CHAPTER
6
Chemical Equilibrium

EXERCISE I (JEE MAIN)

Basic

1. The reaction which proceeds towards completion in the forward direction is

(a) $Fe_2O_3 + 6HCl \rightleftharpoons 2FeCl_3 + 3H_2O$
(b) $SnCl_4 + Hg_2Cl_2 \rightleftharpoons SnCl_2 + 2HgCl_2$
(c) $NH_3 + H_2O + NaCl \rightleftharpoons NH_4Cl + NaOH$
(d) $2CuI + I_2 + 4K^+ \rightleftharpoons 2Cu^{2+} + 4KI$

2. The concentration of a pure solid or liquid phase is not included in the expression of equilibrium constant because

(a) solid and liquid concentrations are independent of their quantities.
(b) solid and liquids react slowly.
(c) solid and liquids at equilibrium do not interact with gaseous phase.
(d) the molecules of solids and liquids cannot migrate to the gaseous phase.

3. For the reversible reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500°C, the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_c, with concentration in mole litre^{-1} is

(a) $\dfrac{1.44\times10^{-5}}{(0.082\times500)^{-2}}$
(b) $\dfrac{1.44\times10^{-5}}{(8.314\times773)^{-2}}$
(c) $\dfrac{1.44\times10^{-5}}{(0.082\times773)^{2}}$
(d) $\dfrac{1.44\times10^{-5}}{(0.082\times773)^{-2}}$

4. When two reactants, A and B are mixed to give products C and D, the reaction quotient Q at the initial stages of the reaction

(a) is zero.
(b) decreases with time.
(c) is independent of time.
(d) increases with time.

5. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by $K_p = \dfrac{4x^2P}{1-x^2}$, where P = total pressure at equilibrium, x = extent of decomposition. Which one of the following statements is true?

(a) K_p increases with increase of P.
(b) K_p increases with increase of x.
(c) K_p increases with decrease of x.
(d) K_p remains constant with change in P and x.

6. For the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, the value of K_P is

(a) P_{CO_2}
(b) $\dfrac{P_{CO_2}}{P_{CaCO_3}}$
(c) $\dfrac{[CaO][CO_2]}{[CaCO_3]}$
(d) $\dfrac{P_{CaCO_3}}{P_{CaO}P_{CO_2}}$

7. $XeF_6 + H_2O \rightleftharpoons XeOF_4 + 2HF$; equilibrium constant = K_1.

$XeO_4 + XeF_6 \rightleftharpoons XeOF_4 + XeO_3F_2$; equilibrium constant = K_2.

The equilibrium constant for the following reaction will be:

$XeO_4 + 2HF \rightleftharpoons XeO_3F_2 + H_2O$

(a) $\frac{K_1}{K_2}$ (b) $K_1 + K_2$

(c) $\frac{K_2}{K_1}$ (d) $K_2 - K_1$

8. K_P for formation of ethane from hydrogen and ethylene is 5.5×10^{18} atm^{-1} and K_P for formation of ethylene from hydrogen and acetylene is 5×10^{26} atm^{-1} at 323 K. What is K_P for the reaction between hydrogen and acetylene to form ethane at 323 K?

(a) 2.75×10^{45} atm^{-2} (b) 1.1×10^{-8}

(c) 9.09×10^{7} (d) 3.63×10^{-46} atm^{2}

9. For a reversible reaction $A + B \rightleftharpoons C$, if the concentrations of the reactants are doubled at a definite temperature, then equilibrium constant will

(a) be doubled (b) be halved

(c) be one fourth (d) remain same

10. The value of $\frac{K_C}{K_P}$ the below for reaction is

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

(a) $\frac{1}{\sqrt{RT}}$ (b) $\sqrt{RT}$

(c) $1/RT$ (d) 1

11. The equilibrium constant for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is K_1 and the equilibrium constant for the reaction $NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ is K_2 both at the same temperature. The value of K_1 and K_2 are related as

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

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

12. Equilibrium constants for some reactions are given. In which of the following case does the reaction go farthest to completion?

(a) $K = 10^2$ (b) $K = 10^{-2}$

(c) $K = 10$ (d) $K = 1$

13. For a reversible reaction, the rate constants for the forward and backward reactions are 0.16 and 4×10^4, respectively. What is the value of equilibrium constant of the reaction?

(a) 0.25×10^6 (b) 2.5×10^5

(c) 4×10^{-6} (d) 4×10^{-4}

14. The following reaction has an equilibrium constant K_C equal to 3.07×10^{-4} at 24°C.

$2NOB(g) \rightleftharpoons 2NO(g) + Br_2(g)$

The correct set of concentrations at which the rate of forward reaction is greater than that of backward reaction is

(a) [NOBr] = 0.06 M, [NO] = 0.015 M, [Br_2] = 0.01 M

(b) [NOBr] = 0.15 M, [NO] = 0.025 M, [Br_2] = 0.014 M

(c) [NOBr] = 0.18 M, [NO] = 0.012 M, [Br_2] = 0.02 M

(d) [NOBr] = 0.045 M, [NO] = 0.0105 M, [Br_2] = 0.01 M

15. 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 metropolitan 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.

16. For the reaction $I_2(g) \rightleftharpoons 2I(g)$, $K_C = 1.0 \times 10^{-2}$ mol lit^{-1}. What volume of the vessel should be taken so that at equilibrium 1 mole of I_2 and 0.5 mole of 'I' are present at equilibrium?

(a) 25 L (b) 0.04 L

(c) 0.25 L (d) 5 L

17. The equilibrium constant for the reaction $3C_2H_2 \rightleftharpoons C_6H_6$ is 4.0 at T K. If the equilibrium concentration of C_2H_2 is 0.5 M, then the concentration of C_6H_6 at equilibrium is

(a) 0.5 M
(b) 1.5 M
(c) 5×10^{-2} M
(d) 0.25 M

18. The equilibrium mixture for the reaction $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ has 1 mole of H_2S, 0.20 mole of H_2 and 0.80 mole of S_2 in a 2 L vessel. The value of K_C for the reaction is

(a) 0.16 M
(b) 0.008 M
(c) 0.016 M
(d) 0.032 M

19. A gaseous mixture contains 0.30 moles of CO, 0.10 moles of H_2, and 0.03 moles of H_2O vapour and an unknown amount of CH_4 per litre. This mixture is in equilibrium at 1200 K.

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$; $K_C = 3.9$

What is the concentration of CH_4 in this mixture?

(a) 0.39 M
(b) 0.039 M
(c) 0.78 M
(d) 0.078 M

20. For the reaction $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$, $\Delta H^\circ = 18$ kcal and $\Delta S^\circ = 30$ cal/K at 300 K. The equilibrium constant K_P° for the reaction at 300 K is

(a) e^{15}
(b) e^{-15}
(c) e^{-18}
(d) e^{-12}

21. For the gas phase reaction $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$; $\Delta H = -43.5$ kcal. Which one of the following is true for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$?

(a) K is independent of T.
(b) K decreases as T decreases.
(c) K increases as T decreases.
(d) K varies with addition of NO.

22. The equilibrium constant for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is 4.0×10^{-4} at 2000 K. In the presence of a catalyst, the equilibrium is attained 10 times faster. Therefore, the equilibrium constant in the presence of the catalyst at 2000 K is

(a) 4×10^{-3}
(b) 4×10^{-5}
(c) 4×10^{-4}
(d) Unpredictable

23. What is the approximate value of log K_P for the following reaction?

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 25°C.

The standard enthalpy of formation of $NH_3(g)$ is −40.0 kJ/mol and the standard entropies of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are 191, 130 and 192 $JK^{-1}\,mol^{-1}$, respectively.

(a) 0.04
(b) 7.05
(c) 8.6
(d) 3.73

24. If K_1 and K_2 are the equilibrium constants for a reversible reaction at T_1 K and T_2 K temperature, respectively ($T_1 < T_2$) and the reaction takes place with neither heat evolution nor absorption, then

(a) $K_1 > K_2$ at high temperature.
(b) $K_1 < K_2$ at high temperature.
(c) $K_1 = K_2$ only at high temperature.
(d) $K_1 = K_2$ at any temperature.

25. From the following data,

(i) $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$; $K_{2000\,K} = 4.4$
(ii) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$; $K_{2000\,K} = 5.31 \times 10^{-10}$
(iii) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$; $K_{1000\,K} = 2.24 \times 10^{22}$

show whether reaction (iii) is exothermic or endothermic or thermal.

(a) Exothermic
(b) Endothermic
(c) Thermal
(d) Cannot say

26. In the decomposition equilibrium of a certain alkaline earth metal carbonate, the partial pressure of CO_2 becomes a hundred fold when the temperature is increased from 400 K to 500 K. What is the mean value of ΔH° for the given range of temperature?

(a) 18.4 kcal/mol
(b) 13.84 kcal/mol
(c) 14.83 kcal/mol
(d) 10.83 kcal/mol

27. The equilibrium constants for the reaction $A_2 \rightleftharpoons 2A$ at 500 K and 1000 K are 1×10^{-10} and 1×10^{-5}, respectively. The reaction is

(a) exothermic
(b) very slow
(c) very fast
(d) endothermic

28. The activation energies for the forward and reverse elementary reactions in the system $A \rightleftharpoons B$ are 10.303 and 8.000 kcal, respectively at 500 K. Assuming the pre-exponential factor to be the same for both the forward and reverse steps, the equilibrium constant of the reaction at 500 K is

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

29. $\Delta G°$ for the reaction $X + Y \rightleftharpoons C$ is – 4.606 kcal at 1000 K. The equilibrium constant for the reverse mode of the reaction is

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

30. For a gaseous equilibrium $2A(g) \rightleftharpoons 2B(g) + C(g)$, K_P has a value 1.8 at 700 K. The value of K_C for the equilibrium $2B(g) + C(g) \rightleftharpoons 2A(g)$ at that temperature is about

(a) 0.031 (b) 32
(c) 57.4 (d) 103.3

Application of Equilibrium Constant

31. The amounts of 0.8 mol of PCl_5 and 0.2 mole of PCl_3 are mixed in a 1 L flask. At equilibrium, 0.4 mole of PCl_3 is present. The equilibrium constant for the reaction, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ will be

(a) 0.05 mol L^{-1} (b) 0.13 mol L^{-1}
(c) 0.013 mol L^{-1} (d) 0.60 mol L^{-1}

32. One mole of pure PCl_5 is placed in an evacuated container and maintained at 250°C. The equilibrium is established at total pressure of 2 atm. What is the partial pressure of chlorine at equilibrium?

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$: $K_P = 1.6$ atm

(a) 0.4 atm (b) 0.67 atm
(c) 0.80 atm (d) 0.64 atm

33. For the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, if initial moles of PCl_5 is 'x', α is the degree of dissociation and P is the total pressure at equilibrium, then $P_{PCl_3} \cdot P^{-1}$ is equal to

(a) $\frac{x}{1+x}$ (b) $\frac{\alpha x}{\alpha + x}$
(c) $\frac{\alpha}{1+\alpha}$ (d) $\frac{\alpha}{x+\alpha x}$

34. In a 5.76 L vessel, 0.5 moles of H_2 gas and 0.5 moles of I_2 vapours are allowed to react to form HI (g) at 447°C, then the total pressure of gases at equilibrium would be ($R = 0.08$ L-atm/K-mol)

(a) 20 atm (b) 10 atm
(c) 5 atm (d) 1 atm

35. In a closed tube, HI(g) is heated at 440°C up to establishment of equilibrium. If it dissociates into $H_2(g)$ and $I_2(g)$ up to 22%, then the dissociation constant is

(a) 0.282 (b) 0.0796
(c) 0.0199 (d) 1.99

36. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the value of equilibrium constant is 9.0. The degree of dissociation of HI will be

(a) 0.5 (b) 0.33
(c) 0.4 (d) 0.67

37. At 444°C, HI is 30% dissociated. If initially 3 moles of HI are taken, then the number of moles of HI at equilibrium is

(a) 0.9 (b) 2.1
(c) 0.45 (d) 1.8

38. One mole of N_2O_4 (g) at 300 K is kept in a closed container under one atm. It is heated to 600 K when 20% by mass of $N_2O_4(g)$ decomposes to $NO_2(g)$. The resultant pressure is

(a) 1.2 atm (b) 2.4 atm
(c) 2.0 atm (d) 1.0 atm

39. For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the relation between the degree of dissociation of $N_2O_4(g)$ at pressure, P with its equilibrium constant K_P is

(a) $\alpha = \frac{K_P/P}{4 + K_P/P}$ (b) $\alpha = \frac{K_P}{4 + K_P}$
(c) $\alpha = \left[\frac{K_P/P}{4 + K_P/P}\right]^{1/2}$ (d) $\alpha = \left[\frac{K_P}{4 + K_P}\right]^{1/2}$

40. At total pressure P_1 atm and P_2 atm, N_2O_4 is dissociated to an extent of 33.33% and 50.00%, respectively. The ratio of pressures P_1 and P_2 is

(a) 3:8 (b) 2:1
(c) 8:3 (d) 1:2

41. At 0°C and 1 atm pressure, 1 L of N_2O_4 decomposes to NO_2 according to the equation $N_2O_4(g) \rightleftharpoons 2NO_2$ (g). To what extent has the decomposition proceeded when the original volume is 25% less than that of existing volume?

(a) 0.67 (b) 0.33
(c) 0.25 (d) 0.75

42. Forty percent of a mixture of 0.2 mol of N_2 and 0.6 mol of H_2 reacts to give NH_3 according to the equation

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

at constant temperature and pressure. Then, the ratio of the final volume to the initial volumes of gases is

(a) 4 : 5 (b) 5 : 4
(c) 7 : 10 (d) 8 : 5

43. An amount of 4 moles of NH_3 gas is introduced with a previously evacuated 1 L container in which it is partially dissociated at high temperature as

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

At equilibrium, 2 mole of $NH_3(g)$ remained. The value of K_C for the reaction is

(a) $1.5M^2$ (b) $6.75M^2$
(c) $0.44M^{-2}$ (d) $2.25M^2$

44. In a closed container maintained at 1 atm pressure and 25°C, 2 moles of $SO_2(g)$ and 1 mole of $O_2(g)$ were allowed to react to form $SO_3(g)$ under the influence of a catalyst.

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

At equilibrium, it was found that 50% of $SO_2(g)$ was converted to $SO_3(g)$. The partial pressure of $O_2(g)$ at equilibrium will be

(a) 0.17 atm (b) 0.5 atm
(c) 0.33 atm (d) 0.20 atm

45. One mole of ethanol is treated with one mole of ethanoic acid at 25ºC. One-fourth of the acid changes into ester at equilibrium. The equilibrium constant for the reaction will be

(a) 1/9 (b) 4/9
(c) 9 (d) 9/4

46. One mole each of A and B and 3 moles each of C and D are placed in 1 L flask. If equilibrium constant is 2.25 for the reaction $A + B \rightleftharpoons C + D$, then equilibrium concentrations of A and C will be in the ratio

(a) 2:3 (b) 3:2
(c) 1:2 (d) 2:1

47. For the reaction $XY_2(g) \rightleftharpoons XY(g) + Y(g)$, the reaction is started with initial pressure of XY_2, 600 mm Hg. The total pressure for gases at equilibrium is 800 mm Hg. Assuming that volume and temperature of the system remains constant, the value of K_P is

(a) 100 atm (b) 100 mm Hg
(c) 0.01 atm (d) 400 mm Hg

48. For the reaction $A + B \rightleftharpoons C + D$, the initial concentration of A and B is equal, but the equilibrium concentration of C is twice that of equilibrium concentration of A. The equilibrium constant is

(a) 4 (b) 9
(c) 1/4 (d) 1/9

49. $I_2 + I^- \rightleftharpoons I_3^-$. This reaction is set up in aqueous medium. We start with 1 mol of I_2 and 0.5 mol of I^- in 1 L flask. After equilibrium is reached, excess of $AgNO_3$ gave 0.25 mol of yellow precipitate. The equilibrium constant is

(a) 1.33 (b) 2.66
(c) 0.375 (d) 0.75

50. The equilibrium constant for the mutarotation, α-D–glucose ⇌ β–D–glucose is 1.8. What percent of the α-form remains under equilibrium?

(a) 35.7 (b) 64.3
(c) 55.6 (d) 44.4

51. For the reaction,

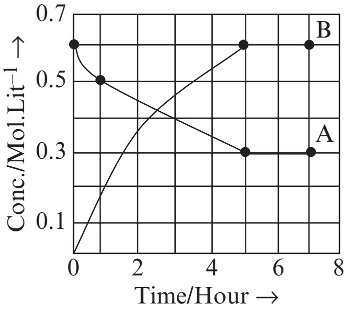
$2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$,

the ratio $\dfrac{K_P}{P}$, where P is the total pressure of gases at equilibrium and $P_{Br_2} = \dfrac{P}{9}$ at a certain temperature is

(a) $\dfrac{1}{9}$ (b) $\dfrac{1}{81}$
(c) $\dfrac{1}{27}$ (d) $\dfrac{1}{3}$

52. The progress of the reaction $A \rightleftharpoons nB$ with time is represented by the graph given below.

The value of n is



(a) 1 (b) 2
(c) 3 (d) 4

53. The value of K_P for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2$ is 640 mm at 775 K. The percentage dissociation of N_2O_4 at equilibrium pressure of 160 mm is

(a) $\frac{100}{\sqrt{2}}$ (b) 50

(c) $\frac{50}{\sqrt{2}}$ (d) $10\sqrt{2}$

54. At 127°C and 1 atm pressure, $PCl_5(g)$ is partially dissociated into $PCl_2(g)$ and $Cl_2(g)$ as $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. The density of the equilibrium mixture is 3.5 g/L. Percentage dissociation of PCl_5 is ($R = 0.08$ L-atm/K-mol, P = 31, Cl = 35.5)

(a) 46.28 (b) 86.16

(c) 15.86 (d) 53.72

55. At T K, a compound $AB_2(g)$ dissociates according to the reaction $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$, with a degree of dissociation 'x' which is small compared with unity. The expression for 'x' in terms of the equilibrium constant, K_P and the total pressure P is

(a) $\frac{K_P}{P}$ (b) $(K_P)^{1/3}$

(c) $\left(\frac{2K_P}{P}\right)^{1/3}$ (d) $\left(\frac{K_P}{P}\right)^{1/3}$

Heterogeneous Equilibrium

56. A quantity of 34 g sample of BaO_2 is heated to 1000 K in a closed and rigid evacuated vessel of 8.21 L capacity. What percentage of peroxide is converted into oxide? (Ba = 138)

$2BaO_2(s) \rightleftharpoons 2BaO(s) + O_2(g)$; $K_P = 0.5$ atm

(a) 20% (b) 50%

(c) 75% (d) 80%

57. For the reaction $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$, $K_P = 3.2 \times 10^{-5}$ atm^3. The total pressure of the gaseous products when sufficient amount of reactant is allowed to achieve equilibrium is

(a) 0.02 atm (b) 0.04 atm

(c) 0.06 atm (d) 0.095 atm

58. At a certain temperature, K_P for the dissociation of solid $CaCO_3$ is 4.5×10^{-2} atm and for the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the K_P value is 2.0 atm. The pressure of carbon monoxide at this temperature, when solid carbon CaO and $CaCO_3$ are mixed together and allowed to attain equilibrium is

(a) 0.09 atm (b) 0.30 atm

(c) 2.1 atm (d) 0.47 atm

59. The value of K_P for the equilibrium $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ at a certain temperature and total 2 atm pressure at equilibrium will be

(a) 0.25 atm^2 (b) 1.0 atm^2

(c) 4.0 atm^2 (d) 1.0 atm

60. Iron fillings and water were placed in a 5 L vessel and sealed. The tank was heated to 1000°C. Upon analysis, the tank was found to contain 1.2 g of $H_2(g)$ and 54.0 g of $H_2O(g)$. If the reaction is represented as $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$, then the value of equilibrium constant is

(a) 0.2 (b) 0.04

(c) 0.008 (d) 0.0016

61. At 1000°C and a pressure of 16 atm, the equilibrium constant of the reaction

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

is such that for every nine moles of CO, there is one mole of CO_2. For what pressure of the mixture, is the ratio CO : CO_2 = 4 : 1? The temperature remains 1000°C.

(a) 40.5 atm (b) 81 atm

(c) 33.75 atm (b) 6.7 atm

62. At a certain temperature, the value of K_P for the reaction: $2CO(g) \rightleftharpoons CO_2(g) + C(\text{graphite})$ is 0.1 atm^{-1}. What is the ratio of partial pressures of CO and CO_2 at equilibrium, taking the total pressure to be 1.1 atm?

(a) 9:1 (b) 10:1

(c) 1:10 (d) 1:9

63. For the equilibrium $LiCl{\cdot}3NH_3(s) \rightleftharpoons LiCl{\cdot}NH_3(s) + 2NH_3(g)$; $K_P = 9$ atm^2 at 27°C. A 8.21 L vessel contains 0.1 mole of $LiCl.NH_3(s)$. How many moles of $NH_3(g)$ should be added to the flask at this temperature to derive the backward reaction for completion?

(a) 0.8 (b) 1.0

(c) 1.2 (d) 1.1

64. The reaction $ZnO(s) + CO(g) \rightleftharpoons Zn(g) + CO_2(g)$ has an equilibrium constant of 1 atm at 1500 K. The equilibrium partial pressure of zinc vapour in a reaction vessel if an equimolar mixture of CO and CO_2 is brought into contact with solid ZnO at 1500 K and the equilibrium is achieved at 1 atm is

(a) 0.68 atm
(b) 0.76 atm
(c) 0.24 atm
(d) 0.5 atm

65. If 0.3 moles of hydrogen gas and 2.0 moles of sulphur solid are heated to 87°C in a 2.0 L vessel, then what will be the partial pressure of H_2S gas at equilibrium? (Given: $R = 0.08$ L-atm/K-mol)

$H_2(g) + S(s) \rightleftharpoons H_2S(g)$: $K_C = 0.08$

(a) 0.32 atm
(b) 0.43 atm
(c) 0.62 atm
(d) 0.48 atm

Le-Chatelier's Principle

66. Consider the following equilibrium in a closed container.

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

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statement holds true regarding the equilibrium constant (K_P) and degree of dissociation (α)?

(a) Neither K_P nor α changes.
(b) Both K_P and α changes.
(c) K_P changes, but α does not change.
(d) K_P does not change, but α changes.

67. Which of the following hypothetical reactions is favoured by the increase of temperature as well as pressure?

(a) $A(s) + 2B(g) \rightleftharpoons C(g) + D(g)$: $\Delta H = +ve$
(b) $A(s) + 2B(g) \rightleftharpoons 2C(g) + D(g)$: $\Delta H = +ve$
(c) $2A(g) + B(g) \rightleftharpoons 2C(g) + D(s)$: $\Delta H = +ve$
(d) $2A(s) + 2B(g) \rightleftharpoons 2C(g) + 2D(g)$: $\Delta H = -ve$

68. In the system $AB(s) \rightleftharpoons A(g) + B(g)$, doubling the quantity of AB(s) would

(a) increase the amount of A to double its value.
(b) increase the amount of B to double its value.
(c) increase the amounts of both A and B to some extent.
(d) cause no changes in the amounts of A and B.

69. In a system $A(s) \rightleftharpoons 2B(g) + 3C(g)$, if the concentration of C at equilibrium is increased by a factor of 2, then it will cause the equilibrium concentration of B to decrease by

(a) two times the original value.
(b) one half of its original value.
(c) $2\sqrt{2}$ times its original value.
(d) 8 times its original value.

70. The reaction $MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$ is in progress. If the number of moles of MgO in the vessel is doubled at an instance,

(a) the reaction quotient Q is halved.
(b) the reaction quotient Q is doubled.
(c) the moles of CO_2 present at equilibrium is halved.
(d) the partial pressure of CO_2 in the vessel remains unchanged.

71. When pressure is applied to the equilibrium system Ice $\rightleftharpoons$ water, which of the following phenomenon will happen?

(a) More ice will be formed.
(b) Ice will sublime.
(c) More water will be formed.
(d) Equilibrium will not disturb.

72. The equilibrium $SOCl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is attained at 25°C in a closed rigid container and helium gas is introduced. Which of the following statements is correct?

(a) Concentration of SO_2 is increased.
(b) More Cl_2 is formed.
(c) Concentrations of all change.
(d) Concentrations will not change.

73. When calcium acetate is dissolved in water, heat is evolved. If the temperature is raised, then the solubility of calcium acetate

(a) increases.
(b) decreases.
(c) is not affected.
(d) first increases and then decreases.

74. The Haber's process for the manufacture of ammonia is usually carried out at about 500ºC. If a temperature of about 250ºC was used instead of 500ºC then,

(a) no ammonia would be formed at all.
(b) the percentage of ammonia in the equilibrium mixture would be too low.
(c) a catalyst would be of no use at all at this temperature.
(d) the percentage of ammonia in the equilibrium mixture would be too high.

75. Densities of diamond and graphite are 3.5 and 2.4 g/ml, respectively. The increase in pressure (at constant temperature) at the equilibrium in C (Diamond) $\rightleftharpoons$ C (Graphite) will

(a) favour the forward reaction.
(b) favour the backward reaction.
(c) have no effect.
(d) increases the equilibrium constant.

76. In a flask, colourless N_2O_4 is in equilibrium with brown coloured NO_2. At equilibrium, when the flask is heated at 100ºC the brown colour deepens and on cooling, it becomes less coloured. The change in enthalpy, ΔH, for the system is

(a) negative (b) positive
(c) zero (d) undefined

77. For the chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of X_3Y at equilibrium is affected by

(a) temperature and pressure.
(b) temperature only.
(c) pressure only.
(d) temperature, pressure and catalyst.

78. What will the change on increasing the pressure at equilibrium water $\rightleftharpoons$ water vapour?

(a) The boiling point of water will increase.
(b) The boiling point of water will decrease.
(c) The boiling point of water will not change.
(d) Boiling point is not related with pressure.

79. In equilibrium:

$$\underset{\text{Colourless}}{SCN^-(aq)} + \underset{\text{Yellow}}{Fe^{+3}(aq)} \rightleftharpoons \underset{\text{Deep red}}{[Fe(SCN)^{2+}](aq)}$$

If thiocyanate ions are added in equilibrium mixture

(a) The solution becomes colourless.
(b) The yellow colour of solution deepens.
(c) The red colour of the solution deepens.
(d) Concentration of $[Fe(SCN)]^{2+}$ ion will decrease.

80. An aqueous solution of volume 500 ml, when the reaction $2Ag^+(aq) + Cu(s) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$ reached equilibrium, the concentration of Cu^{2+} ions was x M. To this solution, 500 ml of water is added. At the new equilibrium, the concentration of Cu^{2+} ions would be

(a) $2x$ M.
(b) x M.
(c) between x and $0.5x$ M.
(d) less than $0.5x$ M.

81. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. In the above reaction, the partial pressure of PCl_3, Cl_2 and PCl_5 are 0.3, 0.2 and 0.6 atm, respectively. If partial pressure of PCl_3 and Cl_2 was increased twice at the new equilibrium, then what will be the new partial pressure of PCl_5 (in atm)?

(a) 0.3 (b) 1.2
(c) 2.4 (d) 0.15

82. In the equilibrium mixture $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the mole ratio of gases are $\sqrt{2} : \sqrt{2} : 10$, respectively. What would be the effect on the mole ratio on adding 5 mole of He gas at constant pressure?

(a) No change
(b) The new molar ratio becomes 1 : 1 : 5.
(c) The new molar ratio becomes 2 : 2 : 5.
(d) The new molar ratio becomes $2 : 2 : 5\sqrt{2}$.

83. One mole of He (g, colourless) is added to the equilibrium mixture containing N_2O_4 (g, colourless) and NO_2 (g, red-brown) present in a cylinder piston arrangement maintained at constant pressure and temperature. It will result in

(a) no change in colour of the equilibrium mixture.
(b) lightening the colour of the equilibrium mixture.
(c) darkening the colour of the equilibrium mixture.
(d) no effect on the equilibrium composition.

84. Consider the formation of SO_3 according to the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $\Delta H = -198$ kJ. Which of the following may change the value of equilibrium constant of the above reaction?

(a) Adding He gas to reaction vessel.
(b) Adding more of O_2 to the reaction vessel.
(c) Increasing the temperature.
(d) Doubling the volume of reaction vessel.

85. For the given chemical equation $2X(g) + Y(g) \rightleftharpoons 2Z(g) + 8$ kcal, which combination of pressure and temperature gives the highest yield of 'Z' at equilibrium?

(a) 1000 atm and 500ºC
(b) 500 atm and 500ºC
(c) 500 atm and 100ºC
(d) 1000 atm and 100ºC

EXERCISE II (JEE ADVANCED)

Section A (Only one Correct)

1. The approach to the following equilibrium was observed kinetically from both directions.

$$PtCl_4^{2-} + H_2O \rightleftharpoons Pt(H_2O)Cl_3^- + Cl^-$$

At 25°C, it was found that

$$-\frac{d\left[PtCl_4^{2-}\right]}{dt} = (3.9 \times 10^{-5}\ s^{-1})\,[PtCl_4^{2-}] - (2.1 \times 10^{-3}\ L\ mol^{-1}s^{-1})\,[Pt(H_2O)Cl_3^-]\,[Cl^-]$$

The value of K_{eq} (equilibrium constant) for the complexation of the fourth Cl^- by Pt (II) is

(a) 53.8 mol L^{-1}
(b) 0.018 mol L^{-1}
(c) 53.8 L mol^{-1}
(d) 0.018 L mol^{-1}

2. The complexion of Fe^{2+} with the chelating agent dipyridyl has been studied kinetically in both the forward and reverse directions.

$Fe^{2+} + 3\ dipy \rightleftharpoons [Fe\ (dipy)_3]^{2+}$

For this reaction, the rates of forward and reverse reactions are $(1.45 \times 10^{13}\ M^{-3}s^{-1})[Fe^{2+}][dipy]^3$ and $(1.22 \times 10^{-4}\ s^{-1})\ [Fe\ (dipy)_3^{2+}]$, at 25ºC. What is the stability constant of the complex?

(a) 1.77×10^9
(b) 8.4×10^{-18}
(c) 1.18×10^{17}
(d) 5.65×10^{-10}

3. The rate constant for the forward reaction: $A(g) \rightleftharpoons 2B(g)$ is $1.5 \times 10^{-3}\ s^{-1}$ at 300 K. If 10^{-5} moles of 'A' and 100 moles of 'B' are present in a 10 litre vessel at equilibrium, then the rate constant of the backward reaction at this temperature is

(a) $1.5 \times 10^{-3}\ M^{-1}s^{-1}$
(b) $1.5 \times 10^{-1}\ M^{-1}s^{-1}$
(c) $1.5 \times 10^{-11}\ M^{-1}s^{-1}$
(d) $1.5 \times 10^{-12}\ M^{-1}s^{-1}$

4. $CuSO_4\ .\ 5H_2O(s) \rightleftharpoons CuSO_4.3H_2O(s) + 2H_2O(g)$, K_P for this equilibrium is 1.0×10^{-4} atm^2 at 25°C. What is the maximum pressure of water vapour (moisture) in the atmosphere, below which the pentahydrate is efflorescent?

(a) 7.60 mm
(b) 0.01 mm
(c) 0.076 mm
(d) 760 mm

5. Ammonia at a pressure of 10 atm and CO_2 at a pressure of 20 atm are introduced into an evacuated chamber. If K_P for the reaction $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2\ (g)$ is 2020 atm^3, then the total pressure after a long time is

(a) less than 30 atm
(b) more than 30 atm
(c) equal to 30 atm
(d) unpredictable

6. The value of K_P for the process: $CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4 \cdot 3H_2O(s) + 2H_2O(g)$ is 1.21×10^{-4} atm^2 at certain temperature. If aqueous tension at that temperature is 40 torr, then at what relative humidity of air will $CuSO_4 \cdot 5H_2O$ effloresces?

(a) Above 40.8%
(b) Below 40.8%
(c) Above 20.9%
(d) Below 20.9%

7. The value of K_P for the reaction: $H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$ is 6.4×10^{-4} atm. On close observation, it is found that the partial pressure of iodine present in vapour state is 1.6×10^{-4} atm, at the same temperature. The value of K_P for the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is

(a) 0.25
(b) 4
(c) 1.024×10^{-7}
(d) 9.76×10^6

8. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the rate law expression is

(a) $-\frac{1}{2}.\frac{d[HI]}{dt} = K_{-1}[HI]^2 - K_1[H_2][I_2]$

(b) $-\frac{1}{2}.\frac{d[HI]}{dt} = \frac{K_1[HI]^2}{K_{-1}[H_2][I_2]}$

(c) $-\frac{1}{2}.\frac{d[HI]}{dt} = K_1[H_2][I_2] - K_{-1}[HI]^2$

(d) $-\frac{1}{2}.\frac{d[HI]}{dt} = K_1K_{-1}[H_2][I_2]$

9. At 200°C, PCl_5 dissociates as $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. It was found that the equilibrium vapours are 62 times as heavy as hydrogen. The percentage dissociation of PCl_5 at 200°C is

(a) 34.1%
(b) 70.3%
(c) 40.5%
(d) 68.1%

10. Under what pressure must an equimolar mixture of Cl_2 and PCl_3 be placed at 250ºC in order to obtain 75% conversion of PCl_3 into PCl_5? Given that $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$; $K_P = 2$ atm^{-1}.

(a) 12 atm
(b) 6 atm
(c) 15 atm
(d) 30 atm

11. In the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ + Heat. One mole of N_2 reacts with three moles of H_2. If at equilibrium 'x' moles of N_2 combined, then the value of 'x' in terms of K_P and the total pressure of gases at equilibrium P is ($x << 1$)

(a) $\dfrac{3P.\sqrt{3.K_P}}{8}$ (b) $\dfrac{8P}{3\sqrt{3.K_P}}$

(c) $\dfrac{3\sqrt{3.K_P}}{8P}$ (d) $\dfrac{8}{P}.\sqrt{\dfrac{K_P}{3}}$

12. For the reaction $X_2(g) + Y_2(g) \rightleftharpoons 2XY(g)$, 2 moles of '$X_2$' was taken in a 2 L vessel and 3 moles of 'Y_2' was taken in a 3 L vessel. Both vessels were then connected. At equilibrium, the concentration of 'XY' is 0.7 M. The equilibrium concentrations of 'X_2' and 'Y_2' would be

(a) 0.65 M, 0.65 M (b) 0.30 M, 0.30 M
(c) 0.25 M, 1.25 M (d) 0.05 M, 0.25 M

13. The equilibrium constant for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is 0.09 at 3500 K. The fraction of equimolar mixture of N_2 and O_2 converted into NO is

(a) 0.13 (b) 0.23
(c) 0.30 (d) 0.357

14. At a certain temperature, the equilibrium constant of the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is 0.0004. Assuming air to be a mixture of four volumes of nitrogen with one volume of oxygen, the percentage of nitric oxide by volume, in the gas produced by allowing air to reach equilibrium at this temperature is

(a) 3.0% (b) 0.8%
(c) 0.04% (d) 8.0%

15. When a mixture of N_2 and H_2 in the volume ratio of 1 : 5 is allowed to react at 700 K and 10^3 atm pressure, 0.4 mole fraction of NH_3 is formed at equilibrium. The value of K_P for the below reaction

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

(a) 2.6×10^{-5} atm^{-2} (b) 2.6×10^{-4} atm^{-2}
(c) 2.6×10^{3} atm^{-2} (d) 5.1×10^{-3} atm^{-2}

16. An amount of 16 moles H_2 and 4 moles of N_2 is confined in a vessel of volume one litre. The vessel is heated to a constant temperature until the equilibrium is established. At equilibrium, the pressure was found to be 9/10th of the initial pressure. The value of K_C for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is

(a) 8100 (b) 6.07×10^{-4}
(c) 1647.75 (d) 8.99×10^{-5}

17. An amount of 3 moles of N_2 and some H_2 is introduced into an evacuated vessel. The reaction starts at $t = 0$ and equilibrium is attained at $t = t_1$. The amount of ammonia at $t = 2t_1$ is found to be 34 g. It is observed that $\dfrac{w(N_2)}{w(H_2)} = \dfrac{14}{3}$ at $t = \dfrac{t_1}{3}$ and $t = \dfrac{t_1}{2}$. The only correct statement is

(a) $w(N_2) + w(H_2) + w(NH_3) = 118$ g at $t = t_1$
(b) $w(N_2) + w(H_2) + w(NH_3) = 102$ g at $t = 2t_1$
(c) $w(N_2) + w(H_2) + w(NH_3) = 50$ g at $t = t_1/3$
(d) $w(N_2) + w(H_2) + w(NH_3)$ cannot be predicted

18. Starting with 2 moles of SO_2 and 1 mol of O_2 in 1 L flask, the equilibrium mixture required 0.4 moles of MnO_4^- for complete reaction in acidic medium. The value of K_C for the reaction: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is

(a) 2 (b) 0.5
(c) 0.25 (d) 4

19. A quantity of 60 g of CH_3COOH and 46 g of CH_3CH_2OH reacts in 5 L flask to form 44 g of $CH_3COOC_2H_5$ at equilibrium. On taking 120 g of CH_3COOH and 46 g of CH_3CH_2OH, $CH_3COOC_2H_5$ formed at equilibrium is

(a) 44 g (b) 29.33 g
(c) 66 g (d) 58.67 g

20. Two moles of an equimolar mixture of two alcohols R_1–OH and R_2–OH are esterified with one mole of acetic acid. If only 80% of the acid is consumed till equilibrium and the quantities of ester formed under equilibrium are in the ratio 3 : 2. What is the value of equilibrium constant for the esterification of R_1–OH?

(a) 0.48 (b) 2.2
(c) 0.32 (d) 3.69

21. For the reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$, NO and Cl_2 are initially taken in mole ratio of 2 : 1. The total pressure at equilibrium is found to be 1 atm. If the moles of NOCl are one-fourth of that of Cl_2 at equilibrium, the value of K_P for the reaction is

(a) $\dfrac{13}{36}$ (b) $\dfrac{13}{256}$

(c) $\dfrac{13}{512}$ (d) $\dfrac{13}{128}$

22. When S in the form of S_8 is heated at 900 K, the initial pressure of 1 atm falls by 30% at equilibrium. This is because of conversion of some $S_8(g)$ to $S_2(g)$. The value of K_P for the reaction is

(a) $0.011\ \text{atm}^{-3}$ (b) $2.96\ \text{atm}^{3}$
(c) $1.71\ \text{atm}^{3}$ (d) $204.8\ \text{atm}^{3}$

23. The Deacon reaction is the oxidation of HCl by O_2 in the following reaction

$$HCl(g) + \frac{1}{4}O_2(g) \rightleftharpoons \frac{1}{2}Cl_2(g) + \frac{1}{2}H_2O(g)$$

at a pressure of 730 mm and with an initial mixture containing 8% of HCl and 92% of O_2, the degree of decomposition of the HCl is 0.08. What is the equilibrium partial pressure of oxygen?

(a) 671.6 mm (b) 659.92 mm
(c) 537.28 mm (d) 670.43 mm

24. The equilibrium constant for the reaction: H_3BO_3 + Glycerin $\rightleftharpoons$ (H_3BO_3 + Glycerin complex) is 0.90. How much glycerin should be added to 1 L of 0.10 M-H_3BO_3 solution, so that 60% of the H_3BO_3 is converted to boric acid–glycerin complex?

(a) Infinite (b) 1.73 M
(c) 0.10 M (d) 2.27 M

25. The process $2A(g) \rightleftharpoons A_2(g)$ has $K_P = 8 \times 10^8\ \text{atm}^{-1}$. If 'A' atoms are taken at 1 atm pressure, then what should be the equilibrium pressure of 'A'?

(a) 0 (b) 2.5×10^{-5} atm
(c) 4×10^4 atm (d) 1.25×10^{-5} atm

26. When $CO_2(g)$ is dissolved in water, then the following equilibrium is established

$$CO_2(aq) + 2H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

for which the equilibrium constant is 3.8×10^{-7}. If the pH of solution is 6.0, then what would be the ratio of concentration of $HCO_3^-(aq)$ to $CO_2(aq)$?

(a) 3.8×10^{-13} (b) 6.0
(c) 0.38 (d) 13.4

27. For the equilibrium $A(g) \rightleftharpoons nB(g)$, the equilibrium constant K_P is related with the degree of dissociation α, and the total pressure of gases at equilibrium P is

(a) $\dfrac{(n\alpha)^n . P^{n-1}}{(1-\alpha).[1+(n-1)\alpha]^{n-1}}$

(b) $\dfrac{(n\alpha)^{n-1} . P^{n-1}}{(1-\alpha).[1+(n-1)\alpha]^{n-1}}$

(c) $\dfrac{\alpha^{n-1} . P^{n-1}}{(1-\alpha).[1+(n-1)\alpha]}$

(d) $\dfrac{n\alpha . P^{n-1}}{(1-\alpha)^{n-1}.[1+(n-1)\alpha]}$

28. The reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$ occurs in a single step. The rate constant of forward reaction is $2.0 \times 10^{-3}\ \text{mol}^{-1}\ \text{L s}^{-1}$. When the reaction is started with equimolar amounts of A and B, it is found that the concentration of A is twice that of C at equilibrium. The rate constant of the backward reaction is

(a) $5.0 \times 10^{-4}\ \text{mol}^{-1}\ \text{L s}^{-1}$
(b) $8.0 \times 10^{-3}\ \text{mol}^{-1}\ \text{L s}^{-1}$
(c) $1.25 \times 10^{2}\ \text{mol}^{-1}\ \text{L s}^{-1}$
(d) $2.0 \times 10^{3}\ \text{mol}^{-1}\ \text{L s}^{-1}$

29. Find the concentration of manomeric dichloroacetic acid in a CCl_4 solution which contains 0.0129 g of the acid in 100 ml of solution. The dissociation constant of the dimeric acid is 5.0×10^{-4}. Assume that the acids are unionized in CCl_4 solution.

(a) 5.0×10^{-4} M (b) 2.5×10^{-4} M
(c) 1.0×10^{-3} M (d) 3.9×10^{-4} M

30. In an evacuated rigid vessel of volume V litre, one mole of solid ammonium carbonate (NH_2CONH_4) is taken and the vessel is heated to T K. The equilibrium total pressure of gases is found to be P atm. The percentage dissociation of solid into $NH_3(g)$ and $CO_2(g)$ is

(a) $\dfrac{100RT}{3PV}\%$ (b) $\dfrac{RT}{3PV}\%$

(c) $\dfrac{100PV}{3RT}\%$ (d) $\dfrac{300PV}{RT}\%$

31. For the equilibrium $SrCl_2 \cdot 6H_2O(s) \rightleftharpoons SrCl_2 \cdot 2H_2O(s) + 4H_2O(g)$, $K_P = 8.1 \times 10^{-7}\ \text{atm}^4$ at 27°C. If 1.642 L of air saturated with water vapour at 27°C is exposed to a large quantity of $SrCl_2 \cdot 2H_2O(s)$, then what mass of water vapour will be absorbed? Saturated vapour pressure of water at 27°C = 30.4 torr.

(a) 12 mg (b) 6.67 mg
(c) 9 mg (d) 48 mg

32. Two systems $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ and $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ are simultaneously in equilibrium in a vessel at constant volume. If some CO is introduced into the vessel, then at the new equilibrium, the moles of

(a) PCl_5 increases.
(b) PCl_5 remains unchanged.
(c) PCl_5 decreases.
(d) Cl_2 increases.

33. In the system, $LaCl_3(s) + H_2O(g) + \text{heat} \rightleftharpoons LaClO(s) + 2HCl(g)$, equilibrium is established. More water vapour is added to disturb the equilibrium. If the pressure of water vapour at new equilibrium is double that of at initial equilibrium, the factor by which pressure of HCl is changed is

(a) 2 times
(b) $\sqrt{2}$ times
(c) $\frac{1}{\sqrt{2}}$ times
(d) 4 times

34. Indicate the correct answer out of the following for the below reaction.

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

(a) The reaction is retarded by the addition of KOH.
(b) The reaction is favoured by the addition of NH_4OH.
(c) The reaction is retarded by the addition of hydrogen ion.
(d) The reaction is favoured by the addition of hydrogen ion.

35. The two equilibria $AB \rightleftharpoons A^+ + B^-$ and $AB + B^- \rightleftharpoons AB_2^-$ are simultaneously maintained in a solution with equilibrium constants K_1 and K_2, respectively. The ratio of A^+ to AB_2^- in the solution is

(a) directly proportional to the concentration of B.
(b) inversely proportional to the concentration of B.
(c) directly proportional to the square of the concentration of B.
(d) inversely proportional to the square of the concentration of B.

36. Solid NH_4HS dissociates into NH_3 and H_2S at a certain temperature, the equilibrium pressure is P atm. If now, NH_3 is pumped into the system so that its partial pressure becomes P atm, then what will be the partial pressure (in atm) of H_2S?

(a) $0.5\ P$
(b) $0.25\ P$
(c) $0.33\ P$
(d) $0.67\ P$

37. In a closed rigid vessel, the following equilibrium partial pressures are measured, where N_2 = 100 mm, H_2 = 400 mm and NH_3 = 1000 mm. Now, nitrogen is removed from the vessel until the pressure of hydrogen at equilibrium is equal to 700 mm. The new equilibrium partial pressure of N_2 is

(a) 11.94 mm
(b) 200 mm
(c) 18.66 mm
(d) 43.78 mm

38. Suppose the gas phase isomerization reactions: $A \rightleftharpoons B$, $A \rightleftharpoons C$ and $B \rightleftharpoons C$ achieve equilibrium simultaneously at a fixed temperature. The equilibrium mole fraction of 'A' in terms of equilibrium constants, K_1, K_2 and K_3 (respectively) is

(a) $\frac{K_1}{K_1 + K_2 + K_3}$
(b) $\frac{1}{1 + K_1 + K_2}$
(c) $\frac{1}{K_1 + K_2 + K_3}$
(d) $\frac{1}{K_1 + K_2}$

39. Methanol (CH_3OH) can be prepared from CO and H_2 as

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$; $K_P = 6.23 \times 10^{-3}$ at 500 K.

What total pressure is required to convert 25% of CO to CH_3OH at 500 K, if CO and H_2 comes from the following reaction?

$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$

(a) 20.48 bar
(b) 21 bar
(c) 10.24 bar
(d) 5.12 bar

40. An amount of 1 mole each of A and D is introduced in 1 L container. Simultaneously the following two equilibria are established.

$A \rightleftharpoons B + C$: $K_C = 10^6$ M and
$B + D \rightleftharpoons A$: $K_C = 10^{-6}\ M^{-1}$

The equilibrium concentration of A will be

(a) 10^{-6} M
(b) 10^{-3} M
(c) 10^{-12} M
(d) 10^{-4} M

41. For a reversible reaction $A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$, the initial molar concentration of A and B are a M and b M, respectively. If x M of A is reacted till the achievement of equilibrium, then x is

(a) $\frac{K_1 a - K_2 b}{K_1 + K_2}$
(b) $\frac{K_1 a - K_2 b}{K_1 - K_2}$
(c) $\frac{K_1 a - K_2 b}{K_1 K_2}$
(d) $\frac{K_1 a + K_2 b}{K_1 + K_2}$

42. For the given reaction $2A(s) + B(g) \rightleftharpoons C(g) + 2D(s) + E(s)$, the extent of reaction of B was found to be 20% at 300 K and 24% at 500 K. The rate of backward reaction

(a) increases with increase in pressure and temperature.

(b) increases with increase in pressure and decrease in temperature.

(c) depends on temperature only and decreases with increases in temperature.

(d) depends on temperature only and increases with increase in temperature.

43. Steam decomposes at high temperature according to the following equation.

$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$; $\Delta H^o = 240$ kJ/mole and $\Delta S^\circ = 50\ JK^{-1}$/mole

The temperature at which the equilibrium constant ($K_P{}^o$) becomes 1.0 is

(a) 4.8 K (b) 4800 K

(c) 480 K (d) impossible

44. $\Delta_f G^o$ for the formation of HI(g) from its gaseous elements is – 2.303 kcal/mol at 500 K. When the partial pressure of HI is 10 atm and of $I_2(g)$ is 0.001 atm, then what must be the partial pressure of hydrogen be at this temperature to reduce the magnitude of ΔG for the reaction to zero?

(a) 1000 atm (b) 10000 atm

(c) 100 atm (d) 31.63 atm

45. When α-D-glucose is dissolved in water, it undergoes a partial conversion to β-D-glucose. This conversion is called mutarotation and it stops when 64.0% of the glucose is in the β-form. Assuming that equilibrium has been attained, what is ΔG^o for the reaction α-D-glucose $\rightleftharpoons$ β-D-glucose, at this experimental temperature?

(a) $-RT\log_{10}(1.6)$ (b) $-RT\log_{10}(1.78)$

(c) $-RT\log_e(1.78)$ (d) $-RT\log_e(1.6)$

46. At chemical equilibrium, a reaction is

(a) spontaneous in forward direction.

(b) spontaneous in backward direction.

(c) spontaneous in both direction.

(d) spontaneous in neither direction.

47. Rate of disappearance of the reactant 'A' in the reversible reaction $A \rightleftharpoons B$ at two temperatures is given as

$$-\frac{d[A]}{dt} = (2.0 \times 10^{-3}\ s^{-1})\,[A] - (5.0 \times 10^{-4}\ s^{-1})\,[B]$$

(at 27°C)

$$-\frac{d[A]}{dt} = (8.0 \times 10^{-2}\ s^{-1})\,[A] - (4.0 \times 10^{-3}\ s^{-1})\,[B]$$

(at 127°C)

The enthalpy of reaction in the given temperature range is

(a) $-\dfrac{2.303\times8.314\times300\times400}{100}\cdot\log(50)\,J/mol$

(b) $-\dfrac{2.303\times8.314\times300\times400}{100}\cdot\log(5)\ J/mol$

(c) $\dfrac{2.303\times8.314\times300\times400}{100}\cdot\log(50)\ J/mol$

(d) $\dfrac{2.303\times8.314\times300\times400}{100}\cdot\log(5)\ J/mol$

48. A certain gas 'A' polymerizes to a very small extent at a given temperature as $nA(g) \rightleftharpoons A_n(g)$. The reaction is started with one mole of 'A' in a container of capacity V. Which of the following is the correct value of $\frac{PV}{RT}$, at equilibrium?

(a) $1-\dfrac{(n-1).K_C}{V^{n-1}}$ (b) $\dfrac{(n-1).K_C}{V^{n-1}}$

(c) $1-\dfrac{n.K_C}{V^{n-1}}$ (d) $1-\dfrac{n.K_C}{V^{n}}$

49. PCl_5 (molecular mass = M) dissociates into PCl_3 and Cl_2 as $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. If the total pressure of the system at equilibrium is P and the density is 'd' at temperature T K. The degree of dissociation of PCl_5 may be represented as

(a) $\dfrac{PM}{dRT}$ (b) $\dfrac{PM}{dRT} - 1$

(c) $\dfrac{dRT}{PM} - 1$ (d) $\dfrac{dRT}{PM}$

50. A 250 ml flask and 100 ml flask are separated by a stopcock. At 350 K, the nitric oxide in the larger flask exerts a pressure of 0.4 atm, and the smaller one contains oxygen at 0.8 atm. The gases are mixed by opening the stopcock. The reactions occurring are as follows.

$2NO + O_2 \rightarrow 2NO_2 \rightleftharpoons N_2O_4$

The first reaction is complete while the second one is at equilibrium. Assuming all the gases to behave ideally, calculate the K_P for the second reaction if the total pressure is 0.3 atm.

(a) 3.5 atm^{-1} (b) 0.87 atm^{-1}
(c) 0.07 atm^{-1} (d) 7.0 atm^{-1}

51. If 'a' is the fraction of ammonia present by volume in an equilibrium mixture made from one volume of N_2 and three volumes of H_2 and P is the total pressure, then

(a) $\frac{a}{1-a} \propto P$ (b) $\frac{a}{(1-a)^2} \propto P$
(c) $\frac{a}{(1+a)^2} \propto P$ (d) $\frac{a}{1+a} \propto P$

52. At 525 K, $PCl_5(g)$ is 80% dissociated at a pressure of 1 atm. Now, sufficient quantity of an inert gas at constant pressure is introduced into the above reaction mixture to produce inert gas partial pressure of 0.9 atm. What is the percentage dissociation of $PCl_5(g)$ when equilibrium is re-established?

(a) 97.3% (b) 80%
(c) 65.6% (d) 4.7%

53. For the reaction: $CuSO_4.3H_2O(s) \rightleftharpoons CuSO_4.H_2O(s) + 2H_2O(g); \Delta H = 3360$ cal. The dissociation pressure is 7×10^{-3} atm at 27°C. What will be the dissociation pressure at 127°C (ln2 = 0.7)?

(a) 9.8×10^{-3} atm (b) 1.4×10^{-2} atm
(c) 1.4×10^{-3} atm (d) 9.8×10^{-2} atm

54. Carbon monoxide in water gas reacts with steam according to the following reaction.

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g); K_{eq} = 0.3333$

If two volumes of water gas (containing 1:1 of CO and H_2) are mixed with five volumes of steam, then the volume ratio of the four gases present at equilibrium is

(a) 1 : 1 : 1 : 1 (b) 1 : 3 : 1 : 1
(c) 1 : 15 : 1 : 5 (d) 1 : 9 : 1 : 3

55. If for the equilibria $NH_2COONH_4(s) \rightleftharpoons N_2 + H_2 + CO + O_2$, the value of K_P at 800 K is $27 \times 2^{\lambda/2}$ and the equilibrium pressure is 22 atm. The value of λ is

(a) 21 (b) 22
(c) 11 (d) 12

56. Solid ammonium carbamate dissociates as: $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_3(g)$. In a closed vessel, solid ammonium carbamate is in equilibrium with its dissociation products. At equilibrium ammonia is added such that the partial pressure of NH_3 at new equilibrium now equals the original total pressure. The ratio of total pressure at new equilibrium to that of original total pressure is

(a) 1 : 1 (b) 27 : 31
(c) 31 : 27 (d) 3 : 4

57. The value of equilibrium constant for the following reaction at 300 K and constant pressure is

$A(g) + B(g) \rightleftharpoons C(g) + D(g) + E(g); \Delta E^\circ = 30$ kcal and $\Delta S^\circ = 100$ cal/K.

(a) e (b) $\frac{1}{e}$
(c) e^2 (d) $\frac{1}{e^2}$

58. $\Delta_f G^\circ$ are 30.426 kJ/mol for *trans*-1,2-dichloroethene and 22.112 kJ/mol for *cis*-1,2-dichloroethene, at 27°C. The molar ratio of *trans* to *cis* isomers at equilibrium at 27°C, is [ln28 = 3.33]

(a) 10 : 3 (b) 3 : 10
(c) 28 : 1 (d) 1 : 28

59. The equilibrium constant for the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ is 3.0 at 500 K. In a 2.0 L vessel, 60 g of water gas [equimolar mixture of CO(g) and $H_2(g)$] and 90 g steam is initially taken. What is the equilibrium concentration of $H_2(g)$?

(a) 1.75 M (b) 3.5 M
(c) 1.5 M (d) 0.75 M

60. The equilibrium $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ is achieved at the equilibrium pressure of 'X' bar at T K. The value of $\Delta_r G^\circ$ for the reaction is

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

Section B (One or More than one Correct)

1. When $NH_4HS(s)$ is vaporized in an empty vessel and maintained at 20ºC, the equilibrium is established $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ and the total pressure of gases at equilibrium is 0.4 atm. When $NH_4HS(s)$ is vaporized in the presence of $NH_3(g)$ in the same vessel at 20ºC, the partial pressure of $NH_3(g)$ at equilibrium is 0.5 atm. Which of the following is/are correct statement(s)?

(a) At second equilibrium, the final partial pressure of $H_2S(g)$ is 0.08 atm.
(b) In second experiment, the initial pressure of $NH_3(g)$ was 0.42 atm.
(c) In the presence of $NH_3(g)$, the extent of dissociation of $NH_4HS(s)$ is decreased.
(d) At second equilibrium, the mole fraction of $H_2S(g)$ is 0.5.

2. Which of the following reaction(s) have $K_P = K_C$?

(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
(c) $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$
(d) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

3. For dissociation of a gas N_2O_5 as $N_2O_5(g) \rightleftharpoons 2NO_2(g) + \frac{1}{2}O_2(g)$. The reaction is performed at constant temperature and volume. If D is the vapour density of equilibrium mixture, P_o is initial pressure of $N_2O_5(g)$ and M is molecular mass of N_2O_5, then the correct information(s) at the equilibrium is/are

(a) the total pressure of gases at equilibrium is $\frac{P_o \cdot M}{2D}$.
(b) the degree of dissociation of $N_2O_5(g)$ is $\frac{M-2D}{3D}$.
(c) the partial pressure of $N_2O_5(g)$ at equilibrium is $\frac{(5D-M)\cdot P_o}{3D}$.
(d) the partial pressure of $O_2(g)$ at equilibrium is $\frac{(M-2D)\cdot P_o}{3D}$.

4. Which of the following is/are correct statement(s)?

(a) The dissociation of $CaCO_3$ is suppressed at high pressure.
(b) The apparent molecular mass of PCl_5 shows lower value on dissociation.
(c) Low pressure is favourable for melting of ice.
(d) Combination of hydrogen atoms to form hydrogen molecule is favourable at high temperature.

5. What is/are true about equilibrium state?

(a) Catalyst has no effect on equilibrium state.
(b) Equilibrium constant is independent of initial concentration of reaction.
(c) The reaction ceases at equilibrium.
(d) Equilibrium constant is independent of pressure.

6. A chemical system is in equilibrium. Addition of a catalyst would result in

(a) increase in the rate of forward reaction.
(b) increase in the rate of reverse reaction.
(c) a new reaction pathway to reaction.
(d) increase the amount of heat evolved.

7. A cylinder fitted with a movable piston contains liquid water in equilibrium with water vapour at 25ºC. Which operation results in a decrease in the equilibrium vapour pressure?

(a) Moving the piston downwards a short distance.
(b) Removing a small amount of vapour.
(c) Removing a small amount of the liquid water.
(d) Dissolving salt in the water.

8. The condition suitable for forming atomic chlorine from molecular chlorine is

(a) Low temperature (b) Low pressure
(c) High temperature (d) High pressure

9. The position of equilibrium will shift in the given direction by the addition of inert gas at constant pressure in which of the following case(s)?

(a) $N_2(g) + 3F_2(g) \rightleftharpoons 2NF_3(g)$; forward direction
(b) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$; 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

10. Two gases A and B, one being the dimer of the other, are at equilibrium. Decreasing of pressure at constant temperature or increasing of temperature at constant pressure favours the formation of more of B. The reaction could not be represented by

(a) $2A \rightleftharpoons B + q$ calories
(b) $2A \rightleftharpoons B - q$ calories
(c) $2B \rightleftharpoons A - q$ calories
(d) $2B \rightleftharpoons A + q$ calories

11. The equilibrium constant for some reactions are given below against each of the reaction.

(i) $2N_2 + 5O_2 \rightleftharpoons 2N_2O_5$; $K = 5 \times 10^{-27}$

(ii) $N_2 + O_2 \rightleftharpoons 2NO$; $K = 2 \times 10^{-15}$

(iii) $N_2 + 2O_2 \rightleftharpoons 2NO_2$; $K = 1.5 \times 10^{-29}$

Which of the following statement is correct?

(a) The least stable oxide is NO_2.

(b) The most stable oxide is NO.

(c) The stability order is $N_2O_5 > NO_2 > NO$.

(d) The stability order is $NO_2 > NO > N_2O_5$.

12. For the gaseous reaction: $CO + H_2O \rightleftharpoons CO_2 + H_2$, the following thermodynamical data are given.

$\Delta H^\circ_{300\ K} = -41.0\ kJ\ mol^{-1}$;
$\Delta S^\circ_{300\ K} = -0.04\ kJ\ K^{-1}\ mol^{-1}$

$\Delta H^\circ_{1200\ K} = -33.0\ kJ\ mol^{-1}$;
$\Delta S^\circ_{1200\ K} = -0.03\ kJ\ K^{-1}\ mol^{-1}$

Assuming partial pressure of each component is 1 bar, the direction of spontaneous reaction is/are

(a) forward at 300 K.

(b) forward at 1200 K.

(c) backward at 300 K.

(d) backward at 1200 K.

13. van 't Hoff equations show the effect of temperature on equilibrium constants K_C and K_P. K_P and K_C varies with temperature according to which of the following relations?

(a) $\log \dfrac{K_{P_2}}{K_{P_1}} = \dfrac{\Delta H}{2.303R}\left[\dfrac{T_1 - T_2}{T_1 T_2}\right]$

(b) $\log \dfrac{K_{P_2}}{K_{P_1}} = \dfrac{\Delta H}{2.303R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

(c) $\log \dfrac{K_{C_2}}{K_{C_1}} = \dfrac{\Delta U}{2.303R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

(d) $\log \dfrac{K_{C_2}}{K_{C_1}} = \dfrac{\Delta U}{2.303R}\left[\dfrac{T_1 - T_2}{T_1 T_2}\right]$

14. For a chemical reaction at the state of equilibrium, which of the following statement(s) is/are correct?

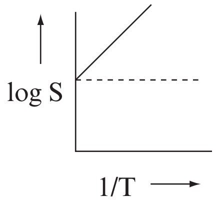
(a) None of the variables like temperature, pressure or volume appear to change.

(b) Reaction system has maximum stability with minimum energy content.

(c) Addition of catalyst disturbs the point of equilibrium.

(d) Addition of inert gas at equilibrium for constant volume system will move the equilibrium in the direction, where more number of moles of gases is present.

15. Solubility of a solute in a solvent (say, water) is dependent on the temperature as given by $S = A.e^{-\Delta H/RT}$, where ΔH is the heat of reaction: solute + $H_2O \rightleftharpoons$ solution. For a given solution, variation of log S with temperature is shown graphically. The solute should be



(a) $CuSO_4 \cdot 5H_2O$

(b) NaCl

(c) Sucrose

(d) CaO

16. At chemical equilibrium, the

(a) enthalpy of system is minimum.

(b) entropy of system is maximum.

(c) free energy of system is minimum.

(d) free energy of system is zero.

17. At –10°C, the solid compound $Cl_2(H_2O)_8$ is in equilibrium with gaseous chlorine, water vapour and ice. The partial pressure of the two gases in equilibrium with a mixture of $Cl_2(H_2O)_8$ and ice are 0.20 atm for Cl_2 and 0.001 atm for water vapour. The processes may be represented as follows.

(i) $Cl_2(H_2O)_8(s) \rightleftharpoons Cl_2(g) + 8H_2O(g)$; K_{P_1}

(ii) $Cl_2(H_2O)_8(s) \rightleftharpoons Cl_2(g) + 8H_2O(s)$; K_{P_2}

Identify the correct statement among the following regarding the processes.

(a) The value of K_{P_1} is $2.0 \times 10^{-25}\ atm^9$.

(b) The value of K_{P_2} is 0.2 atm.

(c) The vapour pressure of ice is 0.001 atm at 263 K.

(d) Process (i) must be exothermic.

18. In an evacuated vessel of capacity 112 L, 4 moles of Ar(g) and 5 moles of $PCl_5(g)$ were introduced and the temperature is maintained at 273°C. At equilibrium, the total pressure of the mixture was found to be 4.8 atm.

(a) The degree of dissociation of $PCl_5(g)$ into $PCl_3(g)$ and $Cl_2(g)$ is 0.6.

(b) K_P for the reaction: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 2.7 atm.

(c) At equilibrium, the total moles of gases are 12.

(d) On removing Ar(g) from the equilibrium mixture at constant pressure and temperature, the extent of dissociation of PCl_5 will increase.

19. In a vessel of 1.0 L capacity, $O_2(g)$ at 0.25 atm pressure and HCl(g) at 1.0 atm pressure are allowed to react in the presence of liquid water at 57°C.

$4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)$; $K_P = 5.0 \times 10^{12}\ atm^{-1}$.

The volume occupied by liquid water is negligible but it is sufficient at achieve equilibrium with water vapour. The vapour pressure of water at 57°C is 0.4 atm. Select the correct statement(s) regarding the equilibrium mixture.

(a) The partial pressure of water vapour at any stage of reaction is 0.4 atm.

(b) The partial pressure of $Cl_2(g)$ at equilibrium is 0.5 atm.

(c) The partial pressure of $O_2(g)$ at equilibrium is 5.0×10^{-4} atm.

(d) The partial pressure of HCl(g) at equilibrium is 2.0×10^{-3} atm.

20. In the following equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, when 5 moles of each is taken and the temperature is kept at 298 K, the total pressure was found to be 20 bar. Given $\Delta_f G^o[N_2O_4(g)]$ = 100 kJ/mol; $\Delta_f G^o[NO_2(g)]$ = 50 kJ/mol.

(a) K_P for the reaction is 1.0 bar.

(b) ΔG^o for the reaction is zero at 298 K.

(c) Under the given condition, the reaction is mainly occurring in backward direction.

(d) The mixture taken is at equilibrium.

21. A gaseous substance $AB_2(g)$ converts to AB(g) in the presence of solid A as $AB_2(g) + A(s) \rightleftharpoons 2AB(g)$. The initial pressure and equilibrium pressure are 0.7 and 0.95 bar, respectively. Now, the equilibrium mixture is expanded reversibly and isothermally till the gas pressure falls to 0.4 bar. Then, which of the following statements is correct?

(a) The volume percent of AB(g) at final equilibrium is nearly 27%.

(b) The volume percent of $AB_2(g)$ at final equilibrium is nearly 32.5%.

(c) K_P for the equilibrium is 5/9.

(c) The ratio of equilibrium pressure of $AB_2(g)$ at initial and final equilibrium is more than 2 but less than 3.

22. An amount of 1 mole of $PCl_3(g)$ and 1 mole of $PCl_5(g)$ is taken in a vessel of 10 L capacity maintained at 400 K. At equilibrium, the moles of Cl_2 is found to be 0.004.

(a) K_C for the reaction: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 0.0004 M.

(b) K_P for the reaction: $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ is $0.0004 \times (0.082 \times 400)$ atm.

(c) If $PCl_3(g)$ is added to the equilibrium mixture, ΔG at the new equilibrium becomes greater than the ΔG at old equilibrium.

(d) After equilibrium is achieved, the moles of PCl_3 are doubled and moles of Cl_2 are halved simultaneously, then the partial pressure of PCl_5 remains unchanged.

23. A reaction at 300 K with $\Delta G^o = -1743$ J consists of 3 moles of A(g), 6 moles of B(g) and 3 moles of C(g). If A, B and C are in equilibrium in 1 L container, then the reaction may be (ln 2 = 0.7, $R = 8.3$ J/K-mol)

(a) $A + B \rightleftharpoons C$ (b) $A \rightleftharpoons B + 2C$

(c) $2A \rightleftharpoons B + C$ (d) $A + B \rightleftharpoons 2C$

24. The equilibrium between gaseous isomers A, B and C can be represented as follows.

$A(g) \rightleftharpoons B(g)$; $K_1 = ?$
$B(g) \rightleftharpoons C(g)$; $K_2 = 0.4$
$C(g) \rightleftharpoons A(g)$; $K_3 = 0.6$

If one mole of A is taken in a closed vessel of volume 1 L, then

(a) [A] + [B] + [C] = 1 M at any moment of reaction.

(b) concentration of C is 1.2 M at equilibrium.

(c) the value of K_1 is 1/0.24.

(d) isomer A is thermodynamically least stable.

25. Consider the equilibrium $HgO(s) + 4I^-(aq) + H_2O(l) \rightleftharpoons HgI_4^{2-}(aq) + 2OH^-(aq)$, which changes will decrease the equilibrium concentration of $HgI_4^{2-}(aq)$?

(a) Addition of 0.1 M-HI(aq).
(b) Addition of HgO(s).
(c) Addition of $H_2O(l)$.
(d) Addition of KOH(aq).

Section C (Comprehensions)

Comprehension I

Equilibrium constants are given for the following reactions at 27ºC.

$$SrCl_2 \cdot 6H_2O(s) \rightleftharpoons SrCl_2 \cdot 2H_2O(s) + 4H_2O\ (g);\ K_P = 2.56 \times 10^{-10}\ atm^4$$

$$Na_2HPO_4 \cdot 12H_2O(s) \rightleftharpoons Na_2HPO_4 \cdot 7H_2O(s) + 5H_2O\ (g);\ K_P = 2.43 \times 10^{-13}\ atm^5$$

$$Na_2SO_4 \cdot 10H_2O(s) \rightleftharpoons Na_2SO_4\ (s) + 10\ H_2O(g);\ K_P = 1.024 \times 10^{-27}\ atm^{10}$$

The vapour pressure of water at 27ºC is 0.04 atm.

1. Which is the most effective drying agent at 27ºC?

(a) $SrCl_2 \cdot 2H_2O$, (b) $Na_2HPO_4 \cdot 7H_2O$
(c) Na_2SO_4 (d) All, equally

2. At what relative humidity will $Na_2SO_4.10H_2O(s)$ be efflorescent when exposed to the air at 27ºC?

(a) Below 50% (b) Above 50%
(c) Above 5% (d) Below 5%

3. At what relative humidity will $Na_2HPO_4.7H_2O(s)$ deliquescent when exposed to the air at 27ºC?

(a) Below 75% (b) Above 75%
(c) Above 7.5% (d) Below 7.5%

Comprehension II

An amount of 0.20 moles of CO taken in a 2.463 L flask is maintained at 750 K along with a catalyst so that the following reaction can take place $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$. Hydrogen is introduced until the total pressure of the system is 7.5 atm at equilibrium and 0.1 mole of methanol is formed.

4. For the reaction, K_P is

(a) 0.16 atm^{-2} (b) 6.25 atm^{-2}
(c) 0.04 atm^{-2} (d) 1.56 atm^{-2}

5. For the reaction, K_C is [Given: $(2.463)^2 = 6.07$]

(a) 6.07 M^{-2} (b) 607 M^{-2}
(c) 151.75 M^{-2} (d) 2428 M^{-2}

6. What is the final pressure if the same amount of CO and H_2 as before used, but with no catalyst so that the reaction does not take place?

(a) 18.75 atm (b) 10.0 atm
(c) 15.0 atm (d) 12.5 atm

Comprehension III

In the esterification reaction,

$$C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

an equimolar mixture of alcohol and acid taken initially, yields under equilibrium, the ester with mole fraction = 0.333.

7. The equilibrium constant is

(a) 10 (b) 4
(c) 100 (d) 16

8. What fraction of the alcohol would be esterified if the initial mole fraction of the alcohol is 0.333? [Given: $\sqrt{12} = 3.45$]

(a) 0.15 (b) 0.85
(c) 0.28 (d) 0.72

9. If in this esterification, initially equal moles of alcohol and acid are taken. At equilibrium, unreacted alcohol and acid, on treatment of sodium, produced H_2 which occupied 44.8 L at 0^oC and 1 atm. The percentage esterification of acid and alcohol is

(a) 25% (b) 33.3%
(c) 50% (d) 66.7%

Comprehension IV

At 444°C, HI undergoes dissociation to the extent of 22.22% at equilibrium

10. What is the equilibrium constant of the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ at 444°C?

(a) 50 (b) 0.02
(c) 0.143 (d) 3.14

11. What is the percentage dissociation of HI at 444^oC if the experiment is started with one mole of HI(g) and one mole of $I_2(g)$?

(a) Less than 22.22%
(b) More than 22.22%
(c) Equal to 22.22%
(d) Nothing can be said

12. What is the percentage dissociation of HI at 444^oC, if the experiment is started with one mole of HI(g) and 1 mole of He(g)?

(a) Less than 22.22%
(b) More than 22.22%
(c) Equal to 22.22%
(d) Nothing can be said

Comprehension V

Le Chatelier performed an experiment in science academy. He introduced excess of solid NH_4HS into a closed 5.0 L vessel containing NH_3 gas at a partial pressure of P mm and at temperature 300 K. Due to it, dissociation of the solid takes place and at equilibrium, he measured the partial pressure of NH_3 gas equal to 625 mm and the total pressure of gases equal to 725 mm.

13. The value of P is

(a) 725 (b) 625
(c) 525 (d) 100

14. The value of K_P for the reaction $NH_3(g) + H_2S(g) \rightleftharpoons NH_4HS(s)$, is

(a) 6.25×10^4 mm^2 (b) 1.6×10^{-5} mm^{-2}
(c) 1.6×10^{-3} mm^{-2} (d) 4.53×10^5 mm^2

15. What would have been the partial pressure of NH_3, if excess solid NH_4HS had been taken in an evacuated vessel of the same volume at the same temperature?

(a) 1000 mm (b) 750 mm
(c) 500 mm (d) 250 mm

16. The minimum mass of $NH_4HS(s)$ needed to establish equilibrium in the same evacuated vessel at the same temperature is

(a) $\dfrac{250 \times 5}{0.0821 \times 300}$ g

(b) $\dfrac{250 \times 5 \times 51}{0.0821 \times 300}$ g

(c) $\dfrac{250 \times 5 \times 51}{0.0821 \times 300 \times 760}$ g

(d) $\dfrac{250 \times 5}{0.0821 \times 300 \times 760}$ g

Comprehension VI

For the system A(g) + B(g) $\rightleftharpoons$ C(g) + D(g), ΔH for the forward reaction is −24.942 kJ/mol. The activation energies of forward and backward reactions are in the ratio of 2 : 3. Assume that the pre-exponential factor is the same for the forward and backward reactions ($A_f = A_b = 1$).

17. What is the equilibrium constant for the reaction at 27°C?

(a) e^4 (b) e^{-4}
(c) e^{10} (d) e^{-10}

18. What is the ratio of rate constant of backward to forward direction at 27°C?

(a) e^4 (b) e^{-4}
(c) e^{10} (d) e^{-10}

19. Which of the following statement is correct at 27°C?

(a) The rate constant of forward reaction is e^{30}.
(b) The rate constant of forward reaction is e^{-30}.
(c) The rate constant of backward reaction is e^{30}.
(d) The rate constant of backward reaction is e^{-30}.

Comprehension VII

The degree of dissociation of NH_3 in a vessel V_1 (initially evacuated) at T K at an equilibrium pressure of 50 atm is same as that of SO_3 (g) at a total equilibrium pressure equal to K_P for

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

A vessel V_2 (capacity 100 L and maintained at T K) initially contains equimolar mixture of NH_3, N_2, H_2 and Ne. The total mass of the mixture containing four gases is 0.134 kg. At equilibrium, N_2 was found to be 52.24% by mass. (Ne = 20).

20. The degree of dissociation of NH_3 at T K in the vessel of volume V_1 is

(a) 0.33 (b) 0.50
(c) 0.67 (d) 0.75

21. The value of K_P for the reaction: $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ at T K is

(a) 2700 atm^2 (b) 2500 atm^2
(c) 3.7×10^{-4} atm^2 (d) 4.0×10^{-4} atm^2

22. The total pressure of gases at equilibrium in the vessel V_2 is

(a) $\sqrt{\dfrac{2700\times 8}{2.5}}$ atm (b) $\sqrt{\dfrac{2700\times 8}{2.5\times 7}}$ atm

(c) $\sqrt{\dfrac{2700\times 81}{2.5\times (3.5)^3}}$ atm (d) $\sqrt{\dfrac{2700\times 81}{3.5\times (2.5)^3}}$ atm

---

Comprehension VIII

In a vessel, the equilibria $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ and $N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g)$ are achieved simultaneously. Initially, the vessel contains N_2 and H_2 in molar ratio of 9 : 13. The equilibrium pressure is $7P_o$ in which due to ammonia, the pressure is P_o and due to hydrogen, the pressure is $2P_o$.

23. The value of K_P for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is

(a) $20\ P_o^2$ (b) $\dfrac{20\ P_o^2}{3}$

(c) $\dfrac{1}{20\ P_o^2}$ (d) $\dfrac{3}{20\ P_o^2}$

24. The value of K_P for the reaction $N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g)$ is

(a) $20\ P_o^2$ (b) $\dfrac{20\ P_o^2}{3}$

(c) $\dfrac{1}{20\ P_o^2}$ (d) $\dfrac{3}{20\ P_o^2}$

Section D (Assertion–Reason)

The following questions consist of two statements. Mark the answer as follows.

(a) If both statements are CORRECT, and **Statement II** is the CORRECT explanation of **Statement I**.

(b) If both statements are CORRECT, and **Statement II** is NOT the CORRECT explanation of **Statement I**.

(c) If **Statement I** is CORRECT, but **Statement II** is INCORRECT.

(d) If **Statement I** is INCORRECT, but **Statement II** is CORRECT.

1. **Statement I:** For the reaction $A(g) \rightleftharpoons B(g)$, equilibrium moles of A and B are, respectively, 'a' and 'b' in 1 L container. If 5 moles of A and 3 moles of B are added, then reaction must move in forward direction.

   Statement II: Even if the amount of reactant added to a system at equilibrium is more than the amount of product added at the same time, the equilibrium can shift in any direction.

2. **Statement I:** Total number of moles in a closed system at new equilibrium is less than the old equilibrium if some amount of a substance is removed from the system (reaction: $A(g) \rightleftharpoons B(g)$).

   Statement II: The number of moles of the substance which is removed, is partially compensated as the system reaches to the new equilibrium.

3. **Statement I:** A net reaction can occur only if a system is not at equilibrium.

   Statement II: All reactions occur to reach a state of equilibrium.

4. **Statement I:** A catalyst does not influence the value of equilibrium constant.

   Statement II: Catalyst influence the rates of both forward and backward reactions by the same factor.

5. **Statement I:** Le Chatelier's principle predicts that an increase in temperature favours an endothermic process.

   Statement II: An endothermic process is one that absorbs heat and hence, tends to minimize the temperature increase.

6. **Statement I:** For a gaseous reversible reaction, K_P can be equal to or less than or even greater than the value of K_C.

   Statement II: The relation between K_P and K_C depends on the change in the number of moles of gaseous reactants and products as well as temperature.

7. **Statement I:** The system $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is said to be at equilibrium when the intensity of brown colour does not change with time.

   Statement II: $N_2O_4(g)$ is colourless while $NO_2(g)$ is coloured.

8. **Statement I:** On cooling in a freezing mixture, the colour of the following mixture turns to pink from deep blue for the reaction:

   $$\underset{\text{Blue}}{Co(H_2O)_6^{2+}}(aq.) + 4Cl^-(aq.) \rightleftharpoons$$
   $$\underset{\text{Pink}}{CoCl_4^{2-}}(aq.) + 6H_2O(l)$$

   Statement II: The reaction is endothermic.

9. **Statement I:** NaCl solution can be purified by passing excess of hydrogen chloride gas through NaCl solution.

   Statement II: Increase in chloride ion concentration in the solution results in the precipitation of NaCl.

10. **Statement I:** Decrease in volume of the system at constant temperature at equilibrium results increase in molar concentration of all the gaseous components involved in the reaction $A(g) + B(s) \rightleftharpoons 3C(g)$.

    Statement II: Decrease in volume of the system at constant temperature at equilibrium results increase in moles of A(g) and decrease in moles of C(g) but no change in the moles of B(s) in the reaction $A(g) + B(s) \rightleftharpoons 3C(g)$.

Section E (Column Match)

1. Match the columns.

Column I	Column II
(A) $Q = K_{eq}$	(P) Reaction is near to completion.
(B) $Q < K_{eq}$	(Q) Reaction is not at equilibrium.
(C) $Q > K_{eq}$	(R) Reaction is fast in forward direction.
(D) $K_{eq} >>> 1$	(S) Reaction at equilibrium.

2. Match the columns.

Column I	Column II
(A) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(P) $K_P = K_C\,(RT)$
(B) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(Q) $K_P = K_C\,(RT)^2$
(C) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(R) $K_P = K_C\,(RT)^{-2}$
(D) $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$	(S) $K_P = K_C$

3. Match the columns.

Column I	Column II
(A) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(P) Unaffected by inert gas addition.
(B) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	(Q) Forward shift by rise in pressure and backward shift by inert gas addition.
(C) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(R) Unaffected by increase in pressure.
(D) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(S) Backward shift by rise in pressure and forward shift by inert gas addition.

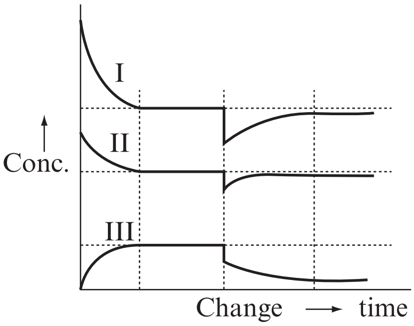
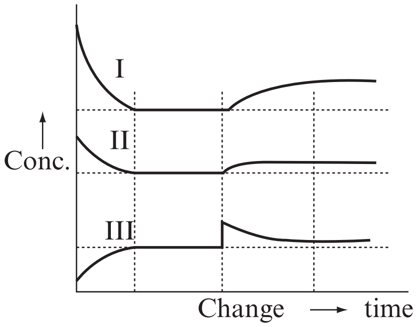
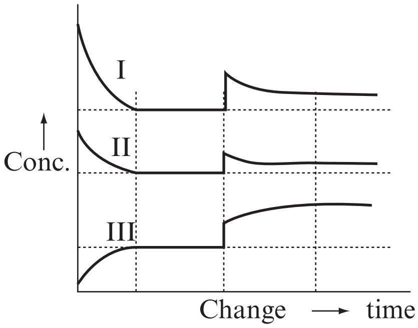
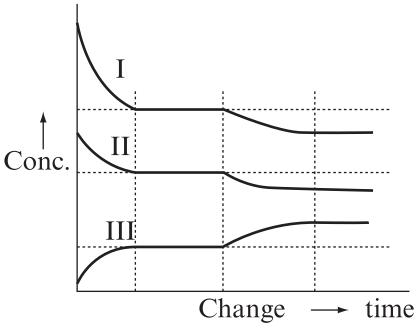
4. Match the columns.

Column I	Column II
(A) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$	(P) Extent of reaction will not increase with increase in pressure.
(B) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$	(Q) Concentration of product will increase with increase in temperature.
(C) $2(CH_3COOH)(g) \rightleftharpoons (CH_3COOH)_2(g)$	(R) Increase in volume will increase moles of reactant.
	(S) Introduction of inert gas at constant pressure will shift the equilibrium in the product side.

5. Match the columns.

Column I	Column II
(A) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$	(P) Introduction of hydrogen gas at constant volume shift equilibrium back.
(B) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(Q) α increases on increasing temperature.
(C) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$	(R) On adding inert gas at constant volume, equilibrium state does not change.
(D) $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$	(S) On increasing the pressure, concentration of all reactants increases.
	(T) α is independent of equilibrium pressure.

6. For an endothermic reaction: $4A(g) + B_2(g) \rightleftharpoons 2A_2B(g)$

Column I	**Column II**
(A) 	(P) Increase in temperature.
(B) 	(Q) Increase in pressure.
(C) 	(R) Addition of A_2B at equilibrium.
(D) 	(S) Addition of inert gas at constant pressure.
	(T) Increase in volume.

7. Match the columns.

Column I	**Column II**
(A) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(P) $K_P > K_C$ at 300 K.
(B) $2NO_2(g) \rightleftharpoons N_2O_4(g)$	(Q) $K_P < K_C$ at 300 K.
(C) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(R) P is increased, reaction moves to right side.
(D) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(S) Inert gas added at constant volume, equilibrium will not be affected.
	(T) Inert gas added at constant pressure, equilibrium will shift right.

8. Match the following for the reaction: $2A(g) \rightleftharpoons 3B(g) + C(s)$; $\Delta H = -$ve.

Column I	**Column II**
(A) Increase in total pressure at equilibrium.	(P) Increase in moles of A.
(B) Increase in volume at equilibrium.	(Q) Increase in moles of B.
(C) Addition of He(g) at constant pressure.	(R) Increase in moles of C.
(D) Increase in temperature at constant volume.	(S) Increase in molar concentration of A.
	(T) Increase in molar concentration of B.

9. For the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; $K_P = 2.463$ atm at 900 K. The reaction is performed in a rigid vessel of 15.0 L capacity maintained at 900 K, starting with the following amounts of $CaCO_3(s)$ (given in Column I). Match the correct information given in Column II for the amount given in Column I.

Column I	**Column II**
(A) 100 g	(P) 50% dissociation of $CaCO_3$
(B) 50 g	(Q) 100% dissociation of $CaCO_3$
(C) 25 g	(R) Addition of small amount of $CO_2(g)$ may result shift of equilibrium in backward direction.
	(S) Addition of 10 g of $CaCO_3(s)$ may result in increasing moles of $CO_2(g)$.

10. Match the columns.

Column I (Reactions)	**Column II (Effect on addition of water)**
(A) $A(aq) \rightleftharpoons 2B(aq) + H_2O(l)$	(P) Moles of 'A' increases.
(B) $3A(aq) \rightleftharpoons 2B(aq)$	(Q) Moles of 'B' increases.
(C) $2A(aq) + H_2O(l) \rightleftharpoons B(aq)$	(R) Molar concentration of 'A' decreases.
(D) $2A(aq) \rightleftharpoons 3B(aq)$	(S) Molar concentration of 'B' decreases.

Section F (Subjective)

Single-digit Integer Type

1. The percent dissociation of $H_2S(g)$ if 0.1 mole of H_2S is kept in 0.4 L vessel at 1000 K for the reaction $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$; $K_C = 1.0 \times 10^{-6}$.

2. $COF_2(g)$ passed over catalyst at 1000°C comes to equilibrium $2COF_2(g) \rightleftharpoons CO_2(g) + CF_4(g)$. Analysis of the equilibrium mixture (after quick cooling to freeze the equilibrium) shows that 500 ml of the equilibrium mixture (STP) contains 300 ml (STP) of $(COF_2 + CO_2)$ taking the total pressure to be 10 atm. The value of K_P for the reaction is

3. The dissociation constant of PCl_5 is 8 atm at 273°C. What pressure (in atm) will be developed when 62.55 g of this substance is vaporized at 273°C in 4480 ml vessel originally full of chlorine gas at 0°C and 1 atm pressure?

4. A mixture of equimolar quantities of ethyl alcohol and acetic acid is prepared. Immediately after mixing, 10 ml of mixture was neutralized by 10 ml of N-NaOH. When the mixture reaches the equilibrium, 10 ml requires 5 ml of N-NaOH for neutralization. What is the equilibrium constant for the formation of ester?

5. The degree of dissociation of HI at a particular temperature of 0.8. Calculate the volume (in litre) of 1.6 M-$Na_2S_2O_3$ solution required to neutralize the iodine present in an equilibrium mixture of a reaction when 2 moles each of H_2 and I_2 are heated in a closed vessel of 2 L capacity.

6. It was found that when 1.0 mole of dichloroacetic acid and 4.0 moles of amylene were heated together at 363 K to equilibrium state, 0.5 moles of ester were formed and the total volume of the mixture was 700 ml. In another experiment, 1.0 mole of the acid was heated at the same temperature with some moles of amylene and the equilibrium mixture now occupied a volume of 720 ml. If the amount of ester at equilibrium is 0.6 mole in the second experiment, then how many moles of amylene was taken initially? Amylene is one of the pentene.

7. The minimum mass (in g) of $CaCO_3$ required to establish the equilibrium:

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, $K_C = 0.05$ M

at a certain temperature in a 1.0 L container is

8. To 500 ml of 0.9 M-$AgNO_3$ solution was added 500 ml of 1.0M-Fe^{2+} solution and the reaction is allowed to achieve equilibrium at 25°C.

$Ag^+ (aq) + Fe^{2+} (aq) \rightleftharpoons Fe^{3+} (aq) + Ag (s)$

For 30 ml of the solution, 25 ml of 0.06 M–$KMnO_4$ was required for oxidation of Fe^{2+} present. The equilibrium constant (in M^{-1}) for the reaction at 25°C is

9. A vessel of 2.5 L was filled with 0.01 mole of Sb_2S_3 and 0.01 mole of H_2 to attain equilibrium at 440°C as

$Sb_2S_3(s) + 3H_2(g) \rightleftharpoons 2Sb(s) + 3H_2S(g)$

After equilibrium, the H_2S formed was analysed by dissolving it in water and treating with excess of Pb^{2+} to give 1.19 g of PbS as precipitate. The value of K_C of the reaction at 440°C is (Pb = 206)

10. At 25°C, 560 g of deuterium oxide, D_2O (d = 1.10 g/ml) and 504 g H_2O (d = 0.997 g/ml) are mixed. The volumes are additive. Fifty percent of the H_2O reacts to form HDO. The value of K_C at 25°C for the reaction $H_2O + D_2O \rightleftharpoons 2HDO$ is

11. The following equilibria are established on mixing two gases A_2 and C.

$3A_2(g) \rightleftharpoons A_6(g)$; $K_P = 1.6\ atm^{-2}$
$A_2(g) + C(g) \rightleftharpoons A_2C(g)$; K_P = 'x' atm^{-1}

When $A_2(g)$ and C(g) are mixed in 2 : 1 molar ratio, the total pressure of gases at equilibrium is found to be 1.4 atm and partial pressure of $A_6(g)$, 0.2 atm. The value of '4x' is

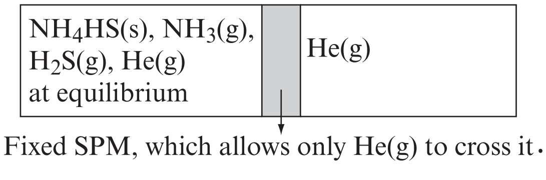
12. A 8.28 g sample of IBr(g) is placed in a container of capacity 164.2 ml and heated to 500 K. The equilibrium pressure of $Br_2(g)$ in the system is 4.0 atm. The value of K_P for the reaction

$2IBr(g) \rightleftharpoons I_2(g) + Br_2(g)$ is (Given: Atomic masses are I = 127, Br = 80)

13. When 1.0 mole of $H_2(g)$ and 3.0 moles of I_2 vapours are allowed to react, 'x' moles of HI(g) is formed at equilibrium. Addition of a further 2.0 moles of $H_2(g)$ gave an additional 'x' moles of HI(g) at new equilibrium. The value of equilibrium constant for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is

14. When $N_2O_5(g)$ is heated to 600 K, it dissociates as $N_2O_5(g) \rightleftharpoons N_2O_3(g) + O_2(g)$; K_C = 2.5 M. Simultaneously, $N_2O_3(g)$ decomposes as $N_2O_3(g) \rightleftharpoons N_2O(g) + O_2(g)$. When initially 4.0 moles of $N_2O_5(g)$ is taken in a 2.0 L flask and allowed to attain equilibrium, the equilibrium concentration of $O_2(g)$ is found to be 2.5 M. The equilibrium concentration of $N_2O(g)$ (in M) is

15.



The entire system is at equilibrium at 300 K. The volume of each chamber is 82.1 L. The total pressure in left chamber is 4 atm and in right chamber, 2 atm. $NH_3(g)$ and $H_2S(g)$ are obtained only from the dissociation of $NH_4HS(s)$. The value of K_P (in atm^2) for the reaction $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ is

Four-digit Integer Type

1. The equilibrium: p–xyloquinone + methylene white $\rightleftharpoons$ p–xylohydroquinone + methylene blue, may be studied conveniently by observing the difference in colour between methylene blue and methylene white. One millimole of methylene blue was added to 1.00 L of solution that was 0.24 M in p–xylohydroquinone and 0.012 M in p–xyloquinone. It was then found that 4.0% of the added methylene blue was reduced to methylene white. What is the equilibrium constant for the above reaction? The equation is balanced with 1 molecule of each of the four substances.

2. The theoretically computed equilibrium constant for the polymerization of formaldehyde to glucose in aqueous solution is $6.4 \times 10^{19}\ \text{M}^{-5}$. If 1 M solution of glucose were taken, what would be the equilibrium concentration of formaldehyde in milligram per litre?

3. A container of capacity V L contains an equilibrium mixture that consists of 2 moles each of PCl_5, PCl_3 and Cl_2 (all as gases). The pressure is 30.3975 kPa and temperature is T K. A certain amount ('x' mole) of $Cl_2(g)$ is now introduced keeping the pressure and temperature constant, until the equilibrium volume becomes $2V$ L. The value of '$90x$' is

4. The standard reaction enthalpy of the reaction $Zn(s) + H_2O(g) \rightleftharpoons ZnO(s) + H_2(g)$ is + 223 kJ/mol and the standard reaction Gibb's functions is +33 kJ mol^{-1} at 1520 K. Assuming that both ΔH^o and ΔS^o remain constant, estimate the minimum temperature (in Kelvin) above which the equilibrium constant becomes greater than one.

5. The diamonds are formed from graphite under very high pressure. Given that the densities of graphite and diamond are, respectively, 2.4 and 3.6 g/cm^3 and are independent of pressure. $\Delta_f G^o$ values for graphite and diamond are zero and 3.0 kJ/mol, respectively. If the equilibrium pressure at which graphite is converted into diamond at 25°C is P bar, then the value of $0.01P$ is

6. For the equilibrium $NiO(s) + CO(g) \rightleftharpoons Ni(s) + CO_2(g)$, $\Delta G^o(\text{cal/mol}^{-1}) = -5320 - 5.6T$ (K). The temperature (in Kelvin) at which the gaseous mixture at equilibrium contains 400 ppm of CO by mole is [ln10 = 2.3, ln2 = 0.7)

7. Assume that the decomposition of HNO_3 can be represented as

   $$4HNO_3(g) \rightleftharpoons 4NO_2(g) + 2H_2O(g) + O_2(g)$$

   and that at a given temperature of 400 K and pressure of 30 atm, the reaction approaches equilibrium. At equilibrium, the partial pressure of $HNO_3(g)$ is 2 atm. The value of K_C (in M^3) for the reaction at 400 K is (R = 0.082 L-atm/K-mol)

8. Gaseous nitrosyl chloride (NOCl) and N_2 are taken in a flask, sealed and heated to some temperature where the total pressure would have been 1.0 bar had not the following equilibrium been established

   $$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

   But the actual pressure was found to be 1.2 bar. Now, into the equilibrium mixture, some Cl_2 gas was introduced at constant volume and temperature so that the total pressure would have been 8.3 bar had no further reaction occurred but the actual pressure was found to be 8.2 bar. The equilibrium constant K_P (in bar) for the decomposition reaction under the given experimental condition is (Answer by multiplying the K_P value with 10)

9. Three ideal gases A, B and D were taken in a vessel of constant volume in molar ratio of 1 : 2 : 3, respectively, causing the following reaction.

   $$A(g) + 2B(g) \rightleftharpoons C(g)$$

   After a long time, when the equilibrium is established, the total pressure was 5/6th of the initial total pressure. At this point, the volume was reduced to half and a catalyst was added starting the following reaction.

   $$2C(g) + D(g) \rightleftharpoons 2F(g)$$

   If at the second equilibrium, moles of A and C are equal and the ratio of equilibrium total pressure at second equilibrium to the equilibrium total pressure at the first equilibrium is 'x : 100', then the value of 'x' is

10. An amount of 0.2 mole of each $A_2(g)$ and $B_2(g)$ is introduced in a sealed flask and heated to 2000 K where the following equilibrium is established.

$A_2(g) + B_2(g) \rightleftharpoons 2\,AB(g)$

At equilibrium, the moles of AB is 0.3. At this stage, 0.1 mole of $C_2(g)$ is added and a new equilibrium is also established as follows.

$A_2(g) + C_2(g) \rightleftharpoons 2\,AC\,(g)$

At the new equilibrium, the moles of AB becomes 0.24. What is the equilibrium constant for the second reaction?

11. At 27°C, the rate of forward reaction at time t is e^4 times greater than that of reverse reaction for the reaction $A + B \rightleftharpoons P$. The magnitude of free energy change involved at that time (in cal) is

12. An amount of 5.0 moles each of ‘A’, ‘B’ and ‘D’ is added to a 1.0 L container.

$A(g) + B(g) \rightleftharpoons C(g);\ K_C = 4 \times 10^{10}\ M^{-1}$

$A(g) + D(g) \rightleftharpoons E(g);\ K_C = 10^{10}\ M^{-1}$

If at equilibrium, the moles of ‘B’ is ‘x’, then the value of ‘$150x$’ is

13. For the reaction $Br_2(l) + Cl_2(g) \rightleftharpoons 2BrCl(g)$; $K_P = 1$ atm. In a closed container of volume 164 L, initially 10 moles of $Cl_2(g)$ are present at 27°C. What minimum mass (in g) of $Br_2(l)$ must be introduced into this container so that the above equilibrium is maintained at a total pressure of 2.25 atm. Vapour pressure of $Br_2(l)$ at 27°C is 0.25 atm. Assume that volume occupied by the liquid is negligible ($R = 0.082$ L-atm/K-mol, Atomic mass of Br = 80).

14. In a 10.0 L container, an equilibrium was established between SO_3, SO_2 and O_2 gases, by starting with SO_3 only. The density of equilibrium mixture was found to be 16 g/litre at a temperature of $\frac{900}{0.0821}$ K. If the degree of dissociation of SO_3 is 40%, then the value of K_P (in atm) for the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ is

15. Equimolar mixture of two gases A_2 and B_2 is taken in a rigid vessel at constant temperature 300 K. The gases achieve equilibrium as follows.

$A_2(g) \rightleftharpoons 2A(g),\ K_P = \boldsymbol{x}$ atm

$B_2(g) \rightleftharpoons 2B(g),\ K_P = \boldsymbol{y}$ atm

$A_2(g) + B_2(g) \rightleftharpoons 2AB(g),\ K_P = 2$

If the initial pressure in the container was 2 atm and the final pressure at equilibrium is 2.75 atm in which the partial pressure of AB(g) is 0.5 atm, ththe value of $\boldsymbol{y} : \boldsymbol{x}$ is $(y > x)$

Answer Keys

Exercise I

Basic

1. (a) 2. (a) 3. (d) 4. (d) 5. (d) 6. (a) 7. (c) 8. (a) 9. (d) 10. (b)
11. (a) 12. (a) 13. (c) 14. (c) 15. (b) 16. (a) 17. (a) 18. (c) 19. (b) 20. (b)
21. (b) 22. (c) 23. (d) 24. (d) 25. (a) 26. (a) 27. (d) 28. (d) 29. (d) 30. (b)

Application of Equilibrium Constant

31. (b) 32. (c) 33. (c) 34. (b) 35. (c) 36. (c) 37. (b) 38. (b) 39. (c) 40. (c)
41. (b) 42. (a) 43. (b) 44. (d) 45. (a) 46. (a) 47. (b) 48. (a) 49. (a) 50. (a)
51. (b) 52. (b) 53. (a) 54. (b) 55. (c)

Heterogeneous Equilibrium

56. (b) 57. (c) 58. (b) 59. (b) 60. (d) 61. (a) 62. (b) 63. (c) 64. (c) 65. (a)

Le-Chatelier’s Principle

66. (d) 67. (c) 68. (d) 69. (c) 70. (d) 71. (c) 72. (d) 73. (b) 74. (a) 75. (b)
76. (b) 77. (a) 78. (a) 79. (c) 80. (d) 81. (c) 82. (a) 83. (c) 84. (c) 85. (d)

Answer Keys — Exercise II

Section A (Only one Correct)

1. (c) 2. (c) 3. (c) 4. (a) 5. (c) 6. (d) 7. (b) 8. (a) 9. (d) 10. (a)
11. (a) 12. (d) 13. (a) 14. (b) 15. (a) 16. (b) 17. (b) 18. (a) 19. (d) 20. (d)
21. (b) 22. (b) 23. (d) 24. (b) 25. (b) 26. (c) 27. (a) 28. (b) 29. (d) 30. (c)
31. (a) 32. (c) 33. (b) 34. (c) 35. (d) 36. (b) 37. (a) 38. (b) 39. (c) 40. (a)
41. (a) 42. (a) 43. (b) 44. (a) 45. (c) 46. (d) 47. (d) 48. (a) 49. (b) 50. (a)
51. (b) 52. (a) 53. (b) 54. (d) 55. (a) 56. (c) 57. (b) 58. (d) 59. (a) 60. (c)

Section B (One or More than one Correct)

1. (a), (b), (c) 2. (a), (b) 3. (a), (b), (c) 4. (a), (b) 5. (a), (b), (d)
6. (a), (b), (c) 7. (d) 8. (b), (c) 9. (b), (c) 10. (a), (b), (d)
11. (a), (b) 12. (a), (d) 13. (b), (c) 14. (a), (b) 15. (d)
16. (a), (b), (c) 17. (a), (b), (c) 18. (a), (c) 19. (a), (b), (c), (d) 20. (a), (b)
21. (b), (c) 22. (a), (d) 23. (c) 24. (a), (c), (d) 25. (c), (d)

Section C

Comprehension I

1. (c) 2. (d) 3. (c)

Comprehension II

4. (a) 5. (b) 6. (d)

Comprehension III

7. (b) 8. (b) 9. (d)

Comprehension IV

10. (b) 11. (a) 12. (c)

Comprehension V

13. (c) 14. (b) 15. (d) 16. (c)

Comprehension VI

17. (c) 18. (d) 19. (d)

Comprehension VII

20. (c) 21. (a) 22. (c)

Comprehension VIII

23. (a) 24. (d)

Section D (Assertion – Reason)

1. (d) 2. (a) 3. (a) 4. (a) 5. (a) 6. (a) 7. (b) 8. (c) 9. (a) 10. (c)

Section E (Column Match)

1. A → S; B → Q, R; C → Q; D → P
2. A → S; B → R; C → P; D → Q
3. A → P, R; B → S; C → Q; D → S
4. A → P, Q, S; B → P, Q; C → R
5. A → P, Q, R, S; B → Q, R, S; C → P, Q, R, S, T; D → Q, R
6. A → S, T; B → R; C → Q; D → P
7. A → P, S, T; B → Q, R, S; C → S; D → Q, R, S
8. A → P, S, T; B → Q, R; C → Q, R; D → P, S
9. A → P, R; B → Q, R; C → Q, S
10. A → Q, R, S; B → P, R, S; C → P, R, S; D → Q, R, S

Section F (Subjective)

Single-digit Integer Type

1. (2) 2. (4) 3. (7) 4. (1) 5. (2) 6. (5) 7. (5) 8. (5) 9. (1) 10. (4)
11. (6) 12. (4) 13. (4) 14. (1) 15. (1)

Four-digit Integer Type

1. (0480) 2. (0015) 3. (0600) 4. (1784) 5. (0180)
6. (0532) 7. (0032) 8. (0032) 9. (0170) 10. (0018)
11. (2400) 12. (0250) 13. (0800) 14. (0016) 15. (0008)

HINTS AND EXPLANATIONS

EXERCISE I (JEE MAIN)

Basic

1. $FeCl_3$ will produce $Fe(OH)_3$ and HCl on hydrolysis.

2. [Solid] or [Pure liquid] $= \dfrac{n}{V} = \dfrac{w/M}{w/d} = \dfrac{d}{M} = \dfrac{\text{Density}}{\text{Molar mass}}$

Thus, it is independent from their quantity.

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

$K_p = K_c.(RT)^{\Delta n_g} = K_c.(RT)^{-2}$

$\therefore K_c = \dfrac{K_p}{(RT)^{-2}} = \dfrac{1.44\times10^{-5}}{(0.0821\times773)^{-2}}$

4. At the initial stage means time after start of reaction, not at $t = 0$.

5. Equilibrium constant is a function of temperature only.

6. $K_p = \dfrac{1.P_{co_2}}{1} = P_{co_2}$

7. Required reaction may be obtained by subtracting the first reaction from second and hence, $K = \dfrac{K_2}{K_1}$.

8. $C_2H_4 + H_2 \rightleftharpoons C_2H_6;\ K_1 = 5.5\times10^{18}\ \text{atm}^{-1}$

$C_2H_2 + H_2 \rightleftharpoons C_2H_4;\ K_2 = 5\times10^{26}\ \text{atm}^{-1}$

$\therefore C_2H_2 + 2H_2 \rightleftharpoons C_2H_6;$

$K_{\text{required}} = K_1.K_2 = 2.75\times10^{45}\ \text{atm}^{-2}$

9. K_{eq} is independent from concentration.

10. $K_p = K_c.(RT)^{\Delta n_g} \Rightarrow \dfrac{K_c}{K_p} = (RT)^{-\Delta n_g} = (RT)^{-\left(-\frac{1}{2}\right)} = \sqrt{RT}$

11. $K_2 = (K_1)^{-1/2} = \dfrac{1}{\sqrt{K_1}} \Rightarrow K_1.K_2^{\,2} = 1$

12. Greater the value of K_{eq}, greater is the extent of reaction.

13. $K_{eq} = \dfrac{K_f}{K_b} = \dfrac{0.16}{4\times10^4} = 4\times10^{-6}$

14. For $r_f > r_b$ means the net reaction in forward direction, the reaction quotient Q should be less than K_{eq}.

15. $Q = \dfrac{[NO_2][O_2]}{[NO][O_3]} = \dfrac{(2.5\times10^{-4})\times(8.2\times10^{-3})}{(1.0\times10^{-5})\times(1.0\times10^{-6})} = 2.05 \times 10^5 < K_C$

Hence, the net reaction is in forward direction.

16. $K_C = \dfrac{[I]^2}{[I_2]} \Rightarrow 10^{-2} = \dfrac{\left(\frac{0.5}{V}\right)^2}{\left(\frac{1}{v}\right)} \Rightarrow V = 25\ \text{L}$

17. $K = \dfrac{[C_6H_6]}{[C_2H_2]^3} \Rightarrow 4 = \dfrac{[C_6H_6]}{(0.5)^3} \Rightarrow [C_6H_6] = 0.5\ \text{M}$

18. $K_C = \dfrac{[H_2]^2[S_2]}{[H_2S]^2} = \dfrac{\left(\frac{0.2}{2}\right)^2\times\left(\frac{0.8}{2}\right)}{\left(\frac{1}{2}\right)^2} = 0.016\ \text{M}$

19. $K_C = \dfrac{[CH_4][H_2O]}{[CO][H_2]^3} \Rightarrow 3.9 = \dfrac{[CH_4]\times0.03}{0.3\times(0.1)^3}$

$\Rightarrow [CH_4] = 0.039\ \text{M}$

20. $\Delta G^\circ = \Delta H^\circ - T.\Delta S^\circ = -RT.\ln K_p^\circ$

or, $18 - 300 \times \dfrac{30}{1000} = -\dfrac{2}{1000} \times 300 \times \ln K_p^\circ$

or, $\ln K_p^\circ = -15 \Rightarrow K_p^\circ = e^{-15}$

21. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$; OH = +43.5 Kcal

For endothermic reactions, K_{eq} increases with the increase in temperature.

22. K_{eq} is independent from catalyst.

23. For the given reaction, $\Delta H^\circ = 2\times(-40) = -80$ KJ

and $\Delta S^\circ = (2\times192) - (191 + 3\times130) = -197$ J/K

Now, $\Delta G^\circ = \Delta H^\circ - \Delta S^\circ = -2.303\ RT \log K^\circ_p$

$\therefore \log K_p = \dfrac{(-80\times1000) - 298\times(-197)}{(-2.303\times8.314\times298)} = 3.73$

24. $\Delta H° = O \Rightarrow K_{eq}$ is independent from T

25. From (i) and (ii),

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$$

$$K_{2000} = \frac{1}{(4.4)^2 \times 5.31 \times 10^{-10}}$$

$$= 9.73 \times 10^7$$

$$K_{1000} = 2.24 \times 10^{22}$$

On increasing temperature, K_{eq} is decreased and hence, $\Delta H° = $ –ve.

26. $MCO_3(S) \rightleftharpoons MO(S) + CO_2(g)$: $K_p = P_{CO_2}$

Now, $\ln \frac{K_2}{K_1} = \frac{\Delta H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

or, $2.303 \times \log 100 = \frac{\Delta H°}{2}\left(\frac{1}{400} - \frac{1}{500}\right)$

$\Rightarrow \Delta H° = 18424$ cal

27. On increasing temperature, K_{eq} is increasing and hence, the reaction is endothermic.

28. $\Delta H = \varepsilon a_f - \varepsilon a_b = 10.303 - 8.000 = 2.303$ kcal

Now, $K_{eq} = \frac{A_f}{A_b} \cdot e^{-\Delta H/RT} = 1 \times e^{-\frac{2.303 \times 10^3}{2 \times 500}} = 0.1$

29. $\Delta G° = -2.303RT \cdot \log K_{eq}$

or, $-4.606 = -2.303 \times \frac{2}{1000} \times 1000 \times \log K_{eq}$

$\Rightarrow K_{eq} = 10$

For reverse reaction, $K'_{eq} = \frac{1}{10} = 0.1$

30. $K_P = K_C \,.\, (RT)^{\Delta Hg}$

or $1.8 = K_C \times (0.0821 \times 700)' \Rightarrow K_C = 0.031$

Hence, for reverse reaction, $K'_C = \frac{1}{K_C} = 31.93$

Application of Equilibrium Constant

31.

	PCl_5	$\rightleftharpoons$	PCl_3	$+$	Cl_2
	0.8 mole		0.2 mole		0
Equilibrium	$0.8 - x$		$0.2 + x$		x
	$= 0.6$		$= 0.4$		$= 0.2$

$\therefore x = 0.2$

Now, $K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{0.4}{1}\right) \times \left(\frac{0.2}{1}\right)}{\left(\frac{0.6}{1}\right)} = 0.133$ M

32.

	PCl_5	$\rightleftharpoons$	PCl_3	$+$	Cl_2
	1 mole		0		0
Equilibrium	$(1 - x)$ mole		x mole		x mole
Equilibrium partial pressure ($P = 2$ atm)	$\frac{1-x}{1+x} \times P$		$\frac{x}{1+x} \times P$		$\frac{x}{1+x} \times P$

$$K_p = \frac{\left(\frac{x}{1+x} \cdot P\right)\left(\frac{x}{1+x} \cdot P\right)}{\left(\frac{1-x}{1+x} \cdot P\right)} = \frac{x^2 \cdot P}{1 - x^2}$$

or $1.6 = \frac{x^2 \times 2}{1 - x^2} \Rightarrow x = \frac{2}{3}$

$\Rightarrow P_{Cl_2} = \frac{x}{1+x} \times P = 0.8$ atm

33.

	PCl_5	$\rightleftharpoons$	PCl_3	$+$	Cl_2
	X mole		0		0
Equilibrium	$x(1 - \alpha)$		$x \cdot \alpha$		$x \cdot \alpha$

E $P_{PCl_3} = \frac{x \cdot \alpha}{x(1+\alpha)} \times P \Rightarrow P_{PCl_3} \cdot P^{-1} = \frac{\alpha}{1+\alpha}$

34. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

As $\Delta n_g = 0$, moles of system is not changing.

$$P = \frac{nRT}{V} = \frac{(0.5 + 0.5) \times 0.08 \times 720}{5.76} = 10 \text{ atm}$$

35.

	$2HI(g)$	$\rightleftharpoons$	$H_2(g)$	$+$	$I_2(g)$
Equilibrium	$1 - \alpha\frac{\alpha}{2}$		$\frac{\alpha}{2}$		
	$= 0.78$		$= 0.11$		$= 0.11$

$$K = \frac{0.11 \times 0.11}{(0.78)^2} = 0.0199$$

36. $K = \dfrac{\frac{\alpha}{2} \cdot \frac{\alpha}{2}}{(1-\alpha)^2} = \dfrac{1}{9} \Rightarrow \alpha = 0.4$

37. $n_{\text{HI}} = 3 - 3 \times \dfrac{30}{100} = 2.1$

38.

$$\begin{array}{lll}
 & N_2O_4 & \rightleftharpoons \; 2NO_2 \\
 & 1 \text{ mole} & 0 \\
\text{Final} & 1 - 0.2 & 2 \times 0.2 \\
 & = 0.8 \text{ mole} & = 0.4 \text{ mole}
\end{array}$$

Now, $\dfrac{P_1}{n_1 T_1} = \dfrac{P_2}{n_2 T_2} \Rightarrow \dfrac{1}{1 \times 300} = \dfrac{P_2}{1.2 \times 600}$

$\Rightarrow P_2 = 2.4$ atm

39.

$$\begin{array}{lll}
 & N_2O_4 \quad \Rightarrow & 2NO_2 \\
\text{Equilibrium} & 1 - \alpha & 2\alpha
\end{array}$$

$$K_p = \frac{P^2_{NO_2}}{p_{N_2O_4}} = \frac{\left(\frac{2\alpha}{1+\alpha} \cdot P\right)^2}{\left(\frac{1-\alpha}{1+\alpha} \cdot P\right)} = \frac{4\alpha^2 \cdot P}{1-\alpha^2}$$

$$\therefore \alpha = \sqrt{\frac{Kp/4p}{1 + Kp/4p}}$$

40. $K_p = \dfrac{4\alpha^2 . P}{1-\alpha^2} = \text{Constant}$

$$\therefore \frac{4 \times \left(\frac{1}{3}\right)^2 \times P_1}{1 - \left(\frac{1}{3}\right)^2} = \frac{4 \times \left(\frac{1}{2}\right)^2 \times P_2}{1 - \left(\frac{1}{2}\right)^2} \Rightarrow \frac{P_1}{P_2} = \frac{8}{3}$$

41.

$$\begin{array}{lll}
 & N_2O_4 & \rightleftharpoons \; 2NO_2 \\
\text{Initial mole} & a & 0 \\
\text{Mole at Equilibrium} & a - x & 2x
\end{array}$$

From question, $(a + x) \times \dfrac{75}{100} = a \Rightarrow \alpha = \dfrac{x}{a} = \dfrac{1}{3}$

42.

$$\begin{array}{llll}
 & N_2 \quad + & 3H_2 \quad \rightleftharpoons & 2NH_3 \\
 & 0.2 \text{ mole} & 0.6 \text{ mole} & 0 \\
\text{Equilibrium} & 0.2 - 0.2 \times \frac{40}{100} & 0.6 - 0.08 \times 3 & 2 \times 0.08 \\
 & = 0.12 & = 0.36 & = 0.16
\end{array}$$

$$\therefore \frac{V_{\text{final}}}{V_{\text{initial}}} = \frac{n_{\text{final}}}{n_{\text{initial}}} = \frac{0.64}{0.80} = \frac{4}{5}$$

43.

$$\begin{array}{llll}
 & 2NH_3 \; \rightleftharpoons & N_2 \; + & 3H_2 \\
 & 4 \text{ mole} & 0 & 0 \\
\text{Equilibrium} & 4 - 2x & x & 3x \\
 & = 2 & = 1 & = 3
\end{array}$$

$\therefore x = 1$

$$\text{Now, } K_C = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{\frac{1}{1} \times \left(\frac{3}{1}\right)^3}{\left(\frac{2}{1}\right)^2} = 6.75 \text{ M}^2$$

44.

$$\begin{array}{llll}
 & 2SO_2 \quad + & O_2 \quad \rightleftharpoons & 2SO_3 \\
 & 2 \text{ mole} & 1 \text{ mole} & 0 \\
\text{Equilibrium} & 2 - 2 \times \frac{50}{100} & 1 - \frac{1}{2} & 1 \\
 & = 1 & = 0.5 &
\end{array}$$

$$\therefore P_{O_2} = \frac{\frac{1}{2}0.5}{2.5} \times 1 = 0.2 \text{ atm}$$

45.

$$\begin{array}{lllll}
 & CH_3COOH \; + & C_2H_5OH \; \rightleftharpoons & CH_3COOC_2H_5 \; + & H_2O \\
 & 1 & 1 & 0 & 0 \\
\text{Equilibrium} & & & & \\
 & 1 - \frac{1}{4} & 1 - \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \\
 & = \frac{3}{4} & \frac{3}{4} & &
\end{array}$$

$$K = \frac{\frac{1}{4} \times \frac{1}{4}}{\frac{3}{4} \times \frac{3}{4}} = \frac{1}{9}$$

46. At equilibrium, $[A]=[B]$ and $[C]=[D]$ and hence

$$K=\frac{[C][D]}{[A][B]}=\frac{[C]^2}{[A]^2}\Rightarrow\frac{[C]}{[A]}=\sqrt{2.25}$$

$$=1.5\Rightarrow\frac{[A]}{[C]}=\frac{2}{3}$$

47.

$$\begin{array}{lccc} & XY_2 & \rightleftharpoons XY & + \ Y \\ & 600\text{ mm} & 0 & 0 \\ \text{Equilibrium} & (600-x)\text{ mm} & x\text{ mm} & x\text{ mm} \end{array}$$

From Question: $(600-x)+x+x=800\Rightarrow x=200$

$$\therefore Kp=\frac{x.x}{(600-x)}=100\text{ mm Hg}$$

48.

$$\begin{array}{lcccc} & A & +\ B & \rightleftharpoons C & +\ D \\ \text{Initial} & c\text{M} & c\text{M} & 0 & 0 \\ \text{Equilibrium} & (c-x)\text{M} & (c-x)\text{M} & x\text{ M} & x\text{ M} \end{array}$$

From Question: $x=2\times(c-x)\Rightarrow x=\frac{2}{3}c$

$$\therefore K=\frac{x.x}{(c-x)(c-x)}=4$$

49. At equilibrium, mole of I^- = mole of AgI (yellow) precipitate

$= 0.25$

$$\begin{array}{lccc} & I_2 & +\ I^- & \rightleftharpoons I_3^- \\ & 1\text{ mole} & 0.5\text{ mole} & 0 \\ \text{Equilibrium} & 1-x & 0.5-x & x \\ & =0.75 & =0.25 & =0.25 \end{array}$$

$\therefore x=0.25$

$$\therefore K=\frac{\left(\frac{0.25}{1}\right)}{\left(\frac{0.75}{1}\right)\times\left(\frac{0.25}{1}\right)}=1.33$$

50.

$$\begin{array}{lcc} & \alpha-\text{D}-\text{Glucose} \rightleftharpoons & b-\text{D}-\text{Glucose} \\ & a & 0 \\ \text{Equilibrium} & a-x & x \end{array}$$

$$K=\frac{x}{a-x}=1.8\Rightarrow x=\frac{9}{14}a$$

$$\therefore \%\text{ of }\alpha-\text{D}-\text{Glucose remained}=\frac{a-x}{a}\times100$$

$$=35.7\%$$

51.

$$\begin{array}{lccc} & 2\text{NOBr} & \rightleftharpoons 2\text{NO} & +\ \text{Br}_2 \\ & P_0 & 0 & 0 \\ \text{Equilibrium} & P_0-2x & 2x & x=\frac{P}{9} \end{array}$$

$$P_{\text{total}}=(P_0-2x)+2x+x=P_0+x$$

$$=P\Rightarrow P_0=\frac{8P}{9}$$

$$\therefore Kp=\frac{(2x)^2\times x}{(P_0-2x)^2}=\frac{\left(\frac{2P}{9}\right)^2\times\frac{P}{9}}{\left(\frac{8P}{9}-\frac{2P}{9}\right)^2}=\frac{P}{81}$$

52.

$$\begin{array}{lcc} & \text{A} & \rightleftharpoons \ \text{nB} \\ & 0.6\text{M} & 0 \\ \text{Equilibrium} & 0.6-x & nx \\ & =0.3\text{ M} & =0.6 \end{array}$$

$\therefore x=0.3$ $\qquad\qquad$ $\therefore n=2$

53. $$K_p=\frac{4\alpha^2\cdot P}{1-\alpha^2}\Rightarrow 640=\frac{4\alpha^2\times160}{1-\alpha^2}\Rightarrow\alpha=\frac{1}{\sqrt{2}}$$

54. $$M_{\text{mix}}=\frac{dRT}{P}=\frac{3.5\times0.08\times400}{1}=112$$

$$\text{Now, }\alpha=\frac{M_{\text{PCl}_5}-M_{\text{mix}}}{(n-1)\cdot M_{\text{mix}}}=\frac{208.5-112}{(2-1)\times112}=0.8616$$

55.

$$\begin{array}{lccc} & 2\text{AB}_2 & \rightleftharpoons 2\text{AB} & +\ \text{B}_2 \\ & 1 & 0 & 0 \\ \text{Equilibrium} & 1-x & x & \frac{x}{2} \end{array}$$

$$K_p = \frac{\left(\dfrac{x}{1+\dfrac{x}{2}} \times P\right)^2 \cdot \left(\dfrac{x/2}{1+x/2} \cdot P\right)}{\left(\dfrac{1-x}{1+x/2} \cdot P\right)^2}$$

$$= \frac{x^3 \cdot P}{2(1-x)^2\left(1+\dfrac{x}{2}\right)}$$

As $x << 1$, $K_p = \dfrac{x^3 \cdot P}{2} \Rightarrow x = \left(\dfrac{2Kp}{P}\right)^{1/3}$

Heterogeneous Equilibrium

56. $$2BaO_2(s) \rightleftharpoons 2BaO(s) + O_2(g)$$

$$\frac{34}{170}\text{ mole} = 0.2$$

$$\begin{array}{llll} \text{Equilibrium} & 0.2x & x & \dfrac{x}{2} \end{array}$$

Now, $K_p = P_{O_2} \Rightarrow 0.5 = \dfrac{\dfrac{x}{2} \times 0.0821 \times 1000}{8.21}$

$\Rightarrow x = 0.1$

$\therefore$ % of BaO_2 decomposed $= \dfrac{0.1}{0.2} \times 100 = 50\%$

57. $K_p = (2p)^2.p \Rightarrow P = \left(\dfrac{3.2 \times 10^{-5}}{4}\right)^{1/3} = 0.02$

$\therefore$ Total pressure $= 2P + P = 0.06$ atm

58. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$;

$K_p = 4.5 \times 10^{-2}$ atm

$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$; $K_p = 2.0$ atm

On adding, $CaCO_3(s) + C(s) \rightleftharpoons CaO(s) + 2CO(g)$;

$Kp = 9 \times 10^{-2}\text{ atm}^2$

or $P_{CO}{}^2 = 9 \times 10^{-2} \Rightarrow P_{CO} = 0.3$ atm

59. $K = \dfrac{[H_2]^4}{[H_2O]^4} = \left(\dfrac{1.2/2}{54/18}\right)^4 = 0.0016$

60. $$\begin{array}{lccccc} & CO_2(g) & + & C(s) & \rightleftharpoons & 2CO(g) \\ \text{Given:} & a\text{ mole} & & & & 9a\text{ mole} \\ \text{Required:} & b\text{ mole} & & & & 4b\text{ mole} \end{array}$$

Now, $K_p = \dfrac{\left(\dfrac{9a}{10a} \times 16\right)^2}{\left(\dfrac{a}{10a} \times 16\right)} = \dfrac{\left(\dfrac{4b}{5b} \times P\right)^2}{\left(\dfrac{b}{5b} \times P\right)}$

$\Rightarrow P = 40.5$ atm

62. $$\begin{array}{llcl} & 2CO & \rightleftharpoons & CO_2 + C(s) \\ \text{Equilibrium} & x\text{ atm} & & y\text{ atm} \end{array}$$

From question, $x + y = 1.1$ and $\dfrac{y}{x^2} = 0.1$

$\therefore \dfrac{x}{y} = \dfrac{10}{1}$

63. Any reaction of heterogeneous equilibrium may complete with respect to solid or pure liquid, maintaining equilibrium with gaseous components.

$$\begin{array}{lll} LiCl.NH_3(s) + & 2NH_3(g) \rightleftharpoons & LiCl.3NH_3(s);\ K_p{}' = \dfrac{1}{9\text{ atm}^2} \\ 0.1\text{ mole} & a\text{ mole} & 0 \\ \text{Equilibrium} & & \\ 0 & (a-0.2)\text{ mole} & 0.1\text{ mole} \end{array}$$

Now, $K_p{}' = \dfrac{1}{P_{NH_3}^2} \Rightarrow P_{NH_3} = 3$ atm

$$= \frac{(a-0.2) \times 0.0821 \times 30}{8.21}$$

$\therefore a = 1.2$

64. $$\begin{array}{lcccc} & ZnO(s) + CO(g) \rightleftharpoons & Zn(g) + & Co_2(g); & K_p = 1\text{ atm} \\ & a\text{ atm} & 0 & a\text{ atm} & \\ \text{Equilibrium} & a-x & x & a+x & \end{array}$$

$$K_p = \frac{P_{Zn} \cdot P_{CO_2}}{P_{CO}} \Rightarrow 1 = \frac{x(a+x)}{a-x}$$

and $(a - x) + x + (a + x) = P_{\text{total}} = 1$ atm

$\therefore x = 0.24$

65.

$$\begin{array}{lccc} & H_2(g) & + \; S(s) & \rightleftharpoons H_2S(g) \\ & 0.3 \text{ mole} & 2 \text{ mole} & 0 \\ \text{Equilibrium} & (0.3-x) \text{ mole} & (2-x) \text{ mole} & x \text{ mole} \end{array}$$

$$H_C = \frac{x/2}{(0.3-x)/2} = 0.08 \Rightarrow 0.022$$

$$\text{Now, } P_{H_2S} = \frac{x \times 0.08 \times 360}{2} = 0.32 \text{ atm}$$

Le-Chatelier's Principle

66. K_p is a function of temperature only. On reducing the volume, equilibrium will shift backward and hence, α will decrease.

67. Increase in temperature favours endothermic direction and increase in pressure favours the direction of decreases in volume (moles of gases).

68. The molar concentration of AB(s) will not change on changing its amount and hence, equilibrium will not be affected.

69. $K = [B]^2[C]^3 = \text{Constant}$

Now, $[B]^2[C]^3 = [B]^2_{\text{new}} \times (2[C])^3 \Rightarrow [B]_{\text{new}} = \dfrac{[B]}{2\sqrt{2}}$

70. MgO is solid.

71. Increase in pressure will shift the equilibrium in the direction of decrease in volume and hence, more water will form.

72. There is no effect of adding inert gas constant volume.

73. Exothermic reactions are unfavoured by increasing temperature.

74. At 250°C, N_2 gas will not react.

75. $V_{\text{Diamond}} < V_{\text{Graphite}}$

On increasing pressure, equilibrium will shift toward diamond.

76. $N_2O_4 \rightleftharpoons 2NO_2$

On increasing temperature, the reaction will shift forward and hence, $\Delta H = +\text{ve}$.

77. Catalyst has no effect on equilibrium.

78. Equilibrium will shift towards water. In order to maintain equilibrium, the temperature should be increased.

79. Addition of reactant will shift the equilibrium in forward direction.

80. If equilibrium were not disturbed, $[Cu^{2+}]_{\text{final}} = \dfrac{x}{2}$.

But as equilibrium will shift backward, its concentration will decrease further.

81. $Kp = \dfrac{P_{PCl_3} \cdot P_{Cl_2}}{P_{PCl_5}} = \text{constant}$

If $P'_{PCl_3} = 2 \times P_{PCl_3}$

and $P'_{Cl_2} = 2 \times P_{Cl_2}$,

then $P'_{PCl_5} = 4 \times P_{PCl_5}$

82. $\Delta n_g = 0$, hence no effect.

83. Equilibrium will shift towards NO_2.

84. K_{eq} is a function of temperature only.

85. For forward reaction (exothermic), temperature should be low. As mole of gas is decreasing, the pressure should be high.

EXERCISE II (JEE ADVANCED)

Section A (Only one Correct)

1. K_{eq} for the reaction in backward direction
$$= \frac{K_b}{K_f} = \frac{2.1\times10^{-3}\,\text{L mol}^{-1}\text{s}^{-1}}{3.9\times10^{-5}\,s^{-1}} = 53.846 \text{ L mol}^{-1}$$

2. Stability constant,
$$K = \frac{K_f}{K_b} = \frac{1.45\times10^{13}}{1.22\times10^{-9}} = 1.1885\times10^{17}$$

3. $$K_{eq} = \frac{K_f}{K_b} = \frac{[B]^2}{[A]}$$
$$\Rightarrow \frac{1.5\times10^{-3}}{K_b} = \frac{(100/10)^2}{(10^{-5}/10)}$$
$$\Rightarrow K_b = 1.5\times10^{-11}\ M^{-1}\ S^{-1}$$

4. For pent hydrate to be efflorescent, $Q < K_p$
or, $P^2_{H_2O} < 10^{-4}\,\text{atm}^2$
$$\Rightarrow P_{H_2O} < 10^{-2}\,\text{atm} = 7.6 \text{ mm}$$

5. $Q_P = P^2_{NH_3}\times P_{CO_2} = 10^2\times20 = 2000 \text{ atm}^3 < K_P$
Hence, the reaction should shift forward. But as solid NH_2COONH_4 is not present initially, the pressure will remain at 30 atm.

6. $Q_P < K_P \Rightarrow P^2_{H_2O} < K_p$
$$\Rightarrow \left(\frac{40}{760}\times\frac{R.H}{100}\right)^2 < 1.21\times10^{-4}$$
$\therefore$ R.H. < 20.9 %

7. $H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$; $K_p = 6.4\times10^{-4}$ atm
$I_2(s) \rightleftharpoons I_2(g)$; $K_p = 1.6\times10^{-4}$ atm
$$\therefore H_2(g) + I_2(g) \rightleftharpoons 2HI(g)\ ;\ K_P = \frac{6.4\times10^{-4}}{1.6\times10^{-4}} = 4$$

8. Net rate of reaction of HI,
$$-\frac{1}{2}\cdot\frac{d[HI]}{dt} = r_b - r_f = K_{-1}[HI]^2 - K_1[H_2][I_2]$$

9. $$\alpha = \frac{M_0 - M}{(n-1)\cdot M} = \frac{208.5-124}{(2-1)\times124} = 0.681$$

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

Initial partial pressure	P_0	P_0	0
Equilibrium partial pressure	$P_0 - 0.75\,P_0$	$P_0 - 0.75\,P_0$	$0.75\,P_0$
	$-0.25\,P_0$	$-0.25\,P_0$	

Now, $$K_P = \frac{P_{PCl_5}}{P_{PCl_3}\times P_{Cl_2}}$$
$$\Rightarrow 2 = \frac{0.75\,P_0}{0.25\,P_0\times0.25\,P_0}$$
$$\Rightarrow P_0 = 6 \text{ atm}$$
$\therefore$ Initial total pressure of mixture $= 2P_0 = 12$ atm

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

Initial moles	1	3	0
Moles at equilibrium	$1-x$	$3-3x$	$2x$

Total moles of gases $= (1-x) + (3-3x) + 2x$
$= 4 - 2x$

Equilibrium partial pressure
$$\frac{1-x}{4-2x}\times P \qquad \frac{3-3x}{4-2x}\times P \qquad \frac{2x}{4-2x}\times P$$

Now, $$K_P = \frac{\left(\frac{2x}{4-2x}\times P\right)^2}{\left(\frac{1-x}{4-2x}\times P\right)\left(\frac{3-3x}{4-2x}\times P\right)^3}$$
$$= \frac{4x^2}{27(1-x)^4}\times\frac{(4-2x)^2}{P^2} \approx \frac{4x^2\times16}{27\times P^2}$$
$$\therefore x = \sqrt{\frac{27\,K_P\cdot P^2}{64}} = \frac{3P\cdot\sqrt{3\,K_P}}{8}$$

12. $$X_2 + Y_2 \rightleftharpoons 2XY$$

Initial moles	2	3	0
Final moles	$2-x$	$3-x$	$2x$

$$[XY] = \frac{2x}{5} = 0.7$$

$$\Rightarrow x = 1.75$$

$$\therefore\ [X_2] = \frac{2-x}{5} = 0.05\ \text{M}$$

$$\text{and } [Y_2] = \frac{3-x}{5} = 0.25\ \text{M}$$

13.

	N_2	$+\ O_2$	$\rightleftharpoons\ 2NO$
Equilibrium moles	$1-x$	$1-x$	$2x$

$$0.09 = \frac{(2x)^2}{(1-x)(1-x)}$$

$$\Rightarrow x = 0.13$$

14.

	N_2	$+\ O_2$	$\rightleftharpoons\ 2NO$
Initial moles	$4a$	a	0
Equilibrium moles	$4a-x$	$a-x$	$2x$

$$\text{Now, } 0.0004 = \frac{(2x^2)}{(4a-x)(a-x)} \approx \frac{4x^2}{4a \cdot a}$$

$$\Rightarrow \frac{x}{a} = 0.02$$

$$\therefore \text{ Per cent of NO} = \frac{2x}{5a} \times 100 = 0.8\%$$

15.

	N_2	$+\ 3H_2$	$\rightleftharpoons\ 2NH_3$
Initial moles	1	5	0
Moles at equilibrium	$1-x$	$5-3x$	$2x$

Total moles = $(1-x) + (5-3x) + 2x = 6-2x$

$$\text{From question, } \frac{2x}{6-2x} = 0.4$$

$$\Rightarrow x = \frac{6}{7}$$

$$K_P = \frac{(2x)^2}{(1-x)\times(5-3x)^3} \times \left(\frac{6-2x}{P}\right)^2$$
$$= 2.6 \times 10^{-4}\ \text{atm}^{-2}$$

16.

	N_2	$+\ 3H_2$	$\rightleftharpoons\ 2NH_3$
Initial moles	4	16	0
Moles at equilibrium	$4-x$	$16-3x$	$2x$

Total moles = $(4-x) + (16-3x) + 2x = 20-2x$

$$\text{From question, } 20 \times \frac{9}{10} = 20-2x$$

$$\Rightarrow x = 1$$

$$\text{Now, } K_C = \frac{(2x)^2}{(4-x)(16-3x)^3} \cdot V^2$$
$$= 6.07 \times 10^{-4}\ \text{M}^{-2}$$

17. If reactants are taken in stoichiometric amount, then their mass ratio does not change at any stage of reaction. For 3 mole N_2, there should be 9 mole H_2. Hence, at any stage, $m_{N_2} + m_{H_2} + m_{NH_3} = 3 \times 28 + 9 \times 2 = 102$ gm.

18.

	$2SO_2$	$+\ O_2$	$\rightleftharpoons\ 2SO_3$
Initial moles	2	1	0
Moles at equilibrium	$2-2x$	$1-x$	$2x$

From question $n_{eq}\ SO_2 = n_{eq}\ MnO_4^-$.

or, $(2-2x) \times 2 = 0.4 \times 5$

$\Rightarrow x = 0.5$

$$\therefore\ K_C = \frac{(2x)^2}{(2-2x)^2 \times (1-x)} = 2\ \text{M}^{-1}.$$

19. $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3C00C_2H_5 + H_2O$

	CH_3COOH	C_2H_5OH	$CH_3C00C_2H_5$	H_2O
Case I	$\frac{60}{60} = 1$ mole	$\frac{46}{46} = 1$ mole	0	0
Moles at Equ.	$1-x$	$1-x$	$x = \frac{44}{88} = 0.5$	x
Case II	$\frac{120}{60} = 2$ mole	$\frac{46}{46} = 1$ mole	0	0
Moles at Equ.	$2-y$	$1-y$	y	y

$$K_{eq} = \frac{x \cdot x}{(1-x)\cdot(1-x)} = \frac{y \cdot y}{(2-y)\cdot(1-y)}$$

$$\Rightarrow y = \frac{2}{3}$$

$\therefore$ Mass of $CH_3COOC_2H_5$ at equilibrium

$$= \frac{2}{3} \times 88 =$$

20. $R_1OH + CH_3COOH \rightleftharpoons CH_3COOR_1 + H_2O$

	R_1OH	CH_3COOH	CH_3COOR_1	H_2O
Initial moles	1	1	0	0
Equ. moles	$1-x$	$1-(x+y)$	x	$x+y$

	R_2OH +	$CH_3COOH \rightleftharpoons$	CH_3COOR_2 +	H_2O
Initial moles	1	1	0	0
Equ. moles	$1 - y$	$1 - (x + y)$	y	$x + y$

From question, $x + y = 0.8$ and $\frac{x}{y} = \frac{3}{2}$

$\therefore$ $x = 0.48$ and $y = 0.32$

Now, $K_1 = \frac{x \cdot (x+y)}{(1-x)[1-(x+y)]} = \frac{0.48 \times 0.8}{0.52 \times 0.2} = 3.69$

21. $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$

	$2NO(g)$	$Cl_2(g)$	$2NOCl(g)$
Initial partial pressure	$2P_0$	P_0	0
Equ. partial pressure	$2P_0 - 2x$	$P_0 - x$	$2x$

From question, $(2P_0 - 2x) + (P_0 - x) + 2x = 1$

$\Rightarrow 3P_0 - x = 1$ (1)

and $2x = \frac{1}{4}(P_0 - x)$ (2)

From (1) and (2), $P_0 = 9x$ and $x = \frac{1}{26}$

$$\therefore\ K_P = \frac{(2x)^2}{(2P_0 - 2x)^2 (P_0 - x)} = \frac{13}{256}\ \text{atm}^{-1}$$

22. $S_8(g) \rightleftharpoons 4\,S_2(g)$

	$S_8(g)$	$4\,S_2(g)$
Initial partial pressure	1 atm	0
Equ. partial pressure	$1 - 0.3$ $= 0.7$ atm	4×0.3 $= 1\ .2$ atm

$$\therefore\ K_P = \frac{(1.2)^4}{0.7} = 2.96\ \text{atm}^3$$

23. $HCl(g) + \frac{1}{4}O_2(g) \rightleftharpoons \frac{1}{2}Cl_2(g) + \frac{1}{2}H_2O(g)$

	$HCl(g)$	$\frac{1}{4}O_2(g)$
Initial partial pressure	$730 \times \frac{8}{100}$ $= 58.4$ mm	$730 \times \frac{92}{100}$ $= 671.6$ mm
Equilibrium partial pressure	$58.4 - 58.4 \times 0.08$	$671.6 - \frac{58.4 \times 0.08}{4}$ $= 670.432$ mm

24. $H_3\,BO_3$ + Glycerin $\rightleftharpoons$ complex

	$H_3\,BO_3$	Glycerin	complex
Initial concent.	0.1	a M	0
Equ. Concert	$0.1 - 0.06$ $= 0.04$ M	$(a - 0.06)$ M	0.06 M

Now, $K_{eq} = 0.9 = \frac{0.06}{(0.04) \times (a - 0.06)}$

$\Rightarrow a = 1.73$ M

25. $2A(g) \rightleftharpoons A_2(g);\ K_P = 8 \times 10^8\ \text{atm}^{-1}$

	$2A(g)$	$A_2(g)$
Initial partial pressure	1 atm	0
Partial pressure on complete reaction	0	0.5 atm
Equilibrium partial pressure	$2x$ atm	$0.5 - x \approx 0.5$ atm

Now, $8 \times 10^8 = \frac{0.5}{P_A^2}$

$\Rightarrow P_A = 2.5 \times 10^{-5}$ atm

26. $K_{eq} = 3.8 \times 10^{-7}\ \frac{10^{-6} \times [HCO_3^-]}{[CO_2]}$

$\Rightarrow \frac{[HCO_3^-]}{[CO_2]} = 0.38$

27. $A(g) \rightleftharpoons nB(g)$

	$A(g)$	$nB(g)$
Initial mole	1(say)	0
Equilibrium mole	$1 - \alpha$	$n\alpha$

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

$$\text{Now}\ K_P = \frac{P_B^n}{P_A} = \frac{\left[\frac{n\alpha}{1+\alpha(n-1)} \cdot P\right]^n}{\left[\frac{1-\alpha}{1+\alpha(n-1)} \cdot P\right]}$$

$$= \frac{(n\alpha)^n \cdot P^{n-1}}{(1-\alpha) \cdot [1+\alpha(n-1)]^{n-1}}$$

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

	A	B	C	D
Initial moles	a	a	0	0
Equilibrium moles	$a - x$	$a - x$	x	x

From question, $[A] = 2[C] \Rightarrow a - x = 2x \Rightarrow a = 3x$

Now, $K_{eq} = \frac{K_f}{K_b} = \frac{x \cdot x}{(a-x) \cdot (a-x)}$

$\Rightarrow \frac{2 \times 10^{-3}}{K_b} = \frac{x \cdot x}{2x \cdot 2x}$

$\therefore$ $K_b = 8 \times 10\ –3\ \text{mol}^{-1}\ \text{L S}^{-1}$

29. $$(Cl_2CHCOOH)_2 \rightleftharpoons 2Cl_2CHOOH$$

Initial Conc.	$\frac{0.0129/258}{100/1000}$ $= 5 \times 10^{-4}$ M	0
Equ. Conc.	$5 \times 10^{-4} - x$	$2x$

Now, $K_{eq} = 5 \times 10^{-4} = \frac{(2x)^2}{(5\times10^{-4} - x)}$

$\Rightarrow x = 1.95 \times 10^{-4}$

$\therefore [Cl_2CHOOH] = 3.90 \times 10^{-4}$ M

30. $$NH_2CONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

Initial moles	1	0	0
Equ. moles	$1 - \alpha$	2α	α

From question, $3\alpha = \frac{P \cdot V}{RT}$

$\therefore$ Percentage dissociation of solid $= 100\alpha\,\%$

$= \frac{100 \cdot PV}{3RT}\%$

31. $P_{H_2O,\,eq} = (K_P)^{1/4} = (8.1 \times 10^{-7}) = 0.03$ atm

$P_{H_2O,\,eq}$, actual $= \frac{30.4}{760} = 0.04$ atm

$\therefore$ Mass of water vapour absorbed

$= \frac{(0.09 - 0.03)\times 1.642}{0.0821 \times 300} \times 18$

$= 0.012$ gm

32. Addition of CO will shift second reaction backward. Decrease in Cl_2 will shift the first reaction forward.

33. $$\frac{P_{H_2O}(g)}{P^2_{HCl(g)}} = \frac{P_{H_2O}(g)\times 2}{P^2_{HCl(g),\,new}}$$

$\Rightarrow P_{HCl\,(g),\,new} = \sqrt{2} \times P_{HCl\,(g)}$

34. Ionic form of the reaction is

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

35. $K_1 = \frac{[A^+][B^-]}{[AB]}$ and $K_2 = \frac{[AB_2^-]}{[AB][B^-]}$

Now, $\frac{[A^+]}{[AB_2^-]} = \frac{K_1}{K_2} \cdot [B^-]^2$

36. $$NH_4HS(s) \rightleftharpoons NH_3\,(g) + H_2S(g)$$

Equ. partial pressure	$\frac{P}{2}$ atm	$\frac{P}{2}$ atm
New Equ.partial pressure	P atm	P' atm

Now, $\frac{P}{2} \times \frac{P}{2} = P \times P'$

$\Rightarrow$ P′ = 0.25 P

37. $$N_2 \quad + \quad 3H_2 \rightleftharpoons 2NH_3$$

Equ. partial pressure	100 mm	400 mm	1000 mm
New equ. partial pressure	$100 - a + x$	$400 + 3x$ $= 700$ mm	$1000 - 2x$ $= 800$ mm

$\therefore x = 100$ mm

Now, $K_P = \frac{1000^2}{100 \times 400^3} = \frac{800^2}{P_{N_2} \times 700^3}$

$\Rightarrow P_{N_2} = 11.94$ mm

$K_1 = \frac{[B]}{[A]}, K_2 = \frac{[C]}{[A]}$

Now, $X_A = \frac{[A]}{[A]+[B]+[C]} = \frac{[A]}{[A]+K_1[A]+K_2[A]}$

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

39. CO and H_2 are initially in 1 : 3 mole ratio, as they are formed by 2nd reaction.

	CO	$+\ 2H_2 \rightleftharpoons$	CH_3OH
Initial moles	1	3	0
Equilibrium moles	$1 - 0.25$ $= 0.75$	$3 - 0.25 \times 2$ $= 2.5$	0.25

Total moles = 0.75 + 2.5 + 0.25 = 3.5

Now, $K_P = \frac{0.25}{0.75 \times (2.5)^2} \times \left(\frac{P}{3.5}\right)^{-2} = 6.23 \times 10^{-3}$

$\therefore P = 10.24$ bar

40.

	$A \rightleftharpoons$	$B +$	$C; K_1 = 10^6$
Initial moles	1	0	0
Equilibrium moles	$1 - x + y$	$x - y$	x

	$B +$	$D \rightleftharpoons$	$A;\quad K_2 = 10^{-6}$
	x	1	1
Equilibrium moles	$x - y$	$1 - y$	$1 + y - x$

As $K_1 >> 1$, we may assume $x \approx 1$

Now, $K_2 = \dfrac{(1+y-x)}{(x-y)(1-y)} \approx \dfrac{y}{(1-y)\cdot(1-y)}$

As $K_2 << 1$, we may assume $y << 1$

$$K_2 = \frac{y}{(1-y)(1-y)} \approx y$$

$\therefore$ [A] $= 1 - x + y \approx y = 10^{-6}$ M

41.

	A $\rightleftharpoons$	B
Initial	a M	b M
Equilibrium	$(a-x)$ M	$(b+x)$ M

Now, $K_{eq} = \dfrac{K_1}{K_2} = \dfrac{b+x}{a-x}$

$$\therefore\ x = \frac{K_1 a - K_2 b}{K_1 + K_2}$$

42. $r_b = K_b \cdot P_{\mathrm{C(g)}}$

43. $\Delta G° = -2.303RT \cdot \ln K_p°$

$\Delta H° - T \cdot \Delta S°$

or $-2.303 \times 8.314 \times T \times \ln 1.0 = 240 \times 10^3 - T \times 50$

$\therefore\ T = 4800\ K$

44. $\Delta G° = -2.303RT \cdot \ln K_{\mathrm{eq}}$

$\Rightarrow -2.303 \times 10^3 = -2.303 \times 2 \times 500 \times \ln K_{\mathrm{eq}}$

$\therefore\ K_{\mathrm{eq}} = 10$

Now, $K_{eq} = \dfrac{P_{\mathrm{HI}}}{P_{\mathrm{H_2}}^{1/2} \times P_{\mathrm{I_2}}^{1/2}}$

$$\Rightarrow \frac{10}{P_{\mathrm{H_2}}^{1/2} \times (0.001)^{1/2}}$$

$\therefore\ P_{\mathrm{H_2}} = 1000$ atm

45. $\Delta G° = -RT \cdot \ln \dfrac{[B]}{[\alpha]} = -RT \cdot \ln \dfrac{64}{36} = -RT \cdot \ln 1.78$

46. There is no net change at equilibrium.

47. K_{eq} at 27°C, $K_1 = \dfrac{2 \times 10^{-3}}{2 \times 10^{-4}} = 4$

and K_{eq} at 127°C, $K_2 = \dfrac{8 \times 10^{-2}}{4 \times 10^{-3}} = 20$

Now, $\ln \dfrac{K_2}{K_1} = \dfrac{\Delta H}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

or, $2.303 \log \dfrac{20}{4} = \dfrac{\Delta H}{R}\left(\dfrac{1}{300} - \dfrac{1}{400}\right)$

$\therefore\ \Delta H = 2.303 \times 8.314 \times 1200 \log(5)$ J/mol

48.

	nA $\rightleftharpoons$	A_n
Initial moles	1	0
Equilibrium moles	$1-x$	$\dfrac{x}{n}$

Now, $K_C = \dfrac{\left(\dfrac{x/n}{V}\right)}{\left(\dfrac{1-x}{V}\right)^n} = \dfrac{x \cdot V^{n-1}}{(1-x)^n \cdot n}$

$$\approx \frac{x \cdot V^{n-1}}{n} (\text{as } x << 1)$$

Now, total moles $= (1-x) + \dfrac{x}{n} = 1 + x \cdot \left(\dfrac{1}{n} - 1\right)$

$$= 1 + \frac{n \cdot KC}{V^{n-1}} \cdot \left(\frac{1-n}{n}\right) = 1 + \frac{(1-n)\cdot K_C}{V^{n-1}}$$

49. $\alpha = \dfrac{\mathrm{M} - \mathrm{M_{mix}}}{(n-1)\cdot \mathrm{M_{mix}}} = \dfrac{\mathrm{M} - \mathrm{M_{mix}}}{(2-1)\cdot \mathrm{M_{mix}}} = \dfrac{\mathrm{M}}{\mathrm{M_{mix}}} - 1$

$$= \frac{\mathrm{M}}{\left(\dfrac{dRT}{P}\right)} - 1 = \frac{PM}{dRT} - 1$$

50. $n_{\mathrm{NO}} = \dfrac{0.4 \times 250}{RT} = \dfrac{100}{RT}$ $\quad n_{\mathrm{O_2}} = \dfrac{0.8 \times 100}{RT} = \dfrac{80}{RT}$

	2 NO +	$\mathrm{O_2}$	$\rightarrow 2\,\mathrm{NO_2} \rightleftharpoons$	$\mathrm{N_2O_4}$
Initial moles	$\dfrac{100}{RT}$	$\dfrac{80}{RT}$	0	0
Final moles	0	$\dfrac{30}{RT}$	$\dfrac{100}{RT} - x$	$\dfrac{x}{2}$

From question, $\dfrac{30}{RT} + \dfrac{100}{RT} - x + \dfrac{x}{2} = \dfrac{0.3 \times 350}{RT}$

$$\therefore\ x = \frac{50}{RT}$$

Now, K_P of second reaction

$$= \frac{P_{N_2O_4}}{P^2_{\mathrm{NO_2}}} = \frac{\dfrac{x}{2}}{\left(\dfrac{100}{RT} - x\right)^2} \times \left(\frac{0.3}{\dfrac{0.3 \times 350}{RT}}\right)^{-1}$$

= 3.5 atm

51.

	$\mathrm{N_2}$ +	$3\mathrm{H_2} \rightleftharpoons$	$2\mathrm{NH_3}$
Initial moles	1	3	0
Equilibrium moles	$1-x$	$3-3x$	$2x$

From question, $\dfrac{2x}{4-2x} = a$

$$\Rightarrow x = \frac{2a}{1+a}$$

Now, $K_P = \frac{(2x)^2}{(1-x)(3-3x)^3}\cdot\left(\frac{P}{4-2x}\right)^{-2}$

$$= \frac{4x^2\cdot(4-2x)^2}{27(1-x)^4\cdot P^2}$$

or, $\sqrt{K_P} = \frac{2x\cdot(4-2x)}{\sqrt{27}(1-x)^2\cdot P} = \frac{2\cdot\left(\frac{2a}{1+a}\right)\cdot\left(4-\frac{4a}{1+a}\right)}{\sqrt{27}\cdot\left(1-\frac{2a}{1+a}\right)^2\cdot P}$

$$= \frac{32a}{\sqrt{27}\cdot(1-a)^2\cdot P}$$

$\therefore \frac{a}{(1-a)^2}\alpha P$

52. $K_P = \frac{\alpha^2\cdot P}{1-\alpha^2}$

$\Rightarrow \frac{(0.3)^2\times 1}{1-(0-3)^2} = \frac{\alpha^2\times 0.1}{1-\alpha^2}$

$\Rightarrow \alpha = 0.973$

53. $K_P = P^2$

Now, $\ln\frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$

or, $\ln\frac{P_2^2}{(7\times 10^{-3})^2} = \frac{3360}{2}\left(\frac{1}{300}-\frac{1}{400}\right)$

$\Rightarrow P_2 = 1.4\times 10^{-2}$ atm

54. $CO(g) + H_2(g) \rightleftharpoons CO_2(g) + H_2(g)$

Initial	1	5	0	1
Equilibrium	$1-x$	$5-x$	x	$1-x$

Now, $K_{eq} = \frac{1}{3} = \frac{x\cdot(1+x)}{(1-x)\cdot(5-x)}$

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

55. $NH_2COONH_4(s) \rightleftharpoons N_2 + 3H_2 + CO + \frac{1}{2}O_2$

Equilibrium partial pressure	$\frac{22}{5.5}$ $= 4$	$\frac{3\times 22}{5.5}$ $= 12$	$\frac{22}{5.5}$ $= 4$	$\frac{22}{2\times 5.5}$ $= 2$

Now, $K_p = 4\times(12)^3\times 4\times(2)^{1/2} = 27\times(2)^{10.5}$

56. $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

Equ. partial pressure	$2P_0$	P_0
New Equ. partial pressure	$3P_0$	P_0

Now, $K_P = (2P_0)^2\cdot P_0 = (3P_0)^2\cdot P$

$\Rightarrow P = \frac{4}{9}P_0$

Now, $\frac{3P_0+P}{3P_0} = \frac{31}{27}$

57. $\Delta H^\circ = \Delta E^\circ + \Delta n_g\cdot RT$

$$= (+30) + (3-2)\times\frac{2}{1000}\times 300 = +30.6 \text{ K cal}$$

Now, $\Delta G^\circ - RT\cdot\ln K_{\text{eq}} = \Delta H^\circ - T\cdot\Delta S^\circ$

or, $-2\times 300\times\ln K_{\text{eq}} = 30.6\times 10^3 - 300\times 100$

$\Rightarrow \ln K_{\text{eq}} =$

$\therefore K_{\text{eq}} = \frac{1}{e}$

58. *trans* $\rightleftharpoons$ *Cis*; $\Delta G^\circ = 22.112 - 30.426 = -8.314$ KJ

Now, $\Delta G^\circ = -RT\cdot\ln\frac{[Cis]}{[trans]}$

$\Rightarrow -8.314\times 10^3 = -8.314\times 300\times\ln\frac{[Cis]}{[trans]}$

$\therefore \frac{[Cis]}{[trans]} = \frac{28}{1}$

59. $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

Initial moles	2	5	0	2
Equilibrium moles	$2-x$	$5-x$	x	$2+x$

Now, $K_{\text{eq}} = 3.0 = \frac{x\cdot(2+x)}{(2-x)(5-x)}$

$\Rightarrow x = 1.5$

$\therefore [H_2] = \frac{2+x}{2} = 1.75$ M

60. $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

$\frac{X}{2}$ bar $\quad \frac{X}{2}$ bar

$\therefore \Delta G^\circ = -RT\cdot\ln K_P^\circ$

$= -\text{RT}\ln\left(\frac{X}{2}, \frac{X}{2}\right) = -2RT(\ln\times - \ln 2)$

Section B (One or More than one Correct)

1. $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

Equ. partial pressure	0.2 atm	0.2 atm
Second Equ. partial pressure	0.5 atm	P atm

Now, $K_P = 0.2 \times 0.2 = 0.5 \times P \Rightarrow P = 0.08$

2. $\Delta ng = 0$

3. $N_2O_5(g) \rightleftharpoons 2NO_2(g) + \frac{1}{2}O_2(g)$

	$N_2O_5(g)$	$2NO_2(g)$	$\frac{1}{2}O_2(g)$
Initial partial pressure	P_0	0	0
Equ. partial pressure	$P_0(1-\alpha)$	$2\,\alpha\,P_0$	$\frac{\alpha P_0}{2}$

and $\alpha = \dfrac{M-2D}{\left(\frac{5}{2}-1\right)\cdot 2D} = \dfrac{M-2D}{3D}$

Total equilibrium pressure $= P_0(1-\alpha) + 2\,\alpha\,P_0 + \dfrac{\alpha P_0}{2} = P_0\left(1+\dfrac{3\alpha}{2}\right)$

4. Le Chatelier's principle

5. Theory based

6. Theory based

7. Vapour pressure of a particular liquid system depends only on temperature.

8. $Cl_2(g) \rightleftharpoons 2Cl(g)$ $\quad T\uparrow \quad P\downarrow$

9. Addition of insert gas at constant pressure shifts the equilibrium in the direction of increase in moles of gases.

10. Decrease in pressure favors the reaction is the direction of increase in moles of gas and hence, B should be monomer.

11. $\Delta_f G^\circ : NO_2 > N_2O_5 > NO$

12. At $300K : \Delta G^\circ = (-41) - 300 \times (-0.04)$
$= -29$ KJ/mol

Hence, the reaction is spontaneous in forward direction.

At 1200 K : $\Delta G^\circ = (-33) - 1200 \times (-0.03)$
$= +3$ KJ/mol

Hence, the reaction is spontaneous in backward direction.

13. Theory based.

14. Theory based.

15. $S = A\cdot e^{-\Delta H/RT}$

$\Rightarrow \ln s = \ln\ A - \dfrac{\Delta H}{RT}$

Positive slope represents that ΔH = negative.

16. Theory based.

17. $K_{P_2} = P_{Cl_2(g)} = 0.2$ atm

$$K_{P_1} = P_{Cl_2(g)} \cdot P^8_{H_2O(g)} = 0.2\times(0.001)^8 = 2\times10^{-25}\ \text{atm}^9$$

$P_{H_2O(g)}$ = Vapour pressure of ice.

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

	$PCl_5(g)$	$PCl_3(g)$	$Cl_2(g)$
Initial moles	5	0	0
Moles at equilibrium	$5-x$	x	x

From question, $(5-x)+x+x+4 = \dfrac{4.8\times112}{0.0821\times546}$

$\Rightarrow x = 3$

$\therefore\ \alpha = \dfrac{x}{5} = 0.6$

and $K_P = \dfrac{x\cdot x}{5-x}\cdot\left(\dfrac{4.8}{12}\right) = 1.8$ atm

19. $4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)$

	$4HCl(g)$	$O_2(g)$	$2Cl_2(g)$	$2H_2O(g)$
Initial partial pressure	1.0 atm	0.25 atm	0	0.4 atm
On completion	0	0	0.5 atm	0.4 atm
Equ. partial pressure	$4x$ atm	x atm	0.5 atm	0.4 atm

$K_P = 5\times10^{12} = \dfrac{(0.5)^2(0.4)^2}{(4x)^4\times x}$

$\Rightarrow x = 5\times10^{-4}$

20. $\Delta G^\circ = 2\times\Delta_f G^\circ_{NO_2(g)} - \Delta_f G^\circ_{N_2O_4(g)} = 0$

$\Rightarrow K_P{}^\circ = 1$

Now, $\Delta G = \Delta G^\circ + \mathrm{RT}\cdot\ln Q = 0 + RT\cdot\ln\dfrac{P^2_{NO_2}}{P_{N_2O_4}}$

$= RT\cdot\ln\dfrac{10^2}{10}$ = positive.

21. $AB_2\,(g) + A(s) \rightleftharpoons 2\,AB(g)$

Initial partial pressure	0.7 bar	0
Equ. partial pressure	$(0.7 - x)$ bar	$2x$ bar
Second equ. partial pressure	y bar	$(0.4 - y)$ bar

From question, $(0.7 - x) + 2x = 0.95$

$\Rightarrow x = 0.25$

$$\therefore\ K_P = \frac{(2x)^2}{(0.7-x)} = \frac{(0.5)^2}{0.45} = \frac{5}{9}$$

$$\text{Now, } \frac{5}{9} = \frac{(0.4-y)^2}{y}$$

$\Rightarrow y = 0.13$

$\therefore$ At second equilibrium, the volume per cent of

$$AB_2 = \frac{0.13}{0.4} \times 100 = 32.5\%$$

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

Initial moles	1	1	0
Equ. moles	$1 - x$	$1 + x$	x
	≈ 1	≈ 1	$= 0.004$

$$\therefore\ K_C = \frac{1 \times 0.004}{1} \times \left(\frac{1}{10}\right) = 0.0004\ \text{M}$$

23. $\Delta G° = -RT \cdot \ln K_P°$

$\Rightarrow -1743 = -\,8.3 \times 300 \times \ln K_P°$

$\therefore\ K_P° = 2$

24. $$K_1 = \frac{1}{K_2 \times K_3} = \frac{1}{0.24}$$

As $\Delta n_g = 0$, $[A] + [B] + [C] = 1$ M

25. Addition of water will shift the reaction in the direction of increase in mole of *aq* species.

Section C (Comprehensions)

Comprehension I

1. For $SrCl_2 \cdot 2H_2O(s)$, $P_{H_2O} = (2.56 \times 10^{-10})^{1/4} = 0.004$ atm

For $Na_2HPO_4 \cdot 7H_2O$ $P_{H_2O} = (2.43 \times 10^{-13})^{1/5} = 0.003$ atm

For $Na_2SO_4(s)$, $P_{H_2O} = (1.024 \times 10^{-27})^{1/10} = 0.002$ atm

As P_{H_2O} is minimum for $Na_2SO_4(s)$, it is the best dehydrating agent.

2. For $Na_2SO_4(s)$, $10H_2O(s)$ to be efflorescent, $P_{H_2O} < 0.002$ atm

or $\left(0.04 \times \dfrac{R.H.}{100}\right) < 0.002$

$\Rightarrow R.H. < 5\%$

3. $Na_2HPO_4 \cdot 7H_2O(s)$ to be deliquescent, $P_{H_2O} >$ 0.003 atm

or, $\left(0.04 \times \dfrac{R.H.}{100}\right) > 0.003$

$\Rightarrow R.H. > 7.5\%$

Comprehension II

4. $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

Initial moles	0.2	a(say)	0
Moles at equ.	$0.2 - x$	$a - 2x$	x
	$= 0.1$	$= a - 0.2$	$= 0.1$

$$\text{Total moles} = 0.1 + (a - 0.2) + 0.1 = \frac{7.5 \times 2.463}{0.0821 \times 750}$$

$\Rightarrow a = 0.3$

$$\text{Now, } K_P = \frac{0.1}{0.1 \times (0.1)^2} \times \left(\frac{7.5}{0.3}\right)^{-2} = 0.16\ \text{atm}^{-2}$$

5. $$K_C = \frac{K_P}{(RT)^{\Delta n_g}} = \frac{0.16}{(0.0821 \times 750)^{-2}} = 607\ \text{M}^{-2}$$

6. $$P = \frac{(0.2 + 0.3) \times 0.0821 \times 750}{2.463} = 12.5\ \text{atm}$$

Comprehension III

7. $$\begin{array}{lcccc} & C_2H_5OH + & CH_3COOH \rightleftharpoons & CH_3COOC_2H_5 + & H_2O \\ \text{Initial moles} & & & & \\ & a & a & 0 & 0 \\ \text{Equilibrium moles} & & & & \\ & a-x & a-x & x & x \end{array}$$

From question, $\frac{x}{2a} = 0.333 = \frac{1}{3}$

$\Rightarrow x = \frac{2}{3}a$

Now, $K_{eq} = \frac{x \cdot x}{(a-x)\cdot(a-x)} = 4$

8. $$\begin{array}{lcccc} & C_2H_5OH + & CH_3COOH \rightleftharpoons & CH_3COOC_2H_5 + & H_2O \\ \text{Initial moles} & & & & \\ & \frac{a}{3} & \frac{2a}{3} & 0 & 0 \\ \text{Equilibrium moles} & & & & \\ & \frac{a}{3}-x & \frac{2a}{3}x & x & x \end{array}$$

Now, $K_{eq} = 4 = \frac{x \cdot x}{\left(\frac{a}{3}-x\right)\left(\frac{2a}{3}-x\right)}$

$\Rightarrow x = 0.2833\ a$

$\therefore$ Fraction of alcohol reacted $= \frac{x}{a/3} = 0.85$

9. Solution of $0.7 = \frac{x}{a} \times 100 = 66.67\%$

Comprehension IV

10. $$\begin{array}{lccc} & 2HI(g) & \rightleftharpoons & H_2(g) + I_2(g) \\ \text{Initial moles} & 1(\text{say}) & & 0 \quad\quad 0 \\ \text{Equilibrium moles} & 1 - 0.2222 = 0.7778 & & 0.1111 \quad 0.1111 \end{array}$$

$\therefore\ K_{eq} = \frac{0.1111 \times 0.1111}{(0.7778)^2} = \frac{1}{49} \approx 0.02$

11. In the presence of $I_2(g)$, the extent of dissociation of HI will decrease.

12. Addition of He(g) will not affect thequilibrium.

Comprehension V

13. $$\begin{array}{lcc} & NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + & H_2S\ (g) \\ \text{Initial partial pressure} & P\ \text{mm} & 0 \\ \text{Equilibrium partial pressure} & (P + x)\text{mm} & x\ \text{mm} \end{array}$$

From question, $P + x = 625$ and $(P + x) + x = 725$

$\therefore\ x = 100$ and $P = 525$

14. $K_P = (P + x) \cdot x = 625 \times 100\ \text{mm}^2$

$\therefore\ K'_P$ (required) $= \frac{1}{K_P} = 1.6 \times 10^{-5}\ \text{mm}^{-2}$.

15. $P_{NH_3} = P_{H_2S} = \sqrt{K_P} = 250$ mm

16. Minimum mass of $NH_4HS\ (s)$ needed.

$$= \frac{\frac{250}{760} \times 5.0}{0.0821 \times 300} \times 51\ \text{gm}$$

Comprehension VI

17. $K_{eq} = \frac{A_f}{A_b} \cdot e^{-\Delta H/RT} = e^{\frac{-(-24.942\times 10^3)}{8.314\times 300}} = e^{10}$

18. $\frac{K_b}{K_f} = \frac{1}{K_{eq}} = e^{-10}$

$\Delta \text{H} = Ea_f - Ea_b = Ea_f - \frac{3}{2} Ea_f \;\; \Rightarrow Ea_f = 2 \cdot (-\Delta \text{H})$

Now, $K_f = A_f \cdot e^{-Ea_f/RT} = 1 \times e^{\frac{-2\times 24.942\times 10^3}{8.314\times 300}} = e^{-20}$

and $K_b = e^{-30}$

Comprehension VII

20.

	$2SO_3 \rightleftharpoons$	$2SO_2$ +	O_2
Equilibrium moles	$1-\alpha$	α	$\frac{\alpha}{2}$

Now. $K_P = \frac{\alpha^2 \cdot \frac{\alpha}{2}}{(1-\alpha)^2} \cdot \left(\frac{K_P}{1+\frac{\alpha}{2}}\right)^{\prime}$

$\Rightarrow \alpha = \frac{2}{3}$

21.

	$2NH_3 \rightleftharpoons$	N_2	+	$3H_2$
Equilibrium moles	$1-\alpha$	$\frac{\alpha}{2}$		$\frac{3\alpha}{2}$
	$=\frac{1}{3}$	$=\frac{1}{3}$		$= 1$

Now, $K_P = \frac{\frac{1}{3}\times 1^3}{\left(\frac{1}{3}\right)^2} \times \left(\frac{50}{\left(\frac{5}{3}\right)}\right)^2 = 2700 \text{ atm}^2$

22. $n_{\text{initial}} \times (17 + 28 + 2 + 20) = 134 \Rightarrow n_{\text{initial}} = 2$

	$2NH_3 \rightleftharpoons$	N_2 +	$3H_2$
Initial moles	2	2	2
Moles at equilibrium	$2 - 2x$	$2 + x$	$2 + 3x$
	$= 1.0$	$= \frac{134\times 0.5224}{28}$	$= 3.5$

$\therefore\; x = 0.5$

Now, $K_P = 2700 = \frac{2.5\times(3.5)^3}{(1.0)^2} \times \left(\frac{P}{9}\right)^2$

$\Rightarrow\; P = \sqrt{\frac{2700\times 81}{2.5\times(3.5)^3}}$ atm

---

Comprehension VIII

	N_2	+ $3H_2$	$\rightleftharpoons$ $2NH_3$; K_{P_1}
Initial partial pressure	$9P$	$13P$	0
Equilibrium partial pressure	$9P - x - y$	$13P - 3x - 2y$	$2x$

	N_2	+ $2H_2$	$\rightleftharpoons$ N_2H_4; K_{P_2}
Initial partial pressure	$9P$	$13P$	0
Equilibrium partial pressure	$9P - y - x$	$13P - 2y - 3x$	y

From question, $P_{NH_3} = 2x = P_0 \;\Rightarrow\; x = \frac{P_0}{2}$

$P_{H_2} = 13P - 3x - 2y = 2P_0$

and $P_{\text{total}} = (9P - x - y) + (13P - 3x - 2y) + 2x + y$
$= 7P_0$

$\therefore\; y = \frac{3P_0}{2}$ and $P = \frac{P_0}{2}$

$K_{P_1} = \frac{P_{NH_3}^2}{P_{N_2} \cdot P_{H_2}^3} = \frac{P_0^2}{\frac{5P_0}{2} \times (2P_0)^3} = \frac{1}{20P_0^2}$

$\therefore\; K_P$ (required) $= 20\, P_0^2$

24. $K_{P_2} = \frac{P_{N_2H_4}}{P_{N_2} \cdot P_{H_2}^2} = \frac{\left(\frac{3P_0}{2}\right)}{\frac{5P_0}{2} \times (2P_0)^2} = \frac{3}{20P_0^2}$

Section D (Assertion–Reason)

1. Direction of shifting of equilibrium will depend on relative values of *a* and *b*.
2. Equilibrium opposes the changes.
3. Theory based
4. Theory based
5. Theory based
6. $K_P = K_C \cdot (RT)^{\Delta n_g}$
7. Theory based
8. Exothermic direction is favoured on lowering temperature.
9. $NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$
10. On decreasing the volume, moles of A(*g*) as well as B(*s*) will increase.

Section E (Column Match)

1. Theory based
2. $K_P = K_C \cdot (RT)^{\Delta n_g}$
3. Le Chatelier's principle
4. Le Chatelier's principle
5. Le Chatelier's principle
6. Le Chatelier's principle
7. Le Chatelier's principle
8. Le Chatelier's principle
9. $P_{CO_2} = K_P = 2.463 \text{ atm}$

   $\therefore\ n_{CO_2}$ at equilibrium $= \dfrac{2.463\times 15}{0.0821\times 900} = 0.5$

   (A) % of $CaCO_3$ decomposed

   $= \dfrac{0.5}{1.0}\times 100 = 50\%\ (\text{Eqn})$

   (B) % of $CaCO_3$ decomposed

   $= \dfrac{0.5}{0.5}\times 100 = 100\%\ (\text{Eqn})$

   (C) % of $CaCO_3$ decomposed $= 100\%$ (non-Eqn)
10. Le Chatelier's principle

Section F (Subjective)

Single-digit Integer Type

1. $2H_2S(g) \rightleftharpoons 2H_2(g) + S(g);\ K_e = 10^{-6}$

	$2H_2S(g)$	$2H_2(g)$	$S(g)$
Initial moles	0.1	0	0
Equilibrium moles	$0.1 - x$ $\simeq 0.1$	x	$\dfrac{x}{2}$

Now,

$$K_C = 10^{-6} = \frac{x^2 \times \frac{x}{2}}{(0.1)^2} \times \left(\frac{1}{0.4}\right)$$

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

$\therefore$ Percentage dissociation $= \dfrac{2\times 10^{-3}}{0.1}\times 100 = 2\%$

2. $V_{CF_4} = 500 - 300 = 200 \text{ ml} = V_{CO_2}$

$\therefore\ V_{COF_2} = 500 - 2\times 200 = 100 \text{ ml}$

Hence, $P_{CF_4} = P_{CO_2} = \dfrac{200}{500}\times 10 = 4 \text{ atm}$

$P_{COF_2} = \dfrac{100}{500}\times 10 = 2 \text{ atm}$

$K_p = \dfrac{4\times 4}{2^2} = 4$

3. Initial: $n_{PCl_5} = \dfrac{62.55}{208.5} = 0.3$ and $n_{Cl_2} = \dfrac{4.48}{22.4} = 0.2$

	$PCl_5 \rightleftharpoons$	PCl_3	$+\ Cl_2$
Initial moles	0.3	0	0.2
Equilibrium moles	$0.3 - x$	x	$0.2 + x$

Now,

$$K_p = \frac{x\cdot(0.2+x)}{(0.3-x)}\cdot\left(\frac{p}{0.5+x}\right) = \frac{x(0.2+x)}{(0.3-x)}\times\frac{RT}{V}$$

$$\text{or, } 8 = \frac{x(0.2+x)}{0.3-x}\times\frac{0.0821\times 546}{4.48}$$

$$\Rightarrow x = 0.2$$

$$\therefore \text{ Final pressure } = \frac{(0.5+x)\times 0.0821\times 546}{4.48}$$

$$= 7 \text{ atm}$$

4. NaOH is used to neutralize acetic acid. From the given data, half of the acid taken is neutralize.

	CH_3COOH +	$C_2H_5OH \rightleftharpoons$	$CH_3COOC_2H_5$ +	H_2O
Initial moles	a	a	0	0
Equilibrium moles	$a-\frac{a}{2}$	$a-\frac{a}{2}$	$\frac{a}{2}$	$\frac{a}{2}$

$$\therefore\ K_{eq} = \frac{\frac{a}{2}\times\frac{a}{2}}{\frac{a}{2}\times\frac{a}{2}} = 1$$

5.

	$2HI \rightleftharpoons$	H_2 +	I_2
Equilibrium moles	$1-0.8$ $=0.2$	0.4	0.4

$$\therefore\ K_{eq} = \frac{0.4\times 0.4}{(0.2)^2} = 4$$

Now,	H_2 +	$I_2 \rightleftharpoons$	$2HI$
Initial moles	2	2	0
Equilibrium moles	$2-x$	$2-x$	$2x$

$$K_{eq} = \frac{1}{4} = \frac{(2x)^2}{(2-x)(2-x)}$$

$\Rightarrow x = 0.4$

Now, n_{eq} of $I_2 = n_{eq}$ of $Na_2S_2O_3$

or, $(2-x)\times 2 = V\times(1.6\times 1)$

$\Rightarrow V = 2$ L

6.

	$Cl_2CHCOOH$ +	$C_5H_{10} \rightleftharpoons$	$Cl_2CHCOOC_5H_{11}$
I: Initial moles	1	4	0
Equilibrium moles	$1-x$	$4-x$	$x = 0.5$
II: Initial moles	1	a	0
Equilibrium moles	$1-y$	$a-y$	$y = 0.6$

$$\text{Now, } K_{eq} = \frac{0.5}{0.5\times 3.5}\times 0.7 = \frac{0.6}{0.4\times(a-0.6)}\times 0.72$$

$\Rightarrow a = 5$

7. n_{CO_2} at equilibrium = 0.05

$\therefore$ Minimum mass of $CaCO_3$ needed = 0.05 × 100
= 5 gm

8. $$Ag^+(aq) + Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

	$Ag^+(aq)$	$Fe^{2+}(aq)$	$Fe^{3+}(aq)$	$Ag(s)$
Initial moles	$\frac{500\times0.9}{1000}$ = 0.45	$\frac{500\times1.0}{1000}$ = 0.50	0	0
Equilibrium moles	$0.45-x$	$0.50-x$	x	x

Now, $n_{eq}\ Fe^{2+} = n_{eq}\ MnO_4^-$

or, $$\frac{(0.50-x)}{1000}\times30\times1 = \frac{25\times0.06}{1000}\times5$$

$\Rightarrow x = 0.25$

$$\therefore\ K_{eq} = \frac{x}{(0.45-x)(0.5-x)} = 5\ M^{-1}$$

9. $$Sb_2S_3(s) + 3H_2(g) \rightleftharpoons 2Sb(s) + 3H_2S(g)$$

	$Sb_2S_3(s)$	$3H_2(g)$	$2Sb(s)$	$3H_2S(g)$
Initial moles	0.01	0.01	0	0
Equ. moles	$0.01-x$	$0.01-3x$ $= 5\times10^{-3}$	$2x$	$3x = \frac{1.19}{238}$ $= 5\times10^{-3}$

Now, $$K_c = \frac{(5\times10^{-3})^3}{(5\times10^{-3})^3} = 1$$

10. $$H_2O + D_2O \rightleftharpoons 2HDO$$

	H_2O	D_2O	$2HDO$
Initial moles	28	28	0
Equ. moles	28 – 14 = 14	28 – 14 = 14	2 × 14 = 28

$$K_C = \frac{(28)^2}{14\times14} = 4$$

11. $$3A_2(g) \rightleftharpoons A_6(g),\ K_{p_1} = 1.6\ atm^{-2}$$

	$3A_2(g)$	$A_6(g)$
Initial partial pressure	$2P_0$	0
Equilibrium partial pressure	$2P_0-3a-b$	a

$$A_2(g) + C(g) \rightleftharpoons A_2C(g),\ K_{p_2} = x\ atm^{-1}$$

	$A_2(g)$	$C(g)$	$A_2C(g)$
Initial partial pressure	$2P_0$	P_0	0
Equilibrium partial pressure	$2P_0-b-3a$	P_0-b	b

From question, $a = 0.2$,

$$\frac{P_{A_6}}{P_{A_2}{}^3} = 1.6 \Rightarrow \frac{0.2}{P_{A_2}{}^3} = 1.6$$

$$\Rightarrow P_{A_2} = 0.5 = 2P_0 - 3a - b$$

and $(2P_0 - 3a - b) + a + (P_0 - b) + b = 1.4$

$\Rightarrow P_0 = 0.7$ and $b = 0.3$

Now, $$K_{p_2} = \frac{b}{(2P_0-3a-b)(P_0-b)} = \frac{0.3}{0.5\times.4}$$
$$= 1.5\ atm^{-1}$$

12. Initial partial pressure of IBr (g)

$$= \frac{8.28}{207}\times\frac{0.0821\times500}{0.1642} = 10$$

$$2IBr(g) \rightleftharpoons I_2(g) + Br_2(g)$$

	$2IBr(g)$	$I_2(g)$	$Br_2(g)$
Initial partial pressure	10	0	0
Equilibrium partial pressure	$10-2x$	x	$x = 4$

$$\therefore\ K_p = \frac{4\times4}{(2)^2} = 4$$

13. $$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

	$H_2(g)$	$I_2(g)$	$2HI(g)$
I: Initial moles	1	3	0
Equilibrium moles	$1-\frac{x}{2}$	$3-\frac{x}{2}$	x
II: Initial moles	3	3	0
Equilibrium moles	$3-x$	$3-x$	$2x$

Now, $K_{eq} = \dfrac{(x)^2}{\left(1-\dfrac{x}{2}\right)\left(3-\dfrac{x}{2}\right)} = \dfrac{(2x)^2}{(3-x)(3-x)}$

$\Rightarrow x = \dfrac{3}{2}$

$\therefore K_{eq} = 4$

14. $N_2O_5(g) \rightleftharpoons N_2O_3(g) + O_2(g);\ K_{C_1} = 2.5\ \text{M}$

Initial moles	4	0	0
Equilibrium moles	$4 - x$	$x - y$	$x + y$

$N_2O_3(g) \rightleftharpoons N_2O(g) + O_2(g);\ K_{C_2}$

	x	0	0
Equilibrium moles	$x - y$	y	$x + y$

From question, $[O_2] = \dfrac{x+y}{2} = 2.5$

$\Rightarrow x + y = 5$

And $K_{C_1} = 2.5 = \dfrac{(x-y)\times 5}{4-x}\times\dfrac{1}{2} = \dfrac{(5-2y)\times 5}{(y-1)}\times\dfrac{1}{2}$

$\Rightarrow y = 2$

$\therefore [N_2O] = \dfrac{y}{2} = 1\ \text{M}$

15. In left chamber, $P_{H_e} = 2$ atm

$\therefore P_{NH_3} = P_{H_2 3} = \dfrac{4-2}{2} = 1\ \text{atm}$

$\therefore K_p = 1\times 1 = 1\ \text{atm}^2$

Four-digit Integer Type

1. P-xyloquinone + M.W $\rightleftharpoons$ P-xylohydroquinone + M.B.

Initial conc.	0.012 M	0	0.24 M	10^{-3} M
Equ. con.	0.012 + 4×10^{-5}	4×10^{-5} M	0.24 – 4 $\times 10^{-5}$	$10^{-3} - \dfrac{4}{100} \times 10^{-3}$
	≈ 0.012		≈ 0.24 M	0.96×10^{-3}m

$\therefore K_{eq} = \dfrac{0.24\times 0.96\times 10^{-3}}{0.012\times 4\times 10^{-5}} = 480$

2. $6HCHO \rightleftharpoons C_6H_{12}0_6;\ K_{eq} = 6.4 \times 10^{19}$

Initial conc.	0	1 M
Equ. con.	$6x$	$1 - x = 1$ M

Now, $K_{eq} = 6.4 \times 10^{19} = \dfrac{1}{[HCHO]^6}$

$\Rightarrow [HCHO] = 5 \times 10^{-4}$ M

$= 5 \times 10^{-4} \times 30$ g/L

$= 15$ mg/L

3. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Initial equ. moles	2	2	2
Moles on adding Cl_2	2	2	$2 + x$
Final Equ. moles	$2 + y$	$2 - y$	$2 + x - y$

From question, $(2 + y) + (2 - y) + 2 + (x - y) = 2 \times 6$

or, $x - y = 6$

and $K_c = \dfrac{2\times 2}{2}\times\dfrac{1}{V} = \dfrac{(2-y)\times(2+x-y)}{(2+y)}\times\dfrac{1}{2V}$

Or, $4 = \dfrac{(8-x)\times 8}{(x-4)} \Rightarrow x = \dfrac{20}{3}$

4. $K^\circ_{eq} = 1 \Rightarrow \Delta G^\circ = 0$

$\Rightarrow T = \dfrac{\Delta H^\circ}{\Delta S^\circ} = \dfrac{223\times 10^3}{\left(\dfrac{223-33}{1520}\times 10^3\right)} = 1784\ \text{K}$

5. Graphite $\rightleftharpoons$ Diamond; $\Delta G^\circ = (3.0 - 0)$ kJ/mol;

$P_1 = 1$ bar

$\Delta G = 0 \quad P_2 = P$

Now, $\Delta(\Delta G) = \Delta V \cdot \Delta P$

or, $(\Delta G - \Delta G^\circ) = (V_{Dia} - V_{Gra})(P_2 - P_1)$

or, $(0 - 3.0 \times 10^3) = \left[\left(\dfrac{12}{3.6} - \dfrac{12}{2.4}\right)\times 10^{-6}\right]\left[P_2 - 10^5\right]$

$\therefore P_2 = 1.8 \times 10^9\ Pa = 1.8 \times 10^4$ bar

6. $K^\circ_P = \dfrac{P_{CO_2}}{P_{CO}} = \dfrac{10^6}{400}$

Now, $\Delta G^\circ = -5320 - 5.6\ \text{T} = -\text{RT}\ln K^\circ_P$

$$= -2 \times T \times \ln \frac{10^6}{400}$$

$\therefore T = 532$ k

7. $4HNO_3\,(g) \rightleftharpoons 4NO_2\,(g) + 2H_2O\,(g) + O_2\,(g)$

	$4HNO_3$	$4NO_2$	$2H_2O$	O_2
Initial partial pressure	P_0	0	0	0
Equ. partial pressure	$P_0 - 4x$	$4x$	$2x$	x

From question, $P_0 - 4x = 2$ atm

and $(P_0 - 4x) + 4x + 2x + x = 30$ atm

$\therefore P_0 = 18$ atm and $x = 4$ atm

$$\text{Now, } K_p = \frac{(4x)^4 \times (2x)^2 \times x}{(P_o - 4x)^4} = 2^{20}\,\text{atm}^3$$

$$\text{and } K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{2^{20}}{(0.08 \times 400)^3} = 32\,\text{M}^3$$

8. Initial: $P_{\text{NOcl}} = P_0$ bar and $P_{N_2} = (1 - P_0)$ bar

$2NOCl \rightleftharpoons 2NO + Cl_2$

	$2NOCl$	$2NO$	Cl_2
Initial partial pressure	P_0	0	0
Eqn. partial pressure	$P_0 - 2x$	$2x$	$x = 1.2 - 1.0 = 0.2$
Par. pre. on adding Cl_2	$P_0 - 2x$	$2x$	$x + (8.3 - 1.2)$
New Equ.partial pre.	$P_0 - 2x + 2y$	$2x - 2y$	$7.1 + x - y$

From question, $y = 8.3 - 8.2 = 0.1$

$$\text{Now, } K_p = \frac{(2x)^2 \times x}{(P_o - 2x)^2} = \frac{(2x - 2y)^2 \times (7.1 + x - y)}{(P_0 - 2x + 2y)^2}$$

$$\text{or, } \frac{0.4^2 \times 0.2}{(P_0 - 0.4)^2} = \frac{0.2^2 \times 7.2}{(P_0 - 0.2)^2} \Rightarrow P_0 = 0.5$$

and $K_p = 3.2$

9. Initial equilibrium:

	A	+ 2B	⇌ C
Initial partial pressure	P_0	$2P_0$	O
Equ. partial pressure	$P_0 - x$	$2P_0 - 2x$	x

From question, $(P_0 - x) + (2P_0 - 2x) + x + 3P_0$

$$= \frac{5}{6} \times 6P_0$$

$$\text{or, } x = \frac{P_0}{2}$$

Second equilibrium:

	A	+ 2B	⇌ C
Initial partial pressure	$2P_0$	$4P_0$	0
Equ. partial pressure	$2P_0 - y$	$4P_0 - 2y$	$y - 2z$

	2C	+ D	⇌ 2F
	y	$6P_0$	0
Equ. partial pressure	$y - 2z$	$6P_0 - z$	$2z$

From question, $2P_0 - y = y - 2z$

Now for the first reaction,

$$K_p = \frac{x}{(P_o - x)(2P_0 - 2x)^2} = \frac{y - 2z}{(2P_0 - y)(4P_0 - 2y)^2}$$

$$\text{or, } \frac{1}{P_0^{\,2}} = \frac{1}{(4P_0 - 2y)^2} \Rightarrow y = \frac{3}{2}P_0 \text{ and } z = \frac{P_0}{2}$$

Total equilibrium pressure:

First equilibrium $= 5P_0$

Second equilibrium $= (2P_0 - y) + (4P_0 - 2y) + (y - 2z) + (6P_0 - z) + 2z = 3.5P_0$

10.

	A_2	+ B_2	⇌ 2AB
Initial moles	0.2	0.2	0
Equ. moles	$0.2 - x$ $= 0.05$	$0.2 - x$ $= 0.05$	$2x = 0.3$

$$K_{\text{eq}} = K_1 = \frac{(0.3)^2}{0.05 \times 0.05} = 36$$

After adding C_2:

	A_2	+ B_2	⇌ 2AB
Initial moles	0.2	0.2	0
Equ. moles	$0.2 - y - z$ $= 0.08 - z$	$0.2 - y$ $= 0.08$	$2y = 0.24$

	A_2	+ C_2	⇌ 2AC
Initial moles	0.2	0.1	0
Equ. moles	$0.2 - z - y$	$0.1 - z$	$2z$

$$\text{Now, } K_1 = 36 = \frac{(0.24)^2}{(0.08 - z) \times 0.08} \Rightarrow z = 0.06$$

$$\therefore K_{\text{eq}} = K_2 = \frac{(0.12)^2}{0.02 \times 0.04} = 18$$

11. $\Delta G = \Delta G° + \text{RT}.\ln Q = -\text{RT}.\ln \dfrac{K_f}{K_b} + \text{RT}.\ln \dfrac{[\text{Product}]}{[\text{Reactants}]}$

$$= \text{RT. ln } \frac{K_b[\text{Product}]}{K_f[\text{Reactants}]} = \text{RT. ln } \frac{r_b}{r_f}$$

$$= 2 \times 300 \times \ln \frac{1}{e^4} = -2400 \text{ cal}$$

12. $A + B \rightleftharpoons C;\ K_1 = 4 \times 10^{10}$

	A	B	C
Initial moles	5	5	0
Equ. moles	$5 - (x + y)$	$5 - x$	x

$A + D \rightleftharpoons C;\ K_2 = 10^{10}$

	A	D	C
Initial moles	5	5	0
Equ. moles	$5 - (x + y)$	$5 - y$	y

As K_1 and K_2 are very large, $(x + y) = 5$ (1)

and $\frac{K_1}{K_2} = 4 = \frac{x}{5-x} \times \frac{5-y}{y} \Rightarrow \frac{x}{y} = 2$ (2)

From (1) and (2), $x = \frac{10}{3}$

$\therefore$ Moles of B at equilibrium $= 5 - x = \frac{5}{3}$

13. $Br_2\,(l) + Cl_2\,(g) \rightleftharpoons 2BrCl\,(g);\ K_p = 1$ atm

	Br_2 (l)	Cl_2 (g)	2BrCl (g)
Initial moles	x	10	0
Equ. moles	≈ 0	$10 - x$	$2x$

$Br_2\,(l) \rightleftharpoons Br_2\,(g);\ K_p = 0.25$ atm

	Br_2 (l)	Br_2 (g)
Initial moles	y	0
Equ. moles	≈ 0	y

From question: $\frac{y \times 0.082 \times 300}{164} = 0.25 \Rightarrow y = \frac{5}{3}$

and $\frac{(10 - x + 2x) \times 0.082 \times 300}{164} = 2.00 \Rightarrow x = \frac{10}{3}$

$\therefore$ Minimum mass of $Br_2(l) = (x + y) \times 160$ gm = 800 gm

14. $2SO_3 \rightleftharpoons 2SO_2 + O_2$

	$2SO_3$	$2SO_2$	O_2
Initial moles	1 (say)	0	0
Equ. moles	$1 - 0.4 = 0.6$	0.4	0.2

$$\therefore M_{av} = \frac{1 \times 80}{1.2}$$

$$\text{Now, } d = \frac{PM}{RT} \Rightarrow 16 = \frac{p \times \frac{80}{1.2}}{0.0821 \times \frac{920}{0.0821}}$$

$$\Rightarrow p = 216 \text{ atm}$$

$$\therefore K_p = \frac{(0.4)^2 \times 0.2}{(0.6)^2} \times \frac{216}{1.2} = 16 \text{ atm}$$

15. $A_2 \rightleftharpoons 2A;\ K_1 = x$ atm

	A_2	2A
Initial partial pressure	1 atm	0
Equ. partial pressure	$1 - (x + z)$	$2x$

$B_2 \rightleftharpoons 2B;\ K_2 = y$ atm

	B_2	2B
Initial partial pressure	1 atm	0
Equ.partial pressure	$1 - (y + z)$	$2y$

$A_2 + B_2 \rightleftharpoons 2AB;\ K_3 = 2$

	A_2	B_2	2AB
Initial partial pressure	1	1	0
Equ. partial pressure	$1 - (x + z)$	$1 - (y + z)$	$2z = 0.5$

(1)

From question, $[1 - (x + z)] + 2x + [1 - (y + z)] + 2y + 2z = 2.75$

$\therefore x + y = 0.75$ (2)

$$\text{Now, } K_3 = \frac{(0.5)^2}{(0.75 - x)(0.75 - y)} = 2$$

$$\Rightarrow x = 0.25 \text{ or } 0.50$$

$$y = 0.50 \text{ or } 0.25$$

$$\therefore \frac{K_2}{K_1} = \frac{\frac{(2y)^2}{1-(y+z)}}{\frac{(2x)^2}{1-(x+z)}} = \frac{(2y)^2 \times (0.75 - x)}{(2x)^2 \times (0.75 - y)} = \frac{1}{8} \text{ or } \frac{8}{1}$$