P_{H_2}^3}{P_{NH_3}^2} = \frac{1 \times 3^3}{6^2} = 0.75\,\text{atm}^2$

26. **(b)**

	$SO_2Cl_{2(g)}$	$\rightleftharpoons$	$SO_{2(s)}$	+	$Cl_{2(g)}$
	100 mm		0		0
	$100 - x$		x		x

Total pressure $= 100 - x + x = 100 + x$ mm

given, $\frac{100 - x}{100 + x} = \frac{1}{3}, x = 50$mm

$K_p = \frac{p_{SO_2} \times p_{Cl_2}}{p_{SO_2Cl_2}} = \frac{x \times x}{(100 - x)} = 50$mm

27. **(c)** $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$n_{H_2} = \frac{6}{2} = 3$ mol; $n_{N_2} = \frac{28}{28} = 1$ mol

500 ml of $1M$ H_2SO_4 = 0.5 mol of H_2SO_4 $\equiv$ 1 mol of NH_3

$[H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4]$

At equilibrium to form 1 mole of NH_3, 0.5 mol of N_2 and 1.5 mol of H_2 must react.

n_{N_2} at equib $= 1 - 0.5 = 0.5$ mol;

n_{H_2} at equib $= 3 - 1.5 = 1.5$ mol

$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{1^2}{0.5 \times 1.5^3} = 0.59\ M^{-2}$

28. **(c)**

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

P = total pressure, α = degree of dissociation

$K_p = \frac{\alpha_1^2 P_1}{1 - \alpha_1^2} = \frac{\alpha_2^2 P_2}{1 - \alpha_2^2}$; $\alpha_1 = 0.5, \alpha_2 = 0.8, P_1 = 4$ atm

Hence $P_2 = 0.75$ atm

29. **(d)** $Ag^{+}_{(aq)} + 2NH_{3(aq)} \rightleftharpoons [Ag(NH_3)_2]^{+}_{(aq)}$

$$\text{Instability constant} = \frac{1}{\text{formation constant}}$$

$$= \frac{K_r}{K_f} = \frac{2.0\times10^{-2}}{1.0\times10^{6}} = 2.0\times10^{-8}$$

30. **(b)** $SO_2Cl_{2(g)} \rightleftharpoons SO_{2(g)} + Cl_{2(g)}$

$$\alpha\,\% = \frac{D-d}{d(y-1)}\times100 \qquad (y=2)$$

$$D = \frac{\text{molar mass of } SO_2Cl_2}{2} = \frac{135}{2} = 67.5;$$

$d = 50.0$ (given)

31. **(c)** $X_2Y_{4(g)} \rightleftharpoons X_{2(g)} + 2Y_{(g)}$

$$\alpha = \frac{D-d}{d(y-1)},\ y=3$$

$$D = \frac{PM}{RT} = \frac{1\times82.1}{0.0821\times400} = 2.5\text{gL}^{-1}$$

$d = 2.0\text{g L}^{-1}$ (given)

32. **(d)** E_a = activation energy for forward reaction
E'_a for backward reaction

$$E_a - E_a^{'} = (8-10.303)\text{kcal} = -2.303\times10^{3}\text{ cal}$$

$$K_c = \frac{-2.303\times10^{3}}{2\times500} = e^{-2.303}$$

$2.303 \log K = -2.303, \quad \log K = -1, K = 0.1$

33. **(d)** $\ln\frac{K_2}{K_1} = \frac{\Delta H}{R}\frac{(T_2-T_1)}{T_1T_2}$

$$= \frac{8.314\times10^{3}\times(500-400)}{8.314\times400\times500} = 0.5$$

34. **(b)** $\frac{n_2}{n_1} = \frac{P_2}{P_1}$ or $\frac{n_2}{4} = \frac{3}{4} \Rightarrow n_2 = 3$ moles

$N_{2(g)}$ +	$3H_{2(g)}$	$\rightleftharpoons$	$2NH_{3(g)}$
1 mol	3 mol		0
$1-x$	$3-3x$		$2x$

Total moles at equib $= 1-x+3-3x+2x$

$= 4-2x = 3\ ; \quad x = 0.5$ mol

$$P_{N_2} = \frac{1-x}{3}\times3 = \frac{0.5}{3}\times3 = 0.5\text{ atm};$$

$$P_{H_2} = \frac{3-3x}{3}\times3 = 3-3\times0.5 = 1.5\text{ atm};$$

$$P_{NH_3} = \frac{2x}{3}\times3 = 2\times0.5 = 1\text{ atm}$$

K_p for dissociation of NH_3

$$= \frac{p_{N_2}\times p_{H_2}}{P^2_{NH_3}} = \frac{(0.5\text{ atm})\times(1.5\text{ atm})^3}{(1\text{ atm})}$$

35. **(c)** $SO_2 \rightarrow SO_3$, Eq. mass = molar mass/2

$Cr_2O_7^{2} \rightarrow 2Cr^{3+}$, Eq. mass = molar mass/6

$\frac{1}{3}$ mol of $K_2Cr_2O_7 = \frac{6}{3} = 2$ equiv. of $K_2Cr_2O_7$

= 2 equiv. of SO_2 = 1 mol of SO_2

$2SO_2$ +	$O_{2(g)}$	$\rightleftharpoons$	$2SO_{3(g)}$
1 mol	1 mol		0 mol
1 mol	10.5 mol		1 mol

$$P_{SO_2} = \frac{1}{2.5}\times5 = 2\text{ atm}, \qquad P_{O_2} = \frac{0.5\times5}{2.5} = 1\text{ atm},$$

$$P_{SO_3} = \frac{1}{2.5}\times5 = 2\text{ atm},$$

$$K_p = \frac{P^2_{SO_3}}{P^2_{SO_2}\times P_{O_2}} = \frac{2^2}{2^2\times1} = 1.0$$

36. **(a)** $I^{-}_{(aq)} + Ag^{+}_{(aq)} \rightarrow AgI_{(s)}$ (0.8 mol at equib.)

x = mol. of I^- reacted = $1.0-0.8 = 0.2$

$I^-_{(aq)}$ +	$I_{2(aq)}$	$\rightleftharpoons$	$I^-_{3(aq)}$	
1 mol	0.25 mol		0 mol	
1–0.2	0.25 – 0.20		0.2	Stability

constant $K = \frac{[I_3^-]}{[I^-][I_2]} = \frac{0.2}{0.8\times0.05} = 5$

37. **(c)** $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

$\frac{120}{60} = 2$mol	$\frac{92}{46} = 2$mol	0	0
$2-x$	$2-x$	x	x

$$K = \frac{[\text{Ester}][H_2O]}{[\text{Acid}][\text{Alcohol}]} = \frac{x^2}{(2-x)^2} = 4 \text{ or } x = \frac{4}{3}$$

$$\text{Mole fraction of ester} = \frac{x}{4} = \frac{4}{3\times4} = 0.333$$

38. **(c)** $K_p = K_c(RT)^{\Delta n}$; $\Delta n = -2$ as shown by the units of K_c; $R = 0.082$ atm K^{-1} mol^{-1}

39. **(d)** $\alpha = \frac{(M-M_e)}{M_e(y-1)} = \frac{208.32-124}{124\times(2-1)} = 0.68$

$y = 2$ for $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

41. **(b)** On multiplying second eq. by 2 and adding to the first eqn.:

$$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$$

$$\Delta G = -457.0 + 2 \times (-28.5) = -514.0\text{kJ}$$

Hence, for $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}, \Delta G = 514.0\,\text{kJ}$

42. **(a)** $\Delta G^\circ = -2.303\,RT\,\log K_p$

$$\log K_p = \frac{-514 \times 10^3}{-2.303 \times 8.314 \times 298} = 90.08$$

43. **(c)** On raising the temp., equilibrium shifts in backward direction. Forward reaction is exothermic, i.e. ΔH is negative.

44. **(d)** $P_{NH_3} = P_{H_2S} = \frac{P}{2}\text{atm}$

$$K_{p=}P_{NH_3}P_{H_2S} = \left(\frac{P}{2}\right)^2 = \frac{P^2}{4}$$

$$\Delta G = -RT \ln k_p = -RT \ln\left(\frac{p}{2}\right)^2 = -2RT\ [\ln p - \ln 2]$$

47. **(c)** All the species are solids and their active masses are unity each.

48. **(c)** The reaction is exothermic and takes place with a decrease in number of molecules of gaseous species. Obviously high pressure and low temperature are the favourable conditions for the shift of equilibrium to products side. However, in continuous flow process optimum elevated temperature is required to have more NH_3 due to high activation energy of the reaction.

50. (d) $NH_4OH_{(aq)} + H^+_{(aq)} \rightleftharpoons NH^+_{4(aq)} + H_2O_{(l)}$

$$K_1 = \frac{[NH_4^+]}{[NH_4OH][H^+]} = 1.80 \times 10^9$$

$$NH_4OH_{(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

$$K_2 = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$\frac{K_2}{K_1} = [H^+][OH^-] = 1.0 \times 10^{-14}$$

or $K_2 = K_1 \times 1.0 \times 10^{-14} = 1.8 \times 10^9 \times 1.0 \times 10^{-14}$

$$= 1.80 \times 10^{-5}$$

51. **(c)** Ice $\rightleftharpoons$ water at $P = 1$ atm and $T = 273.15$K
For $P > 1$ atm and $T = 273.15$K, equilibrium shifts completely in forward direction leading to reduction in volume of the system. i.e., ice melts completely.

52. **(d)** $K_p = K'_x P^2 \quad \Delta n = 1 + 3 - 2 = +2$

$$K_p = K_x(10P)^2 = K'_x \times 100P^2 \text{ or } \frac{K'_x}{K_x} = \frac{1}{100}$$

53. **(c)** $P_{\text{dry air}} = P_{\text{total}} - \text{aqueous tension} = 760 - 20 = 740$ torr $= P_1$

$$\frac{P_1V_1}{V_1} = P_2 \times \frac{V_1}{2}, P_{2(\text{dry})} = 1480 \text{ torr}$$

Resulting pressure = 1480 + 20 = 1500 torr
(Aqueous tension does not change so long T is constant)

55. **(b)** On reversing (i) and (ii) and then adding, we get (iii).

Hence, $K_3 = \frac{1}{K_1K_2}$ or $K_1K_2K_3 = 1$

56. **(d)** $K_p = p^2_{H_2O} = 1.21 \times 10^{-4}$

$\Rightarrow\ p_{H_2O} = 1.1 \times 10^{-2}\text{atm} = 760 \times 1.1 \times 10^{-2} = 8.4\,\text{torr}$

$CuSO_4.5H_2O$ will efforsce when partial pressure of H_2O vapour in air falls below 8.4 torr.

Hence relative humidity of air $< \frac{8.4}{30} \times 100 = 28\%$

57. **(c)** $K_p = 1.0 \times 10^4 = \frac{1}{p^2_{H_2O}}$

$\Rightarrow\ p_{H_2O} = 1.0 \times 10^{-2}\text{atm} = 760 \times 1.0 \times 10^{-2} = 7.6\,\text{torr}$

Relative humidity of air that can be achieved

$$= \frac{7.6}{16} \times 100 = 47.5\%$$

58. **(b)** $2NOBr \rightleftharpoons 2NO + Br_2$

Degree of dissociation, $\alpha = \frac{20}{100} = 0.2$,

$1 - \alpha = 0.8 \qquad \alpha = 0.2 \qquad \frac{\alpha}{2} = 0.1$

Total moles $= 0.8 + 0.2 + 0.1 = 1.1$mol

$$p_{NOBr} = \frac{0.8 \times 1.1}{1.1} = 0.8\text{ atm};$$

$$p_{NO} = \frac{0.2 \times 1.1}{1.1} = 0.2\text{ atm}; \qquad p_{Br_2} = 0.1\text{atm}$$

Hence, $K_p = \frac{P^2_{NO}P_{Br_2}}{P^2_{NOBr}} = \frac{0.2^2 \times 0.1}{0.8^2} = \frac{1}{160}\text{atm}$

59. **(d)** $CO_{2(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)}$

If x is the mole fraction of CO at equilibrium, then $P_{CO} = x.p = x \times 4$

And $P_{CO_2} = (1-x).P = (1-x) \times 4$

Then, $K_p = 9 = \frac{P_{CO}^2}{P_{CO_2}} = \frac{(4x)^2}{4(1-x)}$ or $x = 0.75$

60. **(b)** $2XO + O_2 \rightleftharpoons 2XO_2$; Let x mol of O_2 react at equilibrium. Since K is very-very small $x << 1$,

$[O_2] = 2 - x \approx 2$; $[XO] = 1 - 2x = 1$; $[XO_2] = 2x$

$$K = \frac{[XO_2]^2}{[XO]^2[O_2]} = \frac{[2x]^2}{[1-2x]^2[2-x]}$$

$$= \frac{4x^2}{2} = 2 \times 10^{-4} \text{ (given)} \text{ or } x = 1.0 \times 10^{-2}$$

Mole of $XO_2 = 2x = 2.0 \times 10^{-2}$

61. **(d)** $AB_{(g)} \rightleftharpoons A_{(g)} + B_{(g)}$;

$1-\alpha \qquad \alpha \qquad \alpha$

$P_A = P_B = \frac{\alpha}{1+\alpha}.P$; $P_{AB} = \frac{1-\alpha}{1+\alpha}.P$;

Then ,

$$K_p = \frac{P_A \times P_B}{P_{AB}} \text{ or } \frac{P}{3} = \frac{\left(\frac{\alpha}{1+\alpha}P\right)^2}{\left(\frac{1-\alpha}{1+\alpha}.P\right)} = \frac{\alpha^2 P}{1-\alpha^2}$$

$$\Rightarrow \quad \alpha = \frac{1}{2}$$

64. **(b)** Moles of water gas $(CO + H_2) = \frac{60}{30} = 2$

Mole of CO = mole of $H_2 = 1$; moles of steam $= \frac{18}{18} = 1$

$CO + H_2O \rightleftharpoons CO_2 + H_2$

$1 \quad 1 \quad 0 \quad 1$

$1-x \quad 1-x \quad x \quad 1+x$

$$K = 3 = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{x \times (1+x)}{(1-x)(1-x)}$$

$x = 0.5$ mol of $CO_2 = 22$g

65. **(d)** $2AB_2 \longrightarrow 2AB + B_2$

$1-\alpha \qquad \alpha \qquad \alpha/2$

Total moles $= 1 - \alpha + \alpha + \frac{\alpha}{2} = \frac{2+\alpha}{2}$

$$P_{AB_2} = \frac{(1-\alpha)P}{(2+\alpha)/2} = \frac{2(1-\alpha)P}{2+\alpha};$$

$$P_{AB} = \frac{\alpha P}{(2+\alpha)/2} = \frac{2\alpha P}{2+\alpha}; \quad P_{B_2} = \frac{\frac{\alpha}{2}P}{\frac{(2+\alpha)}{2}} = \frac{\alpha P}{2+\alpha}$$

Hence, $K_P = \frac{P_{AB}^2 P_{B_2}}{P_{AB_2}^2} = \frac{\left(\frac{2\alpha P}{2+\alpha}\right)^2 \times \frac{\alpha P}{2+\alpha}}{\left[\frac{2(1-\alpha)P}{2+\alpha}\right]^2}$

$$= \frac{\alpha^3 P}{2} \qquad (\alpha << 1)$$

66. **(a)** $S_{8(g)} \longrightarrow 4S_{2(g)}$

1 atm 0 atm

$1-x$ atm $4x$ atm

$1 - x + 4x = 1 + 3x = 1.6 \Rightarrow x = 0.2$ atm

$P_{S_8} = 1 - 0.2 = 0.8$; $P_{S_2} = 4 \times 0.2 = 0.8$ atm;

$$K_p = \frac{P_{S_2}^4}{P_{S_8}} = \frac{0.8^4}{0.8} = 0.512 \text{ atm}^3$$

67. **(c)** $2Ag^+ + Cu_{(s)} \longrightarrow Cu^{2+} + 2Ag_{(s)}$;

$$K = \frac{[Cu^+]}{[Ag^+]^2} = \frac{x}{y^2}$$

After dilution, reaction quotient $Q = \frac{\frac{x}{2}}{\left(\frac{y}{2}\right)^2} = \frac{2x}{y^2}$

Under the new situation, $Q > K$, so the equilibrium will shift in backward direction. Hence $[Cu^{2+}] < \frac{x}{2}$;

$[Ag^+] > \frac{y}{2}$

68. **(d)** $-\Delta G^\circ = 2.303RT \log K$,

$-10^3 \times (-4.606) = 2.303 \times 2 \times 1000 \log K$

$\Rightarrow K = 10$; K for reverse mode $= 1/10 = 0.1$

69. **(b)** $RT \ln K = -\Delta G^\circ = T\Delta S^\circ - \Delta H^\circ$;

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

Thus, a plot of ln K versus $1/T$ (abscissa) will be straight line with slope equal to $\frac{-\Delta H^\circ}{R}$ and intercept $\frac{\Delta S^\circ}{R}$.

70. **(c)** K will increase on decreasing temperature. So the reaction is exothermic.

72. **(d)** $A + 2B \rightleftharpoons C + D$; x = mol of A remaining at equilibrium

Moles of A reacted = $1 - x$;

Moles of B reacted = $2(1 - x)$

Moles of B remaining = $3 - 2(1 - x) = 1 + 2x \approx 1$

($\because K$ is very large, $x << 1$)

Moles of C = Moles of $D = 1 - x \approx 1$

$$\text{Hence, } K = 1.0 \times 10^8 = \frac{[C][D]}{[A][B]^2} = \frac{1 \times 1}{x \times [1 + 2x]^2}$$

$$= \frac{1}{x} \Rightarrow x = 1.0 \times 10^{-8}$$

73. **(b)** $2SO_2 + O_2 \rightleftharpoons 2SO_3$; $K = 100 = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

$$= \frac{2^2}{[O_2]} \Rightarrow [O_2] = 0.04 \text{ mol L}^{-1}$$

[At equib. $(SO_3)/(SO_2) = 2$]

74. **(b)** The equilibrium is $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

When CrO_4^{2-} ions are added the equilibrium is shifted backward (Le Chatelier's principle) and it will result in decrease of Ag^+ concentration.

There will be no change in K_{sp}.

75. **(b)** If the solubilities are S_1, S_2, S_3 respectivley, then the K_{SP} values for them are.

For A_2B, $K_{sp} = 4S_1^3$ $[A_2B \rightleftharpoons 2A^+ + B^{2-}]$

For AB, $K_{sp} = S_2^2$ $[AB \rightleftharpoons A^+ + B^-]$

For AB_3, $K_{sp} = 27S_3^4$ $[AB_3 \rightleftharpoons A^{3+} + 3B^-]$

Since the value of K_{sp} is same

$\therefore$ The correct order of solubilities is $AB > A_2B > AB_3$.

76. **(c)** Using the relation $K_P = K_C \cdot (RT)^{\Delta n}$, we get

$$\frac{K_P}{K_C} = (RT)^{\Delta n}$$

Thus $\dfrac{K_P}{K_C}$ will be highest for the reaction having highest value of Δn.

The Δn values for various reactions are

(a) $\Delta n = 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2}$

(b) $\Delta n = 2 - (1 + 1) = 0$

(c) $\Delta n = (1 + 1) - 1 = 1$

(d) $\Delta n = (2 + 4) - (7 + 2) = -3$

Thus maximum value of $\Delta n = 1$

77. **(d)** Given $\alpha = 0.35$ $P = 2$ atmosphere

$$\begin{array}{lll} N_2O_4 & \rightleftharpoons & 2NO_2 \\ (1-\alpha) & & 2\alpha \\ 0.65 & & 2 \times 0.35 \end{array}$$

$$\therefore \quad K_P = \frac{(P_{NO_2})^2}{P_{N_2O_4}}$$

Total number of moles present = $1 + 0.35 = 1.35$

$$\therefore \quad P_{N_2O_4} = \frac{0.65 \times 2}{1.35}$$

$$P_{NO_2} = \frac{2 \times 0.35}{1.35}$$

$\therefore$ $K_P = 0.279$ atm

B COMPREHENSION TYPE

2. **(c)** The pH corresponding to first inflexion point of the titration curve is 3.6. So bromophenol blue with indicator pH range 3.0 – 4.6 will be most suitable.

3. **(b)** Sulphur has 3*d*-subshell which is empty and can take up a pair of electrons. Hence, H_2SO_3 acts as a Lewis acid.

4. **(a)** The presence of catalyst merely causes the equilibrium to reach soon without affecting its position. Since position of the equilibrium is the same in presence and absence of the catalyst, the partial pressures of various reactants and the products would be the same.

5. **(b)** Since the reaction is exothermic, decrease in temperature favours the forward reaction. Hence, partial pressure of SO_3 would increase.

6. **(d)** Mole traction of O_2 in the mixture before equilibrium

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

Hence $p_{O_2} = X_{O_2} P_{Total} = \frac{1}{3} \times 1(\text{atm}) = 0.33$ atm

7. **(b)** $H_2SO_{3(aq)} \longrightarrow H^+_{(aq)} + HSO^-_{3(aq)}$;

$HSO^-_{3(aq)} \rightleftharpoons H^+_{(aq)} + SO^{2-}_{3(aq)}$

Since, the second dissociation constant is very small, the pH will be mainly determined by first ionization.

Step : $[H^+] = [H_2SO_3] = 0.01\ M$; pH = –log 0.01 = 2

8. **(a)** Addition of O_2 will cause the equilibrium to shift in forward direction because that way it is consumed. Reduction in volume i.e., increase in pressure also causes the equilibrium to shift in forward direction leading to smaller number of moles of gases.

9. **(b)** On addition of Cl_2 (product), the equilibrium shifts in reverse direction. Since the reverse reaction is exothermic, the temperature of the system will increase.

10. **(b)** In both reactions, the number of moles of gaseous species on the left side is smaller than right side. Hence, increase in pressure (reduction in volume) makes the equilibria to shift to left.

11. **(b)** In open container, CO_2 formed in the reaction, $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$, passes into atmosphere and equilibrium continues to shift in forward direction leading the reaction to completion.

12. **(c)** On increasing temperature, rate constants of both forward and reverse reactions would increase. The increase for the former, being exothermic, would be smaller.

13. **(b)** Since the slope of the straight line graph between log K and $\frac{1}{T}$ is positive, $\Delta H_{\text{reaction}}$ would be negative, i.e., the forward reaction would be exothermic.

14. **(b)**

	A	+	B	$\rightleftharpoons$	C	+	D
Initial	a		b		0		0
Equi.	$(a-x)$		$(b-x)$		x		x

From the given information $a = 2b$ .....(i)

and $x = 3\,(b-x)$

or $4x = 3b$

or $x = \frac{3}{4}\,b$ ...(ii)

Using law of mass action

$$K = \frac{x \times x}{(a-x)(b-x)}$$

$$= \frac{\left(\frac{3}{4}b\right)^2}{\left(2b-\frac{3}{4}b\right)\left(b-\frac{3}{4}b\right)} \quad [\because x = \frac{3}{4}b, a = 2b\,]$$

$$= \frac{9}{5} \text{ or } 1.8$$

15. **(c)**

	H_2	+	I_2	$\rightleftharpoons$	2HI
Initial :	a		b		0
Equi.	$(a-x)$		$(b-x)$		$2x$

$$a = \frac{0.02}{2} \text{ mole} = 0.01 \text{ mole}$$

$$b = \frac{2.54}{2.54} \text{ mole} = 0.01 \text{ mole}$$

Thus at equilibrium, we have

$H_2 = (0.01 - x)$ mole $\quad I_2 = (0.01 - x)$ mole

$$\therefore K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{4x^2}{(0.01-x)^2}$$

But $(0.01 - x) = 0.0021$ mole [conc. of I_2 at equilibrium]

$x = 0.0079$

$$K_c = \frac{4 \times (0.0079)^2}{(0.01-0.0079)^2} \text{ or } \frac{4 \times (0.0079)^2}{(0.0021)^2}$$

or $K_c = 56.6$

16. **(c)**

	H_2	+	I_2	$\rightleftharpoons$	2HI
Initial	a		b		0
Equi.	$(a-x)$		$(b-x)$		$2x$

$a = 25$ moles, $b = 18$ moles; $2x = 30.8$ moles

or $x = 15.4$ moles

Applying law of mass action

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{4x^2}{(a-x)(b-x)}$$

$$= \frac{4 \times 15.4 \times 15.4}{(25.0-15.4)(18.0-15.4)}$$

$= 38.0$

If α is the degree of dissociation of HI, then at equilibrium we have

$2HI \rightleftharpoons H_2 + I_2$

$(1-\alpha) \quad \alpha/2 \quad \alpha/2$

Then $K_c = \frac{\frac{\alpha}{2} \times \frac{\alpha}{2}}{(1-\alpha)^2} = \frac{1}{38}$ or $\alpha = 0.245$

17. **(d)** Using the relation

$\Delta H° = -2.303\,R \times \text{slope}$

$\Delta H° = -2.303 \times 8.314 \times 4930$

$= -94.39$ kJ

18. **(a)** For an exothermic reaction $\Delta H°$ is negative as in above case. In such a reacion K_p increases as $\frac{1}{T}$ increases (see graph).

19. **(b)** Using Van't Hoff equation, we have

$$\log \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H°}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\text{or } \log \frac{K_{P_2}}{1.22 \times 10^{-3}} = \frac{46190}{2.303 \times 8.314}\left[\frac{1}{298} - \frac{1}{498}\right]$$

$$\text{or } \frac{K_{P_2}}{1.22 \times 10^{-3}} = 1.77 \times 10^3$$

$$\text{or } K_{P_2} = 2.16$$

C Reasoning Type

1. **(a)** $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$; $K_C = \dfrac{[HI]^2}{[H_2][I_2]}$

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

$$K'_C = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{K_C}$$

2. **(a)** $Co(H_2O)_6^{2+}$ (pink) while $CoCl_4^{2-}$ (blue). So, on cooling because of Le Chatelier's principle the reaction tries to overcome the effect of temperature and goes in backward direction.

3. **(d)** $aA + bB \rightleftharpoons cC + dD$, $Q_c = \dfrac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$

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.

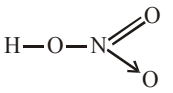
4. **(c)** This is based on common ion effect.

$NaCl \rightleftharpoons Na^+ + Cl^-$ $\qquad$ $HCl \rightleftharpoons H^+ + Cl^-$

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

5. **(a)** In the presence of water as solvent HCl, HNO_3, H_2SO_4 and $HClO_4$ have same strength. This is due to levelling effect of water.

6. **(c)** Among oxyacids, the acidic character increases with increase in oxidation state of the central atom. Hence assertion is correct. Structure of HNO_2 : O—H—N═O ; Structure of HNO_3 :



The assertion is true but the reason is wrong as can be clearly seen from the above structures.

7. **(b)** Both assertion and reason are true but reason is not the correct explanation of assertion.

The solubility is due to the formation of soluble complex KI_3 (or I_3^- ion).

8. **(d)** Assertion in false, reason is true.

There will be a change in state of equilibrium by external factors but there will be no change in the magnitude of equilibrium.

9. **(a)** Both assertion and reason are correct and reason is the correct explanation of assertion.

On increasing pressure, water-ice equilibrium shifts towards water side for the volume of the system decreases on melting of ice. For ice-water equilibrium again, temperature will have to be lowered. In other words melting point of ice decreases.

D Multiple Correct Choice Type

4. **(b, c)** At constant pressure condition addition of inert gas causes equilibrium to shift in the direction leading to increase in no. of moles of gaseous species.

5. **(a, b, d)** Although the reaction is exothermic but requires high energy of activation. For the reaction to go faster in continuous flow process, elevated but optimum temperature of about 450°C is needed.

8. **(a, b, d)** On reducing volume i.e., increasing pressure, equilibrium shifts in the direction of negative Δn(g). In all the three cases equib. shifts in reverse direction.

11. **(c, d)** The reaction is endothermic involving increase in number of moles of gaseous species. Hence conditions (c) and (d) favour forward reaction.

13. **(a,b,c,d)** On addition of inert gas at constant volume, the position of equilibrium is not disturbed (shifted) whether or not $\Delta n_{(g)} = 0$.

14. **(b,c,d)** The reaction is endothermic and takes place with increase in volume. So, low pressure and high temperature will favour the formation of products.

Active mass of carbon (solid) remains constant, independent of its amount and hence its addition does not affect the equilibrium. Increase in pressure of steam (reactant) causes equilibrium to shift in forward direction.

15. **(a,c,d)** (a) For a system to be in equilibrium, $\Delta G = 0$

(c) $\Delta G^\circ = -2.303\,RT \log K = -2.303 \times 8.314 \times 300 \log 10 = -5.74$ kJ

(d) ΔG° is the free energy change when all the reactants having unit concentrations change into the products having unit concentrations.

16. **(b,c)** $\Delta G^\circ = -2.303\,RT \log K$

For larger value of ΔG°, K will be smaller and the reaction will less likely to be spontaneous.

17. **(b,c)** Large value of K suggests that the reaction is spontaneous and goes to an appreciable extent. As a result concentration of free iodine would decrease on addition of I^- ion and hence the solution can dissolve more of iodine.

18. **(b,d)** (a) Addition of NH_2COONH_4 (solid) does not affect the position of the equilibrium.

(b) On addition of NH_3, equilibrium shifts in backward direction leading to decrease in partial pressure of CO_2. To maintain K_P, P_{NH_3} would now be larger.

(c) Addition of CO_2 causes the equilibrium to shift in reverse direction resulting the decrease of, P_{NH_3}.

(d) Dissociation of NH_2COONH_4 is endothermic, favoured by elevated temperature..

19. **(b,d)** Equilibrium constant for the reaction

$$HI \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}I_2$$

$$K' = \left(\frac{1}{K}\right)^{½} = \left(\frac{1}{49}\right)^{½} = \frac{1}{7}$$

(d) $K = \frac{k_f}{k_b} = 49$; Hence $k_f > k_b$

20. **(a, d)** $XY_2(g) \rightleftharpoons XY(g) + Y(g)$

$1-\alpha \qquad \alpha \qquad \alpha$

If P is the equilibrium pressure, then

$$P_{xy_2} = \frac{1-\alpha}{1+\alpha}.P$$

[Total moles : $1 - \alpha + \alpha + \alpha = 1 + \alpha$]

$$P_{xy} = P_y = \frac{\alpha}{1+\alpha}.P$$

Hence, $K_P = \frac{P_{xy} \times P_y}{P_{xy_2}} = \frac{\frac{\alpha}{1+\alpha}.P \times \frac{\alpha}{1+\alpha}.P}{\frac{1-\alpha}{1+\alpha}.P}$

$$= \frac{\alpha^2 P}{1-\alpha^2} = \alpha^2 P \qquad [\because \alpha << 1]$$

or $\alpha = (K_P/P)^{1/2}$ or $\alpha \propto \frac{1}{P^{1/2}}$

Hence, (d) is correct.

Since, V is inversely proportional to P

so $\alpha \propto V^{1/2}$; hence (a) is correct.

Alternatively, $[XY_2] = \frac{1-\alpha}{V}$; $[XY] = [Y] = \frac{\alpha}{V}$

Hence, $K_C = \frac{[XY][Y]}{[XY_2]} = \frac{\alpha/Y \times \alpha/V}{(1-\alpha)/V} = \frac{\alpha^2}{V}$

or $\alpha = (K_C V)^{1/2}$ or $\alpha \propto V^{1/2}$

21. **(a, d)** In each option there are two conditions. If both the given conditions result in shift in the same direction (i.e., backward or forward) we can determine the shift.

If the two conditions tend to shift the reaction in opposite directions, it is not possible to determine the shift because the tendency of the reaction to shift in a particular direction (i.e. backward or forward) are not quantitative.

22. **(a, b, c)** $A(g) \rightleftharpoons n\,B(g)$

$(1-\alpha) \qquad n\alpha$

Total number of moles before dissociation = 1

Total number of moles after dissociation = $1 - \alpha + n\alpha$

$= 1 + \alpha(n-1)$

Since density α $\frac{1}{\text{Volume}}$

and Volume α number of moles

$$\therefore \frac{\text{Density after dissociation}}{\text{Density before dissociation}} = \frac{1}{1+\alpha(n-1)}$$

$$\frac{d}{D} = \frac{1}{1+\alpha(n-1)}$$ [It is option (a)]

Rearranging, $\frac{D}{d} = 1+\alpha(n-1)$ [It is option (b)]

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

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

or $\alpha = \frac{D-d}{d(n-1)}$ [It is option C]

23. **(a, b, d)** K_x (equilibrium constant in terms of mole fraction) is pressure dependent.

24. **(a, b, c)** When $\Delta n = 0$, K_P, K_c and K_x are same. Whenl $\Delta n < 0$, it means there is a decrease in number of moles and thus a decrease in volume. So K_x increases with increasing pressure.

When $\Delta n > 0$, it means there is an increase in number of moles and thus an increase in volume. so K_x decreases with increasing pressure.

[The relation used is $\frac{d \ln K_x}{dp} = -\frac{\Delta V}{RT}$]

E MATRIX-MATCH TYPE

1. A-r; B-p; C-q; D-s

(A) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$;

$\Delta n = -2$; $K_P = K_c(RT)^{-2}$

(B) $2NH_{3(g)} \rightleftharpoons N_2(g) + 3H_{2(g)}$; $\Delta n = +2$

(C) $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$;

$\Delta n = 2$, $K_P = K_c(RT)^2$

(D) $CS_{2(g)} + 4H_{2(g)} \rightleftharpoons CH_{4(g)} + 2H_2S_{(g)}$;

$\Delta n = 3 - 5 = -2$; $K_P = K_x P^{-2}$

2. A-r; B-s; C-q; D-p

(A) As a result of dissociation ($A_{(g)} \longrightarrow n\ B_{(g)}$), number of moles increases and hence the volume of the system increases. Thus $d < D$ and $\frac{D}{d} > 1$

(B) Degree of dissociation $\alpha = \frac{D-d}{d(n-1)} = \frac{D-d}{d(3-1)}$

$\left(\alpha = \frac{50}{100} = \frac{1}{2}\right)$

$\frac{1}{2} = \frac{D-d}{2d}$, $\frac{D}{d} - 1 = 1$, $\frac{D}{d} = 2$

(C) $\alpha_{max} = 1 = \frac{D-d}{2d} \Rightarrow \frac{D}{d} = 3$

(D) $\alpha = \frac{1}{2} = \frac{D-d}{2d} \Rightarrow \frac{D-d}{d} = 1$.

3. A-q; B-s; C-p; D-r

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

(A) Partial pressure of $PCl_5 = 1 - \frac{20}{100} = 0.8$ atm

(B) Partial pressure of $PCl_3 = \frac{20}{100} = 0.2$ atm

(C) Partial pressure of $Cl_2 = 0.2 + 0.2 = 0.4$ atm

(D) K_p for dissociation of

$PCl_5 = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{0.2 \times 0.4}{0.8} = 0.1\ atm$.

4. A-s; B-p; C-q; D-r

(A) $\Delta H < 0$ and $\Delta S > 0$. Hence $\Delta G = \Delta H - T\Delta S$ with be negative at all temperatures.

(B) $\Delta H < 0$ and $\Delta S < 0$. ΔG would be positive at high temperatures and negative at low temperatures.

(C) $\Delta H > 0$ and $\Delta S > 0$. ΔG would be negative at high temperatures and positive at low temperatures.

(D) $\Delta H > 0$ and $\Delta S < 0$. ΔG would be positive at all temperatures. Both energy and entropy factors oppose the process.

5. A-p, s; B-p, s; C-q, r; D-q

(A) Dissolution of CO_2 (or any gas) in water is exothermic and takes place with a decrease in volume.

Hence, low temperature and high pressure favour the process.

(B) $\Delta H < 0$, Δn or $\Delta V < 0$. Low temperature and high pressure favour the process.

(C) $\Delta H = 2H_f^\circ(NO_2) - H_f^\circ(N_2O_4) = 2 \times 33.2 - 9.2 = 57.2$ k J > 0. Δn or $\Delta V > 0$. Hence favourable conditions - high T and low P.

(D) $\Delta H = 2H_f^\circ(NO) - H_f^\circ(N_2) - H_f^\circ(O_2) = 2 \times 90 - 0 - 0 =$ 180 kJ > 0. High temperature favours the reaction. Pressure has no effect, for $\Delta n = 0$

6. A-q, s; B-q, s; C-p; D-q

The reaction in Haber's process is

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

$\Delta H = -$ tive [$\Delta H = -92$ kJmol^{-1}]

The reaction is exothermic and results in decrease in number of moles of gaseous molecules (i.e. $\Delta n < 0$) so it is favoured by decrease in temperature and increase in pressure i.e., Q and S.

The reaction in contact process is

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $\Delta H = -$ tive

[$\Delta H = -175.73$ KJ]

For this exothermic reaction, $\Delta n < 0$

so for it the favourable conditions are same as above.

For Brikland Eyde process,

$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g);\ \Delta H = +\text{tive}$

[$\Delta H = +180.75$ KJ]

for this endothermic reaction, $\Delta n = 0$

so the favourable condition is high temperature i..e, increase in temperature. Pressure has no effect.

Formation of $NO_2(g)$ by the given reaction is exothermic (heat is evolved) and $\Delta n = 0$. Thus the favourable condition is decrease in temperature. Pressure will have no effect.

F NUMERIC/INTEGER ANSWER TYPE

1. **Ans : 1.83**

Moles of all gases at equilibrium

$$n = \frac{PV}{RT} = \frac{12.30 \times 2.5}{0.082 \times 750} = 0.5$$

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$$

Moles of CH_3OH at equilibrium = 0.10

Moles of CO at equilibrium = 0.20 – 0.10 = 0.10

Moles of H_2 at equilibrium = 0.5 – (0.10 + 0.10) = 0.30

Partial pressure of $CH_3OH = X_{CH_3OH}P = \frac{0.1}{0.5} \times 12.3$ atm

= 2.46 atm

Partial pressure of $CO = X_{CO}P = \frac{0.1}{0.5} \times 12.3 = 2.46$ atm

Partial pressure of $H_2 = X_{H_2}P = \frac{0.3}{0.5} \times 12.3 = 7.38$ atm

$$K_P = \frac{P_{CH_3OH}}{P_{CO} \times P_{H_2}^2} = \frac{2.46}{2.46 \times 7.38^2} = 0.0183 \text{ atm}^{-2}$$

$= \mathbf{1.83} \times 10^{-2}$ atm^{-2}

2. **Ans : 1.15**

Mole of $NH_2COONH_4 = \frac{31.2}{78} = 0.40$

Mole of NH_3 initially present $= \frac{1.7}{17} = 0.10$

Ammonium Carbamate dissociates on heating as :

$$NH_2COONH_{4(g)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$$

Mole of NH_2COONH_4 dissociated $= \frac{50}{100} \times 0.4 = 0.20$

Mole of NH_3 formed at equilibrium = 2 × 0.2 = 0.4

Total mole of NH_3 at equilibrium = 0.4 + 0.1 = 0.5

Mole of CO_2 formed = 0.2

K_c for dissociation =$[NH_3]^2\,[CO_2]$ mol^3 L^{-3}

$$= \left(\frac{0.5}{5}\right)^2 \times \left(\frac{0.2}{5}\right) = 4.0 \times 10^{-4} \text{ M}^3$$

$K_P = K_c(RT)^{\Delta n} = 4.0 \times 10^{-4} \times (0.082 \times 350) = 0.0115$ atm^3

= **1.15** × 10^{-2} atm^3

3. **Ans : 2.56 atm**

Vapour density of PCl_5, $D = \frac{208.5}{2} = 104.25$

Vapour density of equilibrium mixture, $d = 100$

Degree of dissociation, $\alpha = \frac{D-d}{d(n-1)}$

$$= \frac{104.25 - 100}{100 \times (2-1)} = 4.25 \times 10^{-2}$$

No. of mole of all species at equilibrium = 1 + α = 1.0 + 0.0425 = 1.0425

Equilibrium pressure $= \frac{nRT}{V} = \frac{1.0425 \times 0.082 \times 300}{10}$

= **2.56 atm**

4. **Ans : 7.5**

Since equilibrium constant for the formation (stability constant) of the complex is of the order of 10^{18}, almost all Ag^+ ions will enter into complex ion formation.

Hence, $[Ag(CN)_2]^- = 0.03\ M$

$[CN^-] = 0.1 - 2 \times 0.03 = 0.04\ M$

$$K = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} = 2.5 \times 10^{18} \text{(given)}$$

$$[Ag^+] = \frac{[Ag(CN)_2^-]}{[CN^-]^2 \times 2.5 \times 10^{18}}$$

$$= \frac{0.03}{0.04^2 \times 2.5 \times 10^{18}} = \mathbf{7.5} \times 10^{-18} M$$

5. **Ans : 0.205 atm**

Total number of moles of gaseous substances in the flask at equilibrium,

$$n = \frac{PV}{RT} = \frac{2.05 \times 100}{0.082 \times 500} = 5$$

On heating PCl_5 dissociates as :

	$PCl_{5(g)} \rightleftharpoons$	$PCl_{3(g)}$ +	$Cl_{2(g)}$
Initial	3	0	0
At equilibrium	3 $(1 - x)$	$3x$	$3x$

(x = degree of dissociation)

Total moles of PCl_5, PCl_3 and Cl_2 = 3 $(1 - x)$ + $3x$ + $3x$ = 3 $(1 + x)$

Since 1 mole of N_2 is present, total number of moles of gaseous substances in the flask

= 1 + 3 $(1 + x)$

But 1 + 3 $(1 + x)$ = 5 $\Rightarrow$ $x = \frac{1}{3}$

$$P_{PCl_5} = X_{PCl_5} \times P = \frac{3(1-x)}{5} \times 2.05 \text{ atm}$$

$$P_{PCl_3} = P_{Cl_2} = \frac{3x \times 2.05}{5} \text{ atm}$$

$$K_P = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{\frac{3x \times 2.05}{5} \times \frac{3x \times 2.05}{5}}{\frac{3(1-x) \times 2.05}{5}}$$

$$= \frac{3x^2 \times 2.05}{5(1-x)} = \frac{3 \times \left(\frac{1}{3}\right)^2 \times 2.05}{5\left(1 - \frac{1}{3}\right)} = \mathbf{0.205 \text{ atm}}$$